RESEARCH LETTER

Wolff–Kishner reduction reactions using a solar irradiation heat source and a green solvent system

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Due to the recognition of the irreversible damage done to the environment through man-made materials, scientists have attempted to transform synthetic procedures into environmentally favorable procedures. Since fossil fuels are used for electrical energy in the USA, the amount of electricity required to complete an experiment has become an environmental concern. Solar parabolic reflectors have been proposed as a means for minimizing the amount of electricity needed to perform chemical reactions. The ability to use the solar reflector as the sole heat source for synthetic reactions is being considered. Another area of environmental concern is the chemical solvent systems involved in synthetic reactions that are not friendly to the environment. The ability to exchange solvent systems for greener solvents is being considered. A comparative study was conducted using an electrical and solar heat source on a series of Wolff–Kishner reduction reactions performed in a green solvent system. The following generalized chemical reaction is representative:

where R is a hydrocarbon chain and R’ is a hydrocarbon chain or hydrogen.

Keywords: solar organic synthesis; solar reflector; Wolff–Kishner reduction; green chemistry; solar energy; reactions and methods

Introduction

The aim of green chemistry is to attempt to make chemicals more sustainable in the environment (1). Several sources have cited that the birth of green chemistry is often associated with the recognition of the irreversible damage that has been done to the environment through man-made materials and the desire to avoid the economic burden of polluted air and water clean-up (2). Because of these concerns the United States Environmental Protection Agency (EPA) established the Office of Pollution Prevention and Toxics (OPPT) to develop new or improve existing chemical procedures to transform them into methods that are not harmful to human health and the environment (3).

There are several areas in which chemical procedures need improving to alleviate waste and reduce hazardous levels. Electricity is one area that needs improving since it is needed for most synthetic chemical procedures. Most of the electricity in the USA is generated from fossil fuels, which all have some form of environmental impact associated with it. For instance, nearly two-thirds of the total greenhouse gas emissions in the USA result from the use of fossil fuels for energy (4). In addition, there are approximately 1.3 billion people globally that live without electricity and do not have the capability to perform chemical reactions nor any other task that would require electricity (5).

Currently, the required thermal heat source that most chemical reactions require comes from the use of either a heating mantle or hot plate. According to the JP Selecta Laboratory Equipment Manufacturer, heating mantles can use between 130 W and 2300 W of power to heat a reaction flask (Table 1) (6). The amount of electricity needed to allow research institutions and universities properly function is far greater than anyone ever imagined.

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Table 1. Power usage of heating mantle.

| Flask capacity (mL) | Power (W) |
|---------------------|-----------|
| 100                 | 130       |
| 250                 | 130       |
| 500                 | 270       |
| 1000                | 410       |
| 2000                | 530       |
| 3000                | 620       |
| 4000                | 700       |
| 5000                | 840       |
| 6000                | 1000      |
| 10000               | 1400      |
| 20000               | 2300      |

Note: Data reported for Fibroman-C heating mantle.

As a solution to the electrical waste problem, solar- and water-based energy generation processes have been engineered and implemented in various parts of the USA. One of the good aspects of solar- and wind-based energy generation is that both forms are virtually greenhouse gas emission-free sources of electricity (7). The solar oven was recently introduced as a possible heat source for chemical reactions has been examined (8). Solar ovens have been observed to heat up to approximately 170°C, far less than the boiling point of several organic solvent systems such as glycerol, ethylene glycol, and diethylene glycol (9).

Several photoreactions have been published recently using solar irradiation as the heat source. The devices in these studies use sunlight-colllecting devices to collect energy from the sunlight and use them as heat sources for chemical reactions. A recent publication examined three different solar reactors that could potentially be used for photochemical synthesis. The first solar reactor was PROPHIS, which is a line-focusing parabolic trough collector that is capable of following the sun by a three-dimensional tracking system. The PROPHIS solar collector works by collecting energy from the sun, and through a heat exchanger, transfers the energy to the reaction vessel (9).

The second sunlight-collecting device that was examined was the Compound Parabolic Collector (CPC) reactor. This system is capable of using part of the diffuse solar radiation; however, it is incapable of tracking the sun. The CPC reactor is run with a fixed slope of 50° to the position of the sun, and reaction mixtures are passed through the absorber tubes during the experiment. For overnight reactions, the reactor is covered with a plastic foil to help maintain heat to the system (10).

The third sunlight-collecting device that has recently been examined was the double-sheet flat bed reactor. The main advantages of this solar collector are the simple design and ability to use direct and diffuse solar radiation. Like the CPC collector, this design is also non-mobile, and is at a fixed slope of 30° to the position of the sun. Due to the design of this collector, two major disadvantages were observed: reacting components were not properly mixed and the solution solidified overnight during the cold weather months (10).

