tone) was always less than 10% of the total weight of ester. The literature value[11] (118°) for the m.p. of guiacol α-naphthylurethan was found to be erroneous. This derivative, both from our product and from an authentic sample, had m.p. and mixed m.p. 134–135° (from chloroform–hexane).

Anal. Calcd. for $C_{18}H_{15}O_3N$: C, 73.70; H, 5.16. Found: C, 73.73; H, 5.20.

Products from *o*-Methylbenzophenone.—The acid from the hydrolysate was obviously a mixture, since on crystallization from hot water two successive fractions melted at 99–101° and 105–115°. In order to determine the composition, 0.60 g. of the total acid was oxidized with alkaline potassium permanganate and the resulting 0.49 g. of colorless solid treated with hot carbon tetrachloride.[12] The insoluble phthalic acid amounted to 0.35 g. and evaporation of the extract left 0.08 g. of benzoic acid. The molar ratio of *o*-toluic to benzoic acid was thus about 3:1. From the phenolic fraction was obtained a small amount of *o*-cresoxyacetic acid by treatment with chloroacetic acid and base. The remainder of this derivative was impure phenoxyacetic acid.

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(11) H. E. French and A. F. Wirtel, This Journal, **48**, 1736 (1926).

(12) W. E. Bachmann and M. X. Barton, *J. Org. Chem.*, **3**, 300 (1938).

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Spectral Detection of a Transient Ion Pair Intermediate in the Reaction of a Triarylmethyl Chloride with Pyrrole in Benzene Solution[1,2]

By C. Gardner Swain, Laura E. Kaiser and Terence E. C. Knee

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Spectral detection of a transient carbonium ion intermediate has been reported previously only by Roberts and Hammett, who observed a transient yellow color in the reaction of 1.3 *M* mercuric nitrate with 1.0 *M* benzyl chloride in 60% dioxane–40% water mixture at 25°.[3] Experiments of this sort if done quantitatively should be able to furnish the concentration of reaction intermediates and the separate kinetic orders and absolute rate constants for their formation and decay. We have investigated the reaction of trianisylmethyl chloride with pyrrole at 25° in benzene solution, which gives α-trianisylmethylpyrrole, and found a transient absorption in the green region of the spectrum. The absorption maximum is at 498 mμ, close to the maximum at 483 mμ observed with trianisylcarbinol or trianisylmethyl chloride in 100% sulfuric acid. It was assumed that both colors are due to the same carbonium ion and that its extinction coefficient is the same in the two media; this was supported by showing that the extinction coefficient of trianisylmethyl perchlorate in benzene differs from that in sulfuric acid by less than a factor of four. Figure 1 is the resulting plot of carbonium concentration *vs.* time for a typical run. Table I gives data for 21 runs in which similar behavior was observed.

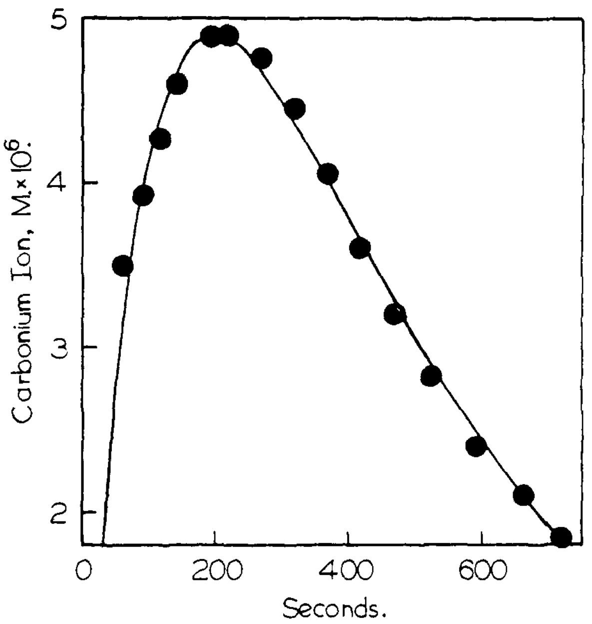

Fig. 1.—Observed points and calculated curve for trianisylmethyl ion concentration *vs.* time in the reaction of trianisylmethyl chloride with pyrrole in benzene solution at 25°, run no. 46.

