The ether was removed on a warm water-bath under a stream of dried nitrogen. The pale yellow residual oil obtained weighed 8.9 g. (70% yield). The oil was cooled in a bath of dry ice and acetone. About 5 ml. of methanol was added. Scratching with a stirring rod soon induced crystallization. The white crystalline mass thus obtained was filtered at once, while cold from the yellow mother liquor. It was then recrystallized twice by dissolving in a mixture containing 40% of a petroleum ether (Skellysolve A) and 60% of methanol at room temperature and cooling to 0°. The yield was 2.3 g. of fine white odorless prisms of irregular shape, m. p. 35.3–35.6° (cor.). An additional 5 g. of crystals melting slightly lower was recovered from the mother liquors.

Anal. Calcd. for $C_8H_{10}O_5NPS$: C, 36.50; H, 3.83; N, 5.32; P, 11.8; S, 12.2. Found: C, 36.43; H, 3.79; N, 5.70; P, 11.4; S, 12.2.

Purification of Crude O,O-Dimethyl O-*p*-Nitrophenyl Thiophosphate.—A mixture of 95 g. of a crude commercial-grade product[3] in the form of a dark viscous liquid of unpleasant odor was placed in a separatory funnel and shaken with two 50-ml. portions of Skellysolve A, which separated as an upper yellow layer and was removed by pipet (toxic substance, use vacuum line) and discarded. The oil was dissolved in 150 ml. of ether and shaken repeatedly with 20-ml. portions of saturated sodium bicarbonate solution until the washings were no longer yellow. It was then washed with water and twice with saturated sodium chloride solution. When the aqueous layer was drawn off, a quantity of suspended sludge was also removed. The dark red ethereal solution was then passed, with the aid of gentle suction, through a column 5 cm. long containing an adsorbent exactly like that described above for the preparation of the synthesized ester. The column was finally washed with 75 ml. of ether. Ether was removed on a warm water (75°)-bath by use of a stream of dried nitrogen to hasten the evaporation. Avoidance of heating is important, since it was found, in a parallel experiment, that heating on the steam-bath caused the residual oil to darken. The orange-red oil, which weighed 77 g., was dissolved in an equal volume of a 40–60 mixture of Skellysolve A and methanol and chilled in the refrigerator at 0°. It was then seeded with a crystal of the pure ester and left to stand in the refrigerator overnight. A bottle of the mixed solvent was placed in the freezing compartment (−20°) of the refrigerator and used the following morning for washing the crystals. Two recrystallizations carried out in this manner yielded fine white irregular prisms melting at 35.0–35.5°. The mother liquors were worked up thus for recovery of additional material. The total yield of crystalline compound melting at 35° or slightly below from the crude starting material was about 40%.

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[3] Sample kindly supplied by R. J. Geary, Geary Chemical Corp., New York, N. Y.

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The Solvolysis of Triphenylmethyl Benzoate[1]

BY GEORGE S. HAMMOND AND JAMES T. RUDESILL

In their 1941 review of the mechanisms of the solvolytic reactions of carboxylic acids and their esters, Day and Ingold[1a] discussed the possibility that the rate controlling step in the reactions of certain esters might be the ionization of the neutral ester.

$$\text{RCOOR} \longrightarrow \text{RCOO}^- + \text{R}^+ \qquad (1)$$

At the time of their review there were no unambiguous examples of reactions involving this mechanism, which they designated as type B″1. It seemed possible, but not certain, that the hydrolysis of the acid phthalates of α-substituted allylic alcohols[2] with dilute base proceeded in this manner. A more clear-cut example was subsequently studied by Kenyon and his co-workers[3] who showed that the solvolysis of the esters of the optically active *p*-methoxybenzhydrols resulted in extensive racemization under all conditions studied. The results are best interpreted in terms of the B″1 mechanism.

