Reduction of 8.47 g. (0.01 mole) of I with excess alkaline glucose at 80° gave 5.77 g. (0.01 mole) of copper phthalocyanine (II) with the liberation of 0.85 g. (0.05 mole) of ammonia. A fluorescein test on the residue indicated the presence of phthalic acid or a derivative.

Pyrolysis of 8.47 g. (0.01 mole) of I at 180° gave 5.50 g. (0.0009 mole) of copper phthalocyanine (II) and 0.17 g. (0.01 mole) of ammonia. Phthalonitrile, m.p. 141°, sublimed and was collected; yield 2.56 g. (0.02 mole).

1-Amino-3-iminoisoindolenine. Phthalonitrile (128 g., 1.0 mole) and liquid ammonia (119 g., 7.0 moles) were placed in a 400-ml. stainless steel pressure vessel sealed with an aluminum gasket. The vessel was heated to 150° and shaken at that temperature for 5 hr. at about 500 p.s.i.g. It was then cooled, vented, and the product was discharged; yield 145 g. (100%). Titration with hydrochloric acid to an endpoint at *p*H 5.25, assuming monobasicity, indicated a purity of 99%.

Anal. Calcd. for $C_8H_7N_3$: C, 66.2; H, 4.83; N, 28.9. Found: C, 65.7, 65.9; H, 4.88, 4.76; N, 28.3; 28.2.

A sample of 1-amino-3-iminoisoindolenine was converted to I by the method of Brooks.[5] The product was identical to that prepared from phthalonitrile.

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[5] R. A. Brooks, U.S. Patent **2,772,285**, Nov. 22, 1956; *Chem. Abstr.*, **50**, 17464 (1956).

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

New Reactions on Decomposition of a Hindered α-Diazoketone[1]

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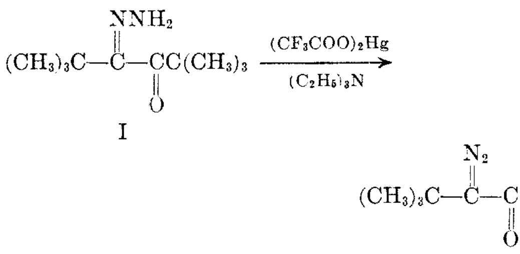
A new procedure for the conversion of monohydrazones of α-diketones to α-diazoketones by oxidation of the hydrazone with mercuric trifluoroacetate in acetonitrile in the presence of triethylamine is described. The rearrangements of 4-diazo-2,2,5,5-tetramethyl-3-hexanone under several conditions are described. The main product of these rearrangements is 2,2,4,5-tetramethyl-4-hexen-3-one, a product in which a methyl migration has occurred.

In connection with work on the synthesis of highly hindered aliphatic compounds we wished to prepare a quantity of di-*t*-butylacetic acid as it represents a disubstituted acetic acid with a *six number*[3] of eighteen. One method which appeared promising was the pyrolysis of 4-diazo,2,2,5,5-tetramethyl-3-hexanone, II, to di-*t*-butylketene (III)[4] a compound which would be expected to yield di-*t*-butylacetic acid on hydration.

The preparation of II was accomplished by a new method which involved oxidation of the monohydrazone of dipivaloyl (I) with mercuric trifluoroacetate and triethylamine in acetonitrile at room temperature. During this treatment about 20% of the theoretical amount of nitrogen to be expected from the diazoketone was evolved.



$$\underset{\text{I}}{(CH_3)_3C-\overset{\overset{\displaystyle NNH_2}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}C(CH_3)_3} \xrightarrow[(C_2H_5)_3N]{(CF_3COO)_2Hg} \underset{\text{II}}{(CH_3)_3C-\overset{\overset{\displaystyle N_2}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}C(CH_3)_3}$$

The entire reaction mixture thus obtained was then treated by three methods in attempts to obtain III. However, only minute amounts (0–3%) of ketene (III) were obtained by heating, either alone or in solvents, by treatment with boron trifluoride etherate, or by irradiation with ultraviolet light at 40°. The small amount of III obtained in any experiment precluded its isolation in sufficient quantity for analysis. However, by means of gas chromatography a homogeneous fraction was isolated which was undoubtedly the ketene (III) as judged by strong infrared absorption bands at 4.83μ and 5.80μ. This ketene III appears to be much more stable than other aliphatic ketenes, as no great tendency to dimerization was apparent. Because of the low yields of III obtained in spite of many attempts at improvement, this method for the synthesis of di-*t*-butylacetic acid was abandoned.[5]

Although the original purpose was not attained, the rearrangements of the diazoketone, II, produced results of interest. These are outlined in Chart 1.

