Bromination of 0.1 g. of the *cis* isomer in 4 ml. of *n*-pentane by addition of 0.09 g. of bromine in 1 ml. of this solvent gave a precipitate of dibromide (complete within a few minutes); yield 0.16 g. (90%); m. p. 159–160°; it was identified by recrystallization from ethanol (m. p. 159.5–160.5°) and by mixture melting point with a sample prepared from the *trans* isomer.[6]

The ultraviolet absorptions of I and II were determined in isoöctane (0.00005 molal) using a Beckman DU Quartz spectrophotometer. For the *trans* isomer, ϵ = 23,600, maximum at 298 mμ (minimum, ϵ = 5,100 at 240 mμ); for the *cis* isomer, ϵ = 14,000 at 248 mμ and 8,950 at 290 mμ (minimum, ϵ = 7,800 at 270 mμ).

---

(6) Allen, Abell and Normington, "Organic Syntheses," Coll. Vol. II, 2nd ed., 1944, p. 205.

Summary

A labile, yellow *cis*-benzalacetophenone has been isolated from an equilibrium mixture obtained by exposure of *n*-pentane or isoöctane solutions of the *trans*-isomer to sunlight.

CHARLOTTESVILLE, VA. RECEIVED FEBRUARY 13, 1950

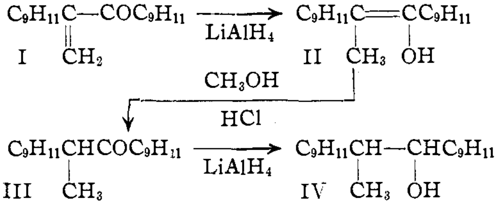
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

1,4-Reduction of an α,β-Unsaturated Ketone by Lithium Aluminum Hydride[1]

BY ROBERT E. LUTZ AND DAVID F. HINKLEY

The demonstration that unsaturated 1,4-diketones react chiefly 1,4 with lithium aluminum hydride as they do with the Grignard reagent[2] suggested the study of a simpler α,β-unsaturated ketone, one possessing structural features which would favor 1,4-addition and render the resulting enol persistent and isolable.

Such a compound, 1,2-dimesitylpropenone (I),[3] reacts readily with lithium aluminum hydride to give the enol (II, known) which is evidently stabilized and protected in the form of the lithium salt. The enol (II), liberated upon hydrolysis of the reaction mixture, is ketonized by methanolic hydrogen chloride to 1,2-dimesitylpropanone (III). The latter compound is reduced to the corresponding alcohol (IV) by lithium aluminum hydride under the conditions used above. Thus 1,4-addition of an α,β-unsaturated ketone is here demonstrated rigorously by actual isolation of the alternatively possible 1,2-addition product (III).



$$\mathrm{I}\quad \mathrm{C_9H_{11}\underset{CH_2}{\underset{\|}{C}}{-}COC_9H_{11}} \xrightarrow[\mathrm{LiAlH_4}]{} \mathrm{II}\quad \mathrm{C_9H_{11}\underset{CH_3}{C}{=}\underset{OH}{C}C_9H_{11}}$$

$$\Big\downarrow\ \begin{matrix}\mathrm{CH_3OH}\\ \mathrm{HCl}\end{matrix}$$

$$\mathrm{III}\quad \mathrm{C_9H_{11}\underset{CH_3}{C}HCOC_9H_{11}} \xrightarrow[\mathrm{LiAlH_4}]{} \mathrm{IV}\quad \mathrm{C_9H_{11}\underset{CH_3}{C}H{-}\underset{OH}{C}HC_9H_{11}}$$

Small but characteristic differences in the ultraviolet absorptions of these and some related compounds are shown in Fig. 1.

