p-**Methylbenzil-C^{14}.**—Similarly 2.3 g. of *p*′-methyldesoxybenzoin-*carbonyl*-C^{14} was treated with 1.82 g. of selenium dioxide in 3.5 ml. of acetic anhydride, to give 1.72 g. (70.2%) of *p*-methylbenzil, m.p. 31°[38]; radioactive assay, 2.38 $\times 10^{-3}$ μc./mg.

p-**Methoxybenzil-C^{14}.**—Acetic anhydride was found to be a poor solvent for the selenium dioxide oxidation of *p*′-methoxydesoxybenzoin, tending to give non-crystallizing oils. The oxidation was successful when 1.66 g. of the material was treated with 0.7 g. of selenium dioxide in 12 ml. of dioxane for three hours, to give 1.54 g. (87%) of *p*-methoxybenzil, m.p. 62.0°[39]; radioactive assay, 2.27 $\times 10^{-3}$ μc./mg.

p-**Chlorobenzilic-C^{14} Acid.**[40]—A 0.9-g. portion of *p*-chlorobenzil was added to 10 ml. of water and 5 ml. of ethanol to which had been added 4 g. of sodium hydroxide. Nitrogen was bubbled through the solution to remove air, and the solution was allowed to stand at room temperature for three days being stirred slowly with a magnetic bar. The solution was extracted with ether, acidified and re-extracted. The solid acid residue after evaporation of the ether was recrystallized several times from aqueous ethanol and dried *in vacuo*. The white crystalline product, m.p. 130°,[41] weighed 0.68 g., or 70% of the theoretical amount; radioactive assay, 4.76 $\times 10^{-3}$ μc./mg.

m-**Chlorobenzilic-C^{14} Acid.**—Following a similar procedure 1.0 g. of *m*-chlorobenzil was converted in alkaline aqueous alcoholic ethanol to 0.56 g. (52.1%) of white crystalline *m*-chlorobenzilic acid, m.p. 98°; radioactive assay, 3.74 $\times 10^{-3}$ μc./mg. *Anal.* Calcd. for $C_{14}H_{11}O_3Cl$: C, 64.11; H, 4.19. Found: C, 64.15; H, 4.21.

p-**Methylbenzilic-C^{14} Acid.**—Similarly, 0.383 g. of *p*-methylbenzil was converted to 0.2737 g. (66.2%) of *p*-methylbenzilic acid, m.p. 133°[38]; radioactive assay, 2.22 $\times 10^{-3}$ μc./mg.

p-**Methoxybenzilic Acid.**—By a similar procedure 440 mg. of *p*-methoxybenzil was converted to 200 mg. (42.3%) of *p*-methoxybenzilic acid, m.p. 148°[42]; radioactive assay, 2.08 $\times 10^{-3}$ μc./mg.

Degradation of *p*-Chlorobenzilic Acid.—All of the benzilic acid degradations were carried out similarly in an apparatus consisting of a 25-ml. reaction vessel with additional funnel and nitrogen inlet tube—connected to a short reflux condenser which was in turn connected to two traps containing barium carbonate solution. Before the barium hydroxide tubes were attached, the solid benzilic acid and dry chromic anhydride were added to the reaction vessel and the system was swept with dry nitrogen. The barium hydroxide tubes were connected, and a few ml. of glacial acetic acid was allowed to flow into the reaction flask. The reaction was allowed to proceed at room temperature with occasional gentle warming and constant magnetic stirring until barium carbonate began to form in the second trap. (The first trap contained an amount of barium hydroxide calculated to react with 90% of the released carbon dioxide.) This required about an hour and a half. The barium carbonate was collected by centrifugation, washed with carbonate-free water and dried at 100° *in vacuo*. The reaction mixture was diluted, neutralized and extracted to isolate the substituted benzophenone, which was purified by crystallization or converted to a derivative for radioactive assay.

In this way 432 mg. of *p*-chlorobenzilic acid was oxidized with 144 mg. of chromic anhydride in 3 ml. of acetic acid to yield 160 mg. of *p*-chlorobenzophenone (74%), m.p. 76°[43]; radioactive assay, *p*-chlorobenzophenone, 3.85 $\times 10^{-3}$ μc./mg.; barium carbonate, 2.0 μc./mg.

