0.33 mole) and methyl-γ-bromo-β-methoxortcyonate,[8] (70 g.; 0.33 mole) were dissolved in 1 liter of tetrahydrofuran (tetrahydrofuran was distilled from calcium hydride and mineral oil and stored over sodium prior to use). This solution was added dropwise through a dropping funnel into a dry 3-neck round bottom flask, equipped with stirrer and reflux condenser and containing finely cut zinc sheet metal (25 g.; 0.38 mole); the zinc metal, immediately prior to the reaction, was sanded, cut into small strips and washed consecutively with 25% hydrochloric acid, water, methanol, acetone and ether, and then dried at 100°. A small crystal of iodine was added to help initiate the reaction and the solution was refluxed with stirring for 5 hr. At the end of this time the reaction mixture (reddish-brown in color) was cooled to room temperature and added to a saturated solution of ammonium chloride (2.5 l.) with stirring. The mixture was extracted twice with $CHCl_3$ (1500 ml. portions) and the combined $CHCl_3$ extracts were washed once with water (500 ml.), filtered through anhydrous sodium sulfate and concentrated on the steam bath *in vacuo* to a resinous mass which on standing overnight at room temperature formed a solid mass of crystals. The material was triturated with ether (500 ml.), filtered and recrystallized from methanol (350 ml.) to give 35 g. (38%) of *dl*-methysticin, m.p. 132–134°. The ultraviolet spectrum showed $\lambda_{\text{max.}}^{\text{alc.}}$ (log ϵ): 226 mμ (4.40), 267 mμ (4.14), 306 mμ (3.93); $\lambda_{\text{min.}}^{\text{alc.}}$ (log ϵ): 218 mμ (4.37), 253 mμ (4.09), 284 mμ (3.80).

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.59; H, 5.15; $—OCH_3$, 11.23; M.W., 274. Found: C, 65.56; H, 5.25; $—OCH_3$, 11.35; M.W. (Rast), 285.

A comparison of the ultraviolet and infrared absorption spectra of this material with those of an authentic sample of natural methysticin showed them to be identical.

7-(3′,4′-methylenedioxyphenyl)-3-methoxy-2,4,6-heptatrienoic acid-1. *dl*-Methysticin was hydrolyzed by the procedure employed by Borsche and co-workers for the hydrolysis of natural methysticin,[9] giving a nearly quantitative yield of methysticic acid. The light yellow crystalline product was recrystallized from hot methanol; m.p. 196–197°.

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.54; H, 5.31.

Upon admixture with an authentic sample of methysticic acid, no depression of melting point was observed. The infrared and ultraviolet absorption spectra were identical.

6-(3′,4′-Methylenedioxy-β-phenethyl)-4-methoxy-5,6-dihydro-2-H-pyran-2-one. dl-Methysticin (300 g.) was dissolved in tetrahydrofuran (1.2 l.) and 10% Pd on carbon catalyst (10 g.) was added. The mixture was hydrogenated on a modified Parr apparatus at a pressure of 35 p.s.i., the uptake being completed within one hour. The solution was filtered free of suspended catalyst and the filtrate was taken to dryness *in vacuo* yielding crystals. The crude product was recrystallized from isopropyl alcohol (1.5 l.) to give needles (270 g.), m.p. 110–111°.

Anal. Calcd. for: $C_{15}H_{16}O_5$: C, 65.21; H, 5.84; $—OCH_3$, 11.23. Found: C, 64.99; H, 5.85; $—OCH_3$, 11.74.

The infrared and ultraviolet absorption spectra of this material were identical with those of an authentic sample of natural dihydromethysticin.

Acknowledgments. We wish to express our thanks to Messrs. C. H. Stimmel and A. Shimamura and Mrs. M. Hansen in the Analytical Section, Research Division, Riker Laboratories, for obtaining the spectral data.

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[8] F. Kogl and O. A. de Bruin, *Rec. Trav. Chim.* **69**, 729 (1950) *Chem. Abs.* **45**, 2416 (1951).

