Anal. Calcd. for $C_{13}H_{15}Cl_2NO_5S$: C, 42.40; H, 4.11. Found: C, 42.64; H, 4.16.

A Kunz hydrolysis[5] of this product yielded a viscous oil which could not be induced to crystallize.

DL-*erythro*-1-(5-Nitro-2-thienyl)-2-dichloroacetamido-1,3-propanediol (VIIIb).—Nitration of the *erythro*-racemate of Vb (m.p. 93.5–94.5°) gave the crystalline 5-nitro compound (VIb), m.p. 123.5–126°. An analytical sample after recrystallization from a 2:1 mixture of petroleum ether–ethylene dichloride had a m.p. of 126.5–127.5°.

Anal. Calcd. for $C_{13}H_{14}Cl_2N_2O_7S$: C, 37.78; H, 3.41; Cl, 17.16. Found: C, 37.83; H, 3.60; Cl, 17.46.

One gram (2.4 millimoles) of VIb (m.p. 127.5–128.5°) was hydrolyzed using 50 ml. of acetone and 50 ml. of 0.1 *N* aqueous sodium hydroxide.[5] The product amounted to 0.51 g., m.p. 125–135°. This was recrystallized twice from 20 ml. of ethylene dichloride yielding 0.10 g., m.p. 167–168°. It was finally recrystallized from 8 ml. of water yielding 0.06 g. of long fine slightly yellow needles, m.p. 168.5–169.5°. A mixture of this product and the *erythro*-racemate of VIIIb prepared above (m.p. 169.5–170.5°) had a m.p. of 169.5–170.5°.

DL-*threo*-1-(5-Nitro-2-thienyl)-2-dichloroacetamido-1,3-propanediol (VIIIb).—Nitration of the *threo*-racemate of Vb (m.p. 123–124°), gave a dark red oil which could not be crystallized. Hydrolysis of 0.90 g. (2.2 millimoles) of this crude nitration product with 50 ml. of acetone and 50 ml. of 0.1 *N* aqueous sodium hyroxide[5] gave 0.22 g., m.p. 121.5–126°. The material was recrystallized successively from 10 ml. of ethylene dichloride, then 10 ml. of water yielding 0.02 g., m.p. 131.5–132.5°. A mixture of this product and the *threo*-racemate of VIIIb prepared above (m.p. 131.5–133°) had a m.p. of 132–133°.

Acknowledgments.—We wish to express our appreciation to Drs. Jonathan W. Williams and Walter A. Gregory for many helpful suggestions during the course of this work. We are also indebted to Eugene B. Cooper, Jr., and Robert O. Bodycot for technical assistance. Microanalyses were carried out by Dr. J. W. Stillman and his group in the Chemical Department at the du Pont Experimental Station, and the ultraviolet absorption spectra were determined by Mr. Charles B. Matthews also in the Chemical Department.

WILMINGTON, DELAWARE

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

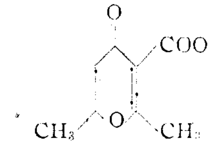
On the Structure of Dehydroacetic Acid

BY JEROME A. BERSON

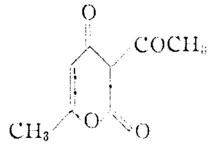
RECEIVED MAY 7, 1952

A consideration of the acidic dissociation constants and ultraviolet spectra of dehydroacetic acid, triacetic lactone and certain of their derivatives provides confirmatory evidence for the presently accepted formulations of these substances.

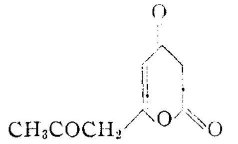
The structure of dehydroacetic acid has been unquestioned since the demonstration[1] that the observed isomerization of the substance by hot 85% sulfuric acid to 2,6-dimethylpyrone-4-carboxylic acid-3 (I) was most easily rationalizable in terms of the Feist structure[2] (II). The possibility that the structure (III) proposed by Collie[3] or some other alternative (*e.g.*, IV) might also be convertible to I under the drastic conditions of the isomerization, as well as the observation (*vide infra*) of certain apparent anomalies in the ultraviolet absorption behavior of the dehydroacetate ion have led us to re-examine the structural question.



