Although presently available information does not allow a definite choice among the three enols, we consider that the expression of the properties of dehydroacetic acid as an enol of the Feist structure (II) is confirmed.

Experimental[18]

Dehydroacetic acid[19] (II) was obtained as white needles from ethanol, m.p. 108–109° (reported[19] m.p. 108°). The ultraviolet spectrum showed maxima at 225 mμ, log ε 3.99 and at 310 mμ, log ε 4.05.[20] In the presence of one or more equivalents of sodium hydroxide, the spectrum showed λ_{max} 294 mμ, log ε 3.91.

Since the acid is sparingly soluble in water, the potentiometric titration (Beckman *p*H meter) was performed by dissolving 0.0358 g. of acid in 15.32 cc. of 0.0225 *N* sodium hydroxide and back titrating with 0.0395 *N* hydrochloric acid. From the titration curve were obtained a neutral equivalent 170 (calcd. 168) and a *pK* 5.30. The excellent agreement with the value *pK* 5.28 found[21] by the conductometric technique is presumably fortuitous, since our figure is not corrected for salt effect.

Triacetic Lactone (V).—As obtained by the procedure of Collie,[4] the lactone, glistening buff needles from water, had m.p. 186–186.5° (reported[4] m.p. 188–189°). The spectrum in ethanol alone or in the presence of a twenty-molar excess of sulfuric acid showed $\lambda\lambda_{max}$ 283 mμ, log ε 3.78 and 345 mμ, log ε 2.45. (Witter and Stotz[5] report λ_{max} 282 mμ, log ε 3.89 for an aqueous solution.) In ethanolic sodium hydroxide (one or more equivalents of alkali), the maximum occurred at 278 mμ, log ε 3.84.

Values for neutral equivalent (129, calcd. 126) and *pK* (5.00) were obtained by potentiometric titration of the lactone in water solution with standard sodium hydroxide.

Triacetic lactone methyl ether,[7a] white needles from ether, m.p. 78–80° (reported[7a] m.p. 81°), showed λ_{max} 280 mμ, log ε 3.76.

Dehydroacetic acid ethyl ether,[22] was obtained as fine, white needles from ether, m.p. 90–91.2° (reported[21] m.p. 93–94°). The compound failed to develop color with ferric chloride at room temperature. On boiling the solution a short time, the color deepened from the pale yellow of the ferric chloride solution to an orange-brown which was visually indistinguishable from the color generated by dehydroacetic acid in ferric chloride.

Potentiometric titration of the ether with standard sodium hydroxide failed to reveal acidic character. The addition of 0.3 equivalent of alkali caused the *p*H to rise to 11. After 0.5 equivalent of alkali had been added, the solution was at *p*H 11.2. We do not attach any quantitative significance to this observation since the *p*H was beyond the reliable range of the conventional Beckman glass electrode instrument.

The ultraviolet spectrum showed $\lambda\lambda_{max}$ 226mμ, log 3.90 and 312 mμ log ε 3.89. The position and intensity of the maxima were unchanged by the addition of 1.25 equivalents of alkali.

Desoxodehydroacetic Acid.—This substance was obtained by catalytic reduction of dehydroacetic acid as rugged, chalk-white prisms, m.p. 188–188.1° (reported[14] m.p. 185°). Potentiometric titration was carried out as for dehydroacetic acid. The curve was not quite steep enough at the equivalence point for accurate determination of a neutral equivalent. The *pK* calculated from the curve was 5.30. The ultraviolet spectrum showed $\lambda\lambda_{max}$ 237 mμ, log ε 2.95 and 290 mμ, log ε 3.92.

(18) All melting points are corrected. The ultraviolet spectra were determined in 95% ethanol with the Beckman spectrophotometer, model DU.

(19) F. Arndt, *Org. Syntheses*, **20**, 26 (1940).

(20) The spectrum in 2,2,4-trimethylpentane solution above 250 mμ has been reported to show λ_{max} at 311 mμ, log ε 4.3 [M. Calvin, T. T. Magel and C. D. Hurd, THIS JOURNAL, **63**, 2174 (1941)].

