SOME AROMATIC REACTIONS
USING AICl$_3$-RICH MOLTEN SALTS

E. Ota
College of Technology, Gunma University
Kiryu, Gunma 376 Japan

ABSTRACT Alkylation, acylation, condensation, and allyl- and aryl-migration were studied using two acidic molten salts with compositions of
\[\text{[AlCl}_3-\text{KCl- NaCl]}(\text{MS-A})\] and \[\text{[AlCl}_3-\text{ethylpyridinium bromide]}(\text{MS-B})\]. In MS-B $\beta$-methylnaphthalene was methylated with MeI and Me$_2$SO yielding mixtures of 1,2-, 2,6-, and 1,3-dimethylnaphthalenes, particularly in a high yield of the 1,3-isomer with Me$_2$SO. $\alpha$- and $\beta$-Binaphthyls both gave perylene as the main product when heated in MS-A. Benzoylation and acetylation of naphthalene in MS-B resulted in a very high $\alpha$-selectivity of 97 and 98%, respectively. At high temperatures $\alpha$-benzoylnaphthalene was proved to isomerize to the $\beta$-isomer through intermolecular mechanism. Anthraquinone was successfully produced from benzene and phthalic anhydride in a yield of 94% by a one pot synthesis involving Friedel-Crafts' acylation and successive intramolecular condensation in MS-B as an acid catalyst and a dehydrating agent.

Friedel-Crafts' and related aromatic reactions were conveniently studied using two kinds of acidic AICl$_3$-rich molten salts shown below as MS-A and MS-B.

\[\text{[AlCl}_3 60- \text{KCl 13.7- NaCl 26.3 mol\%]}, \text{mp 95 °C ...MS-A (1)}\]

\[\text{[AlCl}_3 66.7- \text{N-ethylpyridinium bromide 33.3 mol\%]}, \text{liquid at room temperature ...MS-B (2)}\]

1. ISOMER DISTRIBUTION IN METHYLATION OF $\beta$-METHYLNAPHTHALENE USING MS-A

In connection with our earlier study (3) on isomerization and other reactions of methylnaphthalenes in MS-A, a supplementary study was carried out on methylation of $\beta$-methylnaphthalene with interest of orientation(Scheme 1).
EXPERIMENTAL

A mixture of 0.01 mol of β-methylnaphthalene and 0.01 mol of MeI or 0.005 mol of Me₂SO₄ was added all at once to MS-A, containing 0.6 mol of AlCl₃, at 100°C in an argon stream. After given periods of time specimens of the mixture were taken out, poured into an ice-HCl mixture, extracted with benzene, and subjected to analysis of the products by gas chromatography.

RESULTS AND DISCUSSION

In both reactions quick isomerization of the starting β-methylnaphthalene to the α-isomer was observed and the amounts of both isomers decreased quickly within the first 5 min and then gradually. The methylating agents, especially MeI, seemed to be lost partially by evaporation. The main products were 1,2-, 2,6-, and 1,3-dimethylnaphthalenes commonly in both reactions, but the isomer distribution was different from each other as shown in Fig.1. The high yield of 1,3-dimethylnaphthalene in the reaction with Me₂SO₄ is remarkable.

It is known that α- and β-methylnaphthalene isomerize very fast to each other reaching to the equilibrium (β/α ratio = 4.4) and 1,4-dimethylnaphthalene similarly isomerizes to the 1,3-isomer, both within 2 min under the same reaction conditions as employed in the present experiments (3). From these facts and general rules of orientation of methylnaphthalenes shown in Scheme 2, the reaction path should be as shown in Scheme 3.

According to the orientation rules, such a large amount of the 1,3-compound as observed cannot be produced by direct substitution of both methylnaphthalenes. Formation of the 1,3-isomer from the 1,2- and 2,6-isomers is possible but it is by slow intermolecular rearrangement. Therefore, the major part of the 1,3-compound must be formed by fast intramolecular rearrangement of the 1,4-dimethyl compound, which can be directly formed from α-methylnaphthalene. This indicates that the higher yield of the 1,3-isomer in the reaction with Me₂SO₄ than in the reaction with MeI is attributable to the larger formation of the 1,4-compound in the former reaction than in the latter. This difference should be ascribed to the characteristics of the methylating agents and/or the molten salt used.
2. FORMATION OF PERYLENE FROM BINAPHTHYLS IN MS-A

In connection of our earlier work (1) on condensation of naphthalene as a new way leading aromatics to pitch and carbon, the reaction of binaphthyls was studied. Binaphthyls are the first condensation products from naphthalene and, therefore, their reaction is just the key step in a series of complicated reactions.