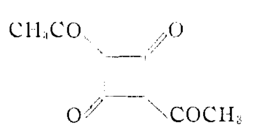
I



II

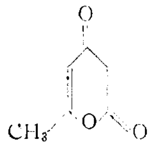


III



IV

With 90% sulfuric acid, dehydroacetic acid is converted to triacetic lactone, formulated as V.[4] Alcoholysis of triacetic lactone leads to ethyl triacetate, formulated as VIa, which on careful saponification yields the unstable triacetic acid (VIb). This acid readily suffers decarboxylation to acetylacetone.[5] Triacetic lactone is regenerated when ethyl triacetate is warmed with 70% sulfuric acid.[6] These observations leave only two possible structures for triacetic acid, VIb and VIIb.

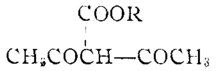


V

$CH_3COCH_2COCH_2COOR$

VIa, R = C_2H_5

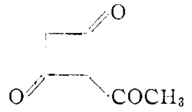
VIb, R = H



$$\overset{COOR}{CH_3CO\overset{|}{C}H{-}COCH_3}$$

VIIa, R = C_2H_5

VIIb, R = H



VIII

β-Lactone structures for triacetic lactone can be rejected in view of the relatively high stability of the lactone to acids and bases.[4,5] There remain, therefore, only two possible structures for triacetic lactone derivable from VIa or VIIa by the loss of alcohol, namely, V and VIII.

Triacetic lactone readily undergoes O-alkylation,[7] is a monobasic acid, gives a blood-red color with ferric chloride and is therefore to be considered

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[1] C. F. Rassweiler and R. Adams, THIS JOURNAL, **46**, 2758 (1924).

[2] F. Feist, *Ann.*, **257**, 253 (1890).

[3] J. N. Collie, *J. Chem. Soc.*, **59**, 179 (1891).

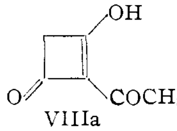
[4] J. N. Collie, *ibid.*, **59**, 619 (1891).

[5] R. F. Witter and E. H. Stotz, *J. Biol. Chem.*, **176**, 485 (1948).

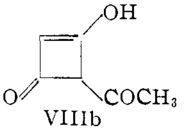
[6] P. R. Johnson, H. M. Barnes and S. M. McElvain, THIS JOURNAL, **62**, 964 (1940).

[7] (a) F. Sproxton, *J. Chem. Soc.*, **89**, 1188 (1906); (b) A. Tamburello, *Chem. Zentr.*, **76**, 1, 348 (1905).

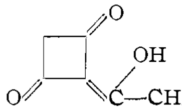
highly enolic. Of the three possible enols of VIII (VIIIa, VIIIb, VIIIc), both VIIIa and VIIIb contain the enolized β-diketone system characteristic of the acidic dimer of methyl ketene[8] (IX). The ultraviolet absorption spectrum of triacetic lactone in neutral or acid solution (Fig. 1, λ_{max} 283 mμ) indicates a considerably higher degree of conjugation in the absorbing species than is normally encountered in simple enolized β-diketones.[9] This result is consistent with the formulation of triacetic lactone as an enol of VIII only if *all three* carbonyl groups are chromophorically active and thus part of the conjugated system. This argument logically implies that VIIIa and VIIIc will form the same anion and consequently that any of the enols (VIIIa, VIIIb or VIIIc) will be acids of at least the same order of strength as IX.[10] Potentiometric titration of triacetic lactone shows that is a weaker acid (*pK* 5.0) than IX (*pK* 2.8) by a factor of about 160. In terms of the cyclobutenolone structures (VIIIa-c) for triacetic lactone, there seems to be only one reasonable explanation for this marked discrepancy in acidity, namely, that there is very effective intramolecular hydrogen-bonding between the enolic hydrogen and one of the carbonyl groups. This type of effect is exemplified by the sharp diminution in acidity of acetylacetone (*pK* 8.938) as compared to dimethyldihydroresorcinol (*pK* 5.253).[11] The existence of strong hydrogen-bonding in the present cases (VIIIa-c) seems unlikely because of the unusual steric requirements resulting from partial inclusion of the enolized β-diketone system in the four-membered ring. In addition, one would expect a marked change in the ultraviolet spectrum of the enol ether of triacetic lactone as compared to that of the free enol.[12] The absence of any such marked effect in the spectrum of triacetic lactone methyl ether (Fig. 1, λ_{max} 280 mμ) we interpret as strong evidence against the hydrogen-bonding hypothesis.



