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V. D. RYABOV and V. L. VAISER

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V. D. RYABOV and V. L. VAISER

CATALYTIC CRACKING OF CERTAIN UNSYMMETRICAL DIARYLETHANES

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Catalytic cracking of unsymmetrical diarylethanes makes it possible to obtain vinylaromatic compounds of various structures in high yield. This method for preparing vinylaromatic compounds has advantages over the others: it consists of two stages—the synthesis of diarylethanes and their cracking over an aluminosilicate catalyst—and, apart from the aromatic compound and acetylene, requires no other reagents. In connection with the development of new processes for producing acetylene using natural hydrocarbon gases and cracking gases, the importance of diarylethanes synthesized on the basis of acetylene will increase. In previous works ([1,2]) we investigated the catalytic cracking of 1,1-(4,4′-dimethyl)-diphenylethane and 1,1-(4,4′-diisopropyl)-diphenylethane. The present work gives the results of the catalytic cracking of other unsymmetrical diarylethanes.

Catalytic cracking of 1,1-(4,4′-diethyl)-diphenylethane. 1,1-(4,4′-Diethyl)-diphenylethane, obtained by the alkylation reaction of ethylbenzene with acetylene and twice distilled under vacuum, had the following constants: b.p. 164—167°/10 mm, n_D^{20} 1.5562; d_4^{20} 0.9646.

Into a quartz catalytic tube were placed 25 ml of aluminosilicate catalyst, and at a temperature of 550° ± 5 there were passed through it 80 ml of 1,1-(4,4′-diethyl)-diphenylethane (space velocity 2.6 hr^{-1}) and 400 ml of distilled water. The catalyzate (76.12 g) was distilled under vacuum on a column of 8 theoretical plates in the presence of hydroquinone. As a result of the distillation the following fractions were obtained: fraction 46—49°/38 mm—19.4 g (n_D^{20} = 1.497, unsaturates by Rosenmund—7.2%); fraction 93—95°/38 mm—31.68 g (n_D^{20} 1.5348; unsaturates 87.4%) and residue 31.68 g (mainly unchanged 1,1-(4,4′-diethyl)-diphenylethane). The fraction 46—49°/38 mm was treated in the cold with concentrated sulfuric acid, washed, dried, and distilled at atmospheric pressure. A fraction 133—134°/748 mm, 16.2 g, was obtained (n_D^{20} 1.4954; d_4^{20} 0.8679); this compound is ethylbenzene (literature data ([3]) for ethylbenzene: n_D^{20} 1.4958; d_4^{20} 0.8670).

M found 105.9; calculated for C_8H_{10} 106. MR found 35.7; calculated 35.54.

The fraction 93—95°/38 mm is 4-ethylstyrene containing 12.6% diethylbenzene.

4-Ethylstyrene was isolated from this fraction by means of ac-

mercury succinate and had the following constants: b.p. 60–61°/5 mm. n_D^{24} 1.5371; n_D^{20} 1.5379; d_4^{20} 0.8935 (literature data (3): n_D^{20} 1.5376, d_4^{20} 0.8924). M found 131.3; calculated for $C_{10}H_{12}$ 132; MR found 46.2; calculated 43.61.

For complete identification of 4-ethylstyrene, its dibromide was obtained in the form of white needle-shaped crystals: m.p. 65.5° (literature data (4): m.p. 66°).

Catalytic cracking of 1,1-(3,3′,4,4′-tetramethyl)-diphenylethane. 1,1-(3,3′,4,4′-Tetramethyl)-diphenylethane (ethylidene-di-*o*-xylene) was obtained by the alkylation reaction of *o*-xylene with acetylene: b.p. 173–174°/5 mm, n_D^{20} 1.5655; d_4^{20} 0.9824. Cracking was carried out at 550°. 100 ml of 1,1-(3,3′,4,4′-tetramethyl)-diphenylethane was passed through a layer of aluminosilicate catalyst (25 ml) at a space velocity of 2.6 hr^{-1}. 400 ml of water was passed through.