Recently, we published an article on the design of a solar reflector that could be used to perform high temperature chemical reaction using only solar irradiation as the heat source (11). In the article, we discussed designing a solar reflector out of recycled satellite dishes and reflective Mylar® tape. A Friedel–Crafts acylation reaction was performed using the solar reflector as the sole thermal heat source. The reaction refluxed at a temperature of 88–90°C for a period of three hours. This process was perceived as a success since the desired product was obtained with a percent yield equivalent to an in-lab comparison study.

Wolff–Kishner reactions are used by organic chemists to reduce aldehydes and ketones to alkanes. The reaction proceeds through the formation of a hydrzone, upon condensation of the aldehyde/ketone with hydrazine. The addition of strong base to the hydrzone initiates the reduction of the carbon, while oxidation of hydrazine to nitrogen gas yields the alkane (12). This reaction is known for requiring high temperatures and long reflux times. Because of these reaction conditions, there is often a general lack of appearance of this reaction in undergraduate laboratory exercises (13). Wolff–Kishner reductions, however, are commonly used throughout industry, especially in pharmaceutical synthesis. One specific industrial reaction that requires the use of this reaction is the synthesis of ibuprofen, in which the carbonyl of isobutyrophenone is reduced to its alkyl form to yield isobutyl benzene (14).

Most chemical reactions that are currently known must be performed in a chemical solvent system. Many chemical solvents involved in synthetic organic reactions are not friendly to the environment. For instance, Wolff–Kishner reduction reactions typically use a solvent system that is comprised of ethylene glycol or diethylene glycol (DEG) (15). DEG has been observed in rat models to be metabolized in the liver into a hydrogen ion, NADH, and 2-hydroxyethoxyacetaldehyde. The enzyme alcohol dehydrogenase (ADH) then metabolizes 2-hydroxyethoxyacetaldehyde into the weak acid 2-hydroxyethoxyacetic acid (HEAA), which is partially filtered in the kidneys for elimination (16). Ethylene glycol, however, is very toxic and is metabolized into oxalic acid, which has toxic effects through contact and ingestion, targeting the kidneys, nerves, blood, and eyes (17). Because of this there is a need to
attempt to exchange the current protocol for the Wolff–Kishner reduction reaction for a more green method.

A more environmentally friendly solvent for Wolff–Kishner reduction reactions would be propylene glycol. Acute oral toxicity of propylene glycol is very low, and large quantities are required to cause health damage in humans (18). Furthermore, propylene glycol is metabolized in the human body into pyruvic acid, which is a normal part of the glucose-metabolism process (19). Yet another benefit of exchanging ethylene glycol for propylene glycol is the cost difference between the two solvents. Currently, the US dollar cost of propylene glycol is slightly less than the price of ethylene glycol per pound of chemical (20). Therefore, it is believed that propylene glycol could potentially be a replacement for more environmentally unfriendly solvents such as ethylene glycol.

The goal of this study is to use the solar reflector heat source that we developed to examine its ability to perform a series of Wolff–Kishner reduction reactions. This particular reaction was chosen based on its current use in synthesis processes used in industry, and because advancements in the reaction are currently needed in order to incorporate it in undergraduate laboratory curricula. To make the synthetic process greener, the solvent for the Wolff–Kishner reductions will be propylene glycol instead of ethylene glycol or diethylene glycol. The results of the solar experiments will be compared to the same reaction performed in-lab and using an electrical heat source. Also, as a result of our work, we hope to develop a method of performing Wolff–Kishner reduction reactions using green chemistry techniques that could potentially be incorporated into undergraduate laboratory curricula.

Experimental

Development of the solar heat source

The same design for the solar reflector was used as the reflector in our previous publication (11). However, we did make one slight adjustment to the set-up. The aluminum heating block which was used in the previous publication as a heat sink was removed. It was discovered that the aluminum block was lowering the heating efficiency of the reflector. In order to use the reflector without the aid of the aluminum heating block as a heat sink, round bottom flasks were painted black up to approximately half-way up the flask using VHT® Flame Proof paint, which can withstand intermittent temperatures of up to 1093°C (Figures 1 and 2). The round bottom flasks were painted black in order to prevent photochemical side reactions and to allow for a more efficient heating process. It was determined that if the flasks were not painted black, the directed sunlight would pass directly though the round bottom and a very low heating efficiency would be observed. By painting the flask black, the black paint absorbs the heat energy from the sun at a more efficient rate.

