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Supplementary Material Available: ^{1}H NMR spectra of 2-4 and 6-10 (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Shape-Selective Synthesis of 2,6-Dicyclohexylnaphthalene over HY Zeolites

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As precursors of 2,6-naphthalenedicarboxylic acid, 2,6-dialkylnaphthalenes are potential starting materials in the production of polyester fibers and plastics with superior properties[1,2] and of thermotropic liquid crystal polymers.[3] The interest of such derivatives is shown by the increasing number of recent patents relevant to their preparation and separation.[3-5] However, the selective formation of 2,6-dialkylnaphthalenes in the alkylation of naphthalene is not obvious, not only with conventional Friedel-Crafts catalysts[6-8] but also over solid catalysts such as silica/alumina[9-11] or zeolites. The latter, which are well-known as shape-selective catalysts for acylation and alkylation of aromatic derivatives,[12,13] have been used in the gas-phase methylation of naphthalene with methanol[14,15] and more recently in the liquid-phase isopropylation of naphthalene with isopropyl bromide[16] or propene.[3,17] It was found that alkylation of naphthalene could be carried out efficiently over such zeolite catalysts with a good selectivity for the formation of 2-alkylnaphthalene and 2,6-/2,7-dialkylnaphthalenes. Unfortunately, the selective formation of the 2,6 isomer was not possible in any case, whatever zeolites and alkylating agents were used.

Such a selectivity might be found with more hindered alkylating agents, such as cyclohexyl derivatives. Our interest[16] in the shape-selective synthesis of a 2,6-dialkylnaphthalene over zeolites was stimulated by the finding that, in the cyclohexylation reaction of naphthalene over aluminum chloride, the 2,6-dicyclohexylnaphthalene was isolated from the reaction mixture by crystallization.[18,19]

We have used the combination of such a property of the 2,6-dicyclohexylnaphthalene with the potential shape-selectivity properties of zeolites in the study of the cyclohexylation reaction of naphthalene with cyclohexyl bromide and cyclohexene over protonic zeolites.

The present paper is concerned with the results obtained, leading to the selective synthesis of 2,6-dicyclohexylnaphthalene, which is known, on the other hand, to yield 2,6-naphthalenedicarboxylic acid by oxidation under the same conditions as those described for other 2,6-dialkylnaphthalenes.[20]

The catalytic activities of a sample of H-mordenite and two samples of HY zeolites were studied in the cyclohexylation reaction of naphthalene at 80 °C and 200 °C, respectively (Table I).

The H-mordenite presents a weak activity in the reaction with cyclohexyl bromide, as shown by the low conversion of naphthalene (6%) at 200 °C, whereas the HY zeolites appear to be very efficient even at lower temperature. The ultrastable zeolite HY (Si/Al ratio = 2.5) and the dealuminated sample (Si/Al ratio = 20) exhibit a similar activity (high conversion ($\simeq$95%) after a 10-min reaction with cyclohexyl bromide at 200 °C) and similar selectivities at the same temperatures.

When cyclohexene is used as the alkylating agent instead of cyclohexyl bromide, a slight difference is observed if the reaction is carried out in the same conditions (naphthalene and alkylating agent put together in the autoclave). When cyclohexene is added drop by drop (run 8) to the stirred mixture, the same results are then obtained, both in conversion and selectivity.

It can be seen, from Table I, that at lower temperature, the main products are monosubstituted derivatives, which consist of a mixture of 1-cyclohexyl- and 2-cyclohexylnaphthalenes. When the temperature is increased, the amount of dicyclohexyl derivatives increases drastically. These compounds are mainly 2,6- and 2,7-dicyclohexylnaphthalenes, formed by consecutive cyclohexylation of the monosubstituted 2-cyclohexylnaphthalene.

This suggests that the α,α and α,β isomers, produced by the cyclohexylation of the 1-cyclohexyl derivative, cannot be formed inside or cannot diffuse through the pores of the Y zeolite because of their steric hindrance. That is not the case for the 2,6- and 2,7-dicyclohexyl derivatives (β,β isomers) for which the pores of the zeolite are large enough to allow their formation and diffusion.

Moreover, the thermodynamic effect favors the β isomer at high temperature as for isopropylnaphthalene derivatives (equilibrium $\alpha \rightleftharpoons \beta$ 1.5-98.5)[8] or *tert*-butylnaphthalene derivatives,[21] and consequently, in a second consecutive step, the formation of β,β-disubstituted isomers.

