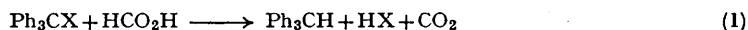


1074. Preparation and Decomposition of Triphenylmethyl Formate.

By R. G. R. BACON and J. KÖCHLING.

The preparation of crystalline triphenylmethyl formate is reported. This easily hydrolysed ester undergoes first-order thermal decomposition above the melting point, giving triphenylmethane as the major product, by reductive decarboxylation, and triphenylmethanol as the minor product, by decarbonylation. Under the conditions examined, decomposition did not occur in benzene, but occurred slowly in methyl cyanide and rapidly in formic acid. The production of triphenylmethane in this last-named solvent is discussed in relation to similar reactions of other triphenylmethyl compounds. In acidified methyl cyanide, triphenylmethyl formate reacted quantitatively with the solvent, giving *N*-triphenylmethylacetamide in a first-order Ritter-type additive process.

TRIPHENYLMETHYL FORMATE has not hitherto been isolated, though it has been postulated¹ as an unstable intermediate in reactions of the type (1) (X = OH, OEt, Cl), which have been carried out in hot formic acid solution:



We have observed a similar reductive decarboxylation in formic acid with triphenylmethyl isothiocyanate (X = NCS).² Several triphenylmethyl esters which are more stable than the formate have been prepared, and the preferred method involves reaction between a suspension of the silver salt of the acid and a solution of triphenylmethyl chloride or bromide,³ or isothiocyanate,² in a hydrocarbon solvent. The advantage of the isothiocyanate lies in its stability towards water and its readily availability in the pure state. We have applied this method to silver formate, and have thus obtained triphenylmethyl formate quantitatively from triphenylmethyl chloride, bromide, or isothiocyanate in benzene at ordinary temperatures. Silver formate has been studied relatively little;⁴⁻⁶ it is known to decompose explosively at 90–100°.⁵

Triphenylmethyl formate was obtained as colourless crystals, which were stable in the absence of moisture, melting without decomposition at 99–101°. It was very readily hydrolysed, and was preferably prepared and handled in a glove-box. Its sensitivity to water was, however, less pronounced than that of triphenylmethyl trifluoroacetate² or nitrate.⁷ In moist air it quickly developed the deep yellow colour of the Ph₃C⁺ ion, as conversion into triphenylmethanol and formic acid proceeded; the same colour resulted if the two hydrolysis products were mixed. Like triphenylmethanol, triphenylmethyl formate also produced the Ph₃C⁺ ion when dissolved in concentrated sulphuric acid. The formate was stable at ordinary temperatures in a dry hydrocarbon solvent, such as benzene, but passage of the solution through a chromatographic column of alumina or silica resulted in quantitative hydrolysis to the alcohol.

Heated above its melting point, triphenylmethyl formate evolved gas, and, if air was absent during reaction, the residue consisted entirely of triphenylmethane and triphenyl-

¹ (a) S. T. Bowden, D. L. Clarke, and W. E. Harris, *J.*, 1940, 874; (b) S. T. Bowden and T. F. Watkins, *J.*, 1940, 1333.

² R. G. R. Bacon, J. Köchling, and T. A. Robinson, preceding Paper.

³ K. D. Berlin, L. H. Gower, J. W. White, D. E. Gibbs, and G. P. Sturm, *J. Org. Chem.*, 1962, 27, 3595.

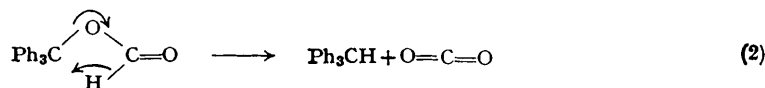
⁴ P. Mars, J. J. F. Scholten, and P. Zwietering, *Adv. Catalysis*, 1963, 14, 35.

⁵ A. Keller and F. Körösy, *Nature*, 1948, 162, 580.

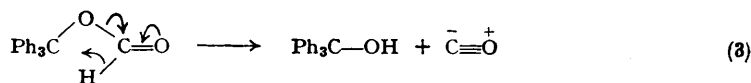
⁶ J. P. Fugassi and G. A. Cowan, U.S.P. 2,630,444/1953.