The importance of the analogous reaction of the conjugate acids of esters is well established, and

$$\text{RCO}\overset{\text{H}}{\text{O}}\text{R}^+ \longrightarrow \text{RCOOH} + \text{R}^+ \qquad (2)$$

Cohen and Schneider[4] have pointed out that such a step is probably generally involved in the acid-catalyzed reactions of the esters of tertiary alcohols. They also predicted that reaction (1) would prove to be of importance in the solvolysis of the esters of polyaryl alcohols in neutral and alkaline solution.

In connection with another problem, we have had occasion to investigate the alcoholysis of triphenylmethyl benzoate. Since the stereochemical criterion used by Kenyon is not applicable in this case we have utilized a familiar kinetic approach to the study of the reaction mechanism.

In anhydrous fifty per cent. methyl ethyl ketone–ethanol solution at 55° the ester reacts at an easily measurable rate to produce benzoic acid and ethyl trityl ether. The nature of the products establishes the alkyl–oxygen bond as the point of cleavage, and the reaction is strictly unimolecular with respect to the ester, showing that catalysis by the weak acid produced in the reaction is unimportant. The rate is increased by the addition of sodium ethoxide but is increased even more by the addition of an equimolar amount of sodium perchlorate. We therefore conclude that the influence of sodium ethoxide may be attributed to a positive salt effect rather than to the incursion of a B″2 reaction between the ester and ethoxide ion.

We wished to analyze benzene solutions which contained both trityl chloride and trityl benzoate by differential alcoholysis. Therefore we solvolyzed mixtures of the two compounds in fifty per cent. benzene–ethanol. The reaction of both compounds was immeasurably rapid unless sufficient base was added to neutralize the hydrogen chloride produced in the alcoholysis of the chloride. This indicates, as would be expected, that in the presence of a strong acid a rapid reaction occurs by mechanism (2). In the presence of excess base the rate of alcoholysis of the

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[1] This research was carried out under contract number NR-056-197 with the Office of Naval Research.

[1a] Day and Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

[2] Kenyon, *et al.*, *J. Chem. Soc.*, 85 (1936); 207 (1937); see also Balfe, Hills, Kenyon, Phillips and Platte, *ibid.*, 556 (1942).

[3] Balfe, Doughty, Kenyon and Poplett, *ibid.*, 605 (1942).

[4] Cohen and Schneider, THIS JOURNAL, **63**, 3382 (1941).

ester was surprisingly close to that observed in the ketone–alcohol solvent whereas the reaction of the halide was still immeasurably rapid. Our kinetic results are presented in Table I.

TABLE I

SOLVOLYSIS OF TRIPHENYLMETHYL BENZOATE AT 54.5 ± 0.5°

Initial molarity of the ester was approximately 0.028 in each run. The solvent was 50% alcohol–methyl ethyl ketone in runs 1–6. The solvent was 50% benzene–alcohol in run 7.

Run	Initial concn. of solutes other than ester	$k \times 10^4$, sec.$^{-1}$	Probable error in $k \times 10^4$	% Ester reacted in last sample[a]
1	None	1.79	0.06	62
2	0.0437 M NaOEt	2.85	.28	85
3	.0437 M NaOEt	2.49	.27	79
4	.0875 M NaOEt	3.05	.25	90
5	.0875 M NaOEt	2.88	.25	89
6	.0437 M $NaClO_4$	5.04	.28	93
7	.0060 M $(C_6H_5)_3CCl$ .0066 M KOH	2.29	.21	78

[a] Disregarding infinite time samples taken to check concentrations.

The precision of our analyses was not high in the runs with added base. At the concentrations of sodium ethoxide employed the concentration of the ester is limited by the solubility of the sodium benzoate produced in the medium. Therefore, the decrease in the titer of the solution during the runs was small relative to the total titer.

Experimental

Triphenylmethyl benzoate was prepared by heating equivalent amounts of sodium benzoate and trityl chloride in refluxing dry acetone for seven hours. The sodium chloride was filtered from the mixture and the solution was concentrated until the ester began to separate from the hot solution. After cooling, solid melting about 145° was collected. Two recrystallizations from methyl ethyl ketone gave material melting in the range 166–169° cor. (highest 168–169°, lit.[5] 164°). The average yield of purified product was 40%. A weighed sample of the ester liberated 98.4% of the theoretical amount of acid when warmed with 95% ethanol.

