

1-diazo-3-phenoxy-2-butanone was obtained by recrystallization from benzene-petroleum ether (b.p. 30–60°); m.p. 34–35° (Kofler hot stage¹²).

Anal. Calcd. for C₁₀H₁₀N₂O₂: C, 63.14; H, 5.30; N, 14.73. Found: C, 63.25; H, 5.47, N, 14.26.

Wolff rearrangement was attempted with the crude solid diazoketone (total residual product from the reaction described immediately above), by the general procedure previously outlined. Gas evolution ceased after 2.5 g. of silver benzoate in 22.5 g. of triethylamine had been added. Isolation of product in the usual manner gave a residual oil, which was distilled under reduced pressure. Three fractions were collected, one of which (4.21 g.), b.p. 110–120° (0.55–0.75 mm.), solidified upon strong cooling. Recrystallization from petroleum ether (b.p. 30–60°) gave a yellow crystalline product, m.p. 34–35°, which in alcohol solution yielded a gas (presumably nitrogen) upon acidification with hydrochloric acid, and was considered to be recovered 1-diazo-3-phenoxy-2-butanone.

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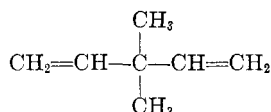
(12) L. Kofler, *Angew. Chem.*, **51**, 703 (1938).

3,3-Dimethyl-1,4-pentadiene¹

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The previously unreported 3,3-dimethyl-1,4-pentadiene (I) is the simplest diene which cannot



conjugate by mere migration of a double bond. As such, we wished to study its catalytic hydrogenation. It is also of interest as model compound for other mechanistic studies.

The readily accessible² 1,5-dichloro-3,3-dimethylpentane (II) would seem an attractive starting material. However, attempts to dehydrochlorinate II directly with a variety of bases failed. The diiodide corresponding to II reacts very rapidly to give good yields of I when refluxed with the hindered amine, 2-methylquinoline. This appears to be an example of the general rule that, in proceeding from chlorides to bromides to iodides, ease of dehydrohalogenation increases even more rapidly than that of nucleophilic substitution.

The preparation may be simplified by refluxing a mixture of II, sodium iodide and 2-methylquinoline under conditions such that the olefin is removed as it is formed.³ This reaction is much slower than

that of the di-iodide. The rate limiting step is apparently substitution of chloride by iodide. Presumably, the sequence of intermediates is chloroiodide, chloroolefin, iodoolefin. Equally good results were obtained in converting 1-chloro-3,3-dimethylpentane to 3,3-dimethyl-1-pentene but the conversion⁴ of 1-chloro-3,3-dimethylbutane to *t*-butylethylene failed, perhaps because of lower refluxing temperatures.

Pyrolysis over calcium chloride of II at about 550° or of the corresponding dibromide at about 450° gave small yields, 5–10%, of I plus a number of difficultly removable by-products.

EXPERIMENTAL

1,5-Dichloro-3,3-dimethylpentane was prepared following Schmerling and West.² We found it important to cool the 1,3-dichloro-3-methylbutane to –40° before adding aluminum chloride and to start the ethylene flow immediately. The reaction flask can then be warmed to –25° but ethylene must be fed as fast as it is absorbed. Under these conditions, little or no hydrogen chloride appears in the small amount of exit gas and the amounts of lower and higher molecular weight materials are minimal. Yields of 70% or better result from final distillation at reduced pressure; n_D^{20} 1.4643, reported² 1.4652.

3,3-Dimethyl-1,4-pentadiene (I). A mixture of 0.5 mole of II, 2 moles of 2-methylquinoline, and 0.1 mole of sodium iodide was refluxed in a flask surmounted by a tubing 40 cm. long with a standard taper plug at the top. Just before this was a connection to a small Vigreux column at the top of which was a condenser and take-off. The reflux had to be interrupted once during a run, the plug removed, and 2-methylquinoline hydrohalide which had distilled into the tubing scraped down into the flask. The reflux rate was maintained so that the temperature at the top of the Vigreux column was between 60 and 70°. The reaction is slow; a few hours elapse before diolefin appears and the entire reaction requires about 8 hr. The product was dried with sodium sulfate and fractionated; yield, 58% at b.p. 70.2° at 750.5 mm. Further possible purification was effected by storage over sodium and azeotropic distillation with methanol, n_D^{20} 1.4067; d_4^{20} 0.7017.

Anal. Calcd. for C₇H₁₂: C, 87.4; H, 12.6. Found: C, 87.9; H, 12.5.

The diolefin absorbs 2 moles of hydrogen in the presence of platinum oxide and forms a hydrocarbon with the infrared spectrum of 3,3-dimethylpentane.

3,3-Dimethyl-1-pentene was made in 88% yield from 1-chloro-3,3-dimethylpentane⁵ by the same process, b.p. 77.2° at 755 mm.; n_D^{20} 1.3978.

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- (4) W. O. Haag and H. Pines, private communication.
(5) L. Schmerling, *J. Am. Chem. Soc.*, **67**, 1152 (1945).

Lithium Cleavages of Triphenyl Derivatives of Some Group Vb Elements in Tetrahydrofuran

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Cleavage of various compounds with alkali metals has often proved to be a valuable tool in

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(2) L. Schmerling and J. P. West, *J. Am. Chem. Soc.*, **74**, 2885 (1952).

(3) We are indebted to Professor L. C. King for suggesting this one-step modification.