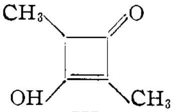
VIIIa



VIIIb



VIIIc



IX

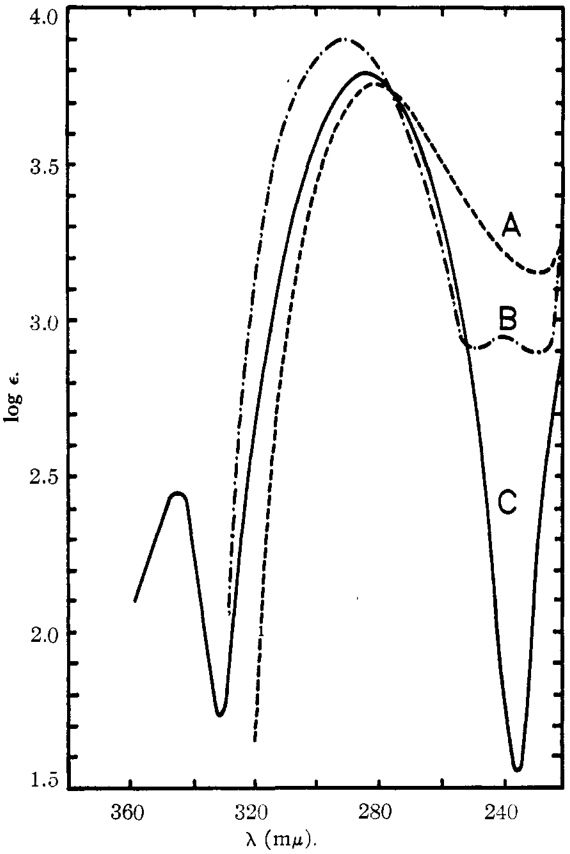


Fig. 1.—A, triacetic lactone methyl ether; B, desoxodehydroacetic acid; C, triacetic lactone.

Having thus eliminated all reasonable interpretations of the properties of this substance in terms of enols derived from VIII, we conclude that triacetic lactone must be an enol of V.

The direct acetylation of triacetic lactone to dehydroacetic acid[13] implies a close structural relationship between these substances. The relationship is clarified by a consideration of the properties of the compound $C_8H_{10}O_3$, m.p. 188° (hereinafter designated as desoxodehydroacetic acid) formed on catalytic reduction of dehydroacetic acid[14] and assigned structure X. Although triacetic lactone potassium salt could not be alkylated to desoxodehydroacetic acid, the O-ethyl ether being obtained instead,[14] the acidity of desoxodehydroacetic acid (*pK* 5.3) and, more particularly, the ultraviolet spectrum (Fig. 1) leave little doubt that the substance is indeed a C-ethyl derivative of V. Of the three possible structures (X, XI and XII), only X and XI are consistent with the observed[14] hydrolysis to 2,4-heptanedione. Since the reduction of dehydroacetic acid involves the change C—COCH$_3$ → C—CH$_2$CH$_3$, there remain only two possible structures for dehydroacetic acid, namely, II and III.

With this delimitation of the structural alterna-

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[8] R. B. Woodward and G. Small, This Journal, **72**, 1297 (1950).