Degradation of *m*-Chlorobenzilic Acid.—A 300-mg. sample of *m*-chlorobenzilic acid was oxidized with 86 mg. of chromic anhydride to give 185 mg. (85.7%) of *m*-chlorobenzophenone, m.p. 84°[44]; radioactive assay, *m*-chlorobenzophenone, 3.70 μc./mg.; barium carbonate, 0.865 $\times 10^{-3}$ μc./mg.

Degradation of *p*-Methylbenzilic Acid.—A 99.49-mg. sample of *p*-methylbenzilic acid was oxidized with 31 mg. of chromic anhydride in one ml. of acetic acid to give 77 mg. (93%) of *p*-methylbenzophenone, m.p. 55°[45]; radioactive assay, *p*-methylbenzophenone, 2.08 $\times 10^{-3}$ μc./mg.; barium carbonate, 1.63 $\times 10^{-3}$ μc./mg.

Degradation of *p*-Methoxybenzilic Acid.—A 60-mg. portion of *p*-methoxybenzilic acid was oxidized by 16 mg. of selenium dioxide in 3 ml. of acetic acid to 39 mg. (79%) of *p*-methoxybenzophenone, m.p. 61°[46]; radioactive assay, *p*-methoxybenzophenone, 0.797 $\times 10^{-3}$ μc./mg.; barium carbonate, 1.57 $\times 10^{-3}$ μc./mg.

Acknowledgment.—We wish to acknowledge helpful and stimulating discussions with Dr. J. D. Roberts of the California Institute of Technology, Dr. Walter M. Lauer of the University of Minnesota, Dr. H. C. Urey and Dr. Weldon G. Brown of the University of Chicago and Dr. G. G. Smith of Washington State College.

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[39] *Cf.* A. McKinsie, E. M. Luis, E. M. Tiffeneau and P. Weill, *Bull. soc. chim.*, **45**, 414 (1929).

[40] The development of a proper nomenclature is difficult for a labeled compound such as this which is actually a mixture of unequal amounts of three kinds of molecules (actually many more than three, if the normal C^{-13} content is taken into account). It seems wiser to treat such compounds as mixtures, which are usually nameless in the absence of a trivial name. The C^{-14} is added to the name for cataloging purposes.

[41] A. H. Ford-Moore, *J. Chem. Soc.*, 952 (1947).

[42] E. Christie, A. McKensie and A. Richtie, *ibid.*, 153 (1935).

[43] *Cf.* R. Montagne, *Rec. trav. chim.*, **26**, 263 (1907).

[44] *Cf.* A. Hantzsch, *Ber.*, **24**, 57 (1891).

[45] *Cf.* T. Zincke, *Ann.*, **161**, 108 (1867).

[46] *Cf.* T. J. Peterson, *Am. Chem. J.*, **46**, 335 (1911).

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NOTRE DAME]

The Reaction of Some Diketones with Sodium Acetylide

BY R. B. DAVIS[1] AND P. HURD

RECEIVED NOVEMBER 22, 1954

A number of diketones were treated with sodium acetylide in liquid ammonia: acetonylacetone, diacetyl, benzil, acetylacetone, allylacetylacetone and diallylacetylacetone. The preparation of allylacetylacetone and diallylacetylacetone is described. It was also found that diacetone alcohol reacted with sodium acetylide to produce 3-methyl-3-hydroxy-1-butyne.

Milas and co-workers[2] and more recently Papa and co-workers[3] added sodium acetylide to acetonylacetone and diacetyl to produce diacetylenic-diols. The purpose of our investigation was to study the reaction of sodium acetylide with a number of diketones.

Sodium acetylide added to acetonylacetone and diacetyl, the former giving 3,6-dimethyl-3,6-dihydroxy-1,7-octadiyne (I) in 34% yield, and the latter, 3,4-dimethyl-3,4-dihydroxy-1,5-hexadiyne in the form of the hemihydrate II in 23% yield. Our results were interesting in that other workers[2,3] isolated compound II in the anhydrous form.

The structures of the products I and II were verified by tests for terminal acetylenic bonds, by char-

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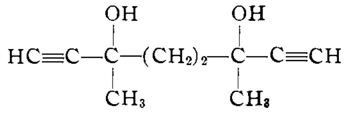
[1] Rev. Ralph B. Davis, C.S.C.

