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

cis-Benzalacetophenone

BY ROBERT E. LUTZ AND ROBERT H. JORDAN

Unsuccessful attempts[1] have been made to obtain a stereoisomer by exposure of ordinary and presumably *trans*-benzalacetophenone (II, Fig. 1) in solvents to the action of sunlight. This transformation has now been accomplished in acetone,[2] isoöctane or *n*-pentane, and it proceeds with rapid equilibration to a favorable mixture which can be separated. The new isomer is bright yellow in color, and melts at 45–46°. It is shown to be the labile *cis* isomer (I, Fig. 1) and not a dimer[3] by analysis and molecular weight determination, by its ready conversion back into the ordinary isomer, which must now be considered as *trans*, by bromination to the same dibromide which was obtained from the *trans* isomer, and by comparison of the ultraviolet and infrared absorption characteristics of the two isomers.[4]

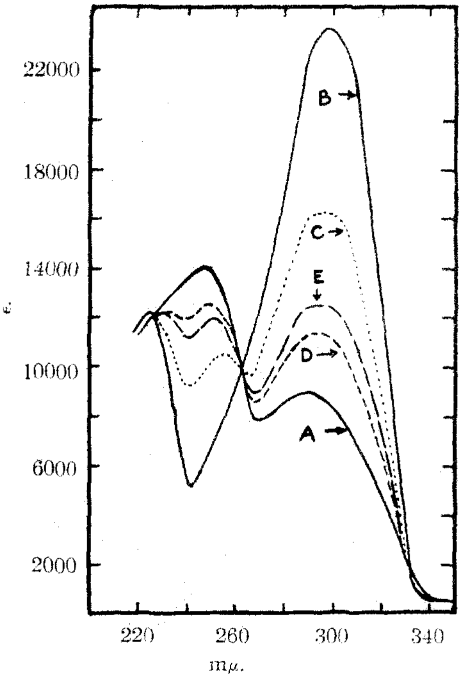

Fig. 1.—Spectra in isoöctane: A, I, *cis*-$C_6H_5CH=CHCOC_6H_5$; B, II, *trans*-$C_6H_5CH=CHCOC_6H_5$; C is II and D is I exposed to sunlight for two minutes; E is I and II exposed twelve minutes.

Because the ultraviolet absorption spectra are quite different (see A and B of Fig. 1) it was possible to follow quantitatively the sunlight interconversions of the two compounds at different time intervals by measurement of the extinction coefficients at the wave lengths 244 and 294 mμ and calculations by proportionation using the values at the wave lengths obtained from the curves of pure compounds. The percentages calculated from extinction coefficients at the two different wave lengths agreed closely in every case. From this study it was found that when 0.00005 molal isoöctane solutions of the isomers were separately exposed for two minutes to sunlight under identical conditions in quartz cells the *cis* isomer became 19% converted to *trans* and the *trans* isomer 50% converted to *cis* (see C and D of Fig. 1). Equilibrium was reached within twelve minutes of exposure as is shown by the then identical absorption curves (E of Fig. 1), and involved 74% of *cis* and 26% of *trans*.[5]

Further studies are in progress on the new *cis* isomer.

Experimental

***cis*-Benzalacetophenone (I).**—A mixture of 20 g. of ordinary (*trans*) benzalacetophenone (II) in 300 ml. of isoöctane or *n*-pentane in a Pyrex erlenmeyer flask was exposed to direct sunlight for two days. There still was present some undissolved *trans* isomer. The mixture was allowed to stand at −20° for two hours. The solution was decanted from the *trans* isomer which had crystallized. After again allowing to stand at −20° (overnight) the *cis* compound (1.5 g.) crystallized in the form of rosettes which adhered to the sides of the flask and were easily distinguished from the *trans* isomer by the deep lemon-yellow color. Recrystallization was accomplished by dissolving the material in 50 ml. of *n*-pentane at room temperature and cooling at −20° until crystallization was complete (yield 1.1 g.); melting point 45–46°. A mixture with the *trans* isomer liquefied at room temperature.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81; mol. wt., 208. Found: C, 86.44; H, 5.93; mol. wt. (freezing point of benzene), 212.