Boiling point analysis

In order to gather data on how much heat the solar dish could generate, several high-boiling organic compounds were tested to determine whether enough heat could be generated to get the organic solvents to boil (Table 2). A 20 mL scintillation vial that contained 10 mL of solvent was attached to the solar reflector. The satellite dish was then proportioned in the sunlight such that focal point was directly centered on the bottom of the round bottom flask. A Fisher Scientific thermocouple (with a temperature...
range of –200°C to +1370°C) was used to monitor the temperature for each solvent. We found that the solar heat source using a painted round bottom flask with direct exposure to the focal point was capable of attaining temperatures well above that of most known chemical reactions at very fast rates. Because of the positive results with the boiling point analysis, we believed that the new set-up for the solar reflector heat source was capable of generating enough heat to drive chemical reactions to completion. A series of Wolff–Kishner reduction reactions were chosen to be the first reactions to be performed using the new design of our solar reflector. Furthermore, in order to make the Wolff–Kishner reactions more environmentally friendly, the typical solvent system of ethylene glycol was exchanged for the more environmentally friendly solvent propylene glycol.

To analyze the outcome of each reaction, analysis using NMR and GC/MS is going to be conducted.

**Experimental methods**

NMR spectra were obtained using a Varian Mercury VX-300 Multi-Nuclear FT-NMR Spectrometer operating at 300 MHz. Chemical shifts for each peak in the spectra were measured in parts per million (ppm) relative to tetramethylsilane (TMS).

A Varian CP-3800 Gas Chromatograph was used with a Varian Saturn 2200 GC/MS/MS detector and a Varian VF-5MS 30MX0.25mm ID DF=0.25 column (Catalog No. CP8944) and CombiPAL auto sampler were used to obtain our GC/MS spectra. A 1:1000 dilution of sample to acetonitrile was found to be the best concentration of the samples. Also, in order to avoid the appearance of nitrogen, oxygen, and water vapor in the spectra, the mass detector was set to detect only ions with a mass over 40 m/z.

**Wolff–Kishner reduction general procedure**

The following conditions are based on a modified version of the Huang-Minlon Wolff–Kishner reduction reaction (27). A solution of propylene glycol and KOH was placed into a 50 mL round bottom flask that had been painted black using VHT® Flame Proof paint. No stir-bar is placed into the flask since the refluxing liquid was determined to be sufficient to mix the solutions. The flask was attached to the solar reflector in the place that the feed horn of the satellite dish was located. Because the reaction was required to reflux for a certain amount of time, a condenser was filled with cold water and capped with pipet bulbs to insure that the water stayed in the condenser. To keep the condenser at a low enough temperature that reflux would persist for the stated time period, condensers were kept on ice and exchanged periodically during the experiment. The solar heat source was then moved into a position in which it was reflecting sunlight. The focal point of the sunlight was directed at the bottom of the round bottom flask to provide a thermal heat source. The solution was allowed to heat until the KOH dissolved into the solution. Once the KOH was dissolved the apparatus was moved such that the focal point was no longer centered on the bottom of the round bottom flask. The solution was allowed to cool until it reached a temperature of 80°C. After the solution had cooled, ketone/aldehyde and neat hydrazine were added to the reaction flask and the solar reflector was moved back into position in which the focal point was directed at the bottom of the round bottom flask. Reflux was initiated for a period of three hours. After acid work-up, propylene glycol went into the water phase and the reduction product was obtained through vacuum distillation. An in-lab study of the same chemical reaction was conducted using the same molar amounts of each reactant, but the reaction was heated using a Thermo Scientific™ Cimarec™ basic stirring hot plate.

**Wolff–Kishner reduction of acetophenone**

A solution of propylene glycol (24.51 mL) and KOH (82.7 mmol (2.5 eq), 4.632 g) was heated to make the basic solvent solution needed for the reaction. After the solution had cooled, acetophenone (29.6 mmol (1 eq), 3.556 g) and neat hydrazine (127 mmol (4 eq),

|                      | Water | Propylene glycol | Ethylene glycol | Diethylene glycol |
|----------------------|-------|------------------|-----------------|------------------|
| Time to begin boiling| 30 sec| 2 min            | 2 min           | 3 min            |
| Solvent temperature at boiling | 100.0°C | 187.6°C | 198.1°C | 235.3°C |
| Average outside temperature | 26.6°C | 26.9°C | 27.1°C | 27.4°C |
| Average solar irradiation to reach boiling temperature | 747 W/m² | 809 W/m² | 761 W/m² | 789 W/m² |
| Average heat energy | 3182 Joules | 4321 Joules | 3880 Joules | 5189 Joules |

*Analysis is average of three points. All samples were analyzed on the same day during a two-hour time period. Estimated error = ±3.13%.

