Cline, *et al.*[9]; yield of recrystallized oxysulfonic acid 115 mg. It did not melt below 300°.

**Raney Nickel Hydrogenolysis of Icthiamin Dihydrobromide.**—Icthiamin dihydrobromide, 420 mg., was dissolved in 25 ml. of water, adjusted to *p*H 7.5–8 with 10% sodium hydroxide and refluxed for two hours with 2.2 ml. of settled Raney nickel catalyst prepared from the alloy by the method of Mozingo, *et al.*[11] The Raney nickel was then removed by filtering the hot suspension. The clear filtrate was adjusted to *p*H 9 with 10% sodium hydroxide and then evaporated to dryness *in vacuo*. The well-powdered residue was then sublimed in a Craig still at 12 mm. over a temperature range of 150–185°. The colorless sublimate weighed 48 mg., m.p. 199°. The picrate of the sublimate was prepared in the usual manner in water; m.p. 224°. The melting points of the sublimate and its picrate were not depressed when mixed, respectively, with authentic 2,5-dimethyl-4-aminopyrimidine and 2,5-dimethyl-4-aminopyrimidine picrate.

NEW YORK 58, N. Y. RECEIVED JUNE 14, 1951

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[11] R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, THIS JOURNAL, **65**, 1013 (1943).

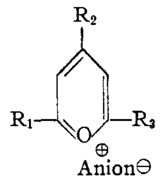
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

# Ring-Chain Tautomerism of Pyrylium Pseudo-bases[1]

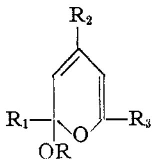
BY JEROME A. BERSON

The ultraviolet and infrared spectra of some triphenylpyrylium pseudo-bases indicate strongly that the predominant species in solutions of these substances are to be represented by the open-chain 1,5-diketone formula. The results are in accord with the infrared spectrum of triphenylpyrylium pseudo-base and with the observed and previously reported chemical behavior of the pseudo-bases.

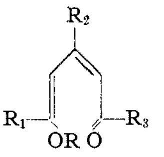
The pseudo-bases derived by treatment of triphenylpyrylium salts (I) with mild alkali have been formulated[2a,b,c,d] as II, III and IV.



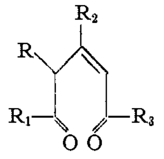
I



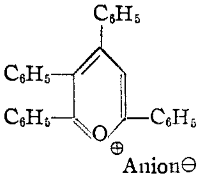
II



III



IV



V

Ia: $R_1, R_2, R_3 = C_6H_5$
Ib: $R_1 = p\text{-}CH_3OC_6H_4;\ R_2, R_3 = C_6H_5$
Ic: $R_1, R_3 = C_6H_5;\ R_2 = p\text{-}CH_3OC_6H_4$
IIa, IIIa, IVa: $R_1, R_2, R_3 = C_6H_5;\ R = H$
IIb, IIIb, IVb: $R_1 = p\text{-}CH_3OC_6H_4;\ R_2, R_3 = C_6H_5;\ R = H$
IIc, IIIc, IVc: $R_2 = p\text{-}CH_3OC_6H_4;\ R_1, R_3 = C_6H_5;\ R = H$
IId, IIId, IVd: $R_1, R_2, R_3 = C_6H_5;\ R = CH_3$

The isolation and interconversion[2d] of two discrete forms (probably a diketone and an enol) of the pseudo-base of tetraphenylpyrylium salts (V) have effectively demonstrated the existence of a mobile equilibrium between at least two such desmotropes in a related case. As a part of a study on pyrylium compounds in progress in this Laboratory, we have undertaken an investigation aimed at determining which, if any, of the hypothetically tautomeric modifications (II, III or IV) predominates in solutions of the triphenylpyrylium pseudo-bases. While this work fails to demonstrate the presence of more than one tautomer, the findings are strongly in favor of the open-chain diketone structure (IV) as the predominant desmotrope.

