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The Transisopropylation of Naphthalene[1)]

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Synopsis. The transisopropylation of naphthalene with *p*-cymene and isopropylxylenes in the presence of aluminum chloride–nitromethane complex as a catalyst was studied. It was observed that the α-isomer initially formed was isomerized to the β-isomer in the reaction with isopropyl-*p*-xylene. However, when *p*-cymene or isopropyl-*o*-xylene was used, the isomer distribution was almost constant from the beginning to the end of the reaction. This was attributed to the fact that the hydride abstraction mechanism plays a role in the latter case.

In the case of the isopropylation of naphthalene, the exclusive or predominant formation of the β-isomer has been reported; this result has been explained as the isomerization of the initially formed α-isomer.[2)]

Farberov *et al.*[3)] showed that the isomeric composition depended on the alkylation conditions, especially on the temperature.

The equilibrium mixture seems to contain 95—96% of the β-isomer.[3,4)]

The isopropylation of naphthalene by transalkylation has also been reported.[5)] Several patents[6)] have claimed that the transalkylation of naphthalenes gave as product the β-isomer predominantly.

Recently, Yumoto[7)] obtained a product of transisopropylation in which the ratio of the α: β isomers was 8.4: 91.6.

One of the present authors (K. S.)[8)] has previously showed that the migration of an isopropyl group of alkylbenzene to another aromatic nucleus proceeded by two different mechanisms according to the structure of the isopropylbenzenes. That is, the transisopropylation of toluene by 1,4-dimethyl-2-isopropylbenzene in the presence of the $AlCl_3$–CH_3NO_2 catalyst gave a product which had a isomer distribution similar to that obtained by the isopropylation with isopropyl bromide. Thus, both reactions seem to proceed by means of the formation of the isopropyl cation. On the other hand, the transisopropylation of toluene with 1,2-dimethyl-4-isopropylbenzene or especially *p*-diisopropylbenzene gave a product rich in *p*-cymene.

In this case, an alkyl substituent on the *p*-position to the isopropyl group may stabilize the *tert*-carbonium ion produced by hydride abstraction from the isopropyl group, and the attack of the bulky phenyldimethyl cation on the *ortho* position of the methyl group of toluene becomes unlikely.

We wish now to report the effect of the structure of isopropylalkylbenzene as a transalkylation reagent on the isomer distribution of the isopropylnaphthalene obtained by the transisopropylation with the $AlCl_3$–CH_3NO_2 catalyst.

Experimental

Materials. The naphthalene was purified by sublimation and was 99.7% pure. The 1,4-dimethyl-2-isopropylbenzene was synthesized from *p*-xylene (purity 99.5% up) and isopropyl bromide with $AlCl_3$ and was distilled twice; 99.0% pure. The 1,3-dimethyl-5-isopropylbenzene was synthesized from m-xylene (purity 99.0% up) and isopropyl bromide as above (purity 96.7%). The 1,2-dimethyl-4-isopropylbenzene was synthesized from *o*-xylene (purity 99.0% up) and isopropyl bromide as above (purity 99.0%).

Commercial *p*-cymene and nitromethane (special grade reagent, Wako Pure Chemical Ind., Ltd.) were used. The *p*-cymene was purified by distillation and was 99.0% pure. The nitromethane was used without further purification.

Reactions. A mixture of 0.1 mol each of naphthalene and one of the isopropylbenzenes in 20 g of *n*-heptane was stirred at 50 °C. To this mixture was then added a catalyst prepared from 0.02 mol of $AlCl_3$ and 0.05 mol of nitromethane. Aliquots of samples were taken off in appropriate times, poured into ice water and ether to decompose the catalyst, washed, and dried. Finally, 0.05 mol of $AlCl_3$ was added to the reaction mixture at 20 °C and the mixture was stirred until the α- and β-isomer composition was equilibrated.

The samples were analyzed by gas chromatography, using an MBMA Golay column (45 m) at 140 °C.

Results and Discussion

1,4-Dimethyl-2-isopropylbenzene: 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 isomerization to the β-position.

Table 1. Isomer distribution in the isopropylation of naphthalene with 1,4-dimethyl-2-isopropylbenzene

Time (min)	Isopropylnaphthalene (%)		Conversion[a)] (%)
	α	β	
10	72	28	1
30	50	50	2
60	38	62	4
180	18	82	11
One day after addition of further cat.	2.9	97.1	50

a) Calculated from the peak area of gas chromatogram Isopropylnaphthalene/naphthalene + isopropylnaphthalene + diisopropylanphthalene

By extrapolation to the time zero, an initial isomer distribution of about 90% α- and 10% β-position was obtained. Isopropylation by isopropyl alcohol with sulfuric acid gave 80% α- and 20% β-isomer.

Thus, the attacking species of the transalkylation in this case was similar to that of the alkylation. That is, the isopropyl cation formed by proton attack on the

Table 2. Isomer distribution in the isopropylation of naphthalene with 1,2-dimethyl-4-isopropylbenzene

Time (min)	Isopropylnaphthalene (%)		Conversion (%)
	α	β	
10	2.8	97.2	2
30	2.8	97.2	4
60	2.8	97.2	8
One day after addition of further cat.	2.5	97.5	44

Table 3. Isomer distribution in the isopropylation of naphthalene with *p*-cymene

Time (min)	Isopropylnaphthalene (%)		Conversion (%)
	α	β	
10	2.5	97.5	0.4
30	2.7	97.3	2
60	2.6	97.4	6
180	2.9	97.1	18
2 hr after addition of further cat.	2.1	97.9	27

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

Time (min)	Isopropylnaphthalene (%)		Conversion (%)
	α	β	
15	48	52	0.1
30	38	62	0.7
60	28	72	2
180	12	88	6
One day after addition of further cat.	2.4	97.6	35

1,4-dimethyl-2-isopropylbenzene reacts mainly with the α-position of naphthalene.

1,2-Dimethyl-4-isopropylbenzene and p-*Cymene*: The isomer distribution and the reaction times are shown in Tables 2 and 3.

The data of the Tables 2 and 3 are quite different from those of Table 1. The ratio of α- and β-isomer was almost constant from the beginning to the end of the reaction.

This means that the attacking species must be a bulky and sterically hindered group. That is, the phenyldimethyl carbonium ion formed by hydride abstraction from the isopropyl group of 1,2-dimethyl-4-isopropylbenzene or *p*-cymene reacts with the β-position of naphthalene.

1,3-Dimethyl-5-isopropylbenzene: The results of the reaction are shown in Table 4.

The results show the two reaction mechanisms work simultaneously.

Thus, it was further confirmed that two different mechanisms, namely, the proton addition and the hydride abstraction mechanism, operated according to the structures of alkylbenzenes, in the transalkylation of such *sec*-alkyl groups as isopropyl.

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