**Heat Energy calculated from** $Q = mC_s\Delta T$. 

**Table 2. Solvent boiling point analysis using satellite dish heat source**.

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4.070 g) were added and the solar reflector was moved back into position in which the focal point was directed at the bottom of the round bottom flask. Reflux was initiated for a period of three hour at a temperature of 136–140°C. After acid work-up, pure ethyl benzene (5.83 mmol, 0.619 g, 19.7%) was collected through vacuum distillation at 4 inHg at a temperature range of 71–73°C. The in-lab study of this chemical reaction was conducted using the same molar amounts of each reactant, but the reaction was heated using a Fisher Scientific hotplate. 1H NMR (CDCl3): δ 7.43–7.30, δ 2.74 (t, J = 7.5 Hz, 2H), δ 1.75 (q, J = 8.1 Hz, 2H), δ 1.49 (sex, J = 7.8 Hz, 2H), δ 1.04 (t, J = 1.2 Hz, 3H). 13C NMR (CDCl3): δ 142.998, δ 128.530, δ 128.339, δ 125.676, δ 35.830, δ 33.851, δ 22.531, δ 14.102. GC: 5.67 min. MS: 51.2 m/z, 65.2 m/z, 77.2 m/z, 91.1 m/z (base peak), 105.1 m/z, 115.2 m/z, 134.0 m/z (m+ peak).

**Wolff–Kishner reduction of propiophenone**

A solution of propylene glycol (19.46 mL) and KOH (87.9 mmol (2.5 eq), 4.932 g) was heated to make the basic solvent solution needed for the reaction. After the solution had cooled, propiophenone (30.9 mmol (1 eq), 4.146 g) and neat hydrazine (127 mmol (4 eq), 4.070 g) were added and the solar reflector was moved back into position in which the focal point was directed at the bottom of the round bottom flask. Reflux was initiated for a period of three hour at a temperature of 138–142°C. After acid work-up, pure propyl benzene (6.91 mmol, 0.831 g, 22.4%) was collected through vacuum distillation at 4 inHg at a temperature range of 91–94°C. The in-lab study of this chemical reaction was conducted using the same molar amounts of each reactant, but the reaction was heated using a Fisher Scientific hotplate. 1H NMR (CDCl3): δ 7.61, δ 2.76 (t, J = 7.2 Hz, 3H). 13C NMR (CDCl3): δ 125.661, δ 29.210, δ 125.897, δ 128.162, δ 128.633, δ 144.469. GC: 3.36 min. MS: 49.0 m/z, 65.0 m/z, 91.1 m/z (base peak), 106.0 m/z (m+ peak).

**Wolff–Kishner reduction of butyrophenone**

A solution of propylene glycol (16.62 mL) and KOH (81.3 mmol (1.6 eq), 4.561 g) was heated to make the basic solvent solution needed for the reaction. After the solution had cooled, isobutyrophenone (50.0 mmol (1 eq), 7.410 g) and hydrazine (154 mmol (3 eq), 4.935 g) were added and the solar reflector was moved back into position in which the focal point was directed at the bottom of the round bottom flask. Reflux was initiated for a period of three hour at a temperature of 139–143°C. After acid work-up, pure isobutyl benzene (28.3 mmol, 3.780 g, 56.3%) was collected through vacuum distillation at 4 inHg at a temperature range of 103–105°C. The in-lab study of this chemical reaction was conducted using the same molar amounts of each reactant, but the reaction was heated using a Fisher Scientific hotplate. 1H NMR (CDCl3): δ 7.33–7.19, δ 2.53 (d, J = 6.9 Hz, 2H), δ 1.87 (n, J = 6.8 Hz, 1H), δ 0.96 (d, J = 6.6 Hz, 6H). 13C NMR (CDCl3): δ 141.718, δ 129.12, δ 128.111, δ 125.661, δ 45.532, δ 30.299, δ 22.421. GC: 5.04 min. MS: 50.3 m/z, 65.2 m/z, 77.2 m/z, 90.9 m/z (base peak), 103.2 m/z, 115.3 m/z, 133.7 m/z (m+ peak).

