

m.p. 122–123°, and anilide, m.p. 80–82° (lit.¹⁸ 125 and 88°, respectively). The latter did not depress the melting point of the anilide prepared from an authentic sample of the acid.¹⁹

3-Methylvaleric acid could only be derived from 3-methyl-3-pentenitrile (a 1,4-adduct) or 3-methyl-4-pentenitrile (a reverse 1,2-adduct). The infrared bands at 10.0 and 10.8 μ characteristic of the unsaturation in 4-pentenitrile were not present in the infrared spectrum of fraction I; therefore, the unsaturated nitrile present was 3-methyl-3-pentenitrile, resulting from a 1,4-addition of hydrogen cyanide to isoprene. Fraction II was shown by analysis to be a monoadduct.

Anal. Calcd. for C₆H₉N: C, 75.7; H, 9.5; N, 14.7. Found: Fraction II, 3, 75.5; H, 9.5; N, 14.3.

Hydrogenation and hydrolysis gave 4-methylvaleric acid, amide m.p. 118–119° (lit.²⁰ 119°), anilide m.p. 108–109° (lit.²¹ 111°). The latter did not depress the melting point of the anilide prepared from an authentic sample of the acid.²² This acid could only be derived from 4-methyl-3-pentenitrile (a 1,4-adduct) or 4-methyl-4-pentanitrile (a reverse 1,2-adduct). The nitrile showed no infrared adsorption at 3.25, 10.1, 10.4 or 11.3 μ , characteristic of terminal unsaturation. Hence, it must be 4-methyl-3-pentenitrile, resulting from 1,4-addition of hydrogen cyanide to isoprene. The two products, 3-methyl-3-pen-

tenitrile and 4-methyl-3-pentenitrile, were obtained in the ratio of about 1:3.

Dicyclopentadiene (run 15) reacted with hydrogen cyanide to give a mononitrile, but the location of the nitrile group was not established.

Anal. Calcd. for C₁₁H₁₂N: N, 8.8. Found: N, 8.5.

Bicyclo[2.2.1]-5-heptene-2-carbonitrile, prepared by the Diels-Alder addition of cyclopentadiene to acrylonitrile,²³ reacted with hydrogen cyanide (run 16) to give a semi-solid product at room temperature which was probably a mixture of geometric and/or position isomers. Filtration at room temperature gave an oil and a white solid.

Anal. Calcd. for C₉H₁₀N₂: C, 74.0; H, 6.9; N, 19.2; mol. wt., 146. Found: (solid) C, 74.4; H, 6.9; N, 18.7; mol. wt., 125, 130. Found: (oil) C, 74.3; H, 6.7; N, 18.2; mol. wt., 151, 145.

The dinitriles were hydrogenated over a cobalt catalyst in ammonia at 125–130° and 250 atm. to obtain a diamine in 90% yield, b.p. 100–101° (1 mm.), *n*_D²⁰ 1.5082, neut. equiv. 77.5 (calcd. for C₉H₁₄(NH₂)₂: neut. equiv., 77.1).

Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride, prepared by Diels-Alder addition of cyclopentadiene to maleic anhydride,²⁴ reacted with hydrogen cyanide (run 17). Recrystallization of the product from toluene-xylene mixture gave 31 g. of white crystals, m.p. 155–167°, probably a mixture of isomers.

Anal. Calcd. for C₁₀H₈O₃N: C, 62.8; H, 4.7; N, 7.3. Found: C, 63.2; H, 5.0; N, 7.8.

(23) H. A. Bruson, *ibid.*, **64**, 2457 (1942).

(24) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

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(18) W. H. Bentley, *J. Chem. Soc.*, **67**, 268 (1895).

(19) "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 416.

(20) W. Marckwald and E. Nolda, *Ber.*, **42**, 1589 (1909).

(21) H. Fourner, *Bull. soc. chim.*, [4] **6**, 924 (1909).

(22) W. A. Noyes, *THIS JOURNAL*, **23**, 393 (1901).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Photolysis of Diazomethyl *t*-Butyl Ketone

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RECEIVED MAY 5, 1954

The photolysis of diazomethyl *t*-butyl ketone has been investigated, and the structures of the products obtained have been determined. The major product was found to be α,γ -di-*t*-butyl- $\Delta^{\beta\gamma}$ -butenolide, and the principal by-product was 2,2,6,6-tetramethyl-4-heptenone-3. The results of the photolysis of diazoacetone and diazoacetophenone suggest that the formation of the butenolide is not a general synthetic method.

The photolysis of diazoketones with ultraviolet light has been investigated in order to determine whether this might be a convenient alternate method for effecting the Wolff rearrangement.¹ The advantages of such a method would be that steric hindrance should not affect this reaction and that diazoketones derived from optically active secondary acids might not be racemized under these conditions.² The ketene which is presumed to be an intermediate³ in the Wolff rearrangement might also be isolated. The results obtained by the irradiation of the pure liquid diazoketones are reported herein, whereas the results obtained in various solvents will be described in a later communication.

