solution was then acidified and the solid obtained was treated with sodium bicarbonate when it dissolved with effervescence. It was filtered and the filtrate acidified. The acid crystallized from acetic acid as white plates, m.p. 285°, yield 0.4 g.

*Anal.* Calcd. for $C_{17}H_{20}O_6$: equiv., 160; C, 63.75; H, 6.25. Found: equiv. (by titration), 159.4; C, 63.57; H, 6.32.

**4,4′-Dimethyl-3′-ethylcoumarino-5′,6′(6,5)-α-pyrone.**—Butyric anhydride (12 ml.), fused sodium butyrate (5 g.) and 5-hydroxy-6-acetyl-4-methylcoumarin (5 g.) were refluxed at 160–170° as before. The product isolated as before crystallized from acetic acid, needles, m.p. 205°; yield, 3 g.

*Anal.* Calcd. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.19. Found: C, 70.94; H, 5.18.

The product was treated with potassium hydroxide and sodium ethoxide as before, but the original compound was recovered unchanged.

**The 2,6-Dimethoxy-5-(α-ethyl-α-carboxy-β-methylvinyl)-β-methylcinnamic Acid.**—The above coumarino-α-pyrone was treated with dimethyl sulfate and alkali as before. The acid isolated as before crystallized from acetic acid; white needles, m.p. 305°.

*Anal.* Calcd. for $C_{18}H_{22}O_6$: equiv., 167; C, 64.67; H, 6.58. Found: equiv. (by titration), 166.6; C, 64.58; H, 6.50.

**4,4′-Dimethyl-3′-phenylcoumarino-5′,6′(6,5)-α-pyrone.**—The coumarin (3 g.), acetic anhydride (10 ml.) and dry sodium phenylacetate (3 g.) were refluxed at 160–170° as before. The product, as obtained previously, crystallized from acetic acid as lustrous needles, m.p. > 300°, yield 2.0 g.

*Anal.* Calcd. for $C_{20}H_{14}O_4$: C, 75.47; H, 4.40. Found: C, 75.50; H, 4.47.

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## The Behavior of Triphenylmethyl Chloride in Nitromethane

BY BILL B. SMITH AND J. E. LEFFLER

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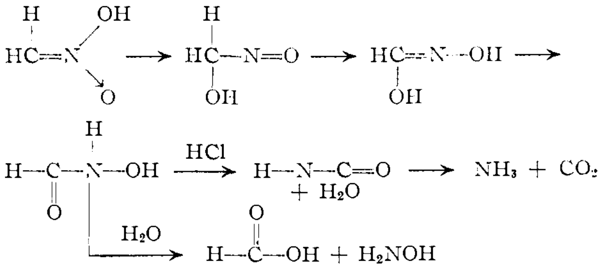
The formation of ion-pairs by triphenylmethyl chloride in nitromethane has been studied spectrophotometrically and the equilibrium constant reported by Bentley, Evans and Halpern.[1] As a preliminary to other work contemplated by us, the equilibrium constant for ion-pair formation has been redetermined by the same method. We find that the optical density of solutions of triphenylmethyl chloride in nitromethane changes with time and that the optical density extrapolated to zero time, from which we have calculated the apparent equilibrium constants for ion-pair formation, depends very much on the method used for purifying the nitromethane.

Using a commercial sample of nitromethane dried over phosphorus pentoxide and distilled (method I), the values of the equilibrium constant are in good agreement with those cited.[1] But some doubt is cast on the interpretation of those values by the fact that ammonium chloride precipitates if the solution is allowed to stand for several days and that the supernatant liquid after evaporation and hydrolysis gives triphenylmethane as well as triphenylcarbinol. Since the sample of triphenylmethyl chloride used was entirely free from triphenylmethane, that product is very likely the result of a reaction with formic acid present as an impurity in the nitromethane. Formic acid has a boiling point very close to that of nitromethane and is known to reduce triphenylmethyl chloride to triphenylmethane.[2]

Even when the nitromethane is purified more elaborately[3] and dry-box or vacuum-line technique is used in making up the solutions the drift in optical density is still observed. Triphenylmethane is no longer detectable as a product but the decay in optical density is even faster and the precipitation of ammonium chloride begins in a few minutes at room temperature rather than after several hours. Another product of the reaction is triphenylmethylamine.

The average value of the apparent equilibrium constant for ion-pair formation in carefully purified nitromethane at a room temperature near 25° is $1.75 \times 10^{-4}$, about half that reported in the literature and about half that found by us for the less elaborately purified solvent. Formic acid causes a notable intensification of the color when it is added to the solution.