**Wolff–Kishner reduction of benzophenone**

A solution of propylene glycol (16.62 mL) and KOH (101 mmol (3 eq), 5.667 g) was heated to make the basic solvent solution needed for the reaction. After the solution had cooled, benzophenone (30.0 mmol (1 eq), 5.466 g) and hydrazine (127 mmol (4 eq), 4.069 g) were added and the solar reflector was moved back into position in which the focal point was directed at the bottom of the round bottom flask. Reflux was initiated for a period of three hour at a temperature of 138–140°C. After acid work-up, pure ethyl diphenylmethan (15.5 mmol, 2.608 g, 51.7%) was collected through vacuum distillation at 4 inHg at a temperature range of 187–191°C. The in-lab study of this chemical reaction was conducted using the same molar amounts of each reactant, but the reaction
was heated using a Fisher Scientific hotplate. ¹H NMR (CDCl₃): δ7.37–7.23, δ4.03 (s, 2H). ¹³C NMR (CDCl₃): δ141.166, δ128.993, δ128.515, δ126.125, δ41.986. GC: 11.14 min. MS: 51.0 m/z, 65.0 m/z, 74.0 m/z, 82.2 m/z, 91.1 m/z, 115.1 m/z, 153.1 m/z, 167.1 m/z (base peak, m⁺ peak).

Wolff–Kishner reduction of vanillin

A solution of propylene glycol (16.06 mL) and KOH (101 mmol (3 eq), 5.667 g) was heated to make the basic solvent solution needed for the reaction. After the solution had cooled, vanillin (29.7 mmol (1 eq), 4.518 g) and hydrazine (143 mmol (4 eq), 4.582 g) were added and the solar reflector was moved back into position in which the focal point was directed at the bottom of the round bottom flask. Reflux was initiated for a period of three hour at a temperature of 138–143°C. After acid work-up, pure isobutyl benzene (33.4 mmol, 4.483 g, 73.5%) was collected through vacuum distillation at 4 inHg at a temperature range of 103–108°C. ¹H NMR (CDCl₃): δ7.23–7.07, δ2.45 (d, J = 6.9 Hz, 2H), δ1.85 (n, J = 6.8 Hz, 1H), δ0.935 (d, J = 6.6 Hz, 3H). ¹³C NMR (CDCl₃): δ141.657, δ129.114, δ128.131, δ125.687, δ45.523, δ30.305, δ22.441. GC: 5.02 min. MS: 50.9 m/z, 65.0 m/z, 77.2 m/z, 90.9 m/z (base peak), 103.5 m/z, 115.5 m/z, 133.8 m/z (m⁺ peak).

Wolff–Kishner reduction of tetralone

A solution of propylene glycol (16.06 mL) and KOH (101 mmol (3 eq), 5.667 g) was heated to make the basic solvent solution needed for the reaction. After the solution had cooled, tetralone (30.1 mmol (1 eq), 4.400 g) and hydrazine (143 mmol (4 eq), 4.582 g) were added and the solar reflector was moved back into position in which the focal point was directed at the bottom of the round bottom flask. Reflux was initiated for a period of three hour at a temperature of 135–141°C. After acid work-up, pure tetralin (8.69 mmol, 1.149 g, 28.9%) was collected through vacuum distillation at 4 inHg at a temperature range of 136–139°C. The in-lab study of this chemical reaction was conducted using the same molar amounts of each reactant, but the reaction was heated using a Fisher Scientific hotplate. ¹H NMR (CDCl₃): δ7.27–7.22, δ2.95 (d, J = 6.3 Hz, 4H), δ1.95 (d, J = 6.3 Hz, 4H). ¹³C NMR (CDCl₃): δ137.239, δ129.295, δ125.573, δ29.563, δ23.414. GC: 7.23 min. MS: 51.0 m/z, 63.0 m/z, 78.0 m/z, 91.1 m/z, 104.0 m/z (base peak), 115.1 m/z, 132.0 m/z (m⁺ peak).

Seasonal and weather limitations

We provided a detailed investigation on the seasonal and weather limitations of the solar reflector heat source in our previous publication (11). The work in that publication demonstrated that the solar reflector heat source can be used successfully during any time of the year as long as there is enough sun present to produce at least approximately 600 W/m² of solar irradiation.