The major product of pyrolysis (or irradiation, or acid-catalyzed rearrangement) was 2,2,4,5-tetramethyl-4-hexen-3-one (IV). In addition small amounts of 2,2,4,5-tetramethyl-5-hexen-3-one (V) and of a saturated (hence cyclic) ketone, $C_{10}H_{18}O$-(VI) were formed. In both IV and V a carbon skele-

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[1] The material herein presented was taken from the Ph.D. thesis, Ohio State University, 1958, of A. Arkell.

[2] This research was supported in part by the United States Air Force under Contract No. AF33(616)-3412, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

[3] M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950); K. L. Loening, A. B. Garrett, and M. S. Newman, *J. Am. Chem. Soc.*, **74**, 3929 (1952).

[4] For an example of the rearrangement of a *t*-butyl group in the decomposition of a diazoketone, see K. B. Wiberg and T. W. Hutton, *J. Am. Chem. Soc.*, **76**, 5367 (1954).

[5] The synthesis of di-*t*-butylacetic acid in good yield by another method will soon be reported.

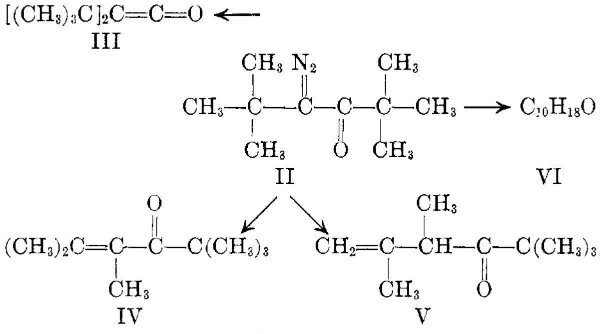

CHART I

tal rearrangement, involving migration of a methyl group to the carbon which held the diazo group, has occurred.[6] The structure of VI is in doubt as infrared spectral studies favor a polymethylated cyclopentanone structure, 2,2,4,4,5-pentamethylcyclopentanone, whereas a study of the NMR spectrum[7] favors formulation as *t*-butyl 2,2-dimethylcyclopropyl ketone, but neither line of evidence seems conclusive. We do not propose to study this compound further since the main purpose of the pyrolysis was the synthesis of di-*t*-butylketene.

The structure, 2,2,4,5-tetramethyl-4-hexen-3-one (IV) was assigned to the major product (near 80%) of the decompositions of II on the basis of the following facts. Analysis of a homogeneous sample, obtained by gas chromatography, indicated a formula of $C_{10}H_{18}O$. The ultraviolet absorption spectrum showed a maximum at 245 mμ (ϵ_{max}, 900), which compares with a maximum at 243 mμ (ϵ_{max}, 1400) for 2,6,6-trimethyl-1-acetylcyclohexene.[8] The very low intensity is typical of hindered α,β-unsaturated ketones.[9] In the present example, IV, the hindrance to coplanarity is severe because of the *t*-butyl group, whereas in other ketones under discussion[8] methyl ketones were involved. Compound IV absorbed strongly at 5.95μ in the infrared and formed a liquid 2,4-dinitrophenylhydrazone. No double bond absorption in the 6.0–6.4 or 11.1–11.3μ regions was observed.

The structure, 2,2,4,5-tetramethyl-5-hexen-3-one (V) present as a minor constituent (1–5%) in the products of decomposition of II by the methods described above, was assigned on the basis of the following facts. Analysis and gas chromatographic characteristics indicated that V was isomeric with IV. The ultraviolet absorption spectrum showed a maximum at 296.5 mμ (ϵ_{max}, 81). As compared to hexamethylacetone which has a maximum[10] at 295 mμ (ϵ_{max}, 20). The absorption maximum for a ketone having an isolated double bond should occur at about the same position as that of the corresponding saturated ketone.[11] In addition a strong band at 11.2μ in the infrared is characteristic of compounds having a terminal methylene group. V formed a 2,4-dinitrophenylhydrazone.