The disproportionation of nitromethane in the presence of hydrogen chloride at 130° to give carbon dioxide and ammonium chloride has been known for some time.[4] The following appears to be a plausible reaction path, especially in view of the observation that formylation of hydroxyl compounds takes place and that hydroxylamine hydrochloride rather than ammonium chloride is produced in the presence of water



We believe that the decay in the color of triphenylmethyl chloride in pure nitromethane is due to a similar reaction in the presence of triphenylmethyl chloride. Although participation of hydrogen chloride produced by the action of traces of water cannot be excluded as a possibility, it is significant that ammonium chloride is produced faster in the more carefully prepared and drier solutions in which hydrolysis of the triphenylmethyl chloride should be at a minimum. Triphenylcarbonium ions perhaps may themselves promote the rearrangement of the hydroxamic acid. On the other hand, the reaction of tris-(*p*-anisyl)-carbinol and perchloric acid in nitromethane is reported to give 1,1,1-tris-(*p*-anisyl)-2-nitroethane.[5] No analogous product was found in our triphenylmethyl chloride–nitromethane reaction mixtures.

### Experimental

**Triphenylmethyl chloride** was prepared from the carbinol.[6]

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[1] A. Bentley, A. G. Evans and J. Halpern, *Trans. Faraday Soc.*, **47**, 711 (1951).

[2] S. T. Bowden and T. F. Watkins, *J. Chem. Soc.*, 1333 (1940).

[3] C. J. Thompson, H. J. Coleman and R. V. Helm, THIS JOURNAL, **76**, 3445 (1954).

[4] A. Pfungst, *J. prakt. Chem.*, **34**, 35 (1886).

[5] H. Burton and G. W. H. Cheeseman, *J. Chem. Soc.*, 832 (1953).

[6] W. E. Bachmann, *Org. Syntheses*, **23**, 100 (1943).

It melted at 112.0 to 113.5 and showed no change in melting point on standing in a desiccator over a period of several weeks. Hydrolysis and chromatography gave only triphenylcarbinol; the chloride was entirely free from triphenylmethane.

**Nitromethane** was purified by two methods, both starting with Matheson nitromethane. Method I, like that used by Bentley, Evans and Halpern,[1] consists of refluxing the nitromethane over phosphorus pentoxide, distilling it, collecting the fraction boiling at 100.0 to 100.5° and storing in a glass-stoppered bottle. Method II is like that of Thompson, Coleman and Helm[3] and consists of washing with dilute sodium bicarbonate, sodium bisulfite and sulfuric acid followed by a preliminary drying over phosphorus pentoxide and distillation from phosphorus pentoxide through a 19-plate bubble cap column into ampoules which are sealed while still attached to the column. A forerun, b.p. 100.0–100.2°, is discarded and the main fraction, b.p. 100.5°, collected for use.

**Spectrophotometry.**—In the first experiments weighed portions of triphenylmethyl chloride were made up to a known volume with nitromethane purified by method I. Measurements were made in 1-cm. ground-glass stoppered Beckman cells at 404 and 434 mμ. The optical density decreased with time and the value extrapolated to zero time was used in calculating the equilibrium constants for ion-pair formation. Curve A of Fig. 1 shows the decay of optical density for a typical solution in nitrobenzene purified by method I. Later experiments were made using nitromethane purified by method II, carrying out the procedure of opening the ampoules, making up the solutions, and filling the cells in a dry-box. The cells were sealed around the top with Apiezon Q (method IIa). In method IIb, which gave the same results as method IIa, an ampoule of the nitromethane purified by method II is introduced into one arm of a vacuum system and allowed to stand over boric acid. An ampoule containing a known amount of triphenylmethyl chloride is fused to the system, the solvent frozen, degassed and transferred onto the triphenylmethyl chloride by distillation at $10^{-5}$ mm. The ampoule containing the triphenylmethyl chloride is then sealed and detached from the apparatus. After the optical density measurements the ampoule is opened, the volume of solution measured, and the ampoule calibrated against a standard Beckman cell.

In both method IIa and IIb precipitation of ammonium chloride greatly hindered accurate observation of the rate of decay of the optical density. In method IIb the ampoules were centrifuged before observation. Curve B of Fig. 1 is a typical result.