[9] Compare dimethyldihydroresorcinol (λ_{max} 255 mμ) [E. R. Blout, V. A. Eager and D. C. Silverman, *ibid.*, **68**, 566 (1946)].

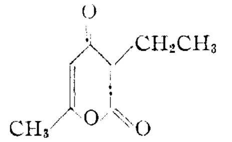
[10] Woodward and Small (ref. 8) have suggested an interesting explanation for the inordinate enhance ment of acidity resulting from the incorporation of the β-diketone system in the four-membered ring of IX.

[11] G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, **23**, 1147 (1940).

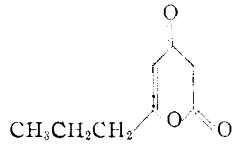
[12] Derivatives of enolized β-diketones and *o*-hydroxyacetophenones in which intramolecular hydrogen-bonding is prevented (*e.g.*, the enol ethers or acetates) show a pronounced shift of the principal absorption maximum toward the violet. Thus, (a) acetylacetone absorbs at 270 mμ while the acetate absorbs at 230 mμ [R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, This Journal, **71**, 1068 (1949)]; (b) dibenzoylmethane absorbs at 345 mμ and *cis*-β-methoxystyryl phenyl ketone at 290 mμ [B. Eistert, F. Weygand and E. Csendes, *Chem. Ber.*, **84**, 745 (1951)]; (c) R. A. Morton, A. Hassan and T. C. Calloway, *J. Chem. Soc.*, 883 (1934), report λ_{max} 345 mμ for dibenzoylmethane and λ_{max} 300 mμ for β-ethoxystyryl phenyl ketone; (d) 2-hydroxy-4-methoxyacetophenone absorbs at 274 mμ and 2,4-dimethoxyacetophenone at 267 mμ [D. J. Cram and F. W. Cranz, This Journal, **72**, 595 (1950)].

[13] W. Dieckmann and F. Breest, *Ber.*, **37**, 3387 (1904).

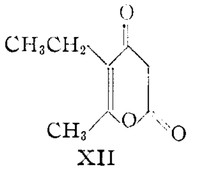
[14] R. Malachowski and T. Wanczura, *Bull. intern. acad. polonaise*, **1933A**, 547 [*C. A.*, **28**, 4421 (1934)].



X

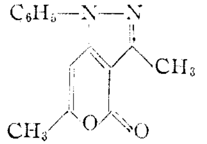


XI



XII

tives, the available chemical evidence strongly indicates the correctness of the Feist structure (II). In addition to the isomerization of dehydroacetic acid by sulfuric acid (*vide supra*), the demonstration[15] that the dehydration product of dehydroacetic acid phenylhydrazone has the structure XIII is, barring an intervening rearrangement, clearly consistent only with II.



XIII

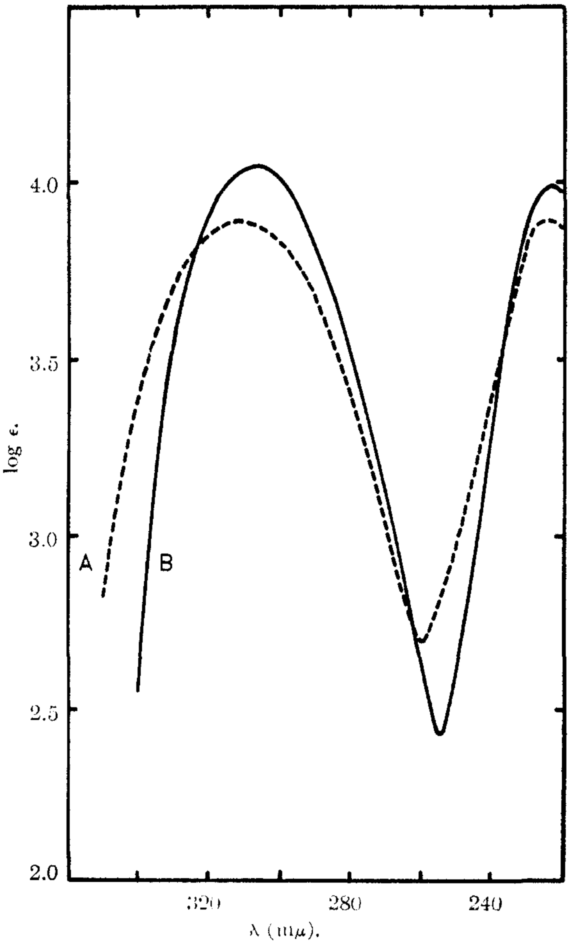
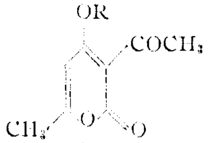
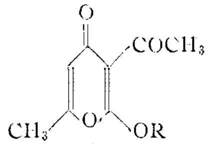