Table I

Maximum Intermediate Concentrations[a]

Run	[RCl], $M \times 10^3$	[PH], M	$I_{\max}$,[a] $M \times 10^6$	$I_{\max}$/ [RCl][PH] $M^{-1} \times 10^3$
2	2.72	0.099	1.34	4.99
5	2.45	.189	2.40	5.19
11	1.58	.198	1.62	5.18
13	3.28	.198	3.31	5.11
14	3.26	.148	2.63	5.45
16	3.26	.247	4.53	5.64
19	2.53	.142	2.24	6.24
20	2.17	.276	3.38	5.65
23	2.17	.294	3.70	5.80
27	2.00	.184	2.12	5.76
28	2.00	.163	1.70	5.22
31	3.41	.113	2.59	6.73
33	1.74	.318	3.73	6.74
35	1.74	.212	1.98	5.37
36	1.74	.269	2.82	6.02
38	2.87	.212	3.25	5.35
39	2.87	.226	3.48	5.37
42	4.10	.283	6.08	5.25
44	2.96	.339	5.84	5.82
46	4.09	.226	4.90	5.31
47	4.09	.113	2.44	5.28
			Av.	5.60 ± 0.39

[a] Maximum intermediate concentrations assuming the same extinction coefficient as in 100% sulfuric acid.

The maximum concentration of intermediate in all runs is proportional to the product of concentrations of chloride and pyrrole. This is demonstrated by the fact that the last column of Table I ($I_{\max}$/[RCl][PH]) has an average deviation of only 7% whereas $I_{\max}$[PH]/[RCl], $I_{\max}$/[RCl], $I_{\max}$/[RCl][PH]^2 and $I_{\max}$/[RCl][PH]^3 have average deviations of 54, 26, 30 and 61%, respectively. This relationship suggests that all steps consuming the intermediate are of lower order by one with respect to pyrrole than the step forming it.

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(1) For complete experimental data see L. E. Kaiser, Ph.D. thesis, M.I.T., February, 1954.

(2) This work was supported by the Office of Naval Research, Contract No. N5ori-07838, Project No. NR 055-198.

(3) I. Roberts and L. P. Hammett, This Journal, **59**, 1063 (1937).

Therefore the mechanism appears to be

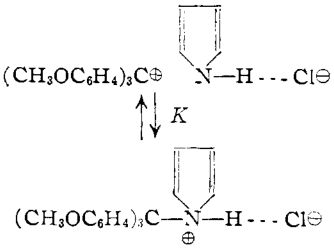
$$\mathrm{RCl} + \mathrm{PH} \underset{k''}{\overset{k}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k'} \text{products}$$

or

$$\mathrm{RCl} + 2\mathrm{PH} \underset{k''}{\overset{k}{\rightleftharpoons}} \mathrm{I} + \mathrm{PH} \xrightarrow{k'} \text{products}$$

where RCl, PH and I represent chloride, pyrrole and intermediate, respectively.

With either of these mechanisms, it is possible to find one set of rate constants (k, k' and k'') which will give plots of I *vs.* t having approximately the same shape and values of $t_{\max}$ as those observed for all 21 runs. Furthermore, this analysis reveals an additional feature of the mechanism. All of the calculated curves have values of $I_{\max}$ about a hundred-fold larger than the observed ones reported in Table I, indicating that the total concentration of intermediate is uniformly higher by 10^2 than the concentration of carbonium ion which we measured. It is possible that most of the intermediate exists in the form of a colorless ammonium ion II which is an isomer or tautomer of the colored carbonium ion I in mobile equilibrium with it with an equilibrium constant K of the order of 10^2.



I

II

The data are too rough to establish the kinetic order of the rate of ionization by a more complete kinetic analysis. Our best fit, which gave an average deviation of 10.5% between calculated and observed maximum intensities for the 21 runs, was obtained by assuming a third-order ionization (second order with respect to pyrrole) and fast equilibrium between I and II with $K = 150$. A calculated curve based on these assumptions is shown in Fig. 1. However, there is not adequate evidence to exclude a second-order ionization (first order with respect to pyrrole).

