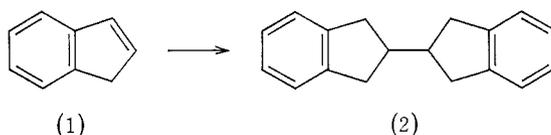


DIMERIZATION OF INDENE WITH LITHIUM NAPHTHALENIDE

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Recently, the authors have reported that lithium naphthalenide dimerizes isoprene in high yields.^{1,2} However, it is well known that lithium naphthalenide is effective for anion polymerization of highly reactive monomer such as indene, styrene, and α -methylstyrene, and the dimerizations of these monomers with lithium naphthalenide are very difficult. This short communication describes the dimerization reaction of indene and other monomers with lithium naphthalenide, using ethylene glycol monobutyl ether as a terminating agent.



To the lithium naphthalenide (2 mol) in tetrahydrofuran, a mixture of indene (1) (1 mol) and ethylene glycol monobutyl ether (1 mol) was added. The reaction mixture was treated in the usual way to selectively give a dimer of (1) in 43% yield. The dimer was identified by spectral and elementary analysis as 2,2'-bi(2,3-dihydroindene) (2). The use of ethylene glycol monobutyl ether as a terminating agent in the reaction is essential in order to obtain this result. A similar experiment with stoichiometric amounts of ethanol present, gave low yields of the compound (2).³ Similar dimerization of styrene and α -methylstyrene gave their corresponding reductive dimers as described in the Experimental section.

Experimental

Reaction of Indene (1) with Lithium Naphthalenide

To a mixture of naphthalene (12.8 g; 0.10 mol) and purified tetrahydrofuran (150 ml), metallic lithium cuttings (2.8 g; 0.4 mol) were added, and the whole was agitated at room temperature under a dry nitrogen atmosphere. After 1 hr, a mixture of indene (1) (23.6 g; 0.2 mol) and ethylene glycol monobutyl ether (23.6 g; 0.2 mol) was gradually added to the dark blue tetrahydrofuran solution, and the mixture was stirred for an additional 2 hr at room

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¹ Suga, K., Watanabe, S., Watanabe, T., and Kuniyoshi, M., *J. appl. Chem.*, 1969, **19**, 318.

² Watanabe, S., and Suga, K., *Aust. J. Chem.*, 1971, **24**, 1301.

³ Richards, D. H., Scilly, N. F., and Williams, F. J., *Chemistry Ind.*, 1970, 1298.

temperature. The reaction mixture was decomposed with methanol, the insoluble matter was dissolved in water, and the organic layer was isolated with isopropyl ether. The ether extracts were washed with water, dried over anhydrous sodium sulphate, and distilled to give unchanged indene (11 g) and a crude dimer (2), b.p. 180–200°/4 mm (10 g). Recrystallization of the product gave the pure dimer (2), m.p. 169·5–170·5°, yield 7 g. I.r.: 3000, 2900, 1470, 1300, 1212, 1150, 980, 794, 750, 740, 672 cm^{-1} . N.m.r. (δ , p.p.m.): 8·3 (s, aromatic protons, 8H), 3·4 (m, PhCH_2 , 4H), 3·1 (m, CH_2CHCH_2 , 2H). U.v. (CH_3OH): λ_{max} 267·5 nm ϵ 3040, 274 nm ϵ 3370. M^+ 234 (Found: C, 92·2; H, 7·7. Calc. for $\text{C}_{18}\text{H}_{18}$: C, 92·3; H, 7·7%).

Dimerization of Styrene

From a mixture of styrene (20·4 g; 0·2 mol), naphthalene (12·8 g; 0·1 mol), metallic lithium cuttings (2·76 g; 0·4 mol), and ethylene glycol monobutyl ether (23·6 g; 0·2 mol) was obtained an oily product (16·0 g), boiling at 140–150°/4–5 mmHg. Redistillation of the oil gave pure 1,4-diphenylbutane (13·5 g), b.p. 144–146°/4–5 mmHg. The infrared absorption spectrum and gas-liquid chromatography were identical with those of authentic 1,4-diphenylbutane.

Dimerization of α -Methylstyrene

From a mixture of α -methylstyrene (11·8 g; 0·1 mol), naphthalene (6·4 g; 0·05 mol), lithium cuttings (1·38 g; 0·2 mol), and ethylene glycol monobutyl ether (11·8 g; 0·1 mol) was obtained an oily product (7 g), boiling at 130–150°/5 mm. Redistillation of the oil gave pure 2,5-diphenylhexane (4·5 g). It was identical with authentic sample which had been prepared as reported previously.⁴

⁴ Richards, D. H., and Scilly, N. F., *J. chem. Soc. (C)*, 1969, 55.