Amberlite™ IRA67: A novel and efficient ion exchange resin catalyst for the synthesis of 1, 8-dioxoxanthene derivatives

Neelaiah Babu G.†, Wubetu Belay† and Teju Endale†

Abstract: The catalytic performance of Amberlite™ IRA67, the heterogeneous weak Base Exchange resin which bears tertiary amine functional group, for the synthesis of 1, 8-dioxoxanthene derivatives were investigated. The Amberlite™ IRA67 heterogeneous resin catalyst was found to be efficient and easily recoverable in the reaction of aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione to their corresponding 1, 8-dioxoxanthene derivatives under novel reaction conditions. Short reaction times, excellent yields (88–98%) and simple experimental procedure with an easy work-up are some of the advantages of the procedure. A total of 11 new compounds have been synthesized with a variety of substituent. The characterization of the compounds was completed using melting point determination, FT-IR, $^1$H-NMR, and $^{13}$C-NMR spectroscopic methods. The Amberlite™ IRA67 catalyst could be easily recovered after reaction completion and reused six times with an excellent durability and without any noticeable loss in activity.

ABOUT THE AUTHORS

Babu G. Neelaiah obtained his Ph.D. from Vikram University, Ujjain, India (in 2012, with Prof. Shubha Jain). Since 2012, he has been working as an Assistant Professor of Organic Chemistry at Haramaya University, Ethiopia. His research interests are focused on synthetic organic chemistry; include the catalysis, synthesis, design, and study of biologically important molecules, with particular emphasis on the heterocyclic compounds.

Wubetu Belay received his M.Sc. degree in organic chemistry from Haramaya University, Ethiopia under the guidance of Dr. Neelaiah Babu G. in 2017. He is currently working as a lecturer and researcher in the Department of Chemistry at Haramaya University, Ethiopia. His scientific interest lies in synthesis and catalysis.

Endale Teju received his Ph.D. degree in analytical chemistry from Addis Ababa University, Ethiopia in 2014, under the supervision of Prof. Negussie Mergesa. He is an Assistant Professor of Analytical Chemistry and Chair of the Department of Chemistry at Haramaya University, Ethiopia. His main research areas include Chromatographic method development, Spectroscopic analyses, Catalysis, Nanochemistry.

PUBLIC INTEREST STATEMENT

The massive increase in use and the broadening range of applications for ion exchange resins in chemistry illustrate the immense significance of their benefits to the chemist. Amberlite™ IRA 67 is an anion exchange resin which has wide applications in water treatment, adsorption of organic acids, metal purification and, pharmaceuticals. The catalytic application of these ion exchange resins is an unexplored area. Therefore, in this paper, an attempt made to use the commercially available Amberlite™ IRA 67 as a heterogeneous catalyst for the synthesis of 1, 8-dioxoxanthene derivatives. These xanthenes are proven to be medicinally significant heterocyclic molecules. The method was fast and the desired products were obtained within a few minutes in high yields under good conditions. Other advantages of this protocol include inexpensive and easily obtainable catalyst, simple work-up, and the recyclability and reusability of the catalyst.
Furthermore, this general and simple method may be of much significance in many of other catalytic applications.

![Diagram of the reaction](image)