(1) Gaydos, R. M. In *Kirk Othmer Encyclopaedia of Chemical Technology*, 3rd ed.; Kirk, R. E., Othmer, D. F., Eds.; Wiley: New York, 1981; Vol 15 p 698.
(2) Kobayaschi, K.; Dogane, I.; Nagao, Y. Japan Kokai Tokkyo Koyo 75 0076 054, 1975.
(3) Fellmann, J. D.; Saxton, R. J.; Wentreck, P. R.; Derouane, E. G.; Massiani, P. PCT Int. Appl. WO 90 03961, 1990.
(4) Tate, K., Sasaki, Y., Sasaki, T. Japan Kokai Tokkyo Koyo 02 264 733, 1990.
(5) Fujita, T., Oono, H., Taniguchi, K., Takahata, K. Japan Kokai Tokkyo Koyo 03 167 139, 1991.
(6) Radt, F. In *Elsevier's Encyclopaedia of Organic Chemistry, Naphthalene*; Radt, F., Ed.; Elsevier Publishing Co.: New York, 1948; Vol. 12B, pp 132-161.
(7) Olah, G. A.; Olah, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 1839.
(8) Olah, G. A. U.S. Patent 4288646, 1979.
(9) Kutz, W. M.; Corson, B. B. *J. Am. Chem. Soc.* **1945**, *67*, 1312.
(10) Teijin Co. Ltd. Japan Patent 74 48949, 1974.
(11) Topchiev, A. V.; Kurashev, M. V.; Gawrilenko, I. F. *Dokl. Akad. Nauk. SSSR* **1961**, *139*, 124.
(12) Chiche, B.; Finiels, A.; Gauthier, C.; Geneste, P.; Graille, J.; Pioch, D. *J. Org. Chem.* **1986**, *51*, 2128.
(13) Kaeding, W. N.; Chu, C.; Young, L. B.; Weinstein, B.; Butter, S. A. *J. Catal.* **1981**, *67*, 159.
(14) Fraenkel, D.; Cherniavsky, M.; Ittah, B.; Levy, M. *J. Catal.* **1986**, *101*, 273.
(15) Eichler, K.; Leupold, E. I. Ger. Offen. DE 3334084, 1985.
(16) Moreau, P.; Finiels, A.; Geneste, P.; Solofo, J. *J. Catal.*, in press.
(17) Katayama, A.; Tobe, M.; Takeuchi, G.; Mizukami, F.; Niwa, S.; Mitamura, S. *J. Chem. Soc., Chem. Commun.* **1991**, 39.
(18) Bodroux, E. *Ann. Chim. Phys.* **1929**, *11*, 535.
(19) Pokrovskaya, E. S.; Stepantseva, T. G. *J. Gen. Chem.* **1939**, *9*, 1953.
(20) Toray, Ind. Inc. Japan Kokai Tokkyo Koho 57 203032, 1982.
(21) Olah, G. A. In *Friedel-Crafts and Related Reactions*; Wiley: New York, 1964; Vol. II, p 68.

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Table I. Catalytic Cyclohexylation of Naphthalene over Zeolites

run	cat.	alkylating agent	T, °C	time, min	naphth convn, %	distribution of products, % MCN[a]	DCN[b]	TCN[c]	selectivity, % 2-MCN/MCN	2,6-DCN/DCN	2,6- + 2,7-DCN/DCN
1	HM	A[d]	200	70	6	56	44		46	16	27
2	HY2.5	A	80	360	85	88	12		38		
3		A	200	10	96	31	67	2	6	43	82
4	HY20	A	80	360	84	90	10		38		
5		A	200	10	94	53	46	1	8	43	79
6		B[e]	80	360	50	99			42		
7		B	200	10	90	85	15		53	20	36
8		B*[f]	200	25[g]	98	44	54	2	7	41	77

[a] MCN = monocyclohexylnaphthalenes. [b] DCN = dicyclohexylnaphthalenes. [c] TCN = tricyclohexylnaphthalenes. [d] A: cyclohexyl bromide. [e] B: cyclohexene. [f] B* corresponds to reaction where cyclohexene is added drop by drop into the autoclave charged with naphthalene and zeolite. [g] 25 min corresponds to the end of the addition of cyclohexene.

Table II. Isopropylation and Cyclohexylation of Naphthalene over Y Zeolites[a]

alkylating agent	time, min	naphth convn, %	distribution of products, % MAN[b]	DAN[c] 2,6	2,7	2,6 + 2,7	others	TAN[d]	β,β selectivity, % 2,6- + 2,7-DAN/DAN
isopropyl bromide	60	97	28	19	20	39	16	17	71
cyclohexyl bromide	10	96	31	29	26	55	12	2	82

[a] Catalyst, ultrastable HY (Si/Al = 2.5); T = 200 °C; solvent, cyclohexane; ratio, alkylating agent/naphthalene = 2/1. [b] MAN: monoalkylnaphthalenes. [c] DAN: dialkylnaphthalenes. [d] TAN: trialkylnaphthalenes.

The comparison of isopropylation[16] with cyclohexylation of naphthalene over the ultrastable zeolite US-HY under the same conditions is given in Table II.

