Anal. Calcd. for $C_{26}H_{23}N_3$: C, 82.72, H, 6.14. Found: C, 82.91, 82.95; H, 6.18, 6.07.[10]

The mother liquors were combined and concentrated to a volume of 160 ml. by distillation. Chilling the solution yielded orange crystals which were recrystallized from 125 ml. of ethyl acetate to yield 0.60 g., m.p. 193–195°; total yield 11.50 g. (84%).

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1-Diazo-3-phenoxy-2-butanone[1]

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The cyclization of β-aryloxypropionic acids and their derivatives to chromanones is well-known. The present note describes a brief study of the Arndt-Eistert reaction for preparation of β-aryloxypropionic acids as potential chromanone precursors.

Phenoxyacetyl chloride (I) reacted with ethereal diazomethane (II) to give a yellow oil, presumably III. Utilization of silver oxide and water to effect Wolff rearrangement of III gave no appreciable yield of β-phenoxypropionic acid. The Newman-Beal modification[2] of the Wolff rearrangement, however, gave the crude methyl ester, which upon hydrolysis yielded β-phenoxypropionic acid,[3] although in low over-all yield.

$$\underset{\text{I, R = H}\quad \text{IV, R = CH}_3}{C_6H_5OCH(R)COCl} + \underset{\text{II}}{CH_2N_2} \longrightarrow C_6H_5OCH(R)COCHN_2 + \text{By-products}$$

III, R = H
V, R = CH_3

α-Phenoxypropionyl chloride (IV) gave with II the crystalline 1-diazo-3-phenoxy-2-butanone (V), which was purified by crystallization from benzene–petroleum ether. As is commonly done,[4] however, the crude diazoketone was employed in the Arndt-Eistert reaction. At least 33% of the V employed was recovered by vacuum distillation of the crude reaction product. The ester of the rearranged acid may have been present, but the data available indicated that the yield of such a product was low. It is apparent that V is unusually stable, both toward heat and metal ion catalysis as used in the Wolff rearrangement.[5]

EXPERIMENTAL[6]

Arndt-Eistert reaction with phenoxyacetyl chloride. An ether solution of diazomethane was prepared by the method of Arndt.[7] The intermediate nitrosomethylurea was prepared from 26 g. of *N*-acetyl-*N'*-methylurea according to the method of Amstutz and Myers.[8] A solution of 5.8 g. (0.034 mole) of phenoxyacetyl chloride in 20 ml. of dry ether was added dropwise over a period of *ca.* 30 min. to the dry diazomethane solution, cooled in ice, and protected by a calcium chloride drying tube. The reaction mixture was allowed to stand overnight at room temperature, and then the solvent was removed under reduced pressure at 20–30°. There remained a residual orange colored oil, which was dissolved in 55 ml. of absolute methanol and placed in a three-necked flask equipped with a mechanical stirrer and dropping funnel. The reaction flask was connected by a rubber hose to a 1-liter graduated cylinder inverted over a pan of water, thus providing a crude gasometer. A solution of 1.25 g. of silver benzoate in 11.4 g. of triethylamine was added over a period of 7 hr., with concomitant evolution of about 83% of the theoretical amount of nitrogen. The reaction mixture was heated under reflux for a few minutes, and the solvent then was removed under reduced pressure. An ether solution of the residual oil was washed first with 100 ml. of saturated sodium bicarbonate solution, then with 75 ml. of a 3% solution of hydrochloric acid. After drying over anhydrous magnesium sulfate, the solvent was removed and the residual oil distilled under reduced pressure. Two fractions were collected: (*a*) 1.00 g., b.p. 84–134° (24 mm.), n_D^{24}, 1.5183; and (*b*) 2.48 g., b.p. 134–138° (24 mm.), n_D^{24}, 1.5086. The literature[9] gives for methyl β-phenoxypropionate n_D^{20}, 1.5071 and b.p. 85° at 0.4 mm.

From a similar run, methyl β-phenoxypropionate (Fraction *b*, 1 g.) was hydrolyzed in 11 ml. of 0.5*N* sodium hydroxide, by heating on a steam bath for *ca.* 1 hr. The mixture was cooled, neutralized with concd. hydrochloric acid, and extracted with ether. The ether phase was then extracted with 5% sodium bicarbonate, which upon acidification gave white crystals of β-phenoxypropionic acid (0.12 g.),[10] m.p. 96–97° (lit.[11] m.p. 97–98°).

1-Diazo-3-phenoxy-2-butanone was prepared by the general method outlined in the preceding section. A solution of 12.4 g. (0.067 mole) of α-phenoxypropionyl chloride in 50 ml. of dry ether was added dropwise over a period of *ca.* 30 min. to a diazomethane solution prepared from the nitrosomethylurea from 49 g. of *N*-acetyl-*N'*-methylurea. The residual yellow oil from solvent removal solidified upon strong cooling. From a similar run, an analytical sample of the yellow

(1) Abstracted from a portion of a thesis submitted in partial fulfillment of requirements for the Ph.D. degree at the University of Nebraska by Loren L. Braun, 1956.

(2) M. S. Newman and P. F. Beal, *J. Am. Chem. Soc.*, **72**, 5161 (1950).

(3) Cyclization of β-phenoxypropionic acid to chromanone has been described by J. D. Loudon and R. D. Razdan, *J. Chem. Soc.*, 4299 (1954).

(4) W. E. Bachman and W. S. Struve, *Org. Reactions*, **I**, 48, 1942.

(5) A limited correlation is possible between our observation of unusual stability of V and that of H. R. Hensel [*Chem. Ber.*, **88**, 527 (1955)], who has noted that α-diazo-γ-(2,4-dichlorophenoxy)acetone retains nitrogen, even on heating with cupric oxide at 60° in petroleum ether, and at 100° with lead tetraacetate in dioxane.

(6) Melting points are uncorrected, and were observed in capillary tubes except where otherwise noted.

(7) F. Arndt, *Org. Syntheses*, **15**, 3 (1935).

(8) E. D. Amstutz and R. R. Myers, *Org. Syntheses*, **Coll. Vol. II**, 462 (1943).

(9) C. E. Rehberg and M. B. Dixon, *J. Am. Chem. Soc.*, **72**, 2205 (1950).

(10) The low yield of the acid is attributed either to impurity of the methyl ester (from incomplete Wolff rearrangement), or difficulty in controlling the hydrolysis of the pure ester. No decision appears possible between these alternative explanations at present.

(11) R. H. Hall and E. S. Stern, *J. Chem. Soc.*, 2035 (1949).

1-diazo-3-phenoxy-2-butanone was obtained by recrystallization from benzene–petroleum ether (b.p. 30–60°); m.p. 34–35° (Kofler hot stage[12]).

Anal. Calcd. for $C_{10}H_{10}N_2O_2$: 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-pentadiene[1]

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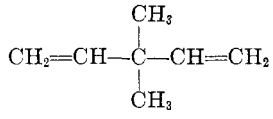
The previously unreported 3,3-dimethyl-1,4-pentadiene (I) is the simplest diene which cannot



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 accessible[2] 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 conversion[4] 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, reported[2] 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 C_7H_{12}: 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-dimethylpentane[5] 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

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF18(603)-132. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(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.