[9] W. Borsche, C. H. Meyer, and W. Peitzsch, *Ber.*, **60**, 2113 (1927).

Novel Rearrangement in the Oxidation of 3-Butylideneacetylacetone by Hydrogen Peroxide

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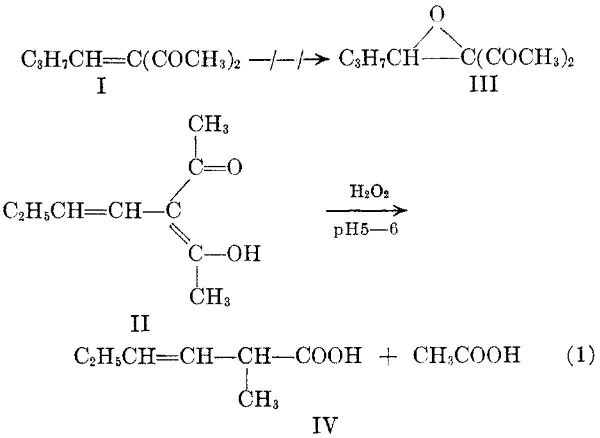
As part of a general survey concerned with the mode of reaction of various unsaturated materials with hydrogen peroxide under controlled *p*H conditions, the product from the condensation of *n*-butyraldehyde with acetylacetone was investigated. It was initially assumed that this product, 3-butylideneacetylacetone, would have structure I, and that it would probably afford the corresponding epoxy diketone (III) on treatment with hydrogen peroxide at the appropriate *p*H.



Surprisingly, *2-methyl-3-hexenoic acid* (IV) rather than III was obtained in 70% yield by the action of hydrogen peroxide at *p*H 5–6 and 38–40° for 1 hr. In view of this result, perhaps the structure of the starting material was not correctly described.

That II, 3-acetyl-2,4-heptadien-2-ol, should better represent this structure was indicated by analogy with the products obtained earlier from the reactions of propionaldehyde[1] and isovaleraldehyde[2] with acetylacetone. This belief was confirmed by infrared analysis which showed the condensation product to possess a highly enolized β-diketone system.[3]

Structure IV was established on the basis of physical constants and analysis as well as by direct comparison of its anilide and saturated anilide with authentic samples.

Confirmation of the position of the double bond in IV was obtained by treatment with iodine-sodium bicarbonate[4] to give the iodo lactone (V) in 87%

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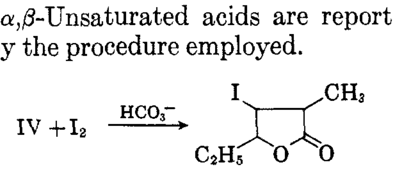
[1] M. E. McEntee and A. R. Pinder, *J. Chem. Soc.*, 4419 (1957).

[2] F. Tiemann and P. Krüger, *Ber.*, **28**, 2121 (1895).

[3] L. J. Bellamy, "Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, 1954, p. 123.

[4] R. P. Linstead and C. J. May, *J. Chem. Soc.*, 2565 (1927).

yield. α,β-Unsaturated acids are reported[4] not to react by the procedure employed.



V

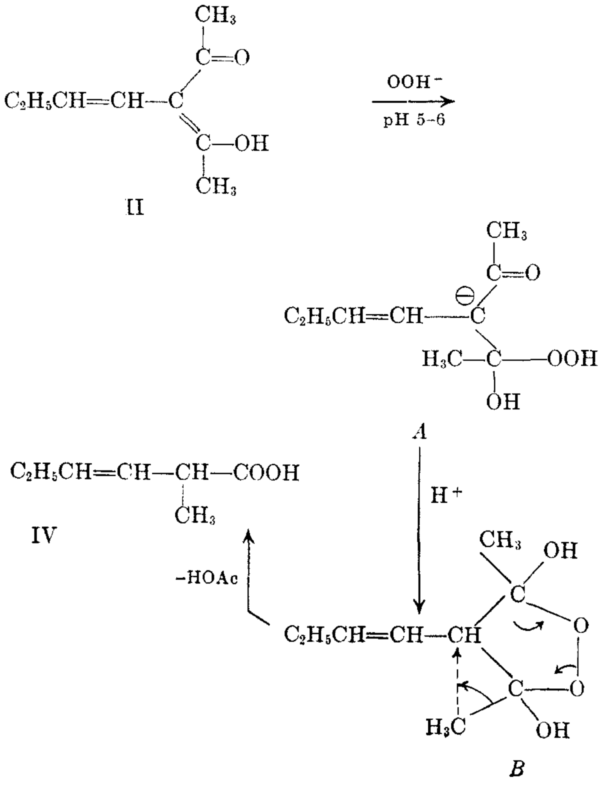
(2)

