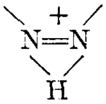
mation concerning the nature of the NH bond. No NH frequency was found below 3000 cm.$^{-1}$ Unfortunately, however, the spectrum of sodium perchlorate had a wide band at about 3200–3300 cm.$^{-1}$, which persisted in all the salts investigated here; this band was probably an overtone of a strong band at about 1600 cm.$^{-1}$ Consequently we were unable to observe any NH frequency in the conjugate acids of the azo compounds in the 3000–3400 cm.$^{-1}$ range, where we had anticipated that the absorption of the  $\overset{\diagdown\ +\ \diagup}{\underset{\diagdown\ \diagup \atop \mathrm{H}}{N{=}N}}$ group[2] would lie.

The infrared spectra of the compounds investigated are strikingly similar to the spectra of the free bases. Unfortunately, however, the spectra of *cis*- and *trans*-azobenzenes are so similar, that no decision can be made on the basis of these spectra concerning the stereochemistry of the conjugate acids.

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(2) H. H. Jaffé and R. W. Gardner, *J. Am. Chem. Soc.*, **80,** 319 (1958).

The Oxidation of 3,5,5-Trimethyl-1,2-cyclohexanedione by Hydrogen Peroxide

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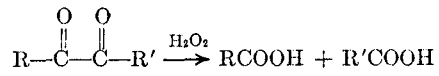
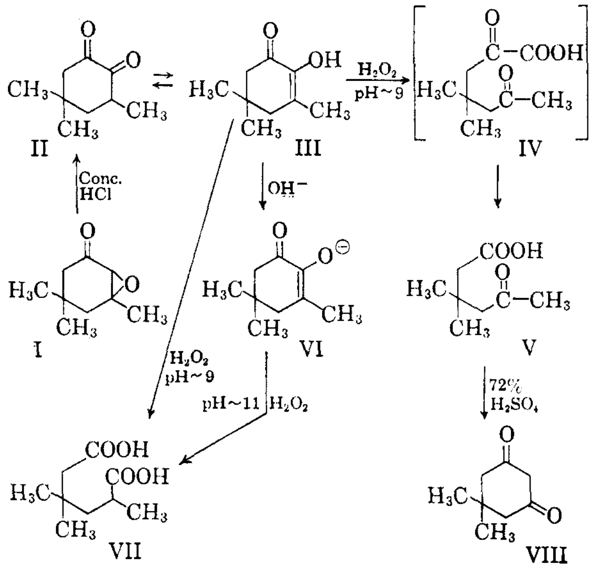
α-Diketones, on oxidation by hydrogen peroxide, are reported[1] to undergo cleavage according to the equation



$$R{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R' \xrightarrow{H_2O_2} RCOOH + R'COOH$$

We have observed, however, that with the *cyclic* α-diketone, 3,5,5-trimethyl-1,2-cyclohexanedione (II), which, by spectroscopic evidence,[2] must exist mainly in an enolic form such as III, the product obtained with hydrogen peroxide depends on the *p*H.

Under mildly alkaline conditions (*p*H *ca.* 9), using excess hydrogen peroxide and adding alkali continuously to neutralize the acidic product, there was obtained a 26% yield of *crude* α,γ,γ-trimethyladipic acid (VII) and a 55% yield of 5-keto-3,3-dimethylhexanoic acid (V). This unexpected product was probably formed by way of the α-keto acid, IV, since carbon dioxide was evolved on acidification of the reaction mixture.[3] Its structure was indicated by physical constants and suitable analyses, and confirmed by its known[4] cyclization to dimedone (VIII).



When one molar equivalent of hydrogen peroxide was added dropwise to the enolate anion, VI (formed by charging equivalent amounts of II and alkali), a mixture resulted. Esterification of the material provided a 23% yield of diethyl α, γ, γ-trimethyl-adipate. This yield was based on unrecovered ketone.

The starting material used in this brief investigation was prepared in 65% yield from isophorone oxide (I) by treatment with cold concentrated hydrochloric acid. The oxide was prepared from isophorone in 84% yield by the action of alkaline peroxide in ethanol at 30–35°.

