Ethylation and Transethylation of Naphthalene[1]

Keizo SHIMADA and Shizuo NAGAHAMA

Central Research Institute, Teijin Limited, Asahigaoka, Hino, Tokyo 191

(Received June 9, 1975)

Transethylation of naphthalene by ethylxylenes and ethylbenzene in the presence of $AlCl_3$ as a catalyst was studied and compared with ethylation by ethyl bromide. When ethylxylenes were used, it was observed that the β-isomer of ethylnaphthalene initially formed (96.8%) was isomerized to the α-isomer. This was attributed to steric hindrance of the α-position in the transition state of reactions proceeding by the hydride abstraction mechanism. However, the formation of considerable proportion of the α-isomer (25%) was observed in the case of transethylation by ethylbenzene, as well as of ethylation with ethyl bromide (60% α-isomer). Thus, the S_N2 mechanism should be operative, at least partly, in the transethylation by ethylbenzene. The rates of transethylation by ethylxylenes were found to be in the order: 1,2-diMe-4-Et-≒1,3-diMe-4-Et-＞1,4-diMe-2-Et-≫1,3-diMe-5-5-Et-benzene. The equilibrium composition of ethylnaphthalene was found to contain 8.7—8.8% α-isomer.

Ethylation of naphthalene has been investigated a long time ago.[2] However, the nature of the isomer distribution of the ethylnaphthalene produced was obscure. Nickels and Kutz[3] described a product of 80% β- and 20% α-isomers by ethylation with ethylene using a silica–alumina catalyst.

Lien and McCaulay[4] reported that the β-isomer was formed exclusively by the transethylation of naphthalene with ethylbenzene in the presence of HF–BF_3. Karakureva *et al.*[5] also reported that the transethylation of naphthalene with ethylbenzene, diethylbenzene, and ethylxylene, prepared *in situ* from xylene and ethylene, in the presence of $AlCl_3$, all produced the β-isomer.

Here, the nature of the isomer distribution of the product obtained by ethylation and transethylation of naphthalene catalyzed by aluminium chloride is reported.

Experimental

1,3-Dimethyl-5-ethylbenzene. To a mixture of 244 g of *m*-xylene (95% pure) and 70 g of $AlCl_3$, 72.3 g of ethyl bromide was added with stirring. The reaction mixture was stirred for 24 h at 30 °C. The lower complex layer was separated and poured onto crushed ice, and the organic layer which appeared was washed with aqueous sodium hydroxide and water, and dried over potassium carbonate. *m*-Xylene was recovered and the residue was fractionated by a spinning band column. A fraction (bp 184 °C) of 97.3% purity was obtained.

1,3-Dimethyl-4-ethylbenzene. To a mixture of 650 g of *m*-xylene and 20 g of $AlCl_3$, 146 g of ethyl bromide was added and the reaction mixture was stirred for 2 h. The upper layer was separated by decantation and treated as above. A fraction (bp 188 °C) 85.7% pure and containing 14.2% 1,3-dimethyl-2-ethylbenzene and 0.1% 1,3-dimethyl-5-ethylbenzene was obtained.

1,4-Dimethyl-2-ethylbenzene was synthesized from *p*-xylene and ethyl bromide with $AlCl_3$ and was distilled. Bp 187 °C, purity 97.5%.

1,2-Dimethyl-4-ethylbenzene was synthesized from *o*-xylene and ethyl bromide as above and distilled by a spinning band column. Bp 190 °C, purity 97.5%.

Naphthalene was purified by sublimation, purity 99.7%.

Reactions. Ethylation was carried out using naphthalene (0.1 mol), ethyl bromide (0.025 mol) and $AlCl_3$ (0.01 mol) in 50 g of *n*-heptane at 30 °C. Transethylation by ethylxylenes was carried out using a mixture containing 0.1 mol each of naphthalene and ethylxylene, 0.02 mol of $AlCl_3$ in 30 g of *n*-heptane at 30 °C. In the case of transethylation by ethylbenzene, 0.2 mol of ethylbenzene was used without *n*-heptane at 20 °C.

Aliquots of the samples were taken at appropriate times, poured into ice water and ether to decompose the catalyst, washed and dried. The samples were analyzed by gas chromatography, using an MB MA Golay column (45 m) at 160 °C.

Results

Ethylation with Ethyl Bromide. The isomer distribution and the reaction time are shown in Table 1. The data clearly show the initial attack favorable to the α-position, followed by rapid isomerization to the β-position. By extrapolating to zero time, an initial isomer distribution of about 60% α-isomer was obtained.

Table 1. Isomer distribution in the ethylation of naphthalene with ethyl bromide

Time (min)	Ethylnaphthalenes (%) α	Ethylnaphthalenes (%) β	Conversion[a] (%)
5	45	55	1.1
10	30	70	2.2
15	16	84	3.5
30	14	86	6.8
90	12	88	9.7
210	10	90	12
24 (h)	8.8	91.2	

a) Calculated from the peak area of the gas chromatogram, (ethylnaphthalene+diethylnaphthalene)/(naphthalene+ethylnaphthalene+diethylnaphthalene).

Transalkylation with Ethylbenzene. The isomer distribution and the reaction time are shown in Table 2. The initial β-attack increased as compared with ethyl bromide ethylation. By extrapolation to zero time, an initial isomer distribution of about 25% α-isomer was obtained.

If transethylation proceeded by the hydride abstraction mechanism, the initial attack would be more probable at the β-position, and thus, isomerization from the β- to the α-isomer may be expected. However, isomerization from the α- to the β-isomer was none the less ob-

Table 2. Isomer distribution in the transethylation of naphthalene with ethylbenzene

Time (min)	Ethylnaphthalenes (%) α	Ethylnaphthalenes (%) β	Conversion (%)
2	20	80	1.5
5	15	85	5.5
15	9.7	90.3	14.5
30	8.9	91.1	19.5
60	8.8	91.2	28

served.