A few related experiments with II and hydrogen peroxide were carried out with the hope of learning something about the mechanism of the reaction. It was found, for example, that the reaction at pH 5–6 was exceedingly more rapid that at "ambient pH". Indeed, the uncatalyzed reaction in ethanol required 2 days at room temperature for 95% reaction or about 4 hr. at reflux. From the latter reaction, IV was secured in 62% yield.

The sulfuric acid-catalyzed reaction proceeded exothermally at 35° but with a consumption of peroxide greater than theory. Compound IV was obtained in 41% yield based on an 85% conversion of II.

That the reaction did not proceed via the enolate anion of II was indicated by a very slow reaction when II and 1 molar equivalent of alkali were treated with hydrogen peroxide. After 3 days at room temperature, the reaction was still only 70% complete; it was not further investigated.

Of the several possible mechanisms considered for this unusual reaction, the following is considered most reasonable. The initial driving force for the reaction would be the formation of carbanion A, resonance stabilized by both ethylenic and carbonylic linkages. A might reasonably be expected to form the symmetrical dihydroxy peroxide B,[5] with simultaneous addition of a proton. Peroxide cleavage with methyl migration in the manner indicated would then afford the observed product.



EXPERIMENTAL

3-Butylideneacetylacetone. To a solution of 443 g. (4.43 moles) of acetylacetone (n_D^{20} 1.4514) in 700 ml. of acetic acid was added a solution of 22 g. of piperidine in 100 ml. of acetic acid. This mixture was stirred at 35–40° while 319 g. (4.43 moles) of freshly distilled n-butyraldehyde was added over 1 hr. After an overnight stand at room temperature, the mixture was poured into 2 liters of water and extracted with two 500 ml. portions of chloroform. The combined chloroform was washed with sodium bicarbonate and then with water. Distillation of the dried solution through a 10-tray Oldershaw column gave 78 g. of recovered diketone, b.p. 30° (10 mm), n_D^{20} 1.4490, and 420 g. (75% yield based on unrecovered acetylacetone) of 3-butylideneacetylacetone, b.p. 83–84° (8 mm), n_D^{20} 1.4840.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.1; H, 9.1. Found: C, 70.0; H, 9.2.

Infrared analysis showed a broad band centered at 6.25 μ, characteristic of enolized β-diketones.[3] The sample also gave a characteristic[1] deep purple color with ferric chloride.

Reaction of 3-butylideneacetylacetone with hydrogen peroxide at pH 5–6. To a 1-liter, 5-neck round-bottom flask equipped with stirrer, thermometer, pH electrodes and dropping funnel, were charged 75 g. (0.49 mole) of 3-butylideneacetylacetone (3-acetyl-2,4-heptadiene-2-ol), 300 ml. of methanol and 42 g. (0.61 mole) of 50% hydrogen peroxide. The mixture was stirred at 38–40° and maintained at a meter pH of 5.1–5.3 (true pH of 5–6 by indicator paper) by the addition of 3N sodium hydroxide; ice bath cooling was required. After 45 minutes, 100 ml. of alkali had been added and an iodometric titration indicated the presence of 0.16 mole of peroxide. Another 25 ml. of alkali raised the pH from 5.2 to 5.4, indicating a strongly buffered solution. No further consumption of peroxide was observed during an additional 0.5 hr. at 30–35°. Another 75 ml. of caustic solution brought the pH to 5.7, while 100 ml. more caused the meter pH to rise to 9. The total alkali consumed amounted to 0.90 equivalent.