**Keywords:** Amberlite™ IRA 67; ion-exchange resin; 1; 8-dioxoxanthene; dimedone

**1. Introduction**

Due to their wide range of pharmacological properties of xanthenes and its derivatives become considerably interested fine chemicals for the synthetic organic chemists. Their activities include anticancer (Mulakayala et al., 2012), anti-nociceptive (Anupam et al., 2016), anti-plasmodial (Fabien et al., 2009), and anti-inflammatory (Hafez, Hegab, El-Gazzar, & Ahmed-Farag, 2008). Furthermore, the Xanthene derivatives have been widely used as organic dyes (Yu, Tetsuo, & Kenjiro, 2015) and useful fluorescent materials (Jixiang, Zhenjun, & Wai-Yee, 2001). Despite the large number of pharmacological and materials applications, efficient procedures for their synthesis of xanthenes and its derivatives are limited. Many reports on heterogeneous catalysts can be found in the literature for the synthesis of one very important derivative of xanthenes is 1, 8-dioxoxanthene. Many reported procedures can be found for the synthesis of 1, 8-dioxoxanthene derivatives involves aromatic aldehydes, 5,5-dimethyl-1,3-cyclohexanediene and the heterogeneous catalytic systems include TMSCl (Srinivas, Rajashaker, & Lingaiah, 2006), Amberlite-15 (Biswanath, Ponnaboina, Mahender, Saidi, & Koteswara, 2006), cyanuric-Cl (Zhan-Hui & Xu-Ye, 2008), SbCl₅/SiO₂ (Zhan-Hui & Yu-Heng, 2008), NaHSO₄·SiO₂ (Zhan-Hui & Yu-Heng, 2008), SiO₂-R-SiO₂-H (Gholam, Mohammad, & Yaser, 2009), DABCO-bromine (Mohammadi, 2010), ZnO(OTf)₂ (Iraj, Majid, Valiollah, Shahram, & Hamid, 2011), [Et₃N-SO₃H]Cl (Abdolkarim et al., 2012), nano-TiO₂ (Ardeshir et al., 2013), SmCl₃ (Andivelu, Subramani, Samraj, & Sundaram, 2011), SO₄²⁻/ZrO₂ (Sandeee, Anand, Sandip, Pepijn, & Radha, 2017), CAN/HY- Zeolite (Paramasivam & Appaswami, 2014), nano-Fe₃O₄·SiO₂-imidazole-SO₃H (Mohammad, Raya, Saeed, Vahid, & Soeidi, 2016), tetrachlorosilane (TCS) (Hanan & Tarek, 2013), and nano-WO₃-supported sulphonie acid (Ali & Salman, 2015). To improve these reactions several methodologies were reported in the literature as mentioned above. Many catalysts are described for the synthesis of xanthenes and its derivatives, but there are still formidable challenges in the design of new immobilized molecular catalysts. Although these procedures provide an improvement, most of them suffer from disadvantages such as long reaction times, harsh reaction conditions, need to excess amounts of the reagent, use of organic solvents and use of toxic reagents. Additionally, only some of them are useful for the synthesis of all of the above-mentioned xanthenes. Therefore, it is important to find more efficient catalysts and methods for the synthesis of these types of compounds.
Inspired by the fact that the need for cheaper and eco-friendly processes there is a growing interest in the application of heterogeneous catalytic methods for the synthesis of fine chemicals. By the proper design of the catalytic systems, result in increased reactivity and high yields of the desired chemicals (Mizuno & Misono, 1998). The use of ion exchange resins in organic synthesis was reviewed by Gelbard in 2004 (Gelbard, 2005). In recent years special attention was given to Amberlite and Amberlyst-based resins for the synthesis of different chemicals that are both chemically and pharmaceutically important. Some examples are polysubstituted pyridenes (Kiumars, Mohammad, Fardin, & Behrooz, 2013), 4H-Benzof[b] pyrans (Mohammad, Kiumars, & Azita, 2010) and Michael Products (Bandini, Fagioli, & Umani-Ronchi, 2004; Das, Damodar, & Chowdhury, 2007) were synthesized by using Amberlite IRA-400(OH\(^-\)). Heterocyclic ketols (Wener & John, 1961), 1,8-dioxooctahydroxanthene (Biswaanath et al., 2006) and 1,8-dioxodecahydroacridenes (Biswaanath et al., 2006) were synthesized by using Amberlyst 15. Azidation of \(\alpha,\beta\)--unsaturated ketones by using Amberlite IRA900N\(_3\) (Luca, Francesco, Luisa, Ferdinando, & Luigi, 2006). In recent past, the use of resins as catalysts in organic transformation has garnered the attention of synthetic organic chemists due to their nontoxicity, low cost, high yield efficiency, reusability and recovery by simple filtration after the completion of the reaction.