Experimental

Trianisylcarbinol.—This compound was prepared from anisylmagnesium bromide and ethyl anisate by the Grignard reaction. The product was recrystallized numerous times from petroleum ether–benzene mixtures and finally yielded white crystals, m.p. 83.2–84.5°.

Trianisylmethyl Chloride.—The compound was prepared from the carbinol and acetyl chloride in benzene solution by utilizing the procedure for triphenylmethyl chloride.[4] The compound was filtered, recrystallized and handled in a dry-box, the air of which was dried to a dew point of −50 to −60° by continuously circulating it through seven 12-inch drying towers filled with Davison Chemical Corp. 6–16 mesh silica gel. The purest compound was obtained by dissolving in benzene containing a few drops of acetyl chloride, then adding low-boiling petroleum ether, allowing the compound to crystallize slowly and repeating this many times in the dry-box. It was filtered with exclusion of air and kept pumped down to 1 mm. pressure in a desiccator over calcium hydride for a day, m.p. 154.7–155.9°. This still showed a slight pink tinge, the light absorption indicating a carbonium ion impurity of 0.01–0.03% if the same extinction coefficient was assumed as that for the carbinol in *100% sulfuric acid*.

Solvents.—Benzene, ethyl ether, 30–60° petroleum ether and methanol were Mallinckrodt analytical reagent grades. Benzene was refluxed either over sodium wire or Metal Hydrides calcium hydride and then distilled, discarding the forerun. The ethers were dried over sodium wire. The methanol was dried with magnesium[5] or by refluxing 500 ml. with 5 g. of calcium hydride and distilling.

Product.—The product from a large scale run of trianisylmethyl chloride and pyrrole in benzene was isolated by removing the solvent under vacuum. The crude product was a gray powder, m.p. 178.1–180.0°, in 94.1% yield. After recrystallization from an ethyl ether–chloroform mixture a white powder was obtained, m.p. 182.7–183.5°. *Anal.* Calcd. for $C_{26}H_{25}NO_3$: C, 78.17; H, 6.11. Found: C, 78.01; H, 6.31. The infrared absorption spectrum of the compound showed an N-H frequency at 2.87 μ, indicating that substitution had taken place on carbon.

Spectrum in Sulfuric Acid.—Sulfuric acid of 100% strength was prepared from du Pont C.P. 98% reagent and Baker and Adamson 30% sulfur trioxide reagent and its analysis checked by density and freezing point measurements.[6] It had no absorption at 483 mμ. Both trianisylcarbinol and trianisylmethyl chloride give an orange color in sulfuric acid, with a maximum at 483 mμ.[7] A calibration chart for relating optical density to concentration was prepared for trianisylmethyl chloride by measuring the maximum absorption for a series of solutions of known concentration in sulfuric acid; from 1×10^{-6} to 6×10^{-6} M this was nearly a straight line corresponding to a molar extinction coefficient of 1×10^5.

Comparison of Optical Densities in Benzene and Sulfuric Acid.—Solutions of known concentration of trianisylmethyl perchlorate in dry benzene and 100% sulfuric acid were prepared in the dry-box, and visual comparison made of their optical densities using Nessler tubes. The sulfuric acid solution was diluted further with sulfuric acid until an equivalent optical density to the benzene solution was obtained.

Kinetic Measurements.—A Cary recording spectrophotometer model 11MS with glass-stoppered silica cells of 1.0, 2.0 and 5.0 cm. light paths was used. Temperature control of 25 ± 0.3° was maintained by pumping water from a 25° thermostat continuously through a hollow, brass cell-holder as well as through the walls of the cell compartment of the instrument. All kinetic measurements were made using only a single beam at 498 mμ, the wave length of maximum absorption. A blank for the solvent and cell only was determined in each case and subtracted from the optical density of the solution. All optical densities mentioned are corrected in this manner.