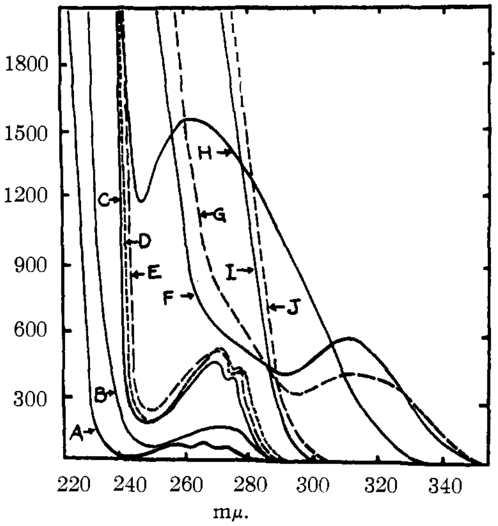


Fig. 1.—(M is mesityl): A, MH; B, $\mathrm{M\underset{OH}{C}HCH_3}$; C, $\mathrm{MCH_2\underset{OH}{C}HM}$; D, $\mathrm{M\underset{CH_3}{C}H{-}\underset{OCH_3}{C}HM}$; E, $\mathrm{M\underset{CH_3}{C}H{-}\underset{OH}{C}HM}$; F, $\mathrm{M\underset{CH_3}{C}H{-}\underset{O}{\underset{\|}{C}}M}$; G, $\mathrm{MCH_2\underset{O}{\underset{\|}{C}}M}$; H, $\mathrm{M\underset{H_2C}{\underset{\|}{C}}{-}\underset{O}{\underset{\|}{C}}M}$; I, $\mathrm{M\underset{H_3C}{C}{=}\underset{OH}{C}M}$; J, $\mathrm{M\underset{CH_3}{C}{=}\underset{OCH_3}{C}M}$.

Experimental

The preparation of α-mesitylacetic acid[4] was modified. A mixture of 13.5 g. of the nitrile and a solution of 13.5 g. of potassium hydroxide in 170 ml. of ethylene glycol was heated at 155° for six hours during which time the reaction was followed to completion by absorbing the evolved ammonia in 0.1 *N* hydrochloric acid. Acidification, filtering and crystallizing the product from acetone gave 12.1 g. (98%) of m. p. 167–168°. The **acid chloride**[5] was made from 25 g. of the acid and 60 ml. of thionyl chloride, refluxing for 45 min., allowing to stand overnight and fractionating under reduced pressure; yield 23.8 g. of b. p. 126–129° (7–10 mm.) (87%).

1,2-Dimesityl-1-propene-1-ol (II)[5] was obtained by adding 2 g. of I in 50 ml. of absolute ether dropwise over eight minutes to 1 g. of lithium aluminum hydride in 75 ml. of ether and refluxing for a half hour. After hydrolysis by 10% sulfuric acid the ether solution was dried and evaporated and the residue (1.8 g. 90%) was crystallized from absolute ethanol; m. p. 126–127°. It showed

---

(1) This work was incidental to synthesis of some 1,2-dimesitylamino ethanols for testing as tumor-necrotizing agents, and owes its support in part to a grant-in-aid from the National Institutes of Health, recommended by the National Cancer Institute.

(2) (a) Lutz and Gillespie, THIS JOURNAL, **71**, 2002 (1949); (b) Lutz and Tyson, *ibid.*, **56**, 1341 (1934).

(3) Fuson, Byers and Rabjohn, *ibid.*, **63**, 2339 (1941).

(4) "Organic Syntheses," **25**, 65 (1945).

(5) Fuson, Corse and McKeever, THIS JOURNAL, **62**, 3250 (1940).

no mixture melting point depression with an authentic sample prepared by platinum catalyzed hydrogenation.[5] Both samples rapidly decolorized potassium permanganate solution. No evidence of the formation of a stereoisomer was observed.

The identification of II was complicated by the fact that a mixture melting point with IV (of m. p. 111–112°) showed no depression. The acetyl derivative and the methyl ether likewise, though melting differently and characteristically, gave no mixture melting point depressions with the corresponding derivatives of IV. These derivatives gave mixture melting point depressions with the parent compounds (II and IV). A qualitative graduated mole-fraction study of mixture melting points of II and IV indicated no compound formation, and isomorphism is therefore presumed. The evidence of non-identity of II and IV consists in the differences in melting points of the two compounds and of their derivatives, the resistance of IV but not II to attack by permanganate, and by differences in ultraviolet absorption spectra.

1,2-Dimesitylpropanol-1 (IV) was made by lithium aluminum hydride reduction of III by the procedure used in the reduction of I (yield 80%). After several crystallizations from absolute ethanol it melted at 111–112°. Careful examination of the residue failed to reveal the diastereoisomer. The compound failed to decolorize permanganate.

Anal. Calcd. for $C_{21}H_{28}O$: C, 85.08; H, 9.52. Found: C, 85.05; H, 9.80.

Platinum and hydrogen in absolute ethanol medium was without effect on III (18 hr. at room temperature, atmospheric pressure).