While the ultraviolet absorption characteristics of desmotropes IIa or IIIa are not easily predictable in the absence of suitable model substances, it is clear that IVa would be expected, as a first approximation, to exhibit absorption due to two insulated chromophoric types, namely, acetophenone and benzalacetophenone. The ultraviolet spectrum of the pseudo-base (IVa) of triphenylpyrylium salts (Ia) (Fig. 1) shows two maxima, $\lambda_{max}$ 247, 298 mμ, which correspond almost exactly in position and intensity to the principal maxima of acetophenone ($\lambda_{max}$ 247 mμ[3]) and benzalacetophenone ($\lambda_{max}$ 299 mμ[4]). Further, a summation of the acetophenone and benzalacetophenone spectra (Fig. 1) corresponds very closely to the spectrum of the pseudo-base.

On the assumption that the long wave length maximum (λ 298 mμ) results from an essentially independent benzalacetophenone-type chromophore in IVa, one would anticipate a strong bathochromic shift of this peak in the spectrum of the pseudo-base (IVc) derived from 2,6-diphenyl-4-*p*-anisylpyrylium salts (Ic) as a consequence of the extension of the conjugated benzalacetophenone system through the methoxyl group.[5] Little or no effect on the position of the short wave length maximum, which is presumably due to the insulated acetophenone chromophore, is to be expected. These conclusions are verified by the absorption curve (Fig. 1): $\lambda_{max}$ 245, 339 mμ. Moreover, the now anticipated bathochromic shift of the short wave length maximum due to extension of the acetophenone chromophore[6] in the pseudo-base (IVb) derived from 2-*p*-anisyl-4,6-diphenylpyrylium salts (Ib) is observed (Fig. 1): $\lambda_{max}$ 285–290 mμ. The absorption due to the unchanged benzalacetophenone chromophore is apparently strongly overlapped and remains only as the sloping shoulder at 300–310 mμ.

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[1] Presented in part at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September 10–13, 1951.

[2] (a) W. Dilthey, *J. prakt. Chem.*, **94**, 53 (1916); (b) *ibid.*, **95**, 107 (1917); (c) *ibid.*, **101**, 177 (1920); (d) W. Dilthey and T. Böttler, *Ber.*, **52B**, 2040 (1919).

[3] H. Mohler and J. Polya, *Helv. Chim. Acta*, **19**, 1222 (1936).

[4] N. H. Cromwell and W. R. Watson, *J. Org. Chem.*, **14**, 411 (1949).

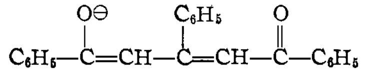
[5] H. Stobbe and A. Hensel, [*Ber.*, **59**, 2255 (1926)], report $\lambda_{max}$ 350 mμ for *p*-anisalacetophenone.

[6] Ramart-Lucas and Rabaté [*Compt. rend.*, **196**, 1493 (1933)] report $\lambda_{max}$ 275 mμ for *p*-methoxyacetophenone.

The infrared spectrum of IVa exhibits no absorption maxima in the region 2.5–2.9 μ (O–H stretching). An intense, partially-resolved doublet at 5.95–5.98 μ indicates the presence of at least one conjugated carbonyl group. (The model substance, benzalacetophenone, shows a maximum at 6.02 μ and acetophenone has been reported[7] to absorb at 5.92 μ.) A strong band at 6.08 μ may possibly be attributable to C=O stretching in the benzalacetophenone moiety of IVa, although an unequivocal assignment does not seem justified.

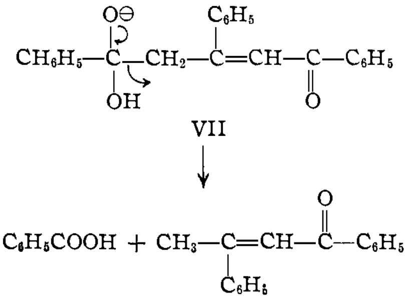
The infrared and ultraviolet spectra are clearly consistent only with the diketone structure (IVa) for triphenylpyrylium pseudo-base.