(21) W. Ostwald, *Z. physik. Chem.*, **3**, 401 (1889).

(22) J. N. Collie and H. R. Le Sueur, *J. Chem. Soc.*, **65**, 254 (1894).

LOS ANGELES 7, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

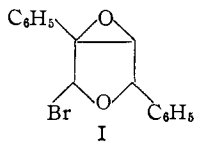
The Self-Condensation of Phenacyl Bromide. The Structure of the Halogen Diphenacyls

BY JEROME A. BERSON

RECEIVED MAY 13, 1952

The 3,4-epoxytetrahydrofuran structures proposed by Widman for the α- and β-bromodiphenacyls are shown to be incorrect. These substances are formulated as epimeric α,β-epoxyketones resulting from normal Darzens-type self-condensation of phenacyl bromide.

The sodium ethoxide catalyzed self-condensation of phenacyl bromide, which occurs according to the stoichiometry $2C_6H_5COCH_2Br \rightarrow C_{16}H_{13}O_2Br + HBr$, leads to two isomeric products: α-bromodiphenacyl (m.p. 129°) and β-bromodiphenacyl (m.p. 159°).[1,2] The investigation of the structure of these products[3–6] culminated in the proposal by Widman[7] that they were stereoisomers of the structure I.



I

The formation of I admittedly[7] requires a singular condensation mechanism. In addition, the reported chemistry of the bromodiphenacyls conflicts seriously in several respects with that predicted by I. These substances are obtained in strongly basic solution, survive prolonged boiling in neutral alcohol,[7] and react sluggishly with water, potassium iodide, potassium cyanide, silver acetate[4] and alcoholic silver nitrate. These properties are in direct contrast to the well-known[8–11] behavior of α-haloethers, which are inordinately responsive to reagents of this type. Further, no mechanism is readily apparent for the facile *base-catalyzed*[7] conversion of α-bromodiphenacyl to the β-isomer.

Although the possibility of the presence of a

(1) V. Fritz, *Ber.*, **28**, 3028 (1895).

(2) C. Paal and C. Demeler, *ibid.*, **29**, 2092 (1896).

(3) C. Paal and H. Stern, *ibid.*, **34**, 1611 (1901).

(4) C. Paal and H. Schulze, *ibid.*, **36**, 2405, 2415, 2416 (1903).

(5) W. L. Evans, *Am. Chem. J.*, **35**, 115 (1906).

(6) O. Widman, *Ber.*, **42**, 3261 (1909).

(7) O. Widman, *Ann.*, **400**, 86 (1913).

(8) A. Genther and H. Laatsch, *ibid.*, **218**, 36 (1883).

(9) F. M. Litterscheid, *ibid.*, **330**, 118, 123 (1904).

(10) H. R. Henze and J. T. Murchison, THIS JOURNAL, **53**, 4077 (1931).

(11) J. B. Conant, W. R. Kirner and R. E. Hussey, *ibid.*, **47**, 488 (1925).

carbonyl group in these substances was dismissed[7] on the grounds that normal carbonyl derivatives could not be obtained, the isomerization strongly implies the presence of such a function in juxtaposition to an asymmetric center. The infrared spectra of the bromodiphenacyls (Fig. 1), which are dominated by strong bands at 5.92 μ, supply direct evidence for the presence of a carbonyl group in each of these molecules. That these carbonyl groups are ketonic is indicated by the stability of the substances to oxidation.[6]