EXPERIMENTAL

A tenth m mol of binaphthyl was added to 0.05 mol of MS-A, kept at 100°C in a test tube, and the mixture was stirred well. After a given reaction time (1 and 10 min) the test tube was immersed into an ice bath to quench the reaction by solidification of the mixture. Then the mixture was dissolved in an ice-HCl mixture and extracted with chloroform. The extract was subjected to analysis of the products by HPLC and UV.

RESULTS AND DISCUSSION

From the results shown in Table 1 it is obvious that perylene was formed from both binaphthyls as the main product after the 10-min reaction and that a very quick isomerization of 1,1'-binaphthyl to the 2,2'-isomer took place. These facts are, of course, important for the purpose of this study mentioned above, and also interesting from viewpoint of aromatic reaction mechanism.

If a working hypothesis that the perylene observed was produced only through the intramolecular condensation of 1,1'-binaphthyl is acceptable, the formation of perylene from 2,2'-binaphthyl demands the reversed isomerization of 2,2'-binaphthyl to the 1,1'-isomer. The absence of 1,1'-isomer among the products from 2,2'-binaphthyl can be explain by assuming that the change of 1,1'-binaphthyl to perylene is faster than its formation from 2,2'-binaphthyl. Based on these facts and consideration, the reaction path should be given as shown in Scheme 4.

3. ISOMER DISTRIBUTION IN ACYLATION OF AROMATIC COMPOUNDS AND RELATED REARRANGEMENT IN MS-B (5)

Some aromatic compounds were acylated with acid chlorides in MS-B with interest of isomer distribution and related isomerization. Solvent effect on isomer distribution is an unsolved problem in Friedel-Crafts' acylation.
EXPERIMENTAL

To a solution of an aromatic compound in MS-B, kept in a flask at a given temperature, an equimolar amount of acylating agent was added dropwise. After planned periods of time, specimens were taken out, poured into an ice-HCl mixture, and extracted with benzene. The extracts were subjected to analysis of the products by GCMS. Some of the results were given in Table 2.

RESULTS AND DISCUSSION

The results of the reactions of naphthalene are noticeable because of the very high selectivity of substitution to the α-position. According to Gore (4), the Friedel-Crafts acylation in organic solvents shows a widely ranging α-selectivity depending on the nature of solvent; i.e., 38–96% in benzylation and 25–91% in acetylation. Compared with these values, the α-selectivity of 97 and 98% observed here presents newly the highest ones.

In contrast to naphthalene, phenanthrene showed a fairly dispersed isomer proportion. This is also interesting since phenanthrene usually shows a similar reactivity to naphthalene in substitution reaction. This difference shall be studied in relation to the characteristics of MS-B.

The α/β-isomer ratio in benzylation of naphthalene did not change at reaction temperatures between -15 and 20°C, while α-benzoylnaphthalene was found to isomerize to the β-isomer at temperatures above ca. 130°C. To examine the mode of this isomerization an equimolar mixture of the α-isomer with phenanthrene was heated at 170°C in MS-B and as a result, at least, three isomeric benzoylphenanthrenes were detected as the cross-rearrangement products as shown in Fig.2. This indicates that the isomerization proceeds through intermolecular mechanism. In Fig.2 formation of benzanethrones is also shown, which must be produced from α-benzoylnaphthalene and benzoylphenanthrenes by the Scholl peri-condensation. This is under investigation now.

4. ONE-POT SYNTHESIS OF ANTHRAQUINONE IN MS-B (6)

Among others there is a commercial preparation method of anthraquinone which consists of two steps of reaction; i.e., preparation of o-benzoylebenzoic acid from benzene and phthalic anhydride by usual Friedel-Crafts’ reaction and its condensation to anthraquinone in sulfuric acid. Here an improved one-pot process (Scheme 5) shall be reported.
EXPERIMENTAL

First, phthalic anhydride (0.11—0.2 mol) was dissolved in MS-B at room temperature and then 0.1 mol of benzene were added dropwise under well-stirring. The mixture was heated up to a given temperature in 1 h and kept there for another 1 h. The mixture was poured into an ice-HCl mixture and the resulting precipitate was filtered and washed. The filtercake was treated with a Na₂CO₃ solution to separate into alkali-soluble and -insoluble matters. The former contained mainly the intermediate o-benzoylbenzoic acid and the latter the final product anthraquinone.