Although a consideration of chemical properties alone does not allow an unambiguous choice among the desmotropes because of the possibility of tautomerism, the behavior of the pseudo-bases toward strong alkali is best formulated in terms of the diketone (IV) as the reactive species. Alkaline solutions of IVa are orange-pink, presumably due to the formation of the resonating enolate ion VI ($\lambda_{max}$ 490 mμ). On standing or warming, the color fades with concomitant formation of benzoic acid and a neutral oil. This facile cleavage seems unexceptional and can be interpreted as involving attack of hydroxyl ion on the vinylogous β-diketone system yielding VII which decomposes as shown.[8]



$$C_6H_5-\overset{\overset{\displaystyle O^{\ominus}}{|}}{C}=CH-\overset{\overset{\displaystyle C_6H_5}{|}}{C}=CH-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$$

VI



$$\underset{\displaystyle VII}{CH_6H_5-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O^{\ominus}}{|}}{C}}-CH_2-\overset{\overset{\displaystyle C_6H_5}{|}}{C}=CH-\underset{\underset{\displaystyle O}{\|}}{C}-C_6H_5}$$

$$\downarrow$$

$$C_6H_5COOH + CH_3-\underset{\underset{\displaystyle C_6H_5}{|}}{C}=CH-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$$

VIII

The suggested mechanism implies a slower hydrolysis of the pseudo-base (IVb) derived from 2-*p*-anisyl-4,6-diphenylpyrylium salts (Ib) as a consequence of the diminished susceptibility of the carbonyl group to anionoid attack due to the resonance effect of the *p*-situated methoxyl group. The prediction is in qualitative agreement with Dilthey's observation[10] that the cleavage of IVb (to anisic acid) is perceptibly more sluggish than that of IVa.

There remains the question of the structure of the "methyl ether" of IVa which is formed when the pseudo-base is treated with methyl iodide in methanolic sodium methoxide. *A priori*, this substance might be represented as the methoxypyran (IId), the enol ether (IIId) or the C-methyl derivative (IVd). The dramatic difference between its ultraviolet spectrum and that of the pseudo-base (Fig. 1), however, permits the rejection of structure IVd. The occurrence in the infrared spectrum of a strong band at 5.97 μ is probably attributable to the presence of a conjugated carbonyl group, an interpretation consistent only with expression IIId.

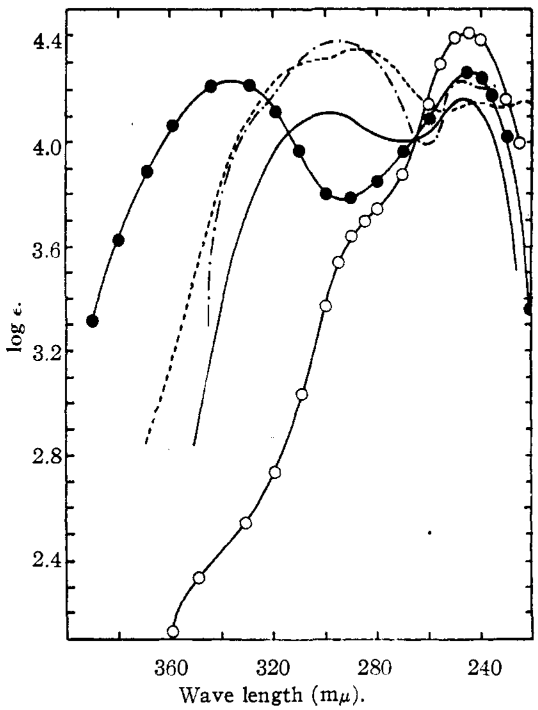
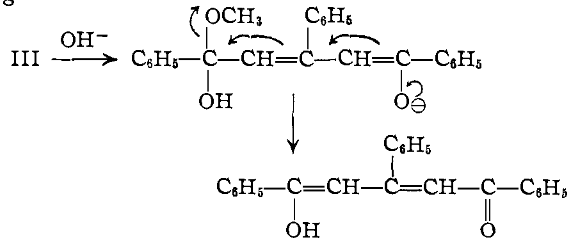


Fig. 1.—Ultraviolet absorption spectra, solvent ethanol: —, IVa; –·–·–., benzalacetophenone + acetophenone; ●-●-●, IVc; - - - -, IVb; -○-○-○-, IIId.