Values of $K$ obtained from the optical densities are shown in Table I. The extinction coefficients used in the calculations were determined from solutions of triphenylcarbinol in concentrated sulfuric acid and were $\epsilon_{404}$ 35,500 and $\epsilon_{434}$ 35,900. These values of the extinction coefficient agree with those in the literature and with those used in the previous measurements.[1,7]

TABLE I

| Concn. of trityl chloride, moles/liter × $10^2$ | Equilibrium constant for ion-pair formation Measured at 434 mμ | Measured at 404 mμ |
|---|---|---|
| 6.72$^a$ | 1.40 | 1.46 |
| 5.61$^b$ | 2.07 | 2.10 |
| 4.01$^b$ | 1.72 | 1.77 |
| 3.12$^a$ | 1.68 | 1.82 |

$^a$ Sealed ampoule technique (method IIb). $^b$ Dry-box technique (method IIa).

**Reaction Products.**—An ampoule containing 300 mg. of triphenylmethyl chloride was filled with pure nitromethane (method II) by the vapor phase transfer method. The evacuated and sealed ampoule, after five days at 92°, was opened and the precipitate removed. It consisted of 28.6 mg. of ammonium chloride, identified by its sublimation in a sealed tube at 330 to 350°, by conversion to ammonia and by conversion (90%) to silver chloride. Triphenylcarbinol and triphenylmethylamine were isolated by chromatography on alumina from the filtrate after hydrolysis. No triphenylmethane or triphenylnitroethane was observed. The amine was identified by its melting point (90–100°), its solubility in hydrochloric acid, and the melting point of its hydrochloride (230–240°).

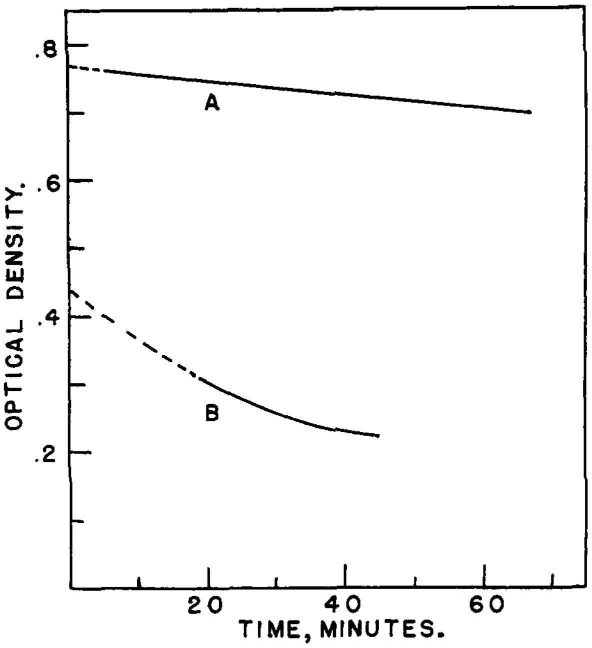

Fig. 1.—Decay of optical density with time (434 mμ): A, 0.0485 $M$ $(C_6H_5)_3CCl$ in nitromethane, method I; B, 0.0561 $M$ $(C_6H_5)_3CCl$ in nitromethane, method IIa.

A similar experiment with nitromethane purified by method I gave triphenylmethane, m.p. 94.5–95.5°, not depressed by an authentic sample.

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(7) W. R. Orndorff, R. C. Gibbs, S. A. McNulty and C. V. Shapiro, THIS JOURNAL, **49**, 1551 (1927).

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## A New Reagent for Dehydrating Primary Amides Under Mild Conditions

BY C. R. STEPHENS, E. J. BIANCO AND F. J. PILGRIM

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In the course of structural studies on Terramycin[1] and on Aureomycin,[2] we have observed previously that arylsulfonyl chlorides in cold pyridine solution convert the antibiotics to nitrile derivatives through dehydration of the primary carboxamido group. The use of the above reagent in converting primary amides to nitriles apparently has not been reported previously, although it is known that certain acyl halides[3] (*e.g.*, 3,5-dinitrobenzoyl chloride) do bring about this transformation in the presence of pyridine. Acyl halide–pyridine

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(1) F. A. Hochstein, C. R. Stephens, L. H. Conover, P. P. Regna, R. Pasternack, P. N. Gordon, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, THIS JOURNAL, **75**, 5455 (1953). Terramycin is the registered trade-mark of Chas. Pfizer & Co., Inc., for the antibiotic oxytetracycline.

(2) C. R. Stephens, L. H. Conover, R. Pasternack, F. A. Hochstein, W. T. Moreland, P. P. Regna, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, *ibid.*, **76**, 3568 (1954). Aureomycin is the registered trade-mark of Lederle Laboratories Division, American Cyanamid Co., for the antibiotic chlorotetracycline.

(3) (a) Q. E. Thompson, THIS JOURNAL, **73**, 5841 (1951); (b) J. Mitchell, Jr., and C. E. Ashby, *ibid.*, **67**, 161 (1945).