RESULTS AND DISCUSSION

As shown in Table 3, anthraquinone was obtained in fairly good yields. The success of this one-pot synthesis is attributable to the dehydrating ability of MS-B in the second step of the reactions. Another point of this process is in the sequence of adding the raw materials to MS-A. When benzene was first added and then phthalic anhydride, the main product was o-dibenzoylbenzene, which rarely changed to anthraquinone even after a prolonged reaction time.

REFERENCES

1. a) E. Ota and S. Otani, Chemistry Lett., 1975, 241.
   b) E. Ota, S. Inoue, M. Horiguchi, and S. Otani, Bull. Chem. Soc. Japan, 52, 3400 (1979).
2. R. A. Osteryoung, J. Amer. Chem. Soc., 98, 5277 (1976).
3. E. Ota, S. Inoue, M. Domae, and S. Otani, Nippon Kagaku Kaishi, 1979, 1210.
4. P. H. Gore, Chemical Reviews, 55, 229 (1955).
5. Partly reported in Reference 6.
6. E. Ota, S. Hagiwara, K. Ishizaki, and O. Shibasaki, The 50th Annual Meeting of Chem. Soc. Japan, Abstract Vol.2, 1228 (1985), Tokyo.
### Table 1. Naphthalene Dimers* in the Products from Biphenyls

| Binaphthyls | Reaction Time(min) | Yields of Dimers(mol%) | 1,1'-' | 2,2''-' | Perylene |
|-------------|--------------------|------------------------|--------|---------|----------|
| 1,1''-'     |                    | 35.0 59.0 6.0          |        |         |          |
|             | 10                 | 0.0 2.1 44.0           |        |         |          |
| 2,2''-'     |                    | 0.0 94.0 5.5           |        |         |          |
|             | 10                 | 0.0 1.7 38.0           |        |         |          |

*Other products were mainly polymers of naphthalene.

### Table 2. Isomer Distribution in Acylation*

| Aromatics Acylating agent | Reaction Conditions | Isomer Ratio |
|---------------------------|---------------------|--------------|
| Toluene Ph-COCl           | Temp.(°C) 30, Time(h) 0.5 | o- 4, m- 1, p-95 |
| Naphthalene Ac-COCl       | Temp.(°C) 20, Time(h) 0.5 | α- 98, β- 2 |
| Naphthalene Ph-COCl       | Temp.(°C) 20, Time(h) 0.5 | α- 97, β- 3 |
| Phenanthrene Ac-COCl      | Temp.(°C) 20, Time(h) 0.5 | 1- 20, 2- 9, 3- 27, 4- Trace, 9- 44 |
| α-Benzoyl-naphthalene Ph-COCl | Temp.(°C) 100, Time(h) 3 | 1,5- 67, 1,8(?)- 8, 1,6(?)- 25 |

*The yields were usually high or almost quantitative.

### Table 3. One-pot Synthesis of Anthraquinone using MS-B

| Raw Materials | Reaction Conditions | Anthraquinone |
|---------------|---------------------|---------------|
| Benzene (mol) | Phthalic Anhydride (mol) | MS-B (unit*) | Temp. (°C) | Time (h) | Yield (%) | mp** (°C) |
| 0.1           | 0.2                 | 5             | 160        | 1        | 88         | 283-4     |
| 0.1           | 0.11                | 3             | 160        | 1        | 53         | 283-4     |
| 0.1           | 0.11                | 3             | 170        | 3        | 94         | 279-80    |

*One "unit" means an amount of MS-B consisting of 0.1 mol of ethylpyridinium bromide and 0.2 mol of AlCl₃.  
**Pure anthraquinone melts at 286°C.
Scheme 1

1st

2nd

Scheme 2

Scheme 3

1008
Scheme 4

\[ 1,1'-\text{Binaphthyl} \xrightarrow{k_{1-p}} \text{Perylene} \xrightarrow{\cdots} \text{Polymers} \]
\[ k_{2-1} \swarrow \quad k_{1-2} \searrow \]

\[ 2,2'-\text{Binaphthyl} \]

Scheme 5

\[ \text{Phthalic Anhydride} \]
\[ \xrightarrow{\text{MS-B}} \]
\[ \begin{align*}
\text{o-Benzoylbenzoic Acide} & \quad \text{Anthraquinone} \\
\text{o-Dibenzyolbenzene} & 
\end{align*} \]
Fig. 1 Product distribution in Methylation of β-Methylnaphthalene

Fig. 2 GC-MS Chromatogram of the Products of Reaction of a Mixture of α-Benzoylnaphthalene and Phenanthrene in MS-B