Dilthey's formulation[2b] of the "methyl ether" as the methoxypyran (IId) is based largely on the failure of the substance to form carbonyl derivatives. However, we find that the "methyl ether" is readily hydrolyzed to benzoic acid by alkali, a reaction best formulated in terms of the enol ether structure (IIId) by analogy to the cleavage of β-alkoxy-α,β-unsaturated ketones and their vinylogs.[11]



$$III \xrightarrow{OH^-} C_6H_5-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OCH_3}{|}}{C}}-CH=\overset{\overset{\displaystyle C_6H_5}{|}}{C}-CH=\underset{\underset{\displaystyle O^{\ominus}}{|}}{C}-C_6H_5$$

$$\downarrow$$

$$C_6H_5-\underset{\underset{\displaystyle OH}{|}}{C}=CH-\overset{\overset{\displaystyle C_6H_5}{|}}{C}=CH-\underset{\underset{\displaystyle O}{\|}}{C}-C_6H_5$$

The proximate product is presumably the pseudo-base, which is then cleaved according to the mechanism suggested above.

## Experimental[12]

The pseudo-bases were prepared by treatment of the corresponding pyrylium chloroferrates with sodium acetate or

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(7) H. M. Randall, *et al.*, "Infrared Determination of Organic Structures," D. Van Nostrand Company, New York, N. Y., 1949, p. 166.

(8) Dilthey's failure[2a] to isolate a discrete product from the neutral fraction is in accord with the well-known[9] instability of dypnone (VIII) in alkaline solution.

(9) See for example "Beilstein's Handbuch der Organischen Chemie," Vol. 7, 2nd Supplement, Springer-Verlag, Berlin, p. 438.

(10) W. Dilthey, *Ber.*, **52**, 1200 (1919).

(11) A recent example is the cleavage of tropolone methyl ether, [W. von E. Doering and L. H. Knox, THIS JOURNAL, **73**, 828 (1951)].

(12) All melting points are corrected. The microanalyses are by Mr. J. Pirie.

sodium bicarbonate according to known procedures: 2,4,6-**triphenylpyrylium pseudo-base** (IVa), buff needles from alcohol, melted at 115–116° (reported,[2a] m.p. 119°); 2,6-**diphenyl-4-*p*-anisylpyrylium pseudo-base** (IVc), pale-yellow needles from ethyl acetate–methanol, melted at 122–122.5° (reported[13] m.p. 122°).

**4,6-Diphenyl-2-*p*-anisylpyrylium pseudo-base** (IVb) was obtained as pale-yellow needles from ether. Although the literature[10] reports m.p. 105°, in our hands the m.p. remained constant at 89.5–90° after the substance had been recrystallized five times.

*Anal.* Calcd. for $C_{24}H_{20}O_2$: C, 80.90; H, 5.66. Found: C, 80.97; H, 5.48.

The "methyl ether" of **IVa** (**IIId**), hard, heavy, white prisms from benzene–Skellysolve A, melted at 140–141° (reported 142–143°).

The ultraviolet spectra (Beckman model DU spectrophotometer) of freshly-prepared 95% ethanol solutions of these substances were determined using material which had been recrystallized to constant melting point and dried *in vacuo*. Although the photodimerization of benzalacetophenone has been reported[4] to cause a rapid diminution in intensity of its absorption maximum, no such changes were observed with any of the pseudo-bases.

The infrared spectra of benzalacetophenone, the "methyl ether" (IIId) and the pseudo-base (IVa) were determined in chloroform solutions with the Perkin–Elmer spectrometer, Model 12-B. The relevant portions of the spectrum were plotted by a point-by-point analysis of the sample and solvent curves.

**Alkaline Hydrolysis of the "Methyl Ether."**—A solution of 0.37 g. of the methyl ether and 0.30 g. of potassium hydroxide in 10 cc. of 90% methanol was heated under reflux. The solution immediately turned bright-red. After an hour, the mixture was evaporated. The residue was taken up in water and the aqueous solution, after having been washed with ether, was acidified with hydrochloric acid. The precipitated acidic material was extracted with chloroform and dried (sodium sulfate). Evaporation of the chloroform solution left 0.11 g. (85%) of benzoic acid, m.p. and mixed m.p. 117–119°.