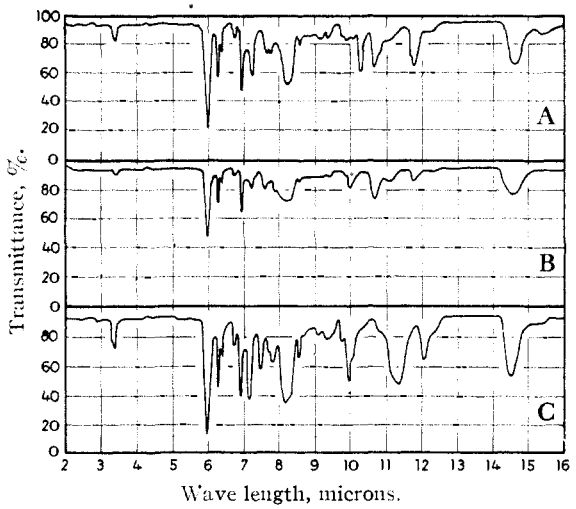
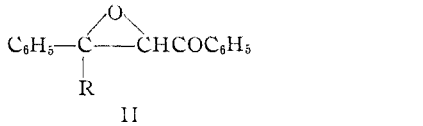


Fig. 1.—Infrared spectra in chloroform: A, α-bromodiphenacyl (10%); B, β-bromodiphenacyl (5%); C, benzalacetophenone oxide (10%).

The presence of an epoxide function in the bromodiphenacyls is established[4,7] by the formation of halohydrin derivatives with hydrogen halides or acetyl halides. These products regenerate the epoxides upon treatment with alkali.

The principal structure features of the bromodiphenacyl molecule may thus be characterized as (i) a conjugated keto group, (ii) an epoxide ring, (iii) an aliphatically bound but unactivated bromine atom,[3,4,5] (iv) a readily epimerizable asymmetric center and (v) two phenyl rings. The several possible structures which incorporate these features have now been examined in the light of two additional requirements (i) that the bromodiphenacyls be derivable from phenacyl bromide under the observed condensation conditions by a reasonable series of changes, and (ii) that the decomposition of β-bromodiphenacyl to *two moles* (68% yield) of benzoylcarbinol acetate upon heating with sodium acetate and acetic acid[5] be accommodated. These considerations lead to the conclusion that the only acceptable representation of the chemistry of the α- and β-bromodiphenacyls is that they are epimers of the structure II (R = CH_2Br).[12]

Confirmatory evidence for this structure is supplied by the close resemblance (in the short wave length region) of the infrared spectra of the bromodiphenacyls to that of the model substance benzalacetophenone oxide (II, R = H) and more dramatically, by the virtual identity of the three ultraviolet spectra (Fig. 2). It is noteworthy that the ultraviolet absorption maximum typical of simple aryl–alkyl ketones (compare acetophenone, λ_{max} 241 mμ[13]) is shifted bathochromically by 9–12 mμ in these α,β-epoxyketones. This apparent ability of small rings to conjugate with adjacent unsaturated centers has been observed previously.[13–16]



II

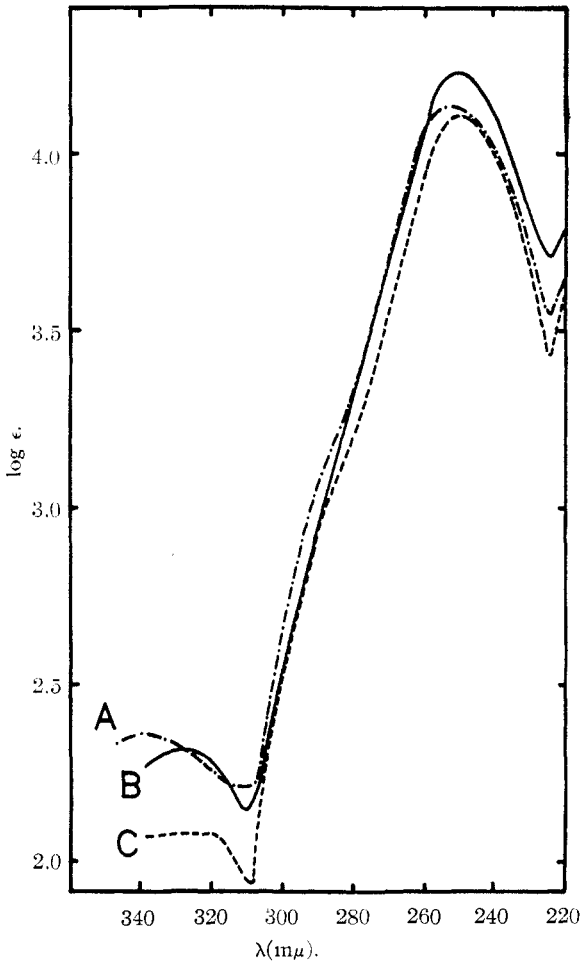


Fig. 2.—Ultraviolet spectra in 95% ethanol: A, α-bromodiphenacyl; B, benzalacetophenone oxide; C, β-bromodiphenacyl.