The tertiary amine functional group bearing heterogeneous weak Base Exchange resin such as Amberlite\textsuperscript{TM} IRA67, could serve as the catalyst for the synthesis of 1, 8-dioxooctahydroxanthene derivatives. In the search for efficient heterogeneous catalysts, up to now, efforts were largely not focused on Amberlite\textsuperscript{TM} IRA67 in connection with organic synthesis. The chemical and physical applications of Amberlite\textsuperscript{TM} IRA67 were (i) product extraction from corn Stover sugars (Benjamin, Keerthi, & Birgitte, 2015), (ii) organic acids (Gluszcz, Jamroz, Sencio, & Ledakowicz, 2004), (iii) adsorption of Lactic acid (Şahika, Ismail, & Hasan, 2011), and (iv) RP-HPLC analysis of common bacteria (Panichayupakaranant, Charoonratana, & Sirikatitham, 2009). However, There is only synthetic application of Amberlite\textsuperscript{TM} IRA67 was found on asymmetric hydrogenation of ketones (Wisdom, Richard, & Jörg, 2013). To the best of our knowledge, only one report was found in the literature, where tertiary amine functional group containing Amberlite\textsuperscript{TM} IRA 67 was used as a base catalyst to deprotonate acetone in Aldol condensation with furfural (Masato & Yu-suke, 2014). But no researchers have yet tried the synthesis of 1, 8-dioxo-octahydroxanthene derivatives using any Amberlite ion exchange resins. Herein, we report a novel catalyst Amberlite\textsuperscript{TM} IRA67 that effectively promotes the synthesis of 1, 8-dioxo-octahydroxanthene derivatives by the reaction of aromatic aldehydes with 5,5-dimethyl-1,3-cyclohexanedi one.

2. Results and discussion

2.1. Optimization of the reaction conditions

The investigation of the catalytic activity of Amberlite\textsuperscript{TM} IRA67 was done on for the synthesis of 9-phenyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydroxanthene-1,8-dione (3a). In the search for the optimal conditions, the reaction of benzaldehyde and two equivalents of dimedone was selected as the model reaction, because of the simplicity of the reactants, to examine the effect of Amberlite\textsuperscript{TM} IRA67 catalyst (1-10 mol %) under a variety of conditions (Table 1).

On the basis of conventional synthesis of 1, 8-dioxo-octahydroxanthene derivatives, we initially investigated reaction conditions using benzaldehyde (1\(a\)) and 5,5-dimethyl-1,3-cyclohexanedione (2) as a model substrate (Table 1). When a reaction was performed with 1 mol % of Amberlite\textsuperscript{TM} IRA67 in aqueous medium at reflux for 45 min, no 1, 8-dioxo-octahydroxanthene derivative was detected (Table 1, entry 1). Thus, to detect the initial 1, 8-dioxooctahydroxanthene derivative formation, the solvent of the reaction was changed to ethyl alcohol, and only 38% of the 1, 8-dioxo-octahydroxanthene derivative was detected (Table 1, entry 2). Subsequently, by keeping catalyst concentration constant 1 mol%, the reaction was tried in tetrahydrofuran as the solvent, this time even only 30% of the 1, 8-dioxo-octahydroxanthene derivative was observed (Table 1, entry 3). In the next try dichloromethane as solvent gave us 59% of the 1, 8-dioxooctahydroxanthene derivative (Table 1, entry 4). Consequently, when acetoni-trile was used as the solvent, the yield was remarkably increased to 75% (Table 1, entry 5) and the
reaction time is decreased to 45 min. On the basis of acetonitrile solvent result, we embarked on to check the formation of the 1, 8-dioxoxanthene derivatives by increasing catalyst concentration gradually by 2, 3, 4, and 5 mol%, respectively. To our surprise, the reaction yields were increased to 98% when acetonitrile used with 5 mol% Amberlite™ IRA 67 at reflux within 15 min (Table 1, entry 9). Furthur, increase in catalyst concentration made no considerable change in increment of yield of 1, 8-dioxoxanthene derivative (Table 1, entry 10).