⁷ (a) S. J. Cristol and J. E. Leffler, *J. Amer. Chem. Soc.*, 1954, 76, 4468; (b) R. T. Merrow and R. H. Boschan, *ibid.*, p. 4622; (c) G. W. H. Cheeseman, *Chem. and Ind.*, 1954, 281.

methanol, consistently obtained (at 148°) in a molecular ratio of about 87:13. The triphenylmethane resulted from a reductive decarboxylation, which can be represented as an intramolecular transfer of hydride ion from an incipient formate ion to an incipient triphenylmethyl carbonium ion:



The accompanying triphenylmethanol could not be attributed to the presence of water in the apparatus, nor, since the thermal decomposition was complete, was it due to subsequent hydrolysis of surviving formate. It could, however, have arisen from a competing decarbonylation process (3), here represented as a heterolytic reaction:



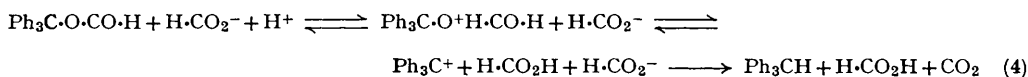
Alternatively, the processes (2) and (3) could be envisaged as homolytic reactions. Carbon monoxide was detected as a reaction product by mass-spectroscopic examination of the gas from the thermal decomposition, generated under argon; the proportion present was in approximate agreement with the proportion of triphenylmethanol in the solid residue. The rate of gas evolution corresponded to a first-order reaction, with a constant of $1.65 \pm 0.1 \times 10^{-2} \text{ min.}^{-1}$ for the combined processes (2) and (3) at 148°. Decomposition was about 50% complete in 30 minutes.

A minor complication was observed if air was present in the reaction vessel. This resulted in the loss of a little of the triphenylmethane by oxidation to benzophenone and phenol, which were isolated, in a typical case, to the extent of about 3 moles per cent:



Conversion of triphenylmethane into benzophenone by oxygen is a known reaction⁸ and presumably has a homolytic mechanism.

The possibility of conducting the decomposition in an anhydrous organic solvent was briefly examined. No change occurred during a few hours in benzene at the boiling point, but in a more polar solvent, methyl cyanide, there was slow formation of triphenylmethane at the boiling point. In formic acid, the decomposition was quite rapid. Even at 20° the ester gave a high yield of the hydrocarbon in four days, whilst at 75° quantitative conversion was observed in about 30 minutes. Solutions of triphenylmethyl formate in formic acid showed the orange colour of the Ph_3C^+ ion, which faded as decomposition proceeded. The ease of this reaction may be attributed to acid catalysis:



Protonation will of course also occur on the carbonyl oxygen, but it is assumed, for this and other hydrolytic reactions depicted in the Paper, that protonation of the oxygen of the $\text{Ph}_3\text{C}-\text{O}$ group provides the reactive species required for fission of this bond.⁹ Hydride-ion transfer may then occur within the ion pair $\text{Ph}_3\text{C}^+\text{H}\cdot\text{CO}_2^-$. Reaction (4) represents a particular case ($\text{X} = \text{O}\cdot\text{CO}\cdot\text{H}$) of the generalised reaction (1). It has been shown,¹⁰ with the

⁸ H. N. Stephens and F. L. Roduta, *J. Amer. Chem. Soc.*, 1935, **57**, 2380.

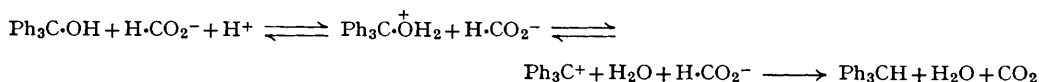
⁹ R. J. Gillespie and J. A. Leisten, *Quart. Rev.*, 1954, **8**, 40.

¹⁰ R. Stewart, *Canad. J. Chem.*, 1957, **35**, 766.

aid of deuterium labelling, that in the case of triphenylmethanol ($X = OH$) reduction is effected by transfer of the non-carboxylic hydrogen of formic acid or formate ion.