The cleavage of β-bromodiphenacyl to benzoylcarbinol acetate is readily rationalized by a scheme involving displacement of the halogen by acetate, opening of the oxide ring, and retrograde aldolization of the resulting β-hydroxyketone

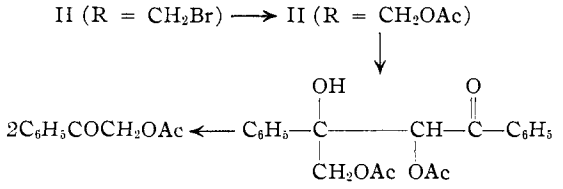
(12) While it is not our intention to reinvestigate the pair of analogous substances, α- and β-chlorodiphenacyl, derived from phenacyl chloride, the complete parallelism of their chemistry to that of the bromo compounds makes it entirely likely that they are epimers of the structure II (R = CH_2Cl).

(13) T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, THIS JOURNAL, **69**, 880 (1947).

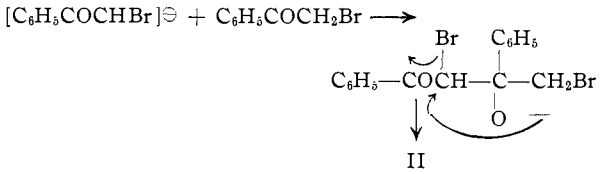
(14) I. M. Klotz, *ibid.*, **66**, 88 (1944).

(15) M. T. Rogers, *ibid.*, **69**, 2544 (1947).

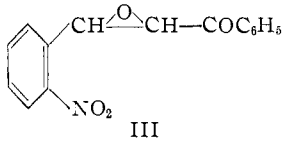
(16) I. M. Heilbron, A. W. Johnson, E. R. H. Jones and A. Spinks, *J. Chem. Soc.*, 727 (1942).



The formation of the bromodiphenacyls may be represented as a normal Darzens condensation[17,18]



If the reaction is carried out using a ratio of 1 mole of sodium ethoxide to 2 moles of phenacyl bromide (stoichiometric quantities), the product is a mixture of 8 parts of α-bromodiphenacyl to 5 parts of the β-isomer.[7] The rate of formation of the α-isomer must then be at least eight-fifths as fast as that of the β-isomer since the equilibrium in the epimerization process[7] favors β-bromodiphenacyl. If the condensation is run in the presence of excess sodium ethoxide, the β-isomer is the sole product. This situation, in which the kinetically-favored product is thermodynamically unstable with respect to a more slowly-formed isomer, is apparently not unique in Darzens reactions. In addition to the direct parallel between the self-condensations of phenacyl bromide and phenacyl chloride,[7] the condensation of *o*-nitrobenzaldehyde with phenacyl bromide leads to a product (III, α-form, m.p. 110°) which is readily converted by ethoxide ion to a β-isomer (m.p. 175°).[19]



III

(17) (a) Darzens, *Compt. rend.*, **139**, 1214 (1904), and many subsequent papers; (b) *cf.* M. S. Newman and B. J. Magerlein, "Organic Reactions," Vol. V, edited by R. Adams, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 413.

(18) While apparently accepting Widman's structure (I), W. Madelung and M. E. Oberwegner, *Ann.*, **490**, 200 (1931), recognized that II would result from a condensation of this type and that it would accommodate much of the chemistry of the bromodiphenacyls.