### 2.2. Study of the efficiency of the Amberlite™ IRA67 in the preparation of 1, 8-dioxoxanthene derivatives (3a–3k)

After the successful optimization of the catalytic application of Amberlite™ IRA67 to the reaction between benzaldehyde and 5,5-dimethyl-1,3-cyclohexanedione, we decided to test its efficacy in the preparation of wide variety of 1, 8-dioxoxanthene derivatives. Under the optimized reaction conditions, 5,5-dimethyl-1,3-cyclohexanedione was reacted with different aromatic aldehydes (including aldehydes bearing electron-withdrawing substituents, electron-releasing substituents, and halogens on their aromatic ring); the corresponding results are summarized in Table 2. As it can be seen in Table 2, Amberlite™ IRA67 was highly efficient in the synthesis of 1, 8-dioxoxanthene derivatives; all reactions proceeded efficiently and the desired products were produced in high yields (88-98%) and short reaction times (15–65 min). Considering the high effectiveness of our novel catalyst Amberlite™ IRA67 in the synthesis of 1, 8-dioxoxanthene derivatives as

| Entry | Conditions | Amberlite™ IRA 67 (mol %) | Temperature (°C) | Time (min) | Yield (%) |
|-------|------------|--------------------------|------------------|------------|-----------|
| 1     | H₂O        | 1                        | reflux           | 90         | No Reaction |
| 2     | CH₃CH₂OH   | 1                        | reflux           | 90         | 38        |
| 3     | THF        | 1                        | reflux           | 90         | 30        |
| 4     | CH₃Cl      | 1                        | reflux           | 90         | 59        |
| 5     | CH₃CN      | 1                        | reflux           | 45         | 75        |
| 6     | CH₃CN      | 2                        | reflux           | 40         | 84        |
| 7     | CH₃CN      | 3                        | reflux           | 35         | 87        |
| 8     | CH₃CN      | 4                        | reflux           | 30         | 90        |
| 9     | CH₃CN      | 5                        | reflux           | 15         | 98        |
| 10    | CH₃CN      | 10                       | reflux           | 15         | 95        |
important organic compounds, we anticipate that it can be applied as a highly efficient catalyst in organic reactions which need the use of tertiary amine-based catalysts to speed up.

To study the generality of the procedure, a series of 1,8-dioxoxanthene derivatives having different electronic properties were synthesized using the optimized conditions. The results are presented in Table 2. As shown in Table, a series of aromatic aldehydes 1 were reacted with 5,5-dimethyl-1,3-cyclohexanedione 2 in the presence of 5 mol% Amberlite™ IRA 67 in acetonitrile at reflux the reaction proceed smoothly to afford the corresponding products 3 in good yields ranging between 88% and 98%. Irrespective of whether the aromatic ring has electron-donating and withdrawing substituent, wide difference in reaction rate could be observed in the formation of the 1, 8-dioxoxanthene (3a-3k). Fortunately, our products were synthesized without byproducts and impurities.

Among the different aromatic aldehydes studied, compounds 3c, 3e, 3f and 3j (Table 2, entries 3, 5, 6 & 10) were recorded relatively faster reaction times ranging between 15 and 25 min. Unsubstituted aromatic compounds studied viz. phenyl 3a and pyridinyl 3k (Table 2, entries 1 and 11) also took a very short time 15 and 25 min respectively to complete the reaction. The remaining mono and

![Diagram of 1,8-dioxoxanthene synthesis](image)