The first diazoketone investigated was diazomethyl *t*-butyl ketone (I). Irradiation of I with ultraviolet light led to nitrogen evolution with an accompanying decrease in the characteristic 4.81 μ

(1) The Wolff rearrangement has been effected by treatment with ultraviolet light in the case of a few aromatic diazoketones (*cf.* L. Horner, E. Spietschka and A. Gross, *Ann.*, **573**, 17 (1951)).

(2) J. F. Lane, J. Willenz, A. Weissberger and E. S. Wallis, *J. Org. Chem.*, **5**, 276 (1940), reported that the rearrangement of diazomethyl 1-phenyl-2-propyl ketone gave largely racemization. This was attributed to enolization on the catalyst surface (J. F. Lane and E. S. Wallis, *ibid.*, **6**, 443 (1941)).

(3) L. Wolff, *Ann.*, **394**, 23 (1912); F. Arndt and B. Eistert, *Ber.*, **68**, 200 (1935).

band of the diazoketone.⁴ The material obtained was distilled giving two compounds. The first (II) was a liquid with an empirical formula C₁₁H₂₀O and the second was a colorless low-melting solid III having the formula C₁₂H₂₀O₂ and was obtained in 62% of the theoretical amount.

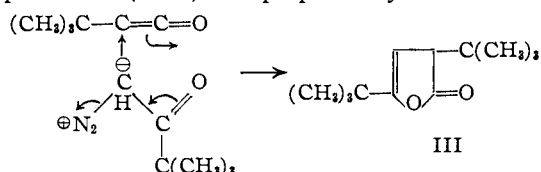
The solid III was found to react with potassium permanganate and with bromine, but it did not react with carbonyl reagents. The product of the reaction with bromine was found to have been formed by the addition of two atoms of bromine. The reduction of III with hydrogen and palladium-on-barium sulfate gave a saturated compound V with the absorption of one mole of hydrogen. The ultraviolet spectrum (λ_{\max} 224 m μ , ϵ_{\max} 2,450) indicated the absence of conjugate unsaturation, as is suggested also by the infrared spectrum. The 5.55 μ band in the infrared is suggestive of a strained ring carbonyl.

Treatment of III with base gave an isomer IV which had a conjugated double bond as indicated by the spectra (λ_{\max} 212 m μ , ϵ_{\max} 11,300; I.R. car-

(4) A. K. Bose and P. Yates, *THIS JOURNAL*, **74**, 4703 (1952) reported that diazoketones have a characteristic N=N band at 4.83 μ and that the carbonyl band is shifted to about 6.2 μ . The infra-red spectra of six diazoketones taken in this Laboratory showed a strong diazo band at 4.80–4.82 μ and a strong carbonyl band at 6.1–6.2 μ .

bonyl band, 5.68 μ). Potassium permanganate did not react with IV, but bromine in carbon tetrachloride did react with the liberation of hydrogen bromide. Hydrogenation of IV also led to the formation of V. These data suggest that III and IV are isomeric butenolides, with the former the β,γ -isomer and the latter the α,β -isomer.⁵ Further support for this type of structure may be found in the reaction of III with methanolic hydrogen chloride to give a mixture of a ketoacid VI and the corresponding methyl ester VII.

A reasonable structure for III would be α,γ -di-*t*-butyl- $\Delta^{\beta\gamma}$ -butenolide, which could be formed by the reaction of the diazoketone with the ketene. The synthesis of this compound was accomplished by the following route. 2,2,5,6,6-Pentamethyl-4-heptenone-3 (VIII) was prepared by the condensa-



tion of pinacolone with itself.⁶ Allylic bromination of VIII with *N*-bromosuccinimide was not satisfactory, and therefore the keto group was first blocked by conversion to the ethylene ketal IX. Treatment of IX with *N*-bromosuccinimide in carbon tetrachloride produced the bromo derivative X which was converted to the acetoxy compound XI by treatment with potassium acetate in dry ethanol. It was not possible to hydrogenate XI using Raney nickel at 70° or Adams catalyst at room temperature. Hydrogenation with palladium-on-barium sulfate proceeded very slowly and led to acetic acid and IX by hydrogenolysis.

Hydrolysis of XI in basic solution gave the ethylene ketal of 5-*t*-butyl-6-hydroxy-2,2-dimethyl-4-hexenone-3 (XII). Hydrogenation of XII resulted in simultaneous hydrogenation and hydrogenolysis of the hydroxyl group. Attempted manganese dioxide oxidation⁷ of XII to the corresponding aldehyde also proved unsatisfactory.

Treatment of XI with aqueous acid removed the ethylene ketal group, giving XIII which could be hydrogenated and hydrolyzed to 5-*t*-butyl-6-hydroxy-2,2-dimethylhexanone-3 (XV). The virtual absence of a carbonyl band in the infrared spectrum indicated that XV existed mainly as the hemiketal XVa. Oxidation of XV at pH 7 with potassium permanganate gave the ketoacid VI previously obtained from III. This keto acid could be converted to the $\Delta^{\alpha,\beta}$ -butenolide IV by heating to 180° in a sealed tube. Since this was not the isomer obtained in the photolysis, III was heated under similar conditions to give IV. This synthesis then established the proposed butenolide structures for III and IV.