After concentration under vacuum to a volume of about 250 ml., the concentrate was acidified with 30% sulfuric acid and extracted with three 100 ml. portions of chloroform. After a water wash, the chloroform extract was concentrated on the steam bath and then distilled through a 0.7 × 50 cm. glass spiral-packed column at 5 mm. pressure. Slow takeoff was required at first for the removal of 6.6 g. of pre-cut, b.p. 80–95°. There was then secured 43.6 g. (70% yield) of 2-methyl-3-hexenoic acid, b.p. 95–96°, n_D^{20} 1.4388 (lit.[6] values: b.p. 121–122° (24 mm); n_D^{25} 1.4382).

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4; neut. equiv., 129. Found: C, 65.6; H, 9.4; neut. equiv., 128.

Acid chloride was prepared from 12 g. of acid by dissolving it in 50 ml. of benzene and adding 25 g. of oxalyl chloride. After standing at ambient temperature for 1 hr., the mixture was allowed to reflux for 2 hr. Claisen distillation afforded 9.7 g. (70% yield) of product, b.p. 150–155°.

Anilide was prepared from the acid chloride by dissolving the latter (9.7 g., 0.066 mole) in 50 ml. of benzene and adding 12.3 g. (0.132 mole) of aniline. The mixture was brought to a boil on the steam bath and held there for 10 minutes. After cooling, this mixture was washed successively with water, dilute acid, dilute alkali and water. After concentration to a volume of 50 ml., 100 ml. of Skellysolve B was added and the

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(5) A cyclic hydroxy peroxide was recently isolated from the alkaline epoxidation of mesityl oxide; see G. B. Payne, *J. Org. Chem.*, **23**, 310 (1958).

(6) A. C. Cope and C. M. Hofmann, *J. Am. Chem. Soc.*, **63**, 3456 (1941).

solution chilled to precipitate 9.0 g. of anilide, m.p. 94–95°. Recrystallization did not alter the melting point.

Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.8; H, 8.4. Found: C, 76.7; H, 8.5.

The anilide (2.03 g.) was *hydrogenated* in 50 ml. of ethanol using 500 mg. of 10% palladium on charcoal catalyst and 50 pounds of hydrogen. One molar equiv. of hydrogen was absorbed in 20 minutes and the product was isolated by precipitation from the concentrated (10 ml.) ethanol solution, m.p. 95–96°.

Authentic samples of both the unsaturated and saturated anilides were prepared as above from authentic 2-methyl-3-hexenoic acid[6] and melted at 94–95° and 95–96°, respectively. The respective mixed melting points were not depressed.

Reaction of 3-butylideneacetylacetone with hydrogen peroxide in ethanol. A solution of 98 g. (0.64 mole) of diketone and 80 g. (0.70 mole) of 30% hydrogen peroxide in 300 ml. of ethanol was allowed to reflux gently for 4.5 hr. and then concentrated to low volume on the steam bath. Distillation of the residue through a 0.7 × 50 cm. glass spiral-packed column gave 13 g. of crude recovered starting material, b.p. 60–90° (5 mm) and 50 g. (62% yield based on ketone charged) of 2-methyl-3-hexenoic acid, b.p. 79–80° (2 mm); n_D^{20} 1.4393.

When the above reaction was carried out at room temperature, 2 days were required for 95% consumption of the theoretical amount of peroxide and after 5 days the mixture was vacuum-flashed *at room temperature* to give 65 mole % of volatile acid. The latter was identified as acetic by means of the *p*-bromophenacyl ester, m.p. and mixed m.p. 83–84°. Claisen distillation of the residue from the flashing operation gave a 70% yield of crude product, b.p. 105–115° (20 mm); the purity was 87% by neut. equiv.