In both reactions, a high conversion of naphthalene is obtained after short reaction times (10 min with cyclohexyl bromide, 1 h with isopropyl bromide).

The use of cyclohexyl bromide, instead of isopropyl bromide as alkylating agent, yields an increasing amount of 2,6- and 2,7-dicyclohexylnaphthalenes, together with a decreasing amount of trialkyl derivatives due to the steric hindrance of the cyclohexyl group, leading to an improvement of the β,β selectivity (82% compared with 71%). Nevertheless, the relative distribution of the 2,6 and 2,7 isomers does not drastically change (2,6/2,7 ratio = 0.95 for isopropyl and 1.1 for cyclohexyl). This confirms our previous findings[16] that Y zeolites increase the β,β selectivity, but do not lead to the predominant formation of one dialkyl isomer.

The advantage of the cyclohexylation in comparison to the isopropylation is directly related to the physical properties of the 2,6-dicyclohexylnaphthalene, which is separated from the mixture by crystallization. Thus, pure 2,6-dicyclohexylnaphthalene is isolated in yields varying from 19 to 27%, depending on the zeolites.[22,23] This crystalline 2,6-dicyclohexylnaphthalene presents a symmetry center which corresponds to a crystallographic center.[24]

In summary, the liquid-phase cyclohexylation reaction of naphthalene can be carried out efficiently over HY zeolites. High conversions are obtained after very short reaction times, and the use of cyclohexyl derivatives as alkylating agents instead of, for example, isopropyl or methyl leads to an improvement of the β,β selectivity. 2,6- and 2,7-dicyclohexylnaphthalenes are predominantly formed, and the 2,6 isomer is easily separated from the mixture by crystallization. The 19–27% yields of pure 2,6-dicyclohexylnaphthalene obtained over HY zeolites constitute a real improvement in the preparation of this material, taking into account the maximum 5% yield reported when aluminum chloride is used as catalyst.[19]

Table III. Properties of Catalysts

cat.	composition (wt %) SiO_2	Al_2O_3	Na_2O	Si/Al molar ratio	specific surface area, $m^2 \cdot g^{-1}$
HM	92.8	7.2	0.01	10.8	510
HY	74.9	25.1	<0.2	2.5	675
HY	95.8	4.1	<0.15	19.5	800

Experimental Section

Catalysts. HY (Si/Al = 2.5) is an ultrastable zeolite from Chemische Fabrik Uetikon, Zurich (Z6-05-01). HY (Si/Al = 19.5) and HM (Si/Al = 10.8) are from Zeocat, Montoir de Bretagne (ZF 520 and ZM 510, respectively). The typical properties of these catalysts are shown in Table III.

Procedure. Naphthalene (0.005 mol), cyclohexyl bromide (0.010 mol), cyclohexane (50 mL), and the catalyst (1.0 g of freshly calcined zeolite) are put together in a 100-mL autoclave operating in a batch mode. The mixture is stirred at 80 °C for 6 h or at 200 °C for 10 min. After cooling, the catalyst is filtered, and the reaction mixture is analyzed by GLC with a 25-m OV1 capillary column.

After cyclohexane is evaporated, the crude product solidifies at room temperature; the solid is filtered and recrystallized from ethanol. After two recrystallizations, white crystals of 2,6-dicyclohexylnaphthalene (mp 152 °C, lit.[18,19] mp 151–152 °C) are obtained. The structure is confirmed by GC–MS and ^1H and ^{13}C NMR spectroscopy, together with X-ray crystallography.[24]

When cyclohexene is used instead of cyclohexyl bromide, the procedure is the following: the autoclave is charged with naphthalene (0.005 mol), cyclohexane (50 mL), and the catalyst (1.0 g), and heating is started. At the same time, cyclohexene (0.010 mol) is added, drop by drop, by means of a stainless steel pressurized funnel, and the mixture is stirred in the same conditions as above. After cooling, the same procedure is used for the isolation and purification of 2,6-dicyclohexylnaphthalene.

In all the cases, the molar ratio alkylating agent/naphthalene is 2/1, the percent conversion is that of naphthalene, and the yields (19–27%) correspond to those in isolated 2,6-dicyclohexylnaphthalene obtained after crystallization and separation and are given in comparison to the converted naphthalene.

(22) Solofo, J.; Moreau, P.; Geneste, P., Finiels, A. PCT Int. Appl. WO 91 01959, 1991.
(23) Solofo, J.; Moreau, P.; Geneste, P.; Finiels, A. Eur. Patent Appl. 0446758 A1, 1991.
(24) Moreau, P.; Solofo, J.; Geneste, P.; Finiels, A.; Rambaud, J.; Declercq, J. P. *Acta. Crystallogr.* 1992, *C48*, 397.