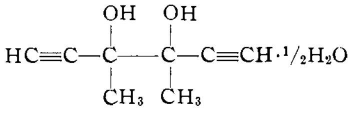
[2] N. A. Milas, R. J. Brown and O. Phillips, THIS JOURNAL, **70**, 2862 (1948).

[3] D. Papa, F. J. Villani and H. F. Ginsberg, *ibid.*, **76**, 4116 (1951).



$\mathrm{HC{\equiv}C{-}\underset{CH_3}{\overset{OH}{C}}{-}(CH_2)_2{-}\underset{CH_3}{\overset{OH}{C}}{-}C{\equiv}CH}$

I



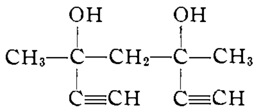
$\mathrm{HC{\equiv}C{-}\underset{CH_3}{\overset{OH}{C}}{-}\underset{CH_3}{\overset{OH}{C}}{-}C{\equiv}CH\cdot {}^1/_2H_2O}$

II

acteristic infrared absorption bands in the region of 4.7 μ,[4] indicating the presence of terminal acetylenic bonds, and by the absence of characteristic carbonyl bands in the region of 5.8 to 6.1 μ.

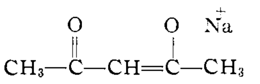
When one mole of benzil was treated with three moles of sodium acetylide in liquid ammonia, the expected addition product was not obtained. Instead, benzamide was obtained in 79% yield, calculated on the basis of an initial cleavage of benzil to benzamide and benzaldehyde. If, indeed, such a cleavage did occur, one would expect to obtain the acetylene addition product of benzaldehyde.[5] However, we were unable to isolate this compound from the viscous tarry material which was obtained along with the benzamide.

In an attempt to prepare the diacetylenic diol (III), acetylacetone was added to a large excess of sodium acetylide in liquid ammonia, an immediate precipitate formed, presumably the sodium salt of acetylacetone (IV) or acetylacetone amine (V), or both. After hydrolyzing the reaction mixture, we isolated acetylacetone amine (V) in 44% yield and the sodium salt of acetylacetone (IV) in 5% yield.



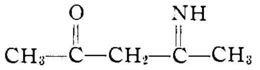
$\mathrm{CH_3{-}\underset{C\equiv CH}{\overset{OH}{C}}{-}CH_2{-}\underset{C\equiv CH}{\overset{OH}{C}}{-}CH_3}$

III



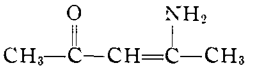
$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH{=}\overset{O\ \overset{+}{Na}}{\overset{|}{C}}{-}CH_3}$

IV



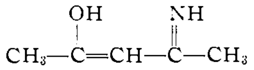
$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{NH}{\overset{\|}{C}}{-}CH_3}$

Va



$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH{=}\overset{NH_2}{\overset{|}{C}}{-}CH_3}$

Vb

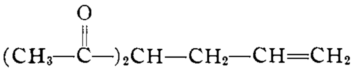


$\mathrm{CH_3{-}\overset{OH}{\overset{|}{C}}{=}CH{-}\overset{NH}{\overset{\|}{C}}{-}CH_3}$

Vc

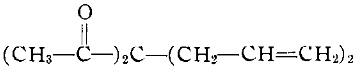
The identity of our product V was verified by the comparison of its properties to those of the compound originally described by Combes and Combes.[6] These authors preferred the structure Vb because their compound readily formed a hydrochloride. The identity of our product IV was verified by comparison to a sample of the same compound prepared from the reaction of acetylacetone and dilute sodium hydroxide.

Since the alkylation of acetylacetone greatly reduces the enolic character[7] of the diketone, it was thought that sodium acetylide might be added successfully to a mono- or dialkylacetylacetone. To this end we prepared allyl- and diallylacetylacetone (VI and VII).