Since Bowden and Watkins had given an account^{1b} of the decomposition of triphenylmethanol in formic acid at 100°, we examined both the alcohol and the formate under similar conditions to theirs. The rate of decomposition of triphenylmethanol corresponded to a first-order reaction, $k = 4.0 \pm 0.3 \times 10^{-2}$ sec.⁻¹ at 100°, but reproducibility was poor ($\pm \sim 10\%$), both at 100°, when the reaction was very fast, and at lower temperatures, when the slow dissolution of the alcohol was a handicap. Data from the experiment described by Bowden and Watkins correspond to a slower first-order reaction than we observed. For decomposition of triphenylmethyl formate, we found a first-order constant, $k = 4.8 \pm 0.5 \times 10^{-2}$ sec.⁻¹ at 100°, which was only slightly higher than that of the alcohol; hence, the ease of protonation and carbonium-ion formation appears to be very little different in the case of the ester. Bowden *et al.*¹ observed the ethyl ether to decompose faster than the alcohol in formic acid.

Although the formate molecule may well have a transient existence, in equilibrium with ionic species, in solutions of triphenylmethanol in formic acid, it is unnecessary to adopt Bowden's suggestion that it is an intermediate through which the decomposition of the alcohol proceeds. The reaction can be depicted as involving the ion Ph_3C^+ , produced directly from the alcohol:

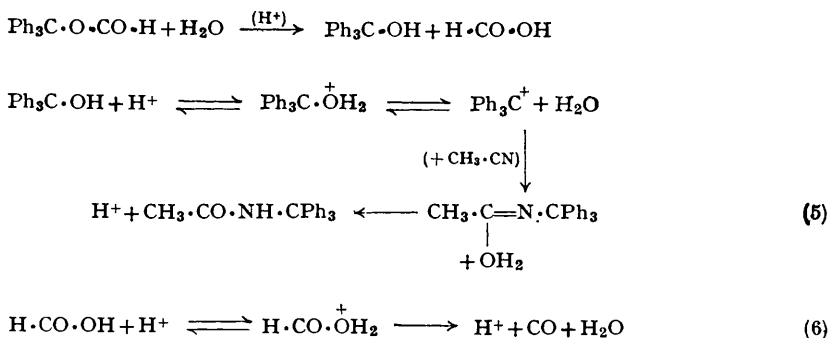


The possibility of acid catalysis of the decomposition of triphenylmethyl formate in a non-acidic organic solvent was also investigated. Anhydrous methyl cyanide was used as solvent and sulphuric acid ($3.5 \times 10^{-5}M$) as the proton source. Reaction was complete in a few minutes at the boiling point and in 1 hour at 50°, but the spectroscopic properties of the evolved gas showed it to be carbon monoxide, and the compound left in solution was exclusively *N*-triphenylmethylacetamide. Measurements of the rate of gas evolution at 50° showed the reaction to be first-order with respect to triphenylmethyl formate, with $k = 0.135 \pm 0.006$ min.⁻¹.

This reaction clearly involves participation of the solvent and is similar in type to that described by Ritter *et al.*¹¹ for the production of amides from cyanides by acid-catalysed addition of secondary or tertiary alcohols. In detail, two interpretations are possible:

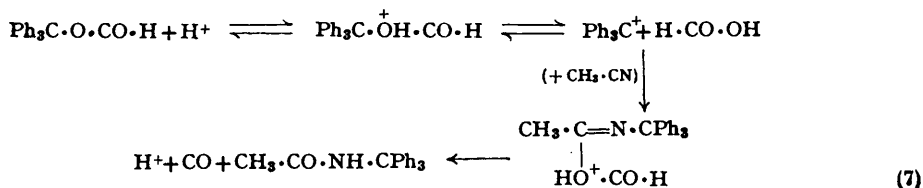
(a) Enough water is adventitiously present to cause complete hydrolysis of the ester to triphenylmethanol and formic acid, which then respectively undergo acid-catalysed addition to the solvent (5) and acid-catalysed decarbonylation (6):

(b) A protonated formate ester molecule reacts additively, like the protonated alcohol,



¹¹ J. J. Ritter and P. P. Minierih, *J. Amer. Chem. Soc.*, 1948, **70**, 4045, and later papers by Ritter *et al.*; N. C. Deno, T. Edwards, and C. Perizzolo, *ibid.*, 1957, **79**, 2108.

with the cyano-group, and the unstable adduct loses both carbon monoxide and a proton in undergoing conversion into the amide:



When triphenylmethanol was tested in place of the formate, under the same conditions, it yielded the amide in accordance with equation (5). On the other hand, when formic acid was similarly tested, it proved to be stable, *i.e.* reaction (6) did not occur under the conditions employed. It is therefore concluded that the formation of the amide involves direct participation of the ester, in accordance with equation (7). This view finds some support from the reported behaviour of triphenylmethyl nitrate.⁷ Like the formate, the latter ester is very easily hydrolysed and is thermally unstable; it forms *N*-triphenylmethylacetamide with methyl cyanide, by way of an intermediate which was regarded^{7a} as the nitrate of the imidol form of the amide.