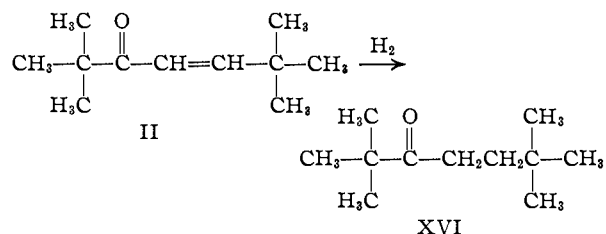
The liquid product II obtained from the photoly-

(5) The α,β -butenolides have a strong maximum (ϵ 9000–15,000) between 210–235 $m\mu$, whereas the β,γ -isomers have only weak absorption in this region ($\epsilon \sim 2000$) (D. W. Goheen, Ph.D. thesis, University of Washington, 1951). Also, the α,β -butenolides have a band at 5.70 μ in the infrared whereas the β,γ -isomers absorb at 5.54 μ (W. G. Dauben and P. D. Hance, *THIS JOURNAL*, **75**, 3352 (1953)).

(6) J. Colonge, *Bull. soc. chim.*, [5] **1**, 1101 (1934).

(7) S. Ball, T. W. Goodwin and R. A. Morton, *Biochem. J.*, **42**, 516 (1948).

sis of diazomethyl *t*-butyl ketone was an α,β -unsaturated ketone (probably β -alkyl substituted) as indicated by the ultraviolet absorption spectrum ($\lambda_{\max}^{\text{EtOH}}$ 228 $m\mu$, ϵ_{\max} 9,400)⁸ and also by the infrared spectrum. If one assumes that the *t*-butyl groups have survived the reaction intact, then the probable structure is 2,2,6,6-tetramethyl-4-heptenone-3.



The 2,4-dinitrophenylhydrazone of II would be expected to have λ_{\max} 376 $m\mu$ ⁹ which is quite different from the observed λ_{\max} 365 $m\mu$ which corresponds to a derivative of a saturated ketone. However, the 2,4-dinitrophenylhydrazone of 2,2,5,6,6-pentamethyl-4-heptenone-3 (VIII) which is structurally very similar to II has λ_{\max} 364 $m\mu$. The Fisher-Hirschfelder models of these derivatives are in accord with the supposition that the lack of conjugation is a consequence of steric crowding.

The hydrogenation of II with Adams catalyst proceeded slowly and gave a saturated ketone XVI whose dinitrophenylhydrazone was identical with that of 2,2,6,6-tetramethylheptanone-3 reported by Bartlett, Friedman and Stiles.¹⁰ Since the tetramethylheptenone II might be formed by loss of carbon monoxide from the lactone III during photolysis, the latter was subjected to irradiation, but failed to give any evidence of reaction. Thus, II was not formed through III as an intermediate.

Since α,γ -disubstituted butenolides are often not easily prepared, the photolysis of diazoketones might possibly be a good method for the preparation of these compounds. In order to test this possibility, the photolysis of diazoacetone and diazoacetophenone was investigated. These diazoketones were chosen because the butenolides which might result are known. When diazoacetone was irradiated, the product was a mixture boiling at a higher temperature than the expected butenolide. Diazoacetophenone, on irradiation, gave a mixture from which 9% of the theoretical amount of a solid, m.p. 287–288° could be isolated. This was identical with the lactone obtained by Anschütz and Montfort¹¹ by heating phenylphenacylacetic acid with acetic anhydride. This lactone, for which Pummerer and Buchta¹² have presented evidence for a dilactone structure XVII, was synthesized by heating phenylphenacylacetonitrile with 70% sulfuric acid.¹³ These results suggest that the irradiation of diazoketones is not a generally applicable

(8) L. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1949, p. 192.