Attempts to obtain a practical *trans* to *cis* conversion using a mercury or tungsten filament lamp were unsuccessful. The *cis* isomer was recovered unchanged upon heating an isoöctane solution on the water-bath for ten minutes.

Conversion from *cis* to *trans* was effected (a) by heating a sample at 280–300° for a few moments, and (b) by boiling for a few seconds a benzene solution containing a small amount of added concd. hydrochloric acid (the yellow color of the solution was immediately discharged). In both cases the *trans* isomer was recovered and identified.

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(1) (a) Dufraisse, *Ann. chim.*, **17**, 182 (1922); (b) *cf.* work on polymorphs, Eisenlohr and Metzer, *Z. phys. Chem.*, **A178**, 350 (1937); LeFèvre, *J. Chem. Soc.*, 1037 (1937).

(2) Previously employed in the isomerization of β-aroylacrylic acids [Lutz and Scott, *J. Org. Chem.*, **13**, 284 (1948)]. However it was the least favorable of the three solvents in the present work.

(3) For dimers of benzalacetophenone (*trans*) see Stobbe and Bremer, *J. prakt. Chem.*, **123**, 1 (1930); Stobbe and Ebert, *Ber.*, **44**, 1291 (1911).

(4) For spectroscopic studies of these and related compounds, see paper in press (Kuhn, Lutz and Bauer).

(5) Cromwell and Watson [*J. Org. Chem.*, **14**, 411 (1949)] observed that the ultraviolet absorption of a heptane solution of *trans*-benzalacetophenone in a quartz cell changed rapidly upon exposure to sunlight, and (we note) seemingly approached an end or equilibrium point within five minutes. These authors interpreted the phenomenon as dimerization although this interpretation was inconsistent with the apparent equilibration involved and with the slowness of the known dimerization reaction[3] which they cited in support of their interpretation.

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).

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.

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

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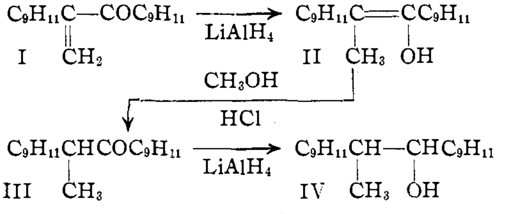
1,4-Reduction of an α,β-Unsaturated Ketone by Lithium Aluminum Hydride[1]

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).



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

$$\text{II} \xrightarrow[\mathrm{HCl}]{\mathrm{CH_3OH}} \text{III}$$

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

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

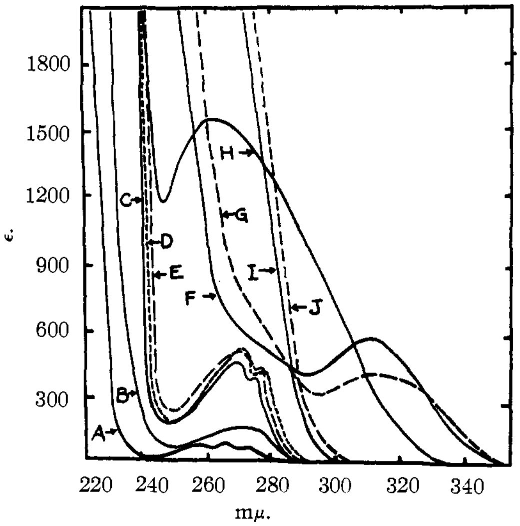


Fig. 1.—(M is mesityl): A, MH; B, $\mathrm{M\underset{OH}{C}HCH_3}$; C, $\mathrm{MCH_2\underset{OH}{C}HM}$; D, $\mathrm{M\underset{CH_3}{C}H{-}\underset{OCH_3}{C}HM}$; E, $\mathrm{M\underset{CH_3}{C}H{-}\underset{OH}{C}HM}$; F, $\mathrm{M\underset{CH_3}{C}H{-}\underset{\overset{\|}{O}}{C}M}$; G, $\mathrm{MCH_2\underset{\overset{\|}{O}}{C}M}$;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

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[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).