The following facts were obtained by a study of a small amount of VI which appeared homogeneous by gas chromatographic separation. Analysis indicated the formula, $C_{10}H_{18}O$, isomeric with IV and V. No hydrogen was absorbed on an attempted hydrogenation. The ketone, VI, absorbed at 286 mμ (ϵ_{max}, 59)[12] and its 2,4-dinitrophenylhydrazone absorbed at 360 mμ (ϵ_{max}, 20,600).[13] The infrared absorption was puzzling as there was a medium band at 5.65μ and a strong band at 5.90μ. Split carbonyl absorption bands have been observed before[14] but in no case has the spread been so large. The band at 5.90μ might be explained by a structure of *t*-butyl 2,2-dimethylcyclopropyl ketone[15] for VI, but one would expect an absorption at a higher wave length for this ketone since methyl cyclopropyl ketone absorbs at 5.87μ and polymethyl substitution in ketones generally increases the wave length of the carbonyl absorption.[16] In view of the latter effect, a structure of 2,2,4,4,5-pentamethyl cyclopentanone appears attractive for VI, except that the NMR evidence rules against this structure.[7]

EXPERIMENTAL[17]

2,2,5,5-Tetramethyl-4-hexanol-3-one (*pivaloin*). To a sodium dispersion prepared by rapid stirring of 93 g. of sodium and 2 g. of oleic acid in 300 ml. of dry toluene was added 850 ml. of toluene and then 260 g. of ethyl pivalate during a 3.5-hr. period. After stirring an hour, an ice cold solution of 210 g. of sulfuric acid in 350 ml. of water was added during 1 hr.

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(6) The formation of an α,β-unsaturated ketone with unrearranged carbon skeleton has been reported by V. Franzen, *Ann.*, **602**, 199 (1957). The rearrangement of triphenylmethyl diazomethane to triphenylethylene has been reported by L. Hellerman and R. L. Garner, *J. Am. Chem. Soc.*, **57**, 139 (1935).

(7) We thank Dr. George V. D. Tiers, Minnesota Mining and Manufacturing Co., for the NMR study and interpretation.

(8) H. B. Henbest and G. Woods, *J. Chem. Soc.*, 1150 (1952).

(9) For examples, see E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3766 (1955); E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3755 (1955); G. D. Hedden and W. G. Brown, *J. Am. Chem. Soc.*, **75**, 3744 (1953); N. J. Leonard and E. R. Blout, *J. Am. Chem. Soc.*, **72**, 434 (1950).

(10) F. O. Rice, *J. Am. Chem. Soc.*, **42**, 727 (1920).

(11) A. E. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy*, Edward Arnold Ltd., London (1954), pp. 62–3.

(12) R. C. Cookson, *J. Chem. Soc.*, 282 (1954) reports that camphor absorbs at 289.5 mμ (ϵ_{max}, 32).

(13) A. Kergomard and C. Sandris, *Bull. soc. chim.*, 1260 (1954) report that the 2,4-dinitrophenylhydrazone of camphor absorbs at 365 mμ (ϵ_{max} 23,100).

(14) See J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 618 (1957), for a discussion of split carbonyl absorption bands. Also P. Yates, N. Yoda, W. Brown, and B. Mann, *J. Am. Chem. Soc.*, **80**, 202 (1958).

(15) This suggestion was made by Dr. Tiers, ref. 7.

(16) P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77**, 2809 (1955).

(17) All melting points uncorrected unless otherwise noted.

The washed and dried toluene layer was cooled at −70° to yield pivaloin, m.p. 80–81°, in 86.5% yield.[18]

2,2,5,5-Tetramethyl-3,4-hexanedione (pivalil). After considerable study the following oxidative procedure was found to give excellent yields of pure pivalil. A pivaloin solution, A, was prepared from 86.2 g. of pivaloin, 210 ml. of acetic acid, 50 ml. of water, and 25 ml. of concentrated sulfuric acid (total volume, 380 ml.). A chromic acid solution, B, was prepared from 50 g. of chromic oxide, 100 ml. of acetic acid, and 50 ml. of water (total volume, 170 ml.). Ten similar small scale oxidations were run. In each 38 ml. of solution A was heated to 75° and with gentle stirring 17 ml. of solution B was added all at once. A vigorous reaction set in and quickly subsided. The hot mixture was then immediately poured on ice. The combined reaction mixtures were extracted with Skellysolve B (petroleum ether, b.p. 65–70°) and the extracts washed with 2% sodium hydroxide, saturated salt solution, and dried by filtration through magnesium sulfate. After removal of solvent and distillation 74.0 g. (87%) of pivalil, b.p. 66–67° and 19–20 mm., n_D^{20} 1.4163, was obtained.[19]

2,2,5,5-Tetramethyl-3,4-hexanedione monohydrazone, I. After refluxing a mixture of 85.2 g. of pivalil, 250 ml. of alcohol, 500 ml. of benzene, 100 g. of 98% hydrazine, and 2 ml. of acetic acid into a column equipped with a phase-separating head for 42 hr., no more aqueous phase was being formed. The reaction mixture was diluted with water and the organic layer distilled to yield 46.0 g. (50%) of solid I and 30.9 g. (36%) of recovered pivalil. A sublimed sample of I melted at 43.4–45.0° and was colorless.[20]

Anal. Calcd. for $C_{10}H_{20}N_2O$: C, 65.2; H, 10.9; N, 15.2. Found:[21] C, 65.2; H, 10.9; N, 15.2.