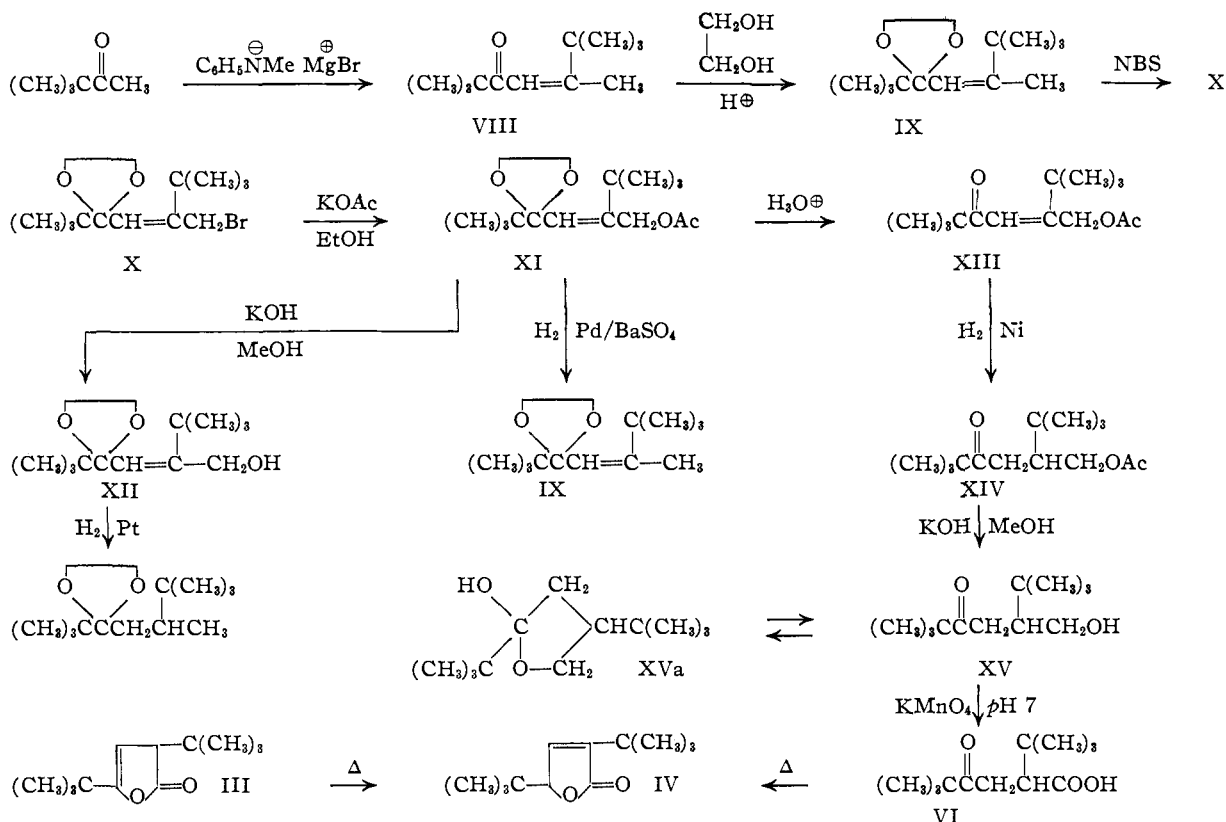
(9) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

(10) P. D. Bartlett, S. Friedman and M. Stiles, *THIS JOURNAL*, **75**, 1771 (1953). A sample of this ketone was kindly supplied by Dr. Bartlett.

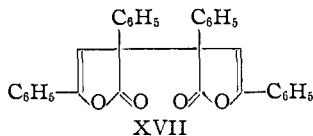
(11) R. Anschütz and W. F. Montfort, *Ann.*, **284**, 1 (1895).

(12) R. Pummerer and E. Buchta, *Ber.*, **69B**, 1005 (1936).

(13) A. C. O. Hann and A. Lapworth, *J. Chem. Soc.*, **85**, 1355 (1904).



method for the synthesis of α,γ -disubstituted butenolides.



Experimental¹⁴

Diazomethyl *t*-Butyl Ketone (I).—To an ether solution of diazomethane prepared from 215 g. (2.1 moles) of *N*-nitrosomethylurea was added 40.5 g. (0.34 mole) of pivaloyl chloride and the resultant solution was allowed to stand overnight. The solvent was then removed under reduced pressure at room temperature, and the residual material was distilled giving 39 g. (92%) of diazomethyl *t*-butyl ketone, b.p. 69° at 15 mm., n_D^{25} 1.4709, d_4^{25} 0.963.

Anal. Calcd. for $C_6H_{10}ON_2$: C, 57.1; H, 8.0; N, 22.2. Found: C, 57.3; H, 7.9; N, 22.0.

The ultraviolet absorption spectrum of I in 95% ethanol had λ_{max} 252 m μ , ϵ_{max} 8,760; λ_{max} 263 m μ (inflection), ϵ_{max} 8,150.

Irradiation of Diazomethyl *t*-Butyl Ketone.—Sixteen grams (0.13 mole) of I was placed in a quartz test-tube and was irradiated with a quartz enclosed 100-watt mercury arc (Hanovia). After three days the diazoketone had been consumed as evidenced by the disappearance of the characteristic 4.81 μ diazo band in the infrared spectrum. The gummy product was fractionated through a 30-inch twisted wire gauze column giving a low-boiling fraction II, b.p. 56–62° at 6 mm. (1.4 g.), n_D^{25} 1.437, followed by a white solid fraction III, b.p. 109–116° at 11 mm. (7.7 g., 62%). After three recrystallizations from ethanol-water, the solid melted at 41.5–42°. This latter fraction was shown to be α,γ -di-*t*-butyl- $\Delta^{\beta\gamma}$ -butenolide.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3; mol. wt., 196. Found: C, 73.2, 73.6; H, 10.5, 10.4; mol. wt., 199.

(14) All melting points are corrected whereas boiling points are uncorrected. Analyses were performed by B. Nist, T. Hutton and A. Elek.

The solid III gave a positive test with bromine and with potassium permanganate, but did not react with *p*-nitrophenylhydrazine or 2,4-dinitrophenylhydrazine. Its ultraviolet spectrum in ethanol had λ_{max} 224 m μ , ϵ_{max} 2,450.