Transethylation with Ethylxylenes. The isomer distributions and the reaction times obtained from the reaction of individual ethylxylene isomers with naphthalene are shown in Tables 3—6.

It is observed, in all cases, that the initial products are rich in the β-isomer compared to the equilibrium composition. Thus, isomerization of the β-isomer to the α-isomer was observed.

Table 3. Isomer distribution in the transethylation of naphthalene with 1,4-dimethyl-2-ethylbenzene

Time (h)	Ethylpaththalenes (%) α	Ethylpaththalenes (%) β	Conversion (%)
1/4	4.2	95.8	3.5
1/2	5.3	94.7	8.7
1	5.3	94.7	17
2	5.7	94.3	32
3	6.0	94.0	40
5	6.2	93.8	46
7	6.4	93.6	48
24	7.8	92.2	57

Table 4. Isomer distribution in the transethylation of naphthalene with 1,3-dimethyl-5-ethylbenzene

Time (h)	Ethylnaphthalenes (%) α	Ethylnaphthalenes (%) β	Conversion (%)
3	3.2	96.8	1.5
5	3.2	96.8	3.4
7	3.9	96.1	10
15	5.1	94.9	38
24	5.9	94.1	54
26	6.3	93.7	57
32	7.3	92.7	62

Table 5. Isomer distribution in the transethylation of naphthalene with 1,3-dimethyl-4-ethylbenzene

Time (h)	Ethylnaphthalenes (%) α	Ethylnaphthalenes (%) β	Conversion (%)
1/12	3.5	96.5	9
1/4	3.5	96.5	23
1/2	3.8	96.2	36
1	4.2	95.8	47
2	5.0	95.0	57
3	5.8	94.2	60
24	8.7	91.3	61

Table 6. Isomer distribution in the ethylation of naphthalene with 1,2-dimethyl-4-ethylbenzene

Time (h)	Ethylbenzenes (%) α	Ethylbenzenes (%) β	Conversion (%)
1/2	3.2	96.8	8
1/4	3.3	96.7	34
1/2	3.3	96.7	50
1	4.3	95.7	59
2	6.7	93.3	59
3	7.0	93.0	60
24	8.7	91.3	61

As a result, the rates of transethylation with ethylxylene isomers decrease in the order 1,2-diMe-4-Et-≧1,3-diMe-4-Et>1,4-diMe-2-Et≫1,3-diMe-5-Et.

The equilibrium composition of ethylnaphthalene was found to contain 8.7—8.8% α-isomer.

Discussion

The mechanism of transethylation has received the attention of many researchers. McCaulay and Lien,[6] and later, Brown and Smoot[7] proposed an S_N2 mechanism without the formation of a free primary carbonium ion. On the other hand, Streitwieser and Reif[8] proposed a hydride abstraction mechanism, in which the formation of a secondary benzyl cation was characteristic, based on an experiment using $GaBr_3$ as the catalyst.

One of the present authors[9] (K.S.) reported on the transethylation of toluene to show that both mechanisms operate with an aluminum chloride catalyst and that the hydride abstraction mechanism is favored when an ethylalkylbenzene of stronger basicity is used. More precisely, ethyl-*m*-xylene produced *p*-ethyltoluene in greater prevalence over its *ortho*-isomer than did ethyl-*o*- and *p*-xylenes.

In the present work, it was found that there is virtually no difference in the initial isomer distribution among the ethylxylene isomers. Namely, 3.2—3.5% α- and 96.8—96.5% β-isomer was obtained. This may be due to the basicity of the reactants which is in the order, naphthalene>ethylxylenes>toluene.

However, the fact that the initial isomer distribution was richer in the β-isomer than at equilibrium, shows the strong steric hindrance of the α-position in the transition state. This means that the hydride abstraction mechanism was operated preferentially as discussed previously.[9]

On the other hand, the formation of considerable proportions of α-ethylnaphthalene was observed in the case of transethylation by ethylbenzene. Therefore, the transethylation of naphthalene with ethylbenzene should, at least partly, proceed by a mechanism, which shows lesser steric hindrance at the α-position as in the ethylation by ethyl bromide, namely, the S_N2-type mechanism.

The authors are indebted to Dr. Shoichi Sakajiri,

Director of the Central Research Institute, Teijin Limited, for his permission to publish this article.

References

1) The Alkylation and Transalkylation Reaction of Aromatic Hydrocarbons V. Part IV: *Sekiyu Gakkaishi*, **18**, 34 (1974).

2) For References on previous researches, see S. H, Patinkin and B. S. Friedman in "Friedel-Crafts and Realted Reactions," edited by G. A. Olah, Vol. 2, Interscience Publishers, New York, N. Y. (1964), pp. 68—71.

3) J. E. Nickels and W. M. Kutz, U. S. 2570263 (1951).

4) A. P. Lien and D. A. McCaulay, U. S. 2837583 (1958).

5) G. I. Karakuleva, A. V. Bondarenko, M. I. Farberov, and Z. V. Smirnova, *Neftekhimiya*, **5**, (6) 856 (1965).

6) D. A. McCaulay and A. P. Lien, *J. Amer. Chem. Soc.*, **75**, 2407, 2411 (1953).

7) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2185 (1956).

8) A. Streitwieser, Jr. and L. Reif, *ibid.*, **82**, 5003 (1960); **86**, 1988 (1964).

9) K. Shimada, *Nippon Kagaku Zassi*, **90**, 1041 (1969).