Fig. 2.—A, dehydroacetic acid ethyl ether; B, dehydroacetic acid.

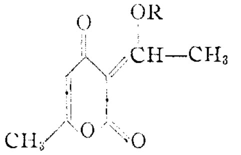
It is now pertinent to examine the consistency of the Feist structure (II) with certain further properties of dehydroacetic acid. The striking similarity of the ultraviolet absorption spectra of dehydroacetic acid and its ethyl ether (Fig. 2) provides compelling evidence that dehydroacetic acid exists as a virtually completely enolized species in solution. The pronounced bathochromic shifts of the maxima in the spectra of dehydroacetic acid (λ_{max} 310 mμ) and the dehydroacetate ion (λ_{max} 294 mμ) relative to the maxima for triacetic lactone (λ_{max} 283 mμ) and the triacetic lactonate ion (λ_{max} 278 mμ) are consistent with the chromophorically active situation of the acetyl group in each of the enol variants of the Feist structure (IIa, IIb, IIc: R = H).



IIa



IIb



IIc

It is noteworthy that maximal absorption for the dehydroacetate and triacetic lactonate ions occurs at *shorter* wave lengths than for the corresponding un-ionized acids. This is in contrast to the observed[9] bathochromic effect of ionization on simple β-dicarbonyl systems.

On the basis of the absorption data (Fig. 2), it seems certain that the conversion of dehydroacetic acid to its ethyl ether occurs with minimum structural change, *i.e.*, with simple replacement of hydrogen by ethyl. Although the ethyl ether IIa (R = C_2H_5) might conceivably be expected to show acidic properties since the methyl group is conjugated with both the lactone and side-chain carbonyl groups, both IIb and IIc (R = C_2H_5) require the absence of acidic character in dehydroacetic acid ethyl ether. The observations that the ether does not consume alkali upon titration, gives a negative ferric chloride reaction and exhibits virtually unchanged spectral characteristics in alkaline solution are thus consistent with at least two of the expressions derived from the Feist structure.[16,17]

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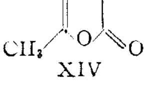
[15] E. Benary, *Ber.*, **43**, 1070 (1910).

[16] The circumstance that none of the enol variants of the Collie structure (III) accommodates the combined requirements (i) that the acetyl group of dehydroacetic acid be chromophorically active and (ii) that dehydroacetic acid ethyl ether be non-acidic, provides further direct evidence of the inadequacy of III.

[17] The formulation of the ethyl ether as a C-ethyl derivative of II (XIV) also accounts for the lack of acidic character. It is, however, inconsistent with the facile hydrolysis to the parent enol.[7a] Further, XIV fails to account for the ultraviolet absorption behavior since it contains only the simple β-acyloxy-α,β-unsaturated ketone chromophore (compare acetylacetone enol acetate, λ_{max} 230 mμ[12a]).



XIV

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 $\lambda\lambda_{max}$ 226 mμ, log ϵ 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.

LOS ANGELES 7, CALIFORNIA

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[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).

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

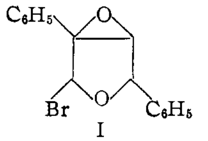
The Self-Condensation of Phenacyl Bromide. The Structure of the Halogen Diphenacyls

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

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[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. Geuther 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).