α,γ -Di-*t*-butyl- $\Delta^{\alpha,\beta}$ -butenolide (IV).—To 0.142 g. of III was added 4 ml. of 15% sodium hydroxide solution, followed by heating on a steam-bath for several hours. It was necessary to shake the flask frequently in order to bring the crystals which sublimed into contact with the solution. After cooling, the solid was filtered from the solution, washed with water and dried. There was obtained 0.099 g. (70%) of white crystals melting at 85°. Sublimation at atmospheric pressure raised the melting point of IV to 92.5–93.5°.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3. Found: C, 73.3; H, 10.1.

The lactone IV failed to decolorize potassium permanganate solution and slowly decolorized a solution of bromine in carbon tetrachloride with the liberation of hydrogen bromide. The ultraviolet spectrum of IV in ethanol had λ_{max} 212 m μ , ϵ_{max} 11,300. It could also be obtained in good yield by dissolving III in 20% aqueous dioxane saturated with ammonia and allowing the solution to stand overnight at room temperature.

Reaction of III with Bromine.—To 0.20 g. of III was added a small excess of 4% bromine in carbon tetrachloride. After the rapid reaction, the solvent was removed giving 0.36 g. (99%) of the dibromide, m.p. 96–99°. After three recrystallizations from hexane, the material was obtained as white needles melting at 112.5–113.2°.

Anal. Calcd. for $C_{12}H_{20}O_2Br_2$: Br, 44.9. Found: Br, 45.2.

The dibromide hydrolyzed slowly on exposure to moist air as evidenced by the evolution of hydrogen bromide.

Hydrogenation of III.—The reduction of 0.182 g. (0.92 mmole) of III was carried out in absolute ethanol using 8% palladium-on-barium sulfate as the catalyst. The hydrogenation required 30 minutes for the consumption of 1.02 equivalents of hydrogen. After filtration, water was added to the solution which was then continuously extracted with pentane. Evaporation of the pentane gave 0.150 g. (83%) of dihydro-III (V) whose m.p. 73–77° was raised to 82–83° on sublimation.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.7; H, 11.2. Found: C, 72.8; H, 11.3.

When 0.088 g. (0.45 mmole) of IV was reduced in a similar manner, 1.10 equivalents of hydrogen was absorbed in seven minutes and 0.088 g. (99%) of V, m.p. 73–77°, was obtained. After sublimation, this material had m.p. 80–83° and did not depress the m.p. of V prepared from III. The infrared spectra of the two samples of V were identical in all respects.

Reaction of α,γ -Di-*t*-butyl- $\Delta^{\beta\gamma}$ -butenolide (III) with Methanolic Hydrogen Chloride.—To 0.70 g. (3.6 mmoles) of III dissolved in 4 ml. of methanol was added 4 ml. of saturated methanolic hydrogen chloride, followed by heating to reflux for three hours. The solution was concentrated to a small volume and then treated with water and extracted several times with small portions of pentane. Evaporation of the aqueous solution gave no residue. The pentane solution was extracted with three 3-ml. portions of 20% potassium hydroxide solution. After removing residual pentane from the aqueous solution under vacuum, it was acidified with 20% sulfuric acid giving 0.04 g. (5%) of a white solid, m.p. 70–75°. After sublimation at atmospheric pressure, α -*t*-butyl- γ,γ,γ -trimethyllevulinic acid (VI) was obtained as long white needles, m.p. 81.5–82.5°.

Anal. Calcd. for $C_{12}H_{22}O_3$: neut. equiv., 214. Found: neut. equiv., 214.

The pentane extract was filtered through anhydrous sodium sulfate and then evaporated giving 0.53 g. (65%) of an oil which on cooling to -20° gave crystalline material VII which was separated from residual oily material on a porous plate. VII had m.p. 34.5–35.5° and had two peaks in the infrared carbonyl region, at 5.77 and 5.84 μ . VII appears to be the methyl ester of VI.

Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.4; H, 10.6. Found: C, 68.3; H, 10.2.

Ethylene Ketal of 2,2,5,6,6-Pentamethyl-4-heptenone-3 (IX).—To 19.6 g. (0.108 mole) of 2,2,5,6,6-pentamethyl-4-heptenone (VIII, b.p. 97–102° at 19 mm., n_D^{25} 1.4483) in 150 ml. of C.P. benzene contained in a 500-ml. flask equipped with a Dean-Stark water separator was added 25 ml. of ethylene glycol and 0.1 g. of *p*-toluenesulfonic acid. After heating for 60 hours, 18.9 ml. of ethylene glycol-water mixture had been separated, and 19 ml. of ethylene glycol was added. After another 72 hours, an additional 21 ml. of ethylene glycol-water mixture had been removed. The benzene solution was washed with 20 ml. of 5% sodium bicarbonate solution, and then concentrated under reduced pressure. Distillation of the residue through a 12-inch packed column gave a forerun (b.p. 63–92° at 9 mm., 3.8 g., 19%) which was mainly unreacted starting material, followed by 14.8 g. (61%) of the ethylene ketal of VIII boiling at 92–99° at 9 mm., n_D^{25} 1.4499.