EXPERIMENTAL[5]

Isophorone oxide. A solution of 138 g. (1.0 mole) of isophorone (redistilled, b.p. 100–102°/20 mm.) in 1300 ml. of ethanol was charged to a 3-liter, round-bottom flask and treated with stirring with a solution of 15 g. of sodium hydroxide in 150 ml. of water. With stirring and cooling at 30–35° was added 165 g. (1.5 moles) of 30% hydrogen peroxide over a period of 20 min. After an additional hour, the mixture was diluted with 2 l. of water and extracted with three 300-ml. portions of chloroform. The combined chloroform extracts were washed with water, dried over magnesium sulfate, and distilled through a 1 × 50 cm. glass helices-packed column to give 129 g. (84% yield) of isophorone oxide, b.p. 68–69° (5 mm.), n_D^{20} 1.4539 [lit.[2a] values: b.p. 70–73° (5 mm.); n_D^{25} 1.4510].

3,5,5-Trimethyl-1,2-cyclohexanedione. To 500 ml. of concentrated hydrochloric acid stirred at 0–5° was added 100 g. (0.65 mole) of isophorone oxide. The mixture was stirred

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(1) A. F. Holleman, *Rec. trav. chim.*, **23,** 169 (1904); J. Boeseken, *Rec. trav. chim.*, **30,** 142 (1911); E. Weitz and A. Scheffer, *Ber.*, **54B,** 2327 (1921).

(2) (a) R. L. Wasson and H. O. House, *J. Am. Chem. Soc.*, **79,** 1488 (1957); (b) H. S. French and E. T. Holden, *J. Am. Chem. Soc.*, **67,** 1239 (1945).

(3) α-Keto acids are readily cleaved by hydrogen peroxide; see ref. 1.

(4) T. Henshall, W. E. Silbermann, and J. G. Webster, *J. Am. Chem. Soc.*, **77,** 6656 (1955).

(5) All melting points are corrected.

in the cold for 3 hr. and then allowed to warm to room temperature over a 3-hr. period. After dilution with 1 l. of water, the solid product was collected by filtration, washed with water, and vacuum dried to a constant weight of 82 g., m.p. 80–85°. Recrystallization from petroleum ether afforded 65 g. (65% yield) of 3,5,5-trimethyl-1,2-cyclohexanedione, m.p. 91–92° (lit.[2a] m.p. 92–93°).

5-Keto-3,3-dimethylhexanoic acid. To a 1-l., 5-neck, round-bottom flask equipped with stirrer, thermometer, *p*H electrodes (connected to a Beckman *p*H meter), and dropping funnel was charged a solution of 38.5 g. (0.25 mole) of 3,5,5-trimethyl-1,2-cyclohexanedione in 300 ml. of methanol. The mixture was stirred at 40° and treated with a solution of 7 g. of potassium hydroxide in 30 ml. of water. One mole of 30% hydrogen peroxide was then added dropwise with cooling over a 15-min. period. During this addition, the meter reading changed from 11 to 8, while indicator paper showed a change from 10 to 7. There was next added dropwise a solution of 21 g. of potassium hydroxide in 90 ml. of water at such a rate as to maintain the meter reading at 9.8–10.0 (true *p*H *ca.* 9). After 1 hr., the alkali addition was complete and another 0.5 mole of hydrogen peroxide was added to compensate for the 0.5 mole loss by decomposition (oxygen evolution followed by means of a wet test meter connected to the system). The mixture was stirred for 1 hr. longer at a steady *p*H of 9.8; no further addition of alkali was necessary

After 12 hr., the mixture was diluted with 200 ml. of water and concentrated under vacuum to a volume of 150 ml. The concentrate was acidified with 30% sulfuric acid and extracted with three 100-ml. portions of chloroform. The combined chloroform extracts were washed with water, dried over magnesium sulfate, and concentrated to low volume on the steam bath. Claisen distillation gave 21.9 g. (55% yield) of 5-keto-3,3-dimethylhexanoic acid, b.p. 73–74° (0.2 mm.), n_D^{20} 1.4469 [lit.[6] values: b.p. 162° (25 mm.), $n_D^{19.5}$ 1.4465] and 11.1 g. of *crude* α,γ,γ-trimethyladipic acid, b.p. 130–135° (0.2 mm.).

Anal. Calcd. for the keto acid, $C_8H_{14}O_3$: C, 60.6; H, 8.9; neut. equiv., 158. Found: C, 60.4; H, 8.9; neut. equiv., 161.

The keto acid gave a positive iodoform test and a crystalline *2,4-dinitrophenylhydrazone* derivative, m.p. 149–150°.

Anal. Calcd. for $C_{14}H_{18}O_6N_4$: N, 16.5. Found: N, 16.4.

The keto acid was cyclized to *dimedone* by the procedure described in the literature[4]: a solution of 5.0 g. of the material in 50 ml. of 72% sulfuric acid was held at 130° for 2 hr. and then poured into 350 ml. of water to precipitate 2.6 g. of dimedone, m.p. and mixed m.p. 145–147°.