### Table 2. Synthesis of 1, 8-dioxoxanthene derivatives (3a-3k) catalyzed by Amberlite™ IRA67

| Entry | Ar             | Product | Time (min.)/Yield (%) | m.p. (°C) (lit.) |
|-------|----------------|---------|-----------------------|-----------------|
| 1     | C6H5           | 3a      | 15/98                 | 200–202 (204–205) (Srinivas et al., 2006) |
| 2     | 2-HOC6H4       | 3b      | 55/92                 | 205–207 (207–208) (Santosh, Gajanan, Arjun, & Rajashri, 2012) |
| 3     | 4-HOC6H4       | 3c      | 15/90                 | 246–248 (246) (Srinivas et al., 2006) |
| 4     | 4-MeOC6H4      | 3d      | 45/93                 | 244–246 (243–245) (Ardeshir et al., 2013) |
| 5     | 4-NO2C6H4      | 3e      | 20/90                 | 224–226 (224–226) (Ardeshir et al., 2013) |
| 6     | 4-ClC6H4       | 3f      | 25/91                 | 230–232 (230–233) (Andivelu et al., 2011) |
| 7     | 4-N(CH3)2C6H4  | 3g      | 65/94                 | 219–221 (220–222) (Srinivas et al., 2006) |
| 8     | 2-MeO,5-BrC6H3 | 3h      | 50/92                 | 203–205 (204–206) (Hitendra, Manisha, & Kaushik, 2007) |
| 9     | 3-MeO,4-OHC6H3 | 3i      | 40/88                 | 225–227 (226–228) (Tong-Shou, Jian-She, Ai-Qing, & Tong-Shuang, 2006) |
| 10    | 3-EtO,4-OHC6H3 | 3j      | 25/90                 | 194–196 (194–196) (Hitendra et al., 2007) |
| 11    | 2-Pyridinyl    | 3k      | 25/89                 | 189–191 (188–190) (Hitendra et al., 2007) |

*isolated yield.*
disubstituted aromatic aldehydes (Table 2, entries 2, 4, 7, 8 and 9) took moderately good time to complete the reaction.

2.3 Regenerating and reusing the catalyst
The recovery of a catalyst is highly preferable for a greener process. For this purpose, the reusability of Amberlite® IRA 67 was examined for six consecutive cycles (fresh + five cycles) for the synthesis of 9-phenyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydroxanthene-1,8-dione (3a). From Scheme 1, it can be seen that Amberlite® IRA 67 can be reused up to 6 runs without the need to reload and the yield difference between the first and sixth runs is only 8% which indicated that the catalyst efficiency is almost completely maintained during six consecutive runs.

Our group proposed a plausible mechanism (Scheme 2) for the formation of 1, 8-dioxoxanthene derivatives from aromatic aldehydes (1) and 5,5-dimethyl-1,3-cyclohexanedione (2) using Amberlite® IRA67 as a catalyst. Initially, the tertiary amine functional group of the polycrylic resin Amberlite® IRA67 to deprotonate at the active methylene site of the 5,5-dimethyl-1,3-cyclohexanedione to form a stable carbanion (I), which then reacting with the electrophilic carbon of the aromatic aldehyde (1) to give an intermediate (II). The intermediate II, thus successfully loses a water molecule to give Knoevenagel Product (III), which in turn undergoes Michael addition with the second molecule of 5,5-dimethyl-1,3-cyclohexanedione (2). Then, Michael adduct (IV) underwent hemiketal (V) formation, followed by dehydration, to give 1, 8-dioxoxanthene derivatives (3).

In addition, to show the efficiency of this method in comparison with other reported procedures, we selected the reaction of benzaldehyde and two equivalents of 5,5-dimethyl-1,3-cyclohexanediione for the synthesis of 9-phenyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydroxanthene-1,8-dione (3a) as a representative model. This comparison is shown in Table 3. It is clear from the data that our method has short reaction times and provides higher yields of the products.

3. Conclusion
In summary, we have reported that Amberlite® IRA67 is a novel heterogeneous, efficient and reusable organocatalyst for the synthesis of 1, 8-dioxoxanthene derivatives. The Amberlite® IRA67 used can be easily recovered and reused 6 times without a significant decrease in the yield of the product. Further, the procedure offers several advantages including high yields, operational simplicity, cleaner reactions, minimal environmental impact, which make it a useful and attractive process for the synthesis of 1, 8-dioxoxanthene derivatives.