Anal. Calcd. for $C_{14}H_{26}O_2$: C, 74.3; H, 11.6. Found: C, 74.1; H, 11.3.

Ethylene Ketal of 6-Bromo-5-*t*-butyl-2,2-dimethyl-4-hexenone-3 (X).—To 100 ml. of C.P. carbon tetrachloride in a 200-ml. flask was added 10.3 g. (0.058 mole) of N-bromosuccinimide (recrystallized from water and air-dried), 13.0 g. (0.055 mole) of IX, 50 mg. of azobisisobutyronitrile and 0.2 g. of magnesium oxide. The solution was irradiated with a 75-watt lamp placed below the flask. After a few minutes, the solution became yellow and in 15 minutes the exothermic reaction was complete. After cooling, the solution was filtered and concentrated under reduced pressure. The residue was distilled, giving 15 g. (89%) of X having b.p. 111–113° at 2.2 mm., n_D^{25} 1.4870, d_4^{25} 1.166; M_D calcd. 75.25, found 75.29.

Anal. Calcd. for $C_{14}H_{26}O_2Br$: C, 55.1; H, 8.3. Found: C, 55.0; H, 8.2.

The 2,4-dinitrophenylhydrazone was prepared and was obtained as a yellow solid, m.p. 175.5–176° after recrystallization from ethanol-ethyl acetate.

Anal. Calcd. for $C_{15}H_{28}O_4N_4Br$: C, 49.0; H, 5.8. Found: C, 49.1; H, 6.0.

Ethylene Ketal of 6-Acetoxy-5-*t*-butyl-2,2-dimethyl-4-hexenone-3 (XI).—To a solution of 14.4 g. (0.047 mole) of X in 50 ml. of absolute ethanol was added 10 g. (0.11 mole) of freshly fused, powdered potassium acetate. After refluxing overnight, the solution was treated with 10 ml. of water and extracted three times with pentane. The pen-

tane solution was washed with 20 ml. of 1% sodium bicarbonate solution and dried over anhydrous sodium sulfate. After concentration, the residue was distilled from a small amount of Raney nickel giving 12.3 g. (92%) of XI, b.p. 87–88° at 0.25 mm., n_D^{25} 1.4572, d_4^{25} 0.987; M_D calcd. 78.48, found 78.54.

Anal. Calcd. for $C_{16}H_{28}O_4$: C, 67.6; H, 9.9; sapn. equiv., 284. Found: C, 67.8; H, 9.7; sapn. equiv., 292.

When the impure bromide X was treated directly with potassium acetate in ethanol, 22.5 g. of IX gave 22.6 g. (83%) of XI, b.p. 121–123° at 2.5 mm., n_D^{25} 1.4572.

Hydrogenation of XI with Raney nickel at 70° and 40 p.s.i. hydrogen pressure or with Adams catalyst at room temperature and atmospheric pressure was not successful. Using 0.5 g. of 8% palladium-on-barium sulfate, 8.83 g. (0.031 mole) of XI in 50 ml. of absolute ethanol consumed 0.88 equivalent of hydrogen in seven days. After filtration, the product was distilled giving a forerun of acetic acid followed by 6.3 g. of compound having b.p. 103–108° at 12 mm., n_D^{25} 1.4490. This material was identical with the ethylene ketal of 2,2,5,6,6-pentamethyl-4-heptenone-3 (IX) and was formed in 90% of the theoretical amount.

Ethylene Ketal of 5-*t*-Butyl-6-hydroxy-2,2-dimethyl-4-hexenone-3 (XII).—To 7.0 g. (0.025 mole) of XI was added a solution of 3.0 g. (0.054 mole) of potassium hydroxide in 30 ml. of methanol. After heating to reflux for one hour, the solution was cooled, treated with an equal volume of water and then extracted with three 30-ml. portions of pentane. The pentane solution was washed with water, dried over anhydrous sodium sulfate and distilled, giving 5.56 g. (92%) of XII having b.p. 117–20° at 3.8 mm., n_D^{25} 1.4648, d_4^{25} 0.972; M_D calcd. 68.98, found 68.91.

Anal. Calcd. for $C_{14}H_{26}O_3$: C, 69.4; H, 10.8. Found: C, 68.8; H, 11.1.

Hydrogenation of 3.47 g. (0.014 mole) of XII using Adams catalyst led to the absorption of 1.37 equivalents of hydrogen and gave as a product 2.21 g. of a compound having b.p. 63–66° at 4.7 mm., n_D^{25} 1.4383. The infrared spectrum showed no strong band corresponding to a hydroxyl group, carbonyl group or a carbon-carbon double bond. The compound is therefore probably the ethylene ketal of 2,2,5,6,6-pentamethylheptanone-3.

Under conditions which led to rapid oxidation of geraniol, XII failed to react with manganese dioxide.