The silica cells and all other glassware were dried in a 175° oven for several hours and cooled under vacuum in a desiccator which was released with dry air. The trianisylmethyl chloride was weighed and made up to volume with benzene directly distilled into the volumetric flask. It was established that exposure of a solution to visible or ultraviolet light for several hours had negligible effect on its absorption. The pyrrole was Eastman Kodak Co. white label grade freshly redistilled in a nitrogen atmosphere before each kinetic run, b.p. 129–130°, and volumetrically diluted with benzene distilled directly into the volumetric flask. Five ml. of each solution at 25° was pipetted into a glass-stoppered erlenmeyer flask and the solution was mixed thoroughly by swirling. Zero time was taken as the time of mixing. The mixture was transferred rapidly to the 2-cm. (6.5 ml.) silica cell, the cell was stoppered, and recording was started. The time interval between zero time and the start of recording was generally about 12–16 sec.

All the solutions of trianisylmethyl chloride absorbed even before adding the pyrrole; *e.g.*, lower limits for the initial carbonium salt impurity are 0.939×10^{-6} M or 19% of the maximum in run 46 and 1.85×10^{-6} M or 72% of the maximum in run 31. Consequently in Fig. 1 for run 46 the time

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(4) W. E. Bachmann, *Org. Syntheses*, **23**, 100 (1943).

(5) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, 2nd ed., p. 360.

(6) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **55**, 1900 (1933).

(7) H. Lund, *ibid.*, **49**, 1346 (1927).

scale for observed points had to be shifted (lengthened) by 50 seconds to obtain agreement with the calculated curve.

Reaction with Methanol.—No absorption at 425 mμ (peak for unsubstituted triphenylcarbonium ion) was detected when triphenylmethyl chloride, thiocyanate, acetate, benzoate or azide was solvolyzed in methanol or in benzene containing methanol or phenol, only ultraviolet absorption of the reactants or products with maxima in the region 230–290 mμ.

With trianisylmethyl chloride in benzene containing methanol (instead of pyrrole), the absorption at 498 mμ showed only a rise to an equilibrium value. For example, with 7×10^{-4} *M* chloride and 1.2×10^{-1} *M* methanol, optical densities at 0, 22, 42, 62, 102, 202, 502 and 942 sec. were 0.210, 0.450, 0.482, 0.505, 0.530, 0.560, 0.610 and 0.650, respectively. If pyridine, di-*n*-propylaniline or N,N-dimethyl-α-naphthylamine was added, discharge of the color was immeasurably fast, and if the amine was present initially no detectable color ever formed.

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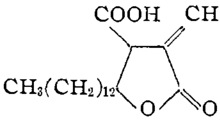
α-Methylene-γ-phenyl-γ-butyrolactone

BY EUGENE E. VAN TAMELEN AND SHIRLEY ROSENBERG BACH[1]

RECEIVED JANUARY 17, 1955

In anticipation of its application to the synthesis of certain natural products, *e.g.*, the labile protolichesterinic acid (I), we should like to disclose a selective and potentially general route to α-methylene lactones, exemplified by the preparation of α-methylene-γ-phenyl-γ-butyrolactone (II). α-Carboxy-γ-phenyl-γ-butyrolactone (III),[2] readily available by hydrolysis of the lactonic ester derived from diethyl malonate and styrene oxide, was allowed to react at room temperature with formaldehyde and diethylamine, whereby it was transformed, with decarboxylation, to α-diethylaminomethyl-γ-phenyl-γ-butyrolactone (IV). This Mannich product was obtained as a stable, distillable oil which could be readily converted to a crystalline methiodide (V). *Treatment of the methiodide with aqueous sodium bicarbonate at room temperature yielded the methylene lactone II.* This ready elimination may be viewed as conforming to the Hofmann type, but greatly facilitated by the lability of the α-hydrogen (*cf.* the transformation of tropinone methiodide to 2,4-cycloheptadienone).[3]