EXPERIMENTAL

Triphenylmethyl Formate.—Silver formate was freshly prepared by adding aqueous ammonium formate (0.12 mole), with stirring, to aqueous silver nitrate (0.1 mole), filtering the precipitate after 2 min., washing it successively with water, acetone, and ether, and keeping the product (90% yield) over a desiccant in a darkened evacuated desiccator. When kept at room temperature, even in the dark, the light-tan silver formate gradually decomposed to dark grey silver.

Triphenylmethyl formate was generally prepared in small samples (~1 g.) freshly, as required; *e.g.*, an excess of fresh, dry silver formate (0.03 mole) was mixed by magnetic stirring, for 12 hr. at room temperature, in a sealed and darkened vessel, with a solution of pure triphenylmethyl chloride, bromide, or (preferably) isothiocyanate (0.003 mole) in freshly distilled benzene (25 ml.). In a glove-box, the silver salts were removed by filtration and the filtrate was evaporated under reduced pressure, giving *triphenylmethyl formate* as colourless needles (100%), m. p. 98—101° (Found: C, 83.5; H, 5.8. C₂₀H₁₆O₂ requires C, 83.3; H, 5.6%). To follow the reaction during preparations of triphenylmethyl formate under varied conditions, samples were examined for changes in the intensity of the infrared absorption due to the NCS group of triphenylmethyl isothiocyanate (broad complex band with maximum at 2046 cm.⁻¹); this showed, *e.g.*, that in light petroleum the conversion had occurred only to the extent of ~50% in 12 hr. The infrared spectrum of triphenylmethyl formate (KBr disc) showed a strong ester-carbonyl peak at 1740 cm.⁻¹. In moist air the ester rapidly acquired a yellow colour, developed the pungent smell of formic acid, and was quantitatively converted into triphenylmethanol, m. p. 162—164°.

Thermal-decomposition Products.—After measurement of the rate of decomposition of samples of the ester (~1 g.) at 148° (see below), the residue was chromatographed on alumina (60 g.) (Peter Spence, Type H, previously neutralised with acetic acid). Yields were reproducible from preparations carried out under standard conditions. After a typical decomposition in an atmosphere of air, elution with light petroleum yielded triphenylmethane (82%), m. p. and mixed m. p. 92—94°. Benzophenone (3%) was then removed by 20:80 benzene–light petroleum, triphenylmethanol (13%), m. p. and mixed m. p. 161—164°, by benzene, and phenol (2%) by ether. The isolation of the benzophenone and phenol was confirmed by infrared spectra and the preparation of derivatives. When decomposed at 148° under argon, triphenylmethyl formate yielded only triphenylmethane (85—86%) and triphenylmethanol (12—13%). The relative proportion of carbon dioxide and carbon monoxide in gas produced under argon was determined in a mass spectrometer. When triphenylmethane was kept in the same apparatus, for 12 hr. at 148°, in an atmosphere of oxygen, chromatography separated benzophenone (10%) and phenol (9%) from unchanged hydrocarbon.

Decomposition in Solvents.—(a) Solutions (0.04M) of triphenylmethyl formate in dry benzene or toluene remained colourless during 3 hr. at the boiling point, and left a colourless residue on evaporation. This was shown to be triphenylmethyl formate by infrared spectroscopy and by

its conversion into triphenylmethanol (100%), m. p. and mixed m. p. 162—165°, on an alumina column.

(b) Methyl cyanide was dehydrated by refluxing with phosphorus pentoxide, distillation, and treatment with molecular sieve Type 5A (Linde Air Products Co.). Solutions of triphenylmethyl formate (0.1M) in this solvent were colourless. After being refluxed for 3 hr. and evaporated, they yielded triphenylmethane (6%) and triphenylmethanol (89%) when chromatographed. After 6 hr. refluxing, the respective yields were 12% and 86%.