4. Experimental

4.1. General procedure for the Amberlitetm IRA67 catalyzed synthesis of 1, 8-dioxoxanthene (3a-3k) derivatives
A mixture of 5,5-dimethyl-1,3-cyclohexanediione (2 mmol), aromatic aldehyde (1 mmol), were placed together in a round-bottom flask containing 5 mL of acetonitrile. Amberlitetm IRA67 catalyst (5 mol %), was added to the mixture. The mixture was magnetically stirred at reflux condition for appropriate time according to Table 2. After completion of the reaction as followed by TLC (n-hexane: ethyl acetate; 9:1), the catalyst was filtered and washed with hot acetonitrile (2 × 5 mL). The recovered catalyst was washed with acetone, dried and stored for other similar consecutive runs. Solvent was removed from the resultant filtrate under reduced pressure to get 1, 8-dioxoxanthene derivatives (3a-3k) as solid, which was then subjected to recrystallization using hot ethanol. The products are known compounds and are characterized by IR and NMR spectroscopy and their melting points are compared with reported values.
Scheme 1. Recycling of Amberlite™ IRA67 for the synthesis of 9-phenyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydroxanthene-1,8-dione (3a).

Scheme 2. Plausible mechanism for the formation of 1, 8-dioxoxanthene derivatives (3a-3k) catalyzed by Amberlite™ IRA67.
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Competing Interests
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Table 3. Comparison of the catalytic efficiency of Amberlite™ IRA67 for the synthesis of 9-phenyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydroxanthene-1,8-dione (3a) with various catalysts reported

| Entry | Catalyst | Condition | Time (min) | Yield (%) | References |
|-------|----------|-----------|------------|-----------|------------|
| 1     | Amberlite™ IRA67 (5 mol %) | CH₂CN/Reflux | 15 | 98 | This work |
| 2     | PDNES (5 mol %) | Neat/90 °C | 60 | 94 | (Ardeshir, Mahshid, Ahmad, & Shahnaz, 2017) |
| 3     | [cmmim][BF₄] ionic liquid | Neat/MW | 2 | 92 | (Abhishek, Vaibhav, & Dipak, 2017) |
| 4     | [cmmim][BF₄] ionic liquid | Neat/Δ | 150 | 87 | (Abhishek et al., 2017) |
| 5     | PEG-SO₃H | Solvent Free/80 °C | 60 | 92 | (Alireza, Mohnes, Marzieh, & Somayeh, 2016) |
| 6     | Nano-TiO₂ (10 mol %) | Solvent Free/100 °C | 30 | 90 | (Ardeshir et al., 2013) |
| 7     | [Et₃N-SO₃H]Cl (25 mol %) | Solvent Free/180 °C | 60 | 97 | (Abdolkarim et al., 2012) |
| 8     | Ceric(IV) ammonium nitrate | Ultrasound/2-propanol/50 °C | 35 | 98 | (Naveen et al., 2012) |
| 9     | SmCl₃ (20 mol %) | Neat/120 °C | 540 | 98 | (Andivelu et al., 2011) |
| 10    | p-toluene sulfonic acid | Solvent Free/80 °C | 30 | 99 | (Bayat, Mohammad, Hossien, & Seyydeh, 2009) |
| 11    | TBAHS (10 mol %) |aq. 1,4-dioxane/Reflux | 210 | 88 | (Hitendra et al., 2007) |
| 12    | DBSA (10 mol %) | H₂O/RT/Ultrasound | 60 | 89 | (Tong-Shou et al., 2006) |
| 13    | TMSCI (20 mmol) | CH₂CN/Reflux | 480 | 84 | (Srinivas et al., 2006) |
| 14    | InCl₃·4H₂O in [Bmim][BF₄] | Neat/80 °C | 240 | 87 | (Xuesen, Xueyuan, Xinying, & Jianji, 2005) |
| 15    | TiO₂/SO₃H | Grinding | 30 | 88 | (Tong-Shou, Jian-She, Ai-Qing, & Tong-Shuang, 2005) |

Wubetu Belay¹
E-mail: wubetubelayye@gmail.com
Teju Endale¹
E-mail: endex72@gmail.com
¹ Department of Chemistry, College of Natural and Computational Sciences, Haramaya University, Dire Dawa, Ethiopia.

Conflict of interest
The authors declare that they have no conflict of interest.

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