The catalyzate (98 g) was distilled under vacuum on a column of efficiency 25 theoretical plates.

Three main fractions were obtained: fraction 55–55.5°/36 mm, 22.6 g; fraction 94–104°/36 mm, 2.7 g; fraction 105–106°/36 mm, 27.2 g. The fraction 55–55.5°/36 mm is *o*-xylene; n_D^{20} 1.5064; d_4^{20} 0.8813 (literature data (3): n_D^{20} 1.5052; d_4^{20} 0.8802).

M found 107.8; calculated for C_8H_{10} 106. MR found 35.80; calculated 35.54.

The fraction 94–104°/36 mm—a mixture of vinylxylene and ethylxylene (n_D^{20} 1.523; unsaturated compounds 46%)—was treated with concentrated sulfuric acid and distilled at atmospheric pressure. 0.8 g of a fraction, 186–188°, was obtained: n_D^{20} 1.5049 (literature data for 1,2-dimethyl-4-ethylbenzene (3): n_D^{20} 1.5031). The fraction 105–106°/36 mm is 3,4-dimethylstyrene: n_D^{20} 1.5465; d_4^{20} 0.9062 (literature data (5): b.p. 94–96/26 mm; n_D^{20} 1.5463; d_{25}^{25} 0.909).

M found 134.9; calculated 132. MR found 46.1; calculated 43.61.

Catalytic cracking of 1,1-di-(2-naphthyl)-ethane. 1,1-Di-(2-naphthyl)-ethane (ethylidene-di-naphthyl) was obtained by alkylating naphthalene with acetylene in carbon tetrachloride solution. It is a very viscous transparent substance with green fluorescence. B.p. 236–238° at 3 mm; n_D^{50}—1.6760. A solution of 87 g of 1,1-di-(2-naphthyl)-ethane in 60 ml of benzene was passed into a catalytic tube containing 25 ml of aluminosilicate catalyst at a rate of 1 ml/min. Water was fed at a rate of 4 ml/min. The cracking temperature was 550°.

After removal of benzene, the catalyzate was distilled under vacuum in a Claisen flask to separate the cracking products from unchanged 1,1-di(2-naphthyl)-ethane. 46.57 g of a fraction 110–150°/8 mm and 25.75 g of residue were obtained. The fraction 110–150°/8 mm, consisting of crystalline and liquid portions, was filtered on a vacuum filter. The crystals on the filter (21.12 g) were twice recrystallized from alcohol and, after sublimation, had m.p. 81–82°. They gave a picrate of m.p. 148–148.5°.

Reference data: m.p. of naphthalene 80°, m.p. of the picrate 149°. The filtrate (25.4 g) was a transparent yellow liquid: n_D^{20} 1.636; unsaturated compounds 74.5%.

Part of the filtrate crystallized on standing. The crystals were separated and, after several recrystallizations from alcohol, had m.p. 65-65.5° (literature data for β-vinylnaphthalene (6): m.p. 66°).

M found 154.5; calculated for $C_{12}H_{10}$ 154.

For identification of β-vinylnaphthalene, bromination of the filtrate was carried out at −20°. Crystals in the form of white needles were obtained, m.p. 86-86.5° (literature data (7): m.p. 86°).

M found 315.5; calculated for $C_{12}H_{10}Br_2$ 314.

Thus, the chemistry of the cracking of the indicated diarylethanes is analogous to the chemistry of the cracking of diarylethanes in our works ([1,2]), namely:

$$R{-}C_6H_4{-}CH(CH_3){-}C_6H_4{-}RarrowC_6H_5{-}R + H_2C{=}CH{-}C_6H_4{-}R + R{-}C_6H_4{-}C_2H_5$$

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Note: Figure translations are in progress. See original paper for figures.