$\mathrm{(CH_3{-}\overset{O}{\overset{\|}{C}}{-})_2CH{-}CH_2{-}CH{=}CH_2}$

VI



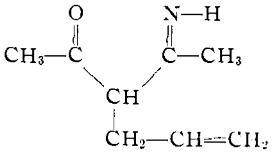
$\mathrm{(CH_3{-}\overset{O}{\overset{\|}{C}}{-})_2C{-}(CH_2{-}CH{=}CH_2)_2}$

VII

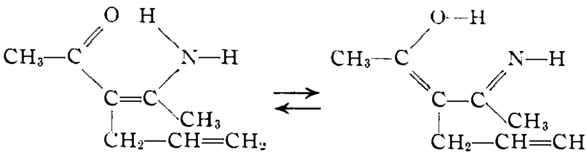
We are reporting the preparation and characterization of VI because the available literature on this matter is not complete. Claisen[8] apparently never published his experimental work, and English[9] with co-workers, although reporting the method of preparation, did not characterize the product. When acetylacetone was allowed to react with an excess of sodium hydroxide in methanol and subsequently with an excess of allyl bromide, VI and VII were obtained in 55 and 17% yields, respectively. As the monoallyl product distilled over a considerable range, and the various fractions showed considerable differences in index of refraction, it was suspected that our products might be contaminated with O-allylacetylacetone and O,C-diallylacetylacetone. However, the lowest and highest boiling fractions of the monoallyl product gave the same derivative with 2,4-dinitrophenylhydrazine and, after standing for four days, all fractions had the same index of refraction, leading us to believe that the original differences were due to the presence of keto and enol forms of the product VI.

That our products were the C-allyl compounds VI and VII, and not the O-allyl compounds was demonstrated by the fact that neither of our products was cleaved by refluxing in alcohol-hydrochloric acid. Corresponding O-allyl compounds are cleaved readily under such conditions.[10] Additional evidence supporting structures VI and VII also was obtained when on subsequent reactions, which will be discussed, our products were partially cleaved in basic solution to allylacetone and α,α-diallylacetone, respectively.

When allylacetylacetone (VI) was treated with sodium acetylide in liquid ammonia, we obtained 36% unreacted allylacetylacetone, allylacetone in 20% yield, indicating partial cleavage of VI, and allylacetylacetone amine (VIII) in 56% yield, which



VIIIa



VIIIb VIIIc

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[4] R. B. Davis and W. F. Erman, THIS JOURNAL, **76**, 3477 (1954).

[5] K. N. Campbell, B. K. Campbell and L. T. Eby, *ibid.*, **60**, 2882 (1938).

[6] A. Combes and C. Combes, *Bull. soc. chim.*, **7**, 778 (1892).

[7] J. B. Conant and A. F. Thompson, Jr., THIS JOURNAL, **54**, 4039 (1932).

[8] L. Claisen, "Beilstein," 4th ed., Vol. 1, p. 804 (412).

[9] J. P. English, J. H. Clark, J. W. Clapp, Doris Seeger and R. H. Ebel, THIS JOURNAL, **68**, 453 (1946).

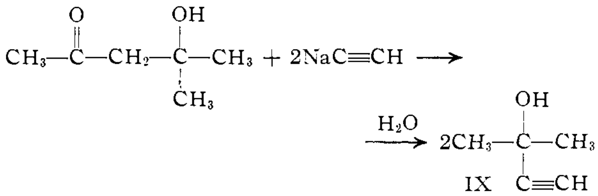
[10] C. D. Hurd and M. A. Pollack, *ibid.*, **60**, 1905 (1938).

was hydrolyzed readily by dilute acid or base to allylacetylacetone (VI).

It is our opinion that the true nature of allylacetylacetone amine is actually a mixture of the tautomeric structures VIIIb and VIIIc. In the case of acetylacetone amine (V), Combes and Combes[6] preferred structure Vb which corresponds to VIIIb on the basis that their product formed a hydrochloride. These authors did not consider the possibility of Vc which corresponds to VIIIc. Both acetylacetone and allylacetylacetone show absorption bands having peaks at approximately 5.85 μ, resulting from the carbonyl group.[11] Our product VIII showed no appreciable absorption in the region of 5.7 to 6.0 μ, which seems to exclude VIIIa. In addition, acetylacetone shows an absorption band in the region of 6.15 μ, resulting from the conjugated system, $\mathrm{HO{-}\underset{|}{C}{=}\underset{|}{C}{-}\underset{|}{C}{=}O}$[11]; allylacetylacetone shows a strong absorption band having a peak at 6.20 μ, resulting from the same conjugated system. Our product VIII shows a double headed absorption band having peaks at 6.22 and 6.32 μ, resulting from the conjugated system $\mathrm{HO{-}\underset{|}{C}{=}\underset{|}{C}{-}\underset{|}{C}{=}NH}$ or $\mathrm{O{=}\underset{|}{C}{-}\underset{|}{C}{=}\underset{|}{C}{-}NH_2}$, or both.