6-Acetoxy-5-*t*-butyl-2,2-dimethyl-4-hexenone-3 (XIII).—To 7.00 g. (0.025 mole) of the ethylene ketal of 6-acetoxy-5-*t*-butyl-2,2-dimethyl-4-hexenone-3 (XI) was added 10 ml. of ethanol, 3 ml. of water and 2 drops of concentrated hydrochloric acid. The solution was heated on a steam-bath for two hours and after cooling, 10 ml. of water was added. Pentane extraction was followed by distillation giving 3.86 g. (65%) of XIII having b.p. 116–120° at 3.7 mm., n_D^{25} 1.4550, d_4^{25} 0.944; M_D calcd. 68.07, found 69.06. XIII had λ_{max} 231 $m\mu$, ϵ_{max} 9,300 (ethanol).

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 70.0; H, 10.1; sapn. equiv., 240. Found: C, 69.3; H, 9.8; sapn. equiv., 238.

6-Acetoxy-5-*t*-butyl-2,2-dimethylhexanone-3 (XIV).—The hydrogenation of 13.0 g. (0.054 mole) of XIII in 90 ml. of absolute methanol was effected using one-third teaspoon of W-4 Raney nickel and one to two atm. hydrogen pressure. After 1.5 hours, 0.59 equivalent of hydrogen had been absorbed, and consumption of hydrogen had ceased. After filtration the solution was distilled giving 8.2 g. (62%) of XIV having b.p. 115–116° at 2.5 mm., n_D^{25} 1.4441. XIV had no carbon-carbon double bond band in the infrared, and did not have a band between 210 and 240 $m\mu$ in the ultraviolet. A portion of the material solidified, and when dried on a porous plate had m.p. 39–41°.

Anal. Calcd. for $C_{14}H_{26}O_4$: C, 69.4; H, 10.8. Found: C, 69.5; H, 10.8.

When XIII was hydrogenated with palladium-on-barium sulfate or Adams catalyst, hydrogenolysis of the acetoxy group occurred in preference to the hydrogenation of the ethylenic group.

5-*t*-Butyl-6-hydroxy-2,2-dimethylhexanone-3 (XV).—To 3.44 g. (0.014 mole) of XIV was added a solution of 1.68 g. (0.03 mole) of potassium hydroxide in 20 ml. of purified methanol. After heating to reflux for two hours, the solution was cooled, diluted with 15 ml. of water and extracted with three 20-ml. portions of pentane. The solution was dried over anhydrous sodium sulfate and distilled giving

2.25 g. (80%) of XV having b.p. 61.5–62° at 0.55 mm., n_D^{25} 1.4476, d_4^{25} 0.923.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 71.9; H, 12.1. Found: C, 71.9; H, 12.0.

The virtual absence of a carbonyl band in the infrared spectrum of XV indicates that it exists mainly as the hemiketal XVa. Distillation of XV at 100° resulted in partial dehydration as evidenced by the appearance of carbon-carbon double bond band in the infrared spectrum.

α -*t*-Butyl- γ,γ,γ -trimethyllevulinic Acid (VI).—In a 125-ml. bottle equipped with a gas inlet tube which reached nearly to the bottom, and a suitable outlet, was placed 50 ml. of distilled water, 1.6 g. (0.008 mole) of XV and 1.70 g. (0.011 mole) of potassium permanganate. A slow stream of carbon dioxide was passed into the bottle while it was shaken until the permanganate had been consumed (9 days). The manganese dioxide was removed by treatment with oxalic acid and, after the solution had been made alkaline, it was extracted with three 20-ml. portions of pentane. Evaporation of the solvent gave 0.5 g. (31%) of unreacted starting material.

The alkaline solution was acidified with 20% sulfuric acid and then extracted with three 25-ml. portions of pentane. After drying over anhydrous sodium sulfate, the pentane solution was evaporated giving 0.51 g. (30%) of VI, m.p. 73–78°. Sublimation afforded pure VI, m.p. 81–82.5°.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.3; H, 10.4; neut. equiv., 214. Found: C, 67.1; H, 10.6; neut. equiv., 216.

Synthetic VI was found to be identical with the acid formed by reaction of III with methanolic hydrogen chloride.

Lactonization of α -*t*-Butyl- γ,γ,γ -trimethyllevulinic Acid.—In a glass tube was sealed 28 mg. of VI which was then heated to 180° for three days. The product was dissolved in pentane and washed with 5% sodium hydroxide solution. Evaporation of the solvent gave a solid which sublimed at 10 mm. and 80° to give 20 mg. (78%) of α,γ -di-*t*-butyl- $\Delta\alpha,\beta$ -butenolide (IV), m.p. 92.5–94°, identical with the material obtained by treatment of III with base. III was found to be converted quantitatively to IV on heating under similar conditions.

2,2,6,6-Tetramethyl-4-heptenone-3 (II).—The low-boiling fraction obtained from the irradiation of diazomethyl *t*-butyl ketone was redistilled through a 12-inch wire gauze packed column. The pure material had b.p. 87° at 29 mm., n_D^{25} 1.4368, d_4^{25} 0.855 λ_{max} 228 m μ , ω_{max} (ethanol).

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.5; H, 12.0. Found: C, 78.6; H, 11.8.