(c) Formic acid was dehydrated¹² by heating with phthalic anhydride for 2 hr. at 90° and distilling; titration with sodium hydroxide indicated 99.6% purity. A suspension of finely powdered triphenylmethyl formate (1 mmole) was vigorously shaken in the formic acid (10 ml.) at room temperature. An orange solution was formed within 15 min., precipitation of triphenylmethane began after 6 hr., and the product (75%), m. p. and mixed m. p. 91—94°, was collected after 90 hr. If an orange solution similarly obtained was kept at 75—80° for 30 min. the colour became pale yellow and pure triphenylmethane was obtained in 96% yield by extraction with light petroleum. The absence of triphenylmethanol in the samples of triphenylmethane was shown by the non-appearance of colour with concentrated sulphuric acid. Triphenylmethanol behaved similarly to the formate with formic acid, at room temperature or on heating.

(d) Methyl cyanide (10 ml.), purified as described in (b), was used to prepare a solution of triphenylmethyl formate (0.002 mole), which was then heated to 50° and treated with 98% sulphuric acid (0.2 ml., 0.0035 mole). The resulting reaction, which was complete within an hour, produced gas, the infrared absorption spectrum of which showed only the broad twin peak at 2100—2200 cm.⁻¹, characteristic of carbon monoxide.¹³ (Carbon dioxide shows a broad band at 2200—2350 cm.⁻¹ and a narrow twin peak at 3500—3650 cm.⁻¹.) Dilution of this solution with water and extraction with methylene chloride gave an almost quantitative yield of *N*-triphenylmethylacetamide, m. p. 212—214° (from 1:2 benzene-light petroleum) (Found: C, 83.7; H, 6.2; N, 4.9. Calc. for C₂₁H₁₉NO: C, 83.7; H, 6.4; N, 4.7%).

Reaction was carried out similarly with triphenylmethanol (0.002 mole) and sulphuric acid (0.0035 mole) in methyl cyanide (10 ml.) for 1 hr. at 50°. *N*-Triphenylmethylacetamide (84%) was similarly isolated. A solution of formic acid (0.002) and sulphuric acid (0.0035 mole) in methyl cyanide produced no carbon monoxide when kept for 1 hr. at 50°.

(e) Triphenylmethyl formate (0.001 mole) was dissolved in 98% sulphuric acid (10 ml.) at room temperature. The orange solution was diluted with water and extracted with methylene chloride to give triphenylmethanol (95%), m. p. and mixed m. p. 163—164°.

Reaction-rate Measurements.—An apparatus was used similar to one devised for measuring volumes of evolved gas, at constant pressure, in decarbonylation reactions.¹⁴ For studying the thermal decomposition of triphenylmethyl formate, the reaction vessel was heated in an oil-bath maintained at 148 ± 0.1° and a weighed sample of the ester was introduced through a wide-bore (15 mm.) tap, in a thin-walled glass tube, which was fractured on entry. Alternatively, and with similar results, a weighed sample of the ester was prepared in the reaction vessel, which was then connected to the apparatus and immersed in the heating bath.

The same apparatus was used for measuring the rate of carbon monoxide evolution from the formate in acidified methyl cyanide solution at 50 ± 0.1°. The apparatus was modified to enable the fast evolution of carbon dioxide from triphenylmethyl formate or triphenylmethanol in formic acid at 100 ± 0.1° to be followed by observation of the increase in pressure at constant volume. These reactions in solvents were initiated by the respective introduction, in glass tubes, of sulphuric acid into a methyl cyanide solution of the formate, or of the ester or alcohol into formic acid. Mixtures were agitated by a magnetic stirrer.

Rate constants were obtained by the usual method, except when initial and final measurements were uncertain, in which case Guggenheim's method of calculation¹⁵ was applied.

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¹² Schering-Kahlbaum A.-G., B.P. 308,731/1929.

¹³ R. H. Pierson, A. N. Fletcher, and E. St. C. Gantz, *Analyt. Chem.* 1956, **28**, 1218.

¹⁴ W. W. Elliott and D. Ll. Hammick, *J.*, 1951, 3402.

¹⁵ E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.