When diallylacetylacetone (VII) was allowed to react with a large excess of sodium acetylide in liquid ammonia, α,α-diallylacetone was obtained in 34% yield, resulting from the cleavage of VII, and 22% of VII was recovered unchanged.

Since the α,γ-diketones did not react with sodium acetylide to yield α,γ-diacetylenic diols, we investigated the possibility of producing a monoacetylenic α,γ-diol from the reaction of diacetone alcohol with sodium acetylide. However, the reaction produced 3-methyl-3-hydroxy-1-butyne (IX) in 32% yield, on the basis of one mole of diacetone alcohol producing two moles of IX.



Experimental[12]

3,6-Dimethyl-3,6-dihydroxy-1,7-octadiyne (I).—Following essentially the method of Campbell, Campbell and Eby,[5] 161 g. (7 moles) of sodium was used to make sodium acetylide, which was then treated with 342 g. (3 moles) of acetonylacetone, producing 169 g. of crude I, m.p. 89–90° (34% yield). The crude product was recrystallized from carbon tetrachloride with 91% recovery, forming needle-like crystals, m.p. 91–92° (lit. 92–92.5°[2] and 93–94°[3]). Compound I gave a positive test for terminal acetylene with ammoniacal silver nitrate. The infrared absorption spectrum of I showed a strong band at 3.05 μ, a weak band at 4.7 μ, and no appreciable absorption from 5.8 to 6.1 μ.

3,4-Dimethyl-3,4-dihydroxy-1,5-hexadiyne Hemihydrate (II).—In a similar manner, using 104 g. (4.5 moles) of sodium and 90 g. (1.04 moles) of diacetyl in 500 ml. of ether II was produced in 23% yield (36 g.), b.p. 76–78° at 6 mm., m.p. 47–49°, recrystallized from carbon tetrachloride, m.p. 48–49°. II gave a positive test for terminal acetylene with ammoniacal silver nitrate. The infrared absorption spectrum of II showed a strong band at 3.05 μ, a very weak band at 4.7 μ, and no appreciable absorption from 5.8 to 6.1 μ.

Anal. Calcd. for $C_8H_{10}O_2 \cdot {}^1/_2H_2O$: C, 65.29; H, 7.53. Found: C, 65.18; H, 7.71.

Preparation of Allylacetylacetone (VI) and Diallylacetylacetone (VII).—Sodium hydroxide, 135 g. (3.4 moles) was dissolved in one liter of methanol. After cooling the mixture using an ice-bath, 300 g. (3 moles) of acetylacetone was added with stirring over a period of one hour. Allyl bromide, 450 g. (3.7 moles), was then added without cooling over a period of two hours. The reaction mixture was refluxed for an additional two hours. It was then cooled and filtered to remove sodium bromide. Methanol and the excess allyl bromide were removed by distillation. Fractionation of the remaining liquid gave 229 g., 55% yield, of VI in five fractions: 32 g., b.p. 81° at 16 mm., $n^{25}\mathrm{D}$ 1.4748; 59 g., b.p. 81–82° at 16 mm., $n^{25}\mathrm{D}$ 1.4762; 42 g., b.p. 82–83° at 16 mm., $n^{25}\mathrm{D}$ 1.4725; 49 g., b.p. 83–85° at 16 mm., $n^{25}\mathrm{D}$ 1.4646; 47 g., b.p. 85–87° at 16 mm., $n^{25}\mathrm{D}$ 1.4568 (after four days of standing, all fractions $n^{25}\mathrm{D}$ 1.4757), density of third fraction, d^{25} 0.9687, derivatives with 2,4-dinitrophenylhydrazine of lowest and highest boiling fractions melted at 186–187°, with no depression on mixing; and 90 g., 17% yield of VII, b.p. 113–114° at 16 mm., $n^{25}\mathrm{D}$ 1.4691, d^{25} 0.9671, derivative with 2,4-dinitrophenylhydrazine decomposed at 235°.