The residual solution from one of the solvolysis runs was extracted with aqueous alkali, dried and evaporated until crystals began to separate and then cooled and filtered. The product was ethyl trityl ether, m. p. 78° (lit.[6] 82°).

Methyl ethyl ketone was dried by distillation from anhydrous potassium carbonate. Anhydrous alcohol was prepared by the method of Lund and Bjerrum.[7] A stock solution of sodium ethoxide was prepared by dissolving freshly cut sodium in anhydrous alcohol.

Sodium perchlorate, anhydrous reagent grade from the G. F. Smith Co., was used without further purification.

Procedure.—Weighed amounts of the ester and trityl chloride were dissolved and made up to the calculated volume in methyl ethyl ketone or benzene. This solution and either pure alcohol or an alcohol solution of the base or sodium perchlorate were brought to temperature in the thermostat. Fifty-ml. aliquots of each were taken, mixed rapidly by inversion, returned to the bath and sampled immediately. Subsequently, 2-ml. aliquots were removed at ten- or twenty-minute intervals and analyzed immediately. Solutions containing excess base were titrated with standard 0.1 N hydrochloric acid and the others with 0.1 N methanolic potassium hydroxide.

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(5) Wieland and Indest, *Ann.*, **532**, 166 (1937).

(6) Beilstein, "Handbuch der organischen Chemie," Fourth ed., Springer, Berlin, 1923, Vol. VI, 716.

(7) Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

Triboluminescence in *cis*-4-Octene[1]

BY MELVERN C. HOFF[2] AND CECIL E. BOORD

In the course of several cryoscopic determinations it was observed that *cis*-4-octene produced flashes of blue-white light when subjected to rapid cooling by immersing a test-tube containing this compound in liquid air. *trans*-4-Octene, *cis*-3-hexene and *trans*-3-hexene were carefully examined but did not produce flashes.

This phenomenon appears to be the same as that observed by Giauque and Ruehrwein[3] with hydrogen cyanide and which they interpreted as an electrical discharge generated by crystal fracture resulting from uneven heating or cooling. The flashes produced in *cis*-4-octene were shown to be electrical discharges by rapidly crystallizing a sample of the olefin under an atmosphere of neon[4] whereupon the flashes exhibited the characteristic red-orange color of an electrical discharge in neon. As was anticipated, no discharges were observed during slow crystallization under nearly equilibrium conditions.

The fact that, of the nearly two hundred hydrocarbons prepared under the auspices of the American Petroleum Institute Research Project 45, only *cis*-4-octene is known to exhibit this phenomenon, indicates either that the phenomenon has taken place unnoticed (it has not been reported by other workers who have crystallized *cis*-4-octene[5,6]) or that the particular crystal structure of this compound is conducive to the phenomenon. As a parallel, it was found to be very difficult to carry out cryoscopic determinations on *cis*-4-octene because of its unusual tendency to form relatively large, intermeshing crystals which cling to the stirrer and the walls of the dewar vessel used in determining freezing and melting points. Normally, under the conditions used in making these determinations, hydrocar-

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[2] Standard Oil Company of Indiana, Whiting, Indiana.

(3) Giauque and Ruehrwein, THIS JOURNAL, **61**, 2626 (1939).

(4) The authors wish to acknowledge their indebtedness to Dr. Thor R. Rubin, of this University, for suggesting the neon experiment. No evidence for an electrical discharge was observed when the flashes were produced in a tube containing a five ohm coil comprising two hundred turns of fine copper wire, connected through the high impedance transfer of an oscillograph.

(5) Henne and Greenlee, THIS JOURNAL, **65**, 2020 (1943).

(6) Campbell and Eby, *ibid.*, **63**, 216 (1941).