α,γ,γ-Trimethyladipic acid. To a stirred solution of 92 g. (0.60 mole) of 3,5,5-trimethyl-1,2-cyclohexanedione, 0.2 g. of magnesium sulfate (stabilizer), and 26 g. (0.65 mole) of sodium hydroxide in 500 ml. of water was added dropwise over 1 hr. 72 g. (0.65 mole) of 30.6% hydrogen peroxide. The temperature was held at 40–45° by means of a cooling bath; the *p*H, as determined by indicator paper, remained about 11 throughout the addition. After completion of the addition, the mixture was allowed to stir for 1 hr. longer before filtration was carried out to allow the recovery of 43 g. (0.28 mole) of starting diketone, m.p. and mixed m.p. 91–92°. Carbon dioxide was bubbled through the filtrate to neutralize excess caustic, and extraction with chloroform gave an additional 2.5 g. of crude starting material. After concentration of the aqueous solution to a volume of 150 ml., it was acidified with 30% sulfuric acid, saturated with solid ammonium sulfate, and extracted with five 200-ml. portions of ether. The combined ether extracts were washed with saturated ammonium sulfate solution, dried over magnesium sulfate, and concentrated to low volume on the steam bath.

Claisen distillation at 0.5 mm. pressure afforded *A*, b.p. 100–140° (11 g.), *B*, b.p. 140–150° (33 g.), and a residue of 3 g.

Fraction *B* represents a 56% yield of *crude* α,γ,γ-trimethyladipic acid based on unrecovered starting material.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.4; H, 8.6; neut. equiv. 94. Found: C, 57.9; H, 8.1; neut. equiv. 120.

Attempts to secure pure acid by recrystallization were unsuccessful, so 24 g. of the crude material was esterified with ethanol using *p*-toluenesulfonic acid catalyst. Distillation of crude ester through a 0.7 × 50 cm. glass spiral-packed column at 5 mm. gave 12.8 g. (23% yield based on unrecovered diketone) of *diethyl* α,γ,γ-*trimethyladipate*, b.p. 115–117°, n_D^{20} 1.4361 (lit.[7] values: b.p. 124°/9 mm.; n_D^{20} 1.4330).

Anal. Calcd. for $C_{13}H_{24}O_4$: C, 63.9; H, 9.9; sapon. equiv., 122. Found: C, 63.9; H, 9.7; sapon. equiv., 122.

The *free acid* was obtained by saponification of the ester with alcoholic sodium hydroxide. It was recrystallized from chloroform-isopentane by allowing the solution to stand for several hours at room temperature, then at 0° for several hours, and finally at −20°. From 10 g. of ester there was obtained 4.5 g. (60%) of recrystallized acid, m.p. 67.5–68.5° (lit.[7] m.p. 68.6–69.2°).

Anal. Calcd. for $C_9H_{16}O_4$: Neut. equiv., 94. Found: Neut. equiv., 95.

The *dianilide* was prepared via the acid chloride (not purified) and recrystallized from benzene, m.p. 162.5–163.5° (lit.[7] m.p. 162.8–163.3°).

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[6] M. Qudrat-I-Khuda, *J. Chem. Soc.*, 207 (1929).

[7] S. F. Birch and E. A. Johnson, *J. Chem. Soc.*, 1493 (1951).

Products of the Reaction between γ-Butyrolactone and Phenylmagnesium Bromide

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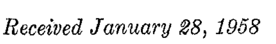
The reaction between phenylmagnesium bromide and γ-butyrolactone has been reported to yield 1,1-diphenylbutane-1,4-diol (I).[1] We have found that an increase in the concentration of acid used to decompose the Grignard adduct results in the formation of two other products, 2,2-diphenyltetrahydrofuran (II) and 1,1-diphenyl-1-butene-4-ol (III). These results are summarized in Table I.

$$(C_6H_5)_2C(OH)CH_2CH_2CH_2OH$$

I



$$(C_6H_5)_2CCH_2CH_2CH_2O$$

II

$$(C_6H_5)_2C{=}CH{-}CH_2CH_2OH$$

III

Examples of the formation of cyclic ethers analogous to II seem to be rare in this type of reaction. This structure was assigned on the basis of the infrared spectrum, which shows the characteristic absorption of the tetrahydrofuran ring at about

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[1] C. Weizmann and F. Bergmann, *J. Am. Chem. Soc.*, **60**, 2647 (1938).