Anal. Calcd. for $C_8H_{12}O_2$ (VI): C, 68.54; H, 8.63. Found: C, 68.73; H, 8.76 (3rd fraction). Calcd. for $C_{11}H_{16}O_2$ (VII): C, 73.30; H, 8.95. Found: C, 73.21; H, 9.13.

In an attempt to cleave VI,[10] 1 g. of this compound was refluxed with 40 ml. of ethanol and 0.5 ml. of concentrated hydrochloric acid for one hour. On cooling, and adding 2,4-dinitrophenylhydrazine, a derivative was obtained, m.p. 186–187°. On similar treatment, VII gave a derivative which decomposed at 237°. VI showed characteristic infrared absorption bands at 5.85 and at 6.20 μ.

Additional Reactions of Diketones with Sodium Acetylide. Benzil.—In the usual manner,[5] 210 g. (1 mole) of benzil was treated with 3 moles of sodium acetylide. After stirring the reaction mixture for four hours, 187 g. (3.5 moles) of ammonium chloride was added portionwise, and stirring was continued for one hour. After most of the liquid ammonia had evaporated, 1 l. of water and 0.5 l. of ether were added with vigorous stirring. The mixture was then centrifuged in portions. The ether and water layers were poured off, and the solid was washed with water and methanol. In all, 96 g. (79% yield) of crude benzamide, m.p. 120–122°, was obtained. After recrystallization from benzene with 80% recovery, the product melted at 130–131°. Upon refluxing 15 g. of the crude product with 150 ml. of 10% sodium hydroxide and then acidifying with 25% sulfuric acid, 9 g. (60% yield) of benzoic acid was obtained, m.p. 120–121°. From the combined ether layers of the centrifuging operation, 64 g. of viscous tarry material was obtained.

Acetylacetone.—Acetylacetone, 150 g. (1.5 moles), in 500 ml. of ether was treated with 4.3 moles of sodium acetylide.[5] After stirring the reaction mixture for four hours, 298 g. (5.5 moles) of ammonium chloride was added, and stirring was continued for one hour. After the liquid ammonia had evaporated, 500 ml. of water and 500 ml. of ether were added with vigorous stirring. The mixture was then filtered, the solid material being saved. The ether layer of the filtrate was separated, washed with brine and dried over magnesium sulfate. The ether was then distilled, the last traces being removed under vacuum. The residue solidified on cooling, 8 g. of V, m.p. 38–40°. The solid material obtained from filtering the reaction mixture was stirred for one hour with 500 ml. of acetone. This mixture was then filtered, and the filtrate was distilled. When most of the acetone had distilled, solid material appeared in the distilling flask. The flask was cooled, and the contents filtered, giving 9 g., 5% yield, of IV, decomposing at 288–292°. The filtrate was distilled under vacuum, yielding 12 g. of material boiling at 25–55° at 15 mm. The residue solidified on cooling, 58 g. of V, m.p. 38–40°. In all 66 g. of V, 44% yield, was obtained.

IV on recrystallization from ethanol–water decomposed at 295°. A sample of IV was prepared by adding acetylacetone to 10% NaOH, and cooling. The crude product

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[11] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, This Journal, **71**, 1068 (1949).

[12] Analyses by Micro-Tech Laboratories, Skokie, Ill.

decomposed at 290-295°; recrystallized from ethanol-water, it decomposed at 295°. Both samples burned in a flame leaving a grayish residue which when moistened with distilled water tested alkaline to litmus. Both samples and acetylacetone gave the same derivatives with 2,4-dinitrophenylhydrazine, melting at 122° (lit. 122°).[13]

Crude V melted at 38–40°, recrystallized from low boiling Skellysolve, m.p. 43° (lit. 43°[6]). After boiling with water, it gave the derivative of acetylacetone with 2,4-dinitrophenylhydrazine, melting at 122°.