However, there are several differences in the synthetic procedures from the previous publication and the work reported in this article. First, the reaction that is being analyzed is different. The previous publication was investigating Friedel–Crafts acylation reactions, while this article is focusing on Wolff–Kishner reduction reactions. Second, the previous publication used an aluminum heating block as a heat sink, while this work focused on heating the reaction mixture via direct exposure to the focal point that was generated. Because of this, Table 4 shows data that were collected for three of the four seasonal periods in which a Wolff–Kishner reaction was performed. Each reaction was performed on a similar mole scale, and the only conditions that changed were the outside weather conditions. All weather conditions and solar irradiation information were obtained from the Millard Oakley STEM Center weather station located on the campus of Tennessee Technological University in Cookeville, TN (22). As observed in Table 3, the average solar irradiation for the three seasonal periods reported is well
above the 600 W/m² needed to provide enough energy to thermally heat the reaction. In each case, analysis was conducted between 12:00 pm and 3:00 pm. However, it has been observed that this set-up can be utilized from essentially early morning to late evening as long as there is sufficient sunlight. A trouble area when using the solar heat source, especially in the winter and spring months, is the presence of wind. Wind is capable of causing notable fluctuations in the reflux temperatures. We were able to solve this problem through the development of a wind blocker, which we discussed in a previous publication \((11)\).

Also, no matter the seasonal period, time required to reach reflux was consistent. For example, an attempted solar Wolff–Kishner reduction of isobutyrophenone was performed on January 7, 2014 at the campus of Tennessee Technological University. During the time period that the reaction was performed, there was approximately 0.5 in of snow on the ground and the outside temperature was between \(-14.4°C\) and \(-13.3°C\) (with a wind chill of \(-20.1°C\); Figure 3a). Consistent with other attempts of this reaction, the reaction reached and maintained a steady reflux at a temperature of \(140–145°C\) (Figure 3b). Provided with this data, we believe that the solar reflector heat source provided an efficient and consistent alternative heat source throughout all seasonal periods investigated.

### Results and discussion

Upon obtaining data from both the solar and electrical reactions, it was concluded that the solar

![Figure 3. (a) Solar reflector set-up. (b) Close-up of solvent refluxing.](image-url)
heat source provided a reliable, efficient alternative heating source that produced similar results to its electrical counterpart study (Table 4).

In each reaction in this series of Wolff–Kishner reactions, the percent yield for the in-lab and solar technique was very similar to one another. The low percent yields (ca. 30%) were determined to be due to attempting to use a minimum amount of base. The Wolff–Kishner reduction of isobutyrophenone was performed using a slight excess of base. Results from an equal molar comparative study provided data that suggest a slight increase in the amount of base can greatly improve reaction yield (solar: 73.5%, 71.6% in-lab).

Initially, we were unable to get successful results using hydrazine hydrate. Therefore, neat hydrazine was used instead. However, upon analysis of the Wolff–Kishner reaction using appropriate amounts of hydrazine hydrate (Wolff–Kishner of isobutyrophenone using excess base), it was discovered to be a successful replacement for neat hydrazine. This discovery allowed for the removal of the more toxic neat hydrazine.

Multiple reactions were performed (with isobutyrophenone as the carbonyl-containing compound) in which several conditions were altered (hydrazine/hydrazine hydrate, amount of base, etc.). As observed in Table 5, the use of hydrazine hydrate over neat hydrazine seemed to have no effect on the outcome of the reaction. Therefore, it is assumed that all reactions can be performed using hydrazine hydrate rather than neat hydrazine.

The Wolff–Kishner reduction of isobutyrophenone was repeated several times. As observed in Tables 5 and 6, the results from each of these reactions seem to be within an expected band of experimental error. Therefore, this technique of using solar energy as a thermal heat source for a Wolff–Kishner reduction reaction is very reproducible.

Through the use of a P4400 Kill A Watt® power meter (23), we were able to determine the energy usage levels in kilowatt-hours (KWH) for the synthesis and

| Isobutyrophenone (mmol) | Thermal heat source | KOH (mmol) | Hydrazine | Hydrazine Hydrate | % Yield |
|-------------------------|---------------------|------------|-----------|-------------------|---------|
| 50.0                    | Solar               | 80         | 150 mmol  | x                 | 51%     |
| 49.8                    | Solar               | 80         | 150 mmol  | x                 | 47%     |
| 50.3                    | Solar               | 80         | 150 mmol  | x                 | 56%     |
| 50.8                    | Electric            | 80         | 150 mmol  | x                 | 55%     |
| 50.1                    | Electric            | 80         | 150 mmol  | x                 | 53%     |
| 50.5                    | Electric            | 80         | 150 mmol  | x                 | 49%     |
| 50.2                    | Solar               | 100        | x         | 150 mmol          | 74%     |
| 50.6                    | Solar               | 100        | x         | 150 mmol          | 77%     |
| 49.9                    | Solar               | 100        | x         | 150 mmol          | 70%     |
| 48.5                    | Electric            | 100        | x         | 150 mmol          | 72%     |
| 50.0                    | Electric            | 100        | x         | 150 mmol          | 78%     |
| 50.3                    | Electric            | 100        | x         | 150 mmol          | 79%     |
| 48.1                    | Solar               | 100        | 150 mmol  | x                 | 70%     |
| 49.4                    | Solar               | 100        | 150 mmol  | x                 | 74%     |
| 49.2                    | Solar               | 100        | 150 mmol  | x                 | 78%     |
| 47.6                    | Electric            | 100        | 150 mmol  | x                 | 73%     |
| 50.9                    | Electric            | 100        | 150 mmol  | x                 | 69%     |
| 51.5                    | Electric            | 100        | 150 mmol  | x                 | 77%     |

