The Base-catalyzed Dimerization of 1,4-Cyclohexadienes[1]

By Ken-ichi MORITA and Zennosuke SUZUKI

The Basic Research Laboratories, Toyo Rayon Company, Ltd., Kamakura

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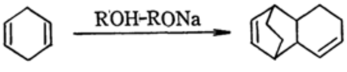
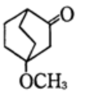
Hoffmann et al.[2] have reported that the treatment of 1,4-cyclohexadiene (I) with *t*-butoxide in dimethylsulfoxide at 55°C gave a mixture of benzene and cyclohexene in a quantitative yield, while an analogous reaction in *t*-butyl alcohol as a solvent has afforded a mixture of I and 1,3-cyclohexadiene.[3] We now wish to report a base-catalyzed dimerization of 1,4-cyclohexadinene derivatives in alcoholic solvents at an elevated temperature.

The reaction of 1,4-cyclohexadiene (I) in alcoholic solvents such as methanol, ethylene glycol or *t*-amyl alcohol in the presence of a base such as potassium alkoxide, sodium alkoxide, potassium hydroxide or sodium hydroxide (10^{-1} to 10^{-3} mol.) at 200—230°C for 15 to 20 hr. afforded dicyclohexadiene (II),[4,8] b. p. 60—61°C/2 mmHg; n_D^{20} 1.5263, in 20 to 30% yields, and a mixture (60—70%) of benzene, cyclohexene and cyclohexadienes.

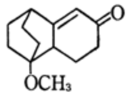


I II

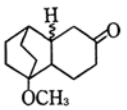
An analogous base-catalyzed dimerization of dihydrotoluene[9] at 250—255°C for 17 hr. furnished a dimeric mixture of dihydrotoluene, b. p. 75—77°C/4 mmHg, in 20 to 25% yields. The treatment of 2-methoxy-1,4-cyclohexadiene[9] (III) (7 g.) with 1 ml. of 10% potassium *t*-amyloxide (in *t*-amyl alcohol) in a glass ampoule[10] at 220°C for 24 hr. furnished a dimer V, $C_{14}H_{20}O_2$, (24%); b. p. 110—115°C/2 mmHg; $\nu_{C=C}^{film}$ 1669 cm^{-1}, 1-methoxy-1,3-cyclohexadiene (IV) (19%), and a mixture (14%) of anisol, III, 1-methoxycyclohexene and benzene. Compound V was identical with a sample prepared in a 16% yield[12] (conversion) by the thermal dimerization of IV[11] at 200—220°C for 32 hr. An acid hydrolysis of V gave the keto ether VI, $C_{13}H_{18}O_2$, $\nu_{C=O}^{film}$ 1715, ν_{OMe}^{film} 1109 cm^{-1}; semicarbazone, m. p. 220—220.5°C decomp. The hydrogenation of VI over a palladium catalyst afforded VII, $C_{13}H_{20}O_2$; b. p. 135—137°C/2 mmHg, $\nu_{C=O}^{film}$ 1714 cm^{-1}, ν_{OMe}^{film} 1109 cm^{-1}. The reaction of pyrrolidyl enamine of 4-methoxybicyclo[2.2.2]octan-2-one (VIII)[14] with methyl vinyl ketone afforded IX., b. p. 145—147°C/1.4 mmHg; τ 6.85 (OMe); 4.37 (doublet, J= 2.5 c. p. s; a vinyl proton); $\nu_{C=O}^{film}$ 1665, $\nu_{C=C}^{film}$ 1632, ν_{OMe}^{film} 1102 cm^{-1}; semicarbazone, m. p. 204—205°C. The hydrogenation of IX over a palladium catalyst gave X, b. p. 135—136°C/2 mmHg, $\nu_{C=O}^{film}$ 1714 cm^{-1}, ν_{OMe}^{film} 1109 cm^{-1}; semicarbazone, m. p. 206—207°C (decomp.).[15] The infrared spectra of VII and X were similar, but some difference was noted in the fingerprint region.



VIII



IX



X

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[1] Bridged Ring Compounds. VII. Paper VI: K. Morita and T. Kobayashi, *J. Org. Chem.*, in press.

[2] J. E. Hoffmann, P. A. Argabright and A. Schriesheim, *Tetrahedron Letters*, **1964**, 1005.

[3] Cf. R. B. Bates, R. H. Carnigham and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3032 (1963).

[4] The identity was established by a comparison of the infrared spectra and the retention time of v. p. c. with those of a sample prepared according to the method of Kazanskii and Svirskaya,[5] who obtained dicyclohexadiene (II), b. p. 110—111°C/14mmHg; n_D^{20} 1.5269 in a 50% yield by the Diels-Alder dimerization of 1,3-cyclohexadiene. Since 1,4-cyclohexadiene (I) can readily be prepared from benzene,[6,7] the method described in this paper provides a convenient way to prepare II. It should be noted that a large amount of polymers have been obtained as by-products in the case of the thermal dimerization of 1,3-cyclohexadiene, whereas only a small amount of polymers were formed in the base-catalyzed dimerization of 1,4-cyclohexadiene.

[5] B. A. Kazanskii and P. I. Svirskaya, *J. Gen. Chem., USSR*, **29**, 2550 (1959). See also K. Alder and G. Stein, *Ann.*, **496**, 197 (1932).

[6] J. P. Wibaut and F. A. Haak, *Rec. trav. chim.*, **67**, 85 (1948).

[7] R. A. Benkeser, E. M. Kaiser and R. F. Lambert, *J. Am. Chem. Soc.*, **86**, 5272 (1964).

[8] The reaction of I with phenyllithium in tetrahydrofuran as a solvent afforded no II, but a moderate yield of biphenyl.

[9] A. L. Wilds and N. A. Nelson, *J. Am. Chem. Soc.*, **75**, 5360 (1953).

[10] An analogous reaction in a stainless steel autoclave gave a trace of V.

[11] J. A. Birch, E. M. A. Shoukry and F. Stansfield, *J. Chem. Soc.*, **1961**, 5376.

[12] It should be noted that the base-catalyzed reaction proceeded somewhat faster than the thermal dimerization. We have found that the Diels-Alder dimerization of 2-methoxy-1,3-butadiene afforded 1-methoxy-4-(1-methoxyvinyl)-1-cyclohexene in a 32% yield when a catalytic amount of potassium *t*-butoxide was added to a reaction mixture, whereas the same reaction proceeded in only a 20% yield without a base.[13]

[13] I. N. Nazarov, G. P. Verkholetova and L. D. Bergel'son, *Izv. Akad. Nauk*, 511 (1948); *Chem. Abstr.*, **43**, 2576i (1949).

[14] K. Morita and T. Kobayashi, *J. Org. Chem.*, **31**, 229 (1966).

[15] All the novel compounds described here gave satisfactory analyses.