Allylacetylacetone (VI).—Similarly, 140 g. (1 mole) of VI was treated with 3.5 moles of sodium acetylide. Fractionation of the products gave 14 g., 20% yield, of allylacetone, b.p. 69° at 100 mm., $n^{25}\text{D}$ 1.4178; 2,4-dinitrophenylhydrazone, m.p. 103–104° (lit. 104°[14]); 39 g., 36%, of unreacted VI, b.p. 82–84° at 16 mm., derivative with 2,4-dinitrophenylhydrazine, m.p. 185–186°, and a residue of 56 g., 56% yield, of crude allylacetylacetone amine (VIII), m.p. 63–66°, recrystallized from low boiling Skellysolve, m.p. 65–67°; derivative with 2,4-dinitrophenylhydrazine, m.p. 185–186°. On heating VIII with 10% sodium hydroxide, ammonia was evolved. The infrared spectrum of VIII showed a double headed absorption band having peaks at 6.22 and 6.32 μ, with no appreciable absorption from 5.7 to 6.0 μ.

Anal. Calcd. for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.07; H, 9.38; N, 10.14.

Diallylacetylacetone (VII).—When 0.47 mole (85 g.) of VII was treated with 4 moles of sodium acetylide in the usual way, the reaction mixture yielded 17 g., 34% yield, of α,α-diallylacetone, b.p. 66–67° at 15 mm., $n^{25}\text{D}$ 1.4448, semicarbazone, m.p. 109–110° (lit. 108°[15]), recrystallized from water-ethanol as the hemihydrate, m.p. 95–96° (lit. 95–96°[15]); and 19 g., 22%, of VII, b.p. 85–86° at 5 mm., $n^{25}\text{D}$ 1.4685, derivative with 2,4-dinitrophenylhydrazine decomposed at 234°.

Reaction of Diacetone Alcohol with Sodium Acetylide.—When 232 g. (2 moles) of diacetone alcohol was treated with 5 moles of sodium acetylide, the only product isolated was 107 g. (32% yield) of 3-methyl-3-hydroxy-1-butyne (IX), b.p. 103.5–104° (lit. 104°[16]), $n^{25}\text{D}$ 1.4187.

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[13] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., p. 262.

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The Acid-catalyzed Reaction of Hydrogen Azide upon Certain Alicyclic Alcohols[1]

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The reaction between hydrogen azide and each of five alicyclic alcohols in concentrated sulfuric acid at 15–25° was investigated. The formation of ketones, cyclic Schiff bases and other products was in agreement with carbonium ion theory.

The first investigations on the acid-catalyzed action between hydrogen azide and alcohols[2] were inadequately understood and the identity of the products obtained was not rigorously established. It was later suggested that the reaction might be explained by a carbonium ion mechanism, but additional experimental data was not offered.[3] A similar explanation was demonstrated for the acid-catalyzed reaction of hydrogen azide upon olefins[4] and accounted for the formation of aniline and acetophenone from both diphenylmethylcarbinol and 1,1-diphenylethylene.[5] Benzhydrol, fluorenol and triphenylcarbinol, curiously enough, were successfully transformed into the corresponding azides by the action of hydrogen azide in sulfuric acid.[6] Azides also were obtained from a series of 1,1-diarylethanols with hydrogen azide in trichloroacetic acid. This suggested that the azides were in equilibrium with their conjugate acids.[7] Presumably a high concentration of a strong acid repressed the dissociation of the conjugate acid. Earlier work on the acid-catalyzed decomposition of alkyl azides[8] was later reinterpreted in terms of initial formation of the protonated azide.[9]

As an outgrowth of investigations on the acid-catalyzed reactions of certain secondary alicyclic azides[10] and of primary azides,[11] a comparison with the acid-catalyzed reaction of hydrogen azide upon alicyclic alcohols was undertaken. This report consists in a reinvestigation of the application of the reaction to 2-methylcyclohexanol[2] and to menthol[2] and an extension of the reaction to cyclopentanol, cyclohexanol and cycloheptanol.

Each of the three unsubstituted alicyclic alcohols apparently was transformed into the corresponding carbonium ion with no rearrangement.[12,13] Whether or not the corresponding azides could be isolated from the acid-catalyzed reactions of alicyclic alcohols and hydrogen azide was not established. Instead the reactions accompanied by the evolution of nitrogen were investigated. The attraction between the electron deficient nitrogen atom, which resulted from the elimination of molecular nitrogen from the conjugate acid of the azide, and an electron pair of an adjacent bond brought about the formation of at least two products each from cyclopentanol, cyclohexanol and cyclohep-

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