When a solution of I was passed through a column of alumina, I was absorbed. On elution with aqueous acetone crystals of a colorless compound, m.p. 43.8–44.2° were obtained in about 80% yield based on I. Absence of the NH band at 3.0μ and depression of melting point when mixed with I showed that a new compound had been formed. We believe this to be the acetone azine of I.

Anal. Calcd. for $C_{13}H_{24}N_2O$: C, 69.6; H, 10.8; N, 12.5. Found: C, 69.6; H, 10.6; N, 12.9.

Preparation and decomposition of 2,2,5,5-tetramethyl-4-diazo-3-hexanone, II. A filtered solution of 42.7 g. of mercuric trifluoroacetate (made by dissolving mercuric oxide in anhydrous trifluoroacetic acid) in 130 ml. of acetonitrile was added dropwise during 7 hr. to a magnetically stirred solution of 18.4 g. of I and 30 g. of triethylamine in 25 ml. of acetonitrile in a flask fitted to an azotometer. During this period, approximately 20% of the theoretical nitrogen was evolved. The filtered solution diluted with low boiling petroleum ether was washed with cold dilute 2% hydrochloric acid until neutral. After drying over magnesium sulfate the solvent was removed under reduced pressure and aliquots of the residual oil treated in one of the following ways: (*A*) heating 1- to 2-g. samples of II at 60–90°; (*B*) irradiation of 5.0 g. of II in 100 ml. of dry tetrahydrofuran for 15 hr. at 24–40°; and (*C*) catalytic decomposition by cuprous chloride in acetonitrile solution (3.0 g. of crude II in 15 ml.) at 24–26° during 12 hr. The products of pyrolysis were analyzed by gas chromatography.[22] By methods *A* and *B* the chief product was 2,2,4,5-tetramethyl-4-hexen-3-one (IV) which was present in 80–90% yield based on starting I. The amounts of di-*t*-butylketene (III) present were too small to allow for more than an infrared absorption spectral analysis which, however, was conclusive as a strong band at 4.83μ indicated the ketone function.[23] The analytical sample of IV had n_D^{20} 1.4424, λ_{max} 245, ϵ_{max} 900. The 2,4-dinitrophenylhydrazone, an oil, had λ_{max} 364, ϵ_{max} 23,200.

Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.8. Found: C, 77.8, 77.6; H, 11.6, 11.6. Calcd. for $C_{16}H_{22}N_4O_4$: C, 57.5; H, 6.6; N, 16.8. Found: C, 57.6; H, 6.6; N, 16.8.

The analytical sample of V had n_D^{20} 1.4324, λ_{max} 296.5, ϵ_{max} 81. The 2,4-dinitrophenylhydrazone of V was not obtained in quantities sufficient for analysis, but spectral analysis showed λ_{max} at 361 mμ, ϵ_{max} 23,200.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.8. Found: C, 77.6; H, 11.8.

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(18) Previously reported yields were 77% (in xylene), H. J. Backer, *Rec. trav. chim.*, **57**, 967 (1937); and 52–60% (in ether), J. M. Snell and S. M. McElvain, *Org. Syntheses* **13**, 36 (1933).

(19) N. J. Leonard and P. M. Mader, *J. Am. Chem. Soc.*, **72**, 5388 (1950) report for pivalil n_D^{20} 1.4144 (50% yield) in an oxidation by chromic acid at 14°. G. F. Hennion and T. F. Banigan, Jr., *J. Am. Chem. Soc.*, **68**, 1202 (1946) report n_D^{20} 1.4157 by oxidation of di-*t*-butylacetylene. Our sample of pivalil, on chromatography or vapor phase chromatography, was homogeneous and had n_D^{20} 1.4163.

(20) This compound was first prepared by G. R. Kahle, Ph.D. Thesis, Ohio State University, 1956, p. 66.

(21) All microanalyses by Galbraith Microanalytical Laboratory, Knoxville, Tenn.

(22) We acknowledge with thanks the valuable assistance of Mr. W. E. Lee and Dr. E. Malmberg in developing this analytical procedure.

(23) A. K. Bose and P. Yates, *J. Am. Chem. Soc.*, **74**, 4703 (1952).