The **acetyl derivative** was made by refluxing a solution of 1 g. of IV in 150 ml. of acetic anhydride for four hours. Hydrolysis of the reaction mixture gave 0.76 g. of product which after three crystallizations from isoöctane melted at 112.5–113°. It gave a 10° mixture melting point depression with starting material (IV) of m. p. 111–112°.

Anal. Calcd. for $C_{23}H_{30}O_2$: C, 81.62; H, 8.94. Found: C, 81.46; H, 8.99.

The **methyl ether** of IV was made by refluxing a solution of 1 g. of IV in 50 ml. of methanol containing 2 ml. of saturated ethereal hydrogen chloride for 18 hr. Concentration of the solution, treatment with 10% sodium carbonate, and extraction with ether, drying and evaporating, gave 0.75 g. It crystallized as cubes from isoöctane; m. p. 155.5–156°.

Anal. Calcd. for $C_{22}H_{30}O$: C, 85.10; H, 9.74. Found: C, 84.75; H, 9.56.

Curve in Fig. 1	Maxima $\epsilon \times 10^{-3}$	Maxima mμ	Minima $\epsilon \times 10^{-3}$	Minima mμ	$\epsilon \times 10^{-3}$ at 220 mμ
A	0.72	259	0.27	240	
	.89	265	.68	260	2.2
	.79	272	.59	270	
B	.16	268	.07	245	5.8
C	.45	270	.17	248	
	.38	275	.37	273	17.7
D	.50	269	.16	249	
	.40	275	.38	274	21.7
E	.51	270	.22	247	
	.43	275	.41	274	23.0
F	.56	310	.38	290	19.7
G	.40	312	.31	295	16.5
H	1.55	259	1.15	244	25.5
I[a]	..	...	..	...	20.2
J	..	...	..	...	25.5

[a] *Cf.* Rodebush and Feldman, THIS JOURNAL, **68**, 896 (1946).

1,2-Dimesitylethanol[6] was obtained from desoxymesitoin in quantitative yield by the above method of reduction with lithium aluminum hydride; m. p. 128.5–129.5°.

The **ultraviolet absorptions** were determined in 0.001 *M* isoöctane solution using a Beckman quartz DU spectrophotometer. None of the curves show maxima other than indicated and they cross the vertical 220 mμ axis at the points listed in the last column of the table of data.

Summary

1,2-Dimesitylpropenone is reduced 1,4 to the metastable enol by lithium aluminum hydride. 1,2-Dimesitylpropanol has been made for comparison with the enol.

---

(6) Fuson, Denton and Best, *J. Org. Chem.*, **8**, 67 (1943).

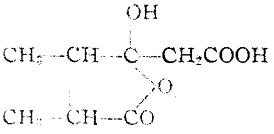
CHARLOTTESVILLE, VA. RECEIVED FEBRUARY 22, 1950

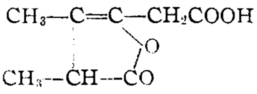
[CONTRIBUTION NO. 74 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

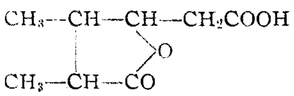
An Isomer of Dihydroanhydromonocrotalic Acid

BY GEORGE P. MUELLER

A new formulation of the structure of monocrotalic acid was recently proposed by Adams and Govindachari[1] and the evidence so far presented in its favor seems very promising. Leading references and discussions of the structure of this acid may be found also in reviews of the subject.[2,3] Of the various formulas considered earlier, structure I was the favored representation of monocrotalic acid. Accordingly, the derivatives, anhydromonocrotalic acid and dihydroanhydromonocrotalic acid, were given the related formulas II and III, with placement of the double bond in the former being uncertain.


I


II


III

The synthesis of structure III by an unequivocal route was undertaken with the hope that isolation and resolution of the proper diastereoisomer could be accomplished to provide a compound identical with the optically active dihydroanhydromonocrotalic acid obtained from

---

(1) Adams and Govindachari, THIS JOURNAL, **72**, 158 (1950).

(2) Wicks, Ph.D. Dissertation, University of Illinois, 1944.

(3) Leonard, "Senecio Alkaloids" in "The Alkaloids, Chemistry and Physiology," edited by Manske and Holmes, Academic Press, Inc., New York N. Y., 1950, p. 138.