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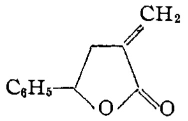
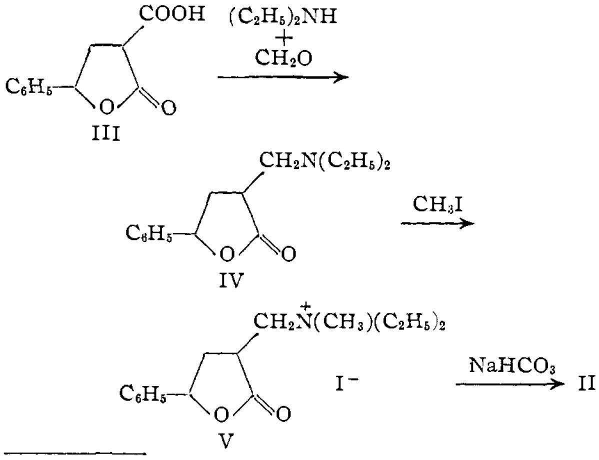
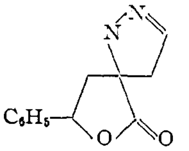


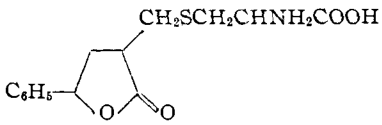
II



Structure proof for II rests upon three pieces of evidence: (i) ultraviolet spectral comparison, the absorption in the 220–240 mμ region compares favorably with that of established α-methylene-γ-lactones (Table I), (ii) catalytic reduction to α-methyl-γ-phenyl-γ-butyrolactone, which was compared with an authentic sample, and (iii) production of formaldehyde by ozonolysis, a result which clearly indicates the exocyclic nature of the double bond. The lactone II was characterized by (i) conversion with diazomethane to a pyrazoline, and (ii) the preparation of the cysteine addition compound; these two products we consider to have the structures VI and VII, respectively.



VI



VII

TABLE I

Extinction coefficients	220 mμ	230 mμ	240 mμ
α-Methylene-γ-phenyl-γ-butyrolactone (II)[a]	4960	2170	990
α-Methylene-γ-butyrolactone[b]	..	2400	500
Protolichesterinic acid (I)[a]	7060	4620	..

[a] Measured with a Cary spectrophotometer; solvent, ethanol. [b] C. J. Cavallito and T. H. Haskell, THIS JOURNAL, **68**, 2332 (1946).

Experimental[4]

α-Diethylaminomethyl-γ-phenyl-γ-butyrolactone (IV).—Three and one-half grams of α-carboxy-γ-phenyl-γ-butyrolactone (m.p. 144.5–145.5°)[2] was added to 7.5 g. of diethylamine in a 50-ml. erlenmeyer flask, after which 3.7 g. of 30% formaldehyde solution was added slowly with swirling. During the addition process, the carboxylactone dissolved smoothly while the mixture effervesced and heat evolved. After standing for two days, the aqueous layer was saturated with potassium carbonate and the upper layer separated. After extracting once with ether, the ether solution was washed twice with water and evaporated *in vacuo*. Upon distillation of the residue at 116–118° (0.2 mm.), 1.6–1.7 g. (40–43%) of colorless α-diethylaminomethyl-γ-phenyl-γ-butyrolactone was obtained.

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.51; N, 5.67. Found: C, 73.23; H, 7.82; N, 5.20.

In order to obtain the **methiodide V**, the basic lactone (2.36 g.) was treated with 10 ml. of *dry* methyl iodide. After about three minutes, pale yellow crystals of the quaternary salt began to precipitate rapidly. Upon completion of the reaction, the solid was triturated with ether, filtered, and dried. The crude salt, obtained in a yield of 3.0 g. (80%), was hygroscopic in that it rapidly became sirupy upon exposure to the atmosphere; in an attempted melting point determination, the solid merely foamed up in the capillary.

α-Methylene-γ-phenyl-γ-butyrolactone (II).—After the addition, with shaking, of 35 ml. of 5% sodium bicarbonate

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[1] Wisconsin Alumni Research Foundation Research Assistant, Feb.-June, 1953; du Pont Summer Research Assistant, 1953.

[2] G. Van Zyl and E. van Tamelen, THIS JOURNAL, **72**, 1357 (1950).

[3] G. Buchi, N. C. Yang, S. L. Emerman and J. Meinwald, *Chemistry and Industry*, 1063 (1953).

[4] All melting points are corrected.