Experimental[20]

β-Bromodiphenacyl[7] was obtained as white needles from ethyl acetate, m.p. 158–158.5° (reported[7] m.p. 161°). The ultraviolet spectrum showed λ_{max} 251 mμ, log ϵ 4.11. A plateau occurred at *ca.* 320–340, log ϵ 2.06. Calcd. for $C_{16}H_{13}O_2Br$: mol. wt., 317. Found: (in camphor), mol. wt., 314.

α-Bromodiphenacyl[7] was obtained as rosettes of white needles from ethyl acetate–methanol, m.p. 134–135° (reported m.p. 129°). The ultraviolet spectrum showed $\lambda\lambda_{max}$ 253 mμ, log ϵ 4.17 and 340 mμ, log ϵ 2.35.

Benzalacetophenone oxide,[21] m.p. 88.5–89.2° (reported m.p. 90°), showed $\lambda\lambda_{max}$ 250 mμ, log ϵ 4.21 and 330 mμ, log ϵ 2.31.

(19) S. Bodforss, *Ber.*, **51**, 192 (1918).

(20) Melting points are corrected. The infrared spectra were determined in chloroform by Mr. S. M. Nagy of the Massachusetts Institute of Technology using the Baird Associates spectrophotometer. The ultraviolet spectra were determined in 95% ethanol with the Beckman spectrophotometer, model DU.

(21) E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

LOS ANGELES 7, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

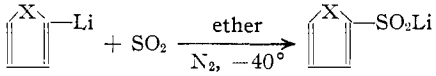
Sulfination of Organolithium Derivatives of Thiophene and Furan

BY WILLIAM E. TRUCE AND ERIC WELLISCH

RECEIVED MAY 22, 1952

Lithium 2-thiophenesulfinate and lithium 2-furansulfinate were prepared by the metalation of thiophene and furan with *n*-butyllithium followed by sulfination with sulfur dioxide. Reaction of these lithium sulfinates with methyl vinyl sulfone gave the corresponding γ-disulfones, 1-(2-thiophenesulfonyl)-2-methanesulfonylethane and 1-(2-furansulfonyl)-2-methanesulfonylethane, in good yield. It was also found that excess lithium 2-thiophenesulfinate caused the cleavage of 1-(2-thiophenesulfonyl)-2-methanesulfonylethane.

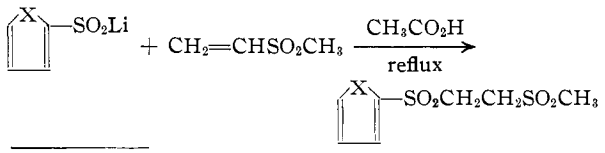
The principal objective of the present work was to develop a convenient synthesis of α-thiophenesulfinic acid[1] and α-furansulfinic acid, an unknown compound. Organolithium compounds have been employed to good advantage recently for the preparation of sulfinic acids.[2] This method was employed in the present work.



(where X is S or O)

The sulfination of 2-thienyllithium[3] was carried out by adding this compound with vigorous stirring to an ethereal solution of sulfur dioxide at −30°. For optimum yields, lithium 2-furansulfinate was prepared by the reverse addition of an ethereal solution of sulfur dioxide to the 2-furyllithium reagent.[4] Presumably this result is a consequence of the sensitivity of furan compounds to acid-catalyzed ring opening.

The lithium sulfinates were converted to the corresponding γ-disulfones by treatment with methyl vinyl sulfone.[5] The products, 1-(2-thio-



(1) L. Weitz, *Ber.*, **17**, 800 (1884); A. Biedermann, *ibid.*, **19**, 1615 (1886).

(2) W. E. Truce and J. F. Lyons, THIS JOURNAL, **73**, 126 (1951).

(3) H. Gilman and D. A. Shirley, *ibid.*, **71**, 1870 (1949).

(4) R. A. Benkeser and R. B. Currie, *ibid.*, **70**, 1780 (1948).

(5) H. Ufer, German Patent 663,992 (1938); *C. A.*, **33**, 174 (1939).