LOS ANGELES 7, CALIF. RECEIVED JULY 16, 1951

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[13] W. Dilthey, *Ber.*, **53** 252 (1920).

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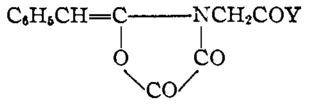
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# The Condensation Products of Oxalyl Chloride with Monosubstituted Amides: Structure and Reactions

BY JOHN C. SHEEHAN AND ELIAS J. COREY[1]

An investigation has been made of the structure of the reaction products of oxalyl chloride with phenylacetamides and the methods by which the resulting heterocyclic system can be degraded to the original monosubstituted amides. The correctness of the 2-benzylidene-3-oxazolidine-4,5-dione structures assigned to the condensation products has been established unequivocally by, *inter alia*, the preparation of the isomeric pyrrolidine-2,3,5-triones, which represent the alternative formulation. The pyrrolidine-2,3,5-triones appear to be formed readily only by base catalyzed cyclization. It is concluded that aminolysis represents the most practical procedure for obtaining phenylacetamides from 2-benzylidene-3-oxazolidine-4,5-diones. The possible application of 2-benzylidene-4,5-diketo-3-oxazolidineacetyl chloride in the indirect synthesis of benzylpenicillin and its analogs is discussed.

Compounds containing the 2-benzylidene-3-oxazolidine-4,5-dione nucleus appear to be promising intermediates in the synthesis of β-lactamthiazolidines bearing the 6-phenylacetylamino substituent characteristic of benzylpenicillin. For example, the successful use of 2-benzylidene-4,5-diketo-3-oxazolidineacetyl chloride (II)[2] in the acid chloride–thiazoline reaction previously disclosed,[3] followed by removal of the oxalyl grouping from the heterocyclic ring, would lead to structures like that of benzylpenicillin.



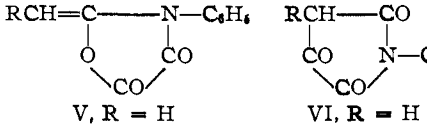
I, Y = OH  III, Y = $NHC_6H_5$

II, Y = Cl  IV, Y = $OCH_2C_6H_5$

Treatment of II with aniline or benzyl alcohol resulted in formation of the corresponding anilide (III) or benzyl ester (IV). The benzyl ester IV could be obtained more readily and in 91% yield by treatment of benzyl phenaceturate with oxalyl chloride. The infrared spectra of I–IV exhibit bands in the double bond region at 5.50, 5.73 and 5.95 μ which are highly characteristic of the heterocyclic system.

At the beginning of the present work the available information concerning the conversion of oxazolidinediones to acylamino compounds was meager. An investigation of the chemistry of these compounds with particular emphasis on ring-cleavage reaction was therefore undertaken.

Structures involving the oxazolidinedione nucleus were first postulated by Stollé and Luther[4] as the products of the reaction of oxalyl chloride with anilides. These investigators considered the product of the reaction of oxalyl chloride with acetanilide as being best represented by the oxazolidinedione structure V rather than the isomeric pyrrolidinetrione structure VI, because it reacted readily with water to form acetic acid and oxanilic acid. The compound also gave no coloration with ferric chloride solution. Additional support for the oxazolidinedione structure for these products may be drawn from the work of Wislicenus and Sattler,[5] who prepared the pyrrolidinetrione VII by the base-catalyzed condensation of ethyl oxalate with propionanilide. The structure was inferred from analytical data and from the fact that the compound



V, R = H  VI, R = H

VIII, R = $CH_3$  VII, R = $CH_3$

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[1] Bristol Laboratories Fellow, 1948–1950.

[2] Prepared in high yield by interaction of phenaceturic acid and oxalyl chloride in dioxane followed by phosphorus pentachloride, G. B. Brown, *Arch. Biochem.*, **24**, 429 (1949).

[3] J. C. Sheehan, E. L. Buhle, E. J. Corey, G. D. Laubach and J. J. Ryan, THIS JOURNAL, **72**, 3828 (1950).

[4] R. Stollé and M. Luther, *Ber.*, **53**, 314 (1920).

[5] W. Wislicenus and W. Sattler, *ibid.*, **24**, 1245 (1891).