The 2,4-dinitrophenylhydrazone was obtained as a yellow

solid, m.p. 145–146° after recrystallization from ethanol. The ultraviolet spectrum had λ_{max} 365 m μ , ϵ_{max} 29,000 (ethanol).

Anal. Calcd. for $C_{17}H_{24}O_4N_4$: C, 58.6; H, 6.9. Found: C, 58.6, 58.7; H, 6.8, 6.9.

2,2,6,6-Tetramethylheptanone-3,2,4-dinitrophenylhydrazone.—The reduction of 0.166 g. (0.99 mmole) of II was carried out in 15 ml. of absolute ethanol using Adams catalyst. In 25 minutes, 0.81 equivalent of hydrogen had been used. A solution of 0.32 g. (1.6 mmoles) of 2,4-dinitrophenylhydrazine in alcohol was added to the hydrogenated material. After concentration to 20 ml. and cooling, 0.203 g. of the 2,4-dinitrophenylhydrazone was obtained, m.p. 98–103°. The crude material was dissolved in 3:1 hexane-benzene and chromatographed through alumina giving 0.200 g. of material having m.p. 127–128° which could be raised to 129–129.3° after recrystallization from ethanol. Water was added to the original filtrate which was then continuously extracted with hexane. The hexane solution was chromatographed giving an additional 0.023 g. of the dinitrophenylhydrazone (total 65%). It had λ_{max} 363 m μ , ϵ_{max} 22,000 (ethanol).

Anal. Calcd. for $C_{17}H_{24}O_4N_4$: C, 58.3; H, 7.5. Found: C, 58.2; H, 7.7.

A sample of 2,2,6,6-tetramethylheptanone-3 was kindly supplied by Dr. Bartlett.¹⁰ The 2,4-dinitrophenylhydrazone of this ketone was identical with the above derivative by m.p., infrared and ultraviolet spectra.

Photolysis of Diazoacetophenone.—Diazoacetophenone was prepared in the conventional manner from benzoyl chloride and diazomethane. After recrystallization from hexane, it had m.p. 46–46.5°.

In a 250-ml. flat-bottom quartz flask was placed 6.0 g. (0.041 mole) of diazoacetophenone which was irradiated for five days. The dark product was triturated with 50 ml. of acetonitrile and the cream-colored solid was filtered. There was obtained 0.42 g. (8.6%) of material having m.p. 255–258°. On recrystallization from anisole, dimethylformamide and anisole, the m.p. was raised to 268–270°.

The α,γ -diphenylbutenolide was prepared from benzylidene acetophenone by the method of Hann and Lapworth.¹³ After recrystallization, it had m.p. 268–270°. The material obtained in the photolysis was shown to be identical with this material by mixed m.p. and infrared spectrum. The butenolide was reported to have m.p. 288^{0.11,12} and it was noted that if the temperature of the melting point block was raised rapidly to 285° and then slowly raised, the butenolide had m.p. 287–288°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Deuterium Isotope Effect of Some Ionic Reactions of Benzaldehyde

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RECEIVED MAY 10, 1954

The chromic acid oxidation, Cannizzaro reaction and benzoin condensation have been studied using benzaldehyde- d_1 . The chromic acid oxidation was found to have a deuterium isotope effect, k_H/k_D , of 4.3, indicating that the cleavage of the carbon-hydrogen bond of the aldehyde is the rate-determining step. Since the reaction is acid catalyzed, the formation of an ester intermediate similar to that in the permanganate oxidation of benzaldehyde is suggested. The Cannizzaro reaction was found to have an isotope effect of 1.8. The observation of an isotope effect is in accord with the currently accepted mechanism, but the value is unusually low for an ionic reaction. The benzoin condensation appeared to give an isotope effect which evidenced itself as an induction period with the labeled aldehyde. It was also shown that exchange of the aldehyde hydrogen with the solvent occurred during the reaction at about the same rate as the condensation. These observations are not in agreement with the Lapworth mechanism.

Introduction

The deuterium isotope effect has proved to be of value in the elucidation of the mechanisms of a number of reactions,^{1,2} particularly oxidation proc-

(1) P. D. Bartlett and F. A. Tate, *THIS JOURNAL*, **75**, 91 (1953); R. P. Bell, "Acid-Base Catalysis," Oxford University Press, New York, N. Y., 1941, p. 146.

(2) (a) F. H. Westheimer and N. Nicolaidis, *ibid.*, **71**, 25 (1949); F. A. Loewus, F. H. Westheimer and B. Vennessland, *ibid.*, **75**, 5018 (1953); (b) K. B. Wiberg and R. Stewart, Abst. 124th Meeting, A.C.S., Chicago, Ill., 1953, p. 67.

esses.² Unfortunately, little is known concerning the magnitude of the effect for different types of reactions, and of the effect of substituents. It is therefore planned to measure the deuterium isotope effect for a number of reactions of benzaldehyde, toluene and their ring-substituted derivatives. The results of a study of the chromic acid oxidation, the Cannizzaro reaction and the benzoin condensation of benzaldehyde and benzaldehyde- c_1 are described herein.