Reaction of 2-methyl-3-hexenoic acid with iodine. The procedure used was that described in the literature.[4] A 2.19 g. (0.0171 mole) sample of unsaturated acid was dissolved in 25 ml. of saturated sodium bicarbonate solution and treated with 3 gram-atoms of iodine (from a solution made from 25 g. of iodine, 40 g. of potassium iodide and 125 ml. of water). After 2 hr. at room temperature, the solution was treated with 5 g. of sodium carbonate and extracted with ether. The ether extract was washed with dilute sodium thiosulfate solution, water, and dried. Concentration under vacuum gave 3.78 g. (87% yield) of crude solid product. Recrystallization from petroleum ether afforded 2-methyl-3-iodo-4-hexanolactone, m.p. 28–30°.

Anal. Calcd. for $C_7H_{11}IO_2$: C, 33.1; H, 4.4; I, 49.9; sapon. equiv., 254. Found: C, 33.2; H, 4.3; I, 49.0; sapon. equiv., 260.

EMERYVILLE, CALIF.

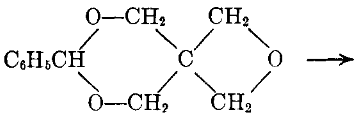
7-Phenyl-2:6:8-trioxaspiro(3,5)nonane: A High Yield Reduction with Lithium Aluminum Hydride[1]

RIYAD F. NASSAR AND COSTAS H. ISSIDORIDES[2]

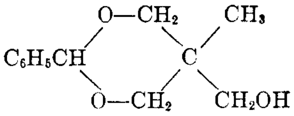
Received July 7, 1959

In recent years, several reports have appeared in the literature on the reductive cleavage of oxetanes by lithium aluminum hydride. In 1954, Büchi[3] prepared 2-phenyl-3,3,4-trimethyl oxetane and attempted to reduce it with lithium aluminum hydride, but reported that no detectable reaction took place even at elevated temperatures. The stability of a highly substituted 1,3 oxide to lithium aluminum hydride has also been noticed by Allen.[4] The first successful reductive cleavage of oxetanes was reported almost simultaneously by this laboratory[5] and by Searles, Pollart and Lutz.[6] In their excellent and thorough study of ten oxetanes having two or fewer alkyl substituents, Searles and his coworkers found that the ease of cleavage was markedly affected by substitution, particularly by *gem*-dialkyl substitution at position 3, which caused marked deactivation. This deactivation was attributed to two factors: The Thorpe-Ingold effect and the relatively low basicity of such oxetanes.

In conjunction with other work carried out in this laboratory on derivatives of pentaerythritol, we had the opportunity to prepare 7-phenyl-2:6:8-trioxaspiro (3,5) nonane (I). Since this oxetane has a spirocyclic structure in addition to having two substituents at position 3, we thought it of interest to study its response to lithium aluminum hydride. The reaction proceeded smoothly in tetrahydrofuran, giving 5-methyl-5-hydroxymethyl-2-phenyl-1,3-dioxane (II) in excellent yield (90%).



(I)



(II)

The structure of (II) was proved by independent synthesis from benzaldehyde and trimethylolethane.

In view of the strong deactivation associated with 3,3 dialkyl substitution in the reaction of oxetanes with lithium aluminum hydride, it is remarkable that (I) is cleaved by this reagent in nearly quantitative yield. The reason why the spirocyclic compound is so vulnerable to this reagent is not entirely clear. One possible explanation lies in the fact that in (I) the substituents at position 3 are "held back" by the six membered ring thus failing to diminish the distortion of the

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[1] Abstracted in part from the M.S. thesis of Riyad F. Nassar, American University of Beirut, June 1959.

[2] To whom requests for reprints should be addressed.

[3] G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, 76, 4327 (1954).

[4] W. S. Allen, S. Bernstein, M. Heller, and R. Littell, *J. Am. Chem. Soc.*, 77, 4784 (1955).

[5] C. H. Issidorides and N. S. Aprahamian, *J. Org. Chem.*, 21, 1534 (1956).

[6] S. Searles, K. A. Pollart, and E. F. Lutz, *J. Am. Chem. Soc.*, 79, 948 (1957).