Table 5. Comparison of reaction conditions.

| Isobutyrophenone Wolff–Kishner Reaction | 95% confidence interval |
|----------------------------------------|-------------------------|
| Solar – 80 mmol KOH/150 mmol hydrazine | (50.9, 51.1)            |
| Electric – 80 mmol KOH/150 mmol hydrazine | (51.9, 52.1)            |
| Solar – 100 mmol KOH/150 mmol hydrazine hydrate | (73.9, 74.1)            |
| Electric – 100 mmol KOH/150 mmol hydrazine hydrate | (75.9, 76.1)            |
| Solar – 100 mmol KOH/150 mmol hydrazine | (73.9, 74.1)            |
| Electric – 100 mmol KOH/150 mmol hydrazine | (72.9, 73.1)            |
purification of a Wolff-Kishner reduction reaction (reaction using isobutyrophenone with excess base). It was determined that this particular reaction used 1.07 KWH for the synthetic/reflux part of the procedure. Furthermore, it was determined that 0.13 KWH was used in the purification of the product (vacuum distillation). Thus, the total synthetic/purification procedure for a typical Wolff-Kishner reduction reaction used 1.20 KWH of energy.

Since there is no energy consumption in the synthetic step when using solar energy as the thermal heat source, the only energy requirements for this process would be the 0.13 KWH used during the purification step. Thus, using the current step-up as proposed, 1.07 KWH of energy is saved for each Wolff-Kishner reaction that is performed. This result would be observed on both small-scale reactions as reported or for industrial-scale reactions. The only difference when comparing the small-scale reactions to industry-scale reactions is that the KWH for the synthetic and purification steps would scale due to the larger volume. However, by using the solar reflector thermal heat source, all energy usage for the synthetic process would be removed, and the only energy consumption would come from the purification process.

Comparing the absolute energy savings that can be realized by the solar process rather than a fossil-generated heat source is effectively a process of determining what is referred to as the “Second-law efficiency.” Nevers and Seader (24) have outlined a detailed procedure for computing the Second-law efficiency. Such calculations, while worthy of being done, depend on very specific process designs and are therefore currently outside the scope of the present study.

Using the current set-up that employs the use of an HD satellite dish (32" × 22") we have successfully developed a technique to use solar energy to provide enough thermal heat to perform a Wolff-Kishner reduction reaction on the millimolar scale. This type set-up would work very well in an educational setting teaching students the principles and applications of green chemistry. Currently, investigations are being conducted to determine the scale limitations of the current set-up for other solar reflectors with larger dimensions (25).

**Conclusion**

This work has demonstrated that the solar heat source that has been modified from the previous publication can be used successfully in the place of an electric heating source. The solar heat source was able to synthesize the product from a well-known, high temperature reaction, generating with yields that were comparable to the same scale reaction performed using an electric heat source. Furthermore, seasonal variations do not seem to affect as long as sunlight is present.

It is believed that modifications that have been made to the solar reflector heat source since the last publication have aided in the sustainability of the reflector as a valid replacement for electric heat sources. By exposing the round bottom flasks to direct contact with the focal point, we have established a method to thermally heat a chemical reaction without using electricity. Furthermore, by painting the flasks black with very high temperature paint, it has allowed for the prevention of unwanted photochemical side reactions, as well as an absorbent for the solar energy so that it does not transmit through the glass flask. By using the solar reflector heat source, no electrical waste is being generated since the only energy being used is the energy from the sun, which is renewable.

In the future, we plan to continue attempting to extend the efficiency of this reflector as a heat source. One area that is currently being investigated is the modification of the reflux condenser set-up that is currently being used. If not careful, solvent/product vapors could escape from the condenser given the set-up currently being used. We are currently looking at incorporating a recently published, water-saving condenser into our set-up (26). Currently, we are investigating various techniques that could be employed during the purification step to remove the consumption of energy during this step. Other well-known chemical reactions are also currently being investigated using the solar reflector, as well as multi-step organic synthesis reactions used to synthesize commercial products that are highly valued by the general public. The results of using our solar reflector in other organic synthesis reactions, and its further development will be released in future publications (27).

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**References**

(1) Woodhouse, E.J.; Breyman, S. *Sci Technol Human Values*. 2005, 30, 199–222.

(2) Albini, A.; Fagnoni, M. *Green Chem*. 2004, 6, 1–6.

(3) Hjeresen, D.L.; Boese, J.M.; Schutt, D.L. *J Chem Educ*. 2000, 77, 1543.
(4) Pryor, S.C.; Barthelmie, R.J. *PNAS*. 2011, 108, 8167–8171.
(5) International Energy Agency. http://www.worldenergyoutlook.org/resources/energydevelopment/energyaccessdatabase/ (accessed Feb 2, 2014).
(6) Selecta, J.P. http://www.grupo-selecta.com/pdfs/en/cats/heating%20mantles%20and%20hotplates.pdf (accessed Jan 10, 2014).
(7) Chu, S.; Arun, M. *Nature*. 2012, 488, 294–303.
(8) Murray, H.; Swartling, D.J. *Abstracts of Papers*, 245th ACS National Meeting and Exposition, New Orleans, LA, Apr 7–11, 2013; CHED-1051. CAPLUS: Washington, DC.
(9) Monroe, L.; Swartling, D.J. *Abstracts of Papers*, 243rd ACS National Meeting and Exposition, San Diego, CA, Mar 25–29, 2012; CHED-1124. CAPLUS: Washington, DC.
(10) Schiel, C.; Oelgemoller, M.; Ortner, J.; Mattay, J. *Green Chem*. 2001, 3, 224–228.
(11) Agee, B.; Mullins, G.; Swartling, D. Friedel-Crafts Acylation Using Solar Irradiation *ACS Sustainable Chem. Eng*. 2013, 1 (12), 1580–1583.
(12) Carey, F.A.; Robert, M.G. *Organic Chemistry*, 8th ed.; McGraw Hill: New York, 2011. Print.
(13) Dicks, A. *Green Organic Chemistry in Lecture and Laboratory*, 1st ed.; CRC Press: Boca Raton, FL, 2012. Print.
(14) Kumudhavalli, M.V.; Margret, C.; Sripriya, D.; Jayakar, B. Studies on Synthesis, Method Development, Characterization, and Antimicrobial Activities of Ibuprofen Lysinate. *Int. J. Pharm. Biol. Sci*. 2010, 1, 1–25.
(15) Hutchins, R.O.; Hutchins, M.K. *Comp. Org. Syn.* 1991, 8, 327–343.
(16) Kraut, J.A.; Kurtz, I. *Clin. J. Am. Soc. Nephrol*. 2008, 3, 208–225.
(17) Ethylene Glycol; *MSDS* [Online]; Sigma Aldrich: Saint Louis, MO, Posted 22 May 2013. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDPage.do?country=US&language=en&productName=324558&brand=SIAL&PageToGoURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fslow%2F324558%3Flang%3Den (accessed Aug 7, 2013).
(18) National Library of Medicine. Propylene Glycol Is Used in Antifreezes. Human Toxicity Excerpts. CAS: 57–55–6. 2005.
(19) Miller, D.N; Bazzano, G. *Ann. NY Acad. Sci*. 1965, 119, 957–973.
(20) I.C.I.S. http://www.icis.com/chemicals/channel-info-chemicals-a-z/ (accessed Feb 14, 2014).
(21) Durham, L.J.; McLeod, D.J.; Cason, J. *Organic Syntheses*. 1958, 38, 34.
(22) Millard Oakley Stem Center. http://www.wunderground.com/weatherstation/WXDailyHistory.asp?ID=KTNCOOKE16 (accessed Feb 20, 2014).
(23) P3 International Corporation. 71 West 23rd Street, Suite 1201. New York, NY 10010-4102. Tel: 212-741-7289.
(24) de Nevers, N.; Seader, J.D. *Lat. Am. J. Heat Mass Transfer*. 1984, 8, 77–105.
(25) Agee, B.; Mullins, G.; Swartling, D. Synthesis of Biodiesel Using Solar Irradiation and Using Biodiesel Waste as a Green Reaction Solvent. *Sustainable Chem. Processes*. in press.
(26) Grist, M.; Perkins, D.; Barber, D. *ACS Sustainable Chem. Eng*. 2013, 1 (12), 1498–1501.
(27) Agee, B.; Swartling, D. 18th ACS Green Chemistry & Engineering Conference. Bethesda, MD, June 17–19, 2014.