and the latter distilled to yield 2 fractions, the first, 69 g. (49%) of ethyl perfluoro-*n*-octanoate, b.p. 74–76° at 18 mm., n_D^{20} 1.3119 and the second, 37% of perfluoro-*n*-octanoic acid.

Anal. Calcd. for $C_{10}H_5F_{15}O_2$: C, 27.17; H, 1.14. Found: C, 26.59; H, 1.49.

Reaction of ethyl trifluoroacetate with sodium ethoxide. A cold solution of freshly prepared sodium ethoxide [6.9 g. (0.30 g.-atom) of sodium in 100 ml. of absolute ethanol] was mixed with a solution of 43 g. (0.30 mole) of ethyl trifluoroacetate in 15 ml. of ethanol. The cool reaction mixture was attached to a reflux condenser in series with a sulfuric acid bubbler, a Dry Ice trap, and a liquid nitrogen trap. The whole system was blanketed under dry nitrogen and the mixture was warmed to reflux whence gas began evolving at a measurable rate. After approximately 4 hr. the gas evolution ceased. A total of 9.0 g. (43%) of fluoroform identified by its infrared spectrum and its molecular weight (found 70.5, 70.5; calcd. 70.0) collected in the liquid nitrogen trap. The reaction mixture gave a strong test for fluoride. No diethyl carbonate was obtained on distillation of the reaction mixture. Presumably, this compound was decomposed by long exposure to ethoxide.

Reaction of ethyl pentafluoropropionate with sodium ethoxide. When ethyl pentafluoropropionate was subjected to the above reaction conditions, a 72% yield of pentafluoroethane, was evolved during a 20-min. period. Distillation of the fluoride free reaction mixture yielded 1 g. of diethyl carbonate, b.p. 126°, n_D^{25} 1.3821.

Reaction of ethyl heptafluoro-n-butyrate with sodium ethoxide. When a solution of 0.10 mole of ethyl heptafluoro-*n*-butyrate in 50 ml. absolute ethanol was added all at once to a solution of 2*N* sodium ethoxide in ethanol and the resulting solution was refluxed, a 71% yield of heptafluoropropane, free of perfluoropropene, evolved over a 15-min. period. Distillation of the fluoride free reaction mixture yielded 30% of diethyl carbonate, b.p. 126°, n_D^{25} 1.3827.

Reaction of ethyl perfluoro-n-octanoate with sodium ethoxide. A solution of 0.14 g.-atom of sodium in 40 ml. of absolute ethanol was mixed with a solution of 55 g. (0.124) mole of ethyl perfluoro-*n*-octanoate in 20 ml. of ethanol and refluxed for one hour. Distillation of the fluoride free reaction mixture yielded 44.5 g., b.p. 69–70°, of an ethanol azeotrope with 1-*H*-pentadecafluoroheptane. In addition, 10.5 g., b.p. 124–125°, n_D^{18} 1.3845–1.3855 was obtained, corresponding to a 72% yield of diethyl carbonate. The azeotrope was washed with saturated calcium chloride and redistilled from phosphorous pentoxide to give 33.5 g. (73%) yield of pentadecafluoroheptane, b.p. 94.0° at 762 mm.

Anal. Calcd. for C_7HF_{15}: C, 22.71; H, 0.27. Found: C, 22.53; H, 0.93.

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A New Synthesis for Triphenylene[1]

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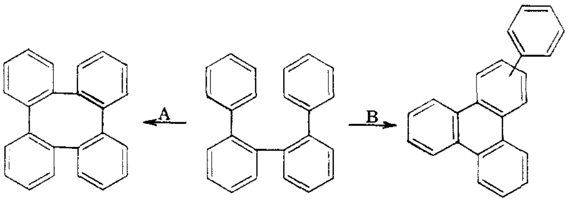
Although several different methods for the synthesis of triphenylene and its derivatives have been devised,[3–9] none offers a convenient route with good yield.

We have discovered that triphenylene can be made in approximately 10% yield in the one step dehydrocyclization of 1,2-diphenylbenzene. 1,2-Diphenylbenzene is a commercial product. The material used in this work is called Santowax and was supplied by the Monsanto Chemical Company. We have found that the dehydrogenation of the crude Santowax gives as good yields as the dehydrogenation of pure 1,2-diphenylbenzene.

This synthesis of triphenylene was suggested by the results we obtained in an attempted synthesis of 1,2,3,4,5,6,7,8-tetrabenzocyclooctatetraene. The dehydrocyclization of 2,2′-diphenylbiphenyl did not give the cyclooactatetraene as was hoped, but instead the reaction seems to have gone by path B to give either 1-, or 2-phenyltriphenylene.



The compound we obtained from the above dehydrogenation did not form a picrate and melted at 183–184°. Rapson[10] reports a melting point of 233° for the tetrabenzocylcooctatetraene. Although 1-phenyltriphenylene is what would be expected to form it is very likely that this would rearrange to the 2-isomer which would be more stable because of less steric strain. It has been shown, for example, that 1-phenylnaphthalene rearranges at 350° over silica gel to 2-phenylnaphthalene.[11]

EXPERIMENTAL[12]

Phenyltriphenylene. 2,2′-Diphenylbiphenyl (8 g. in liquid form) was processed over 10 ml. of 8% chromia on alumina catalyst[13] at 615° during a period of 27 min. The 5.8 g. of condensate obtained was chromatographed over 180 g. of alumina. First the alumina column was eluted with six 100-ml. portions of petroleum ether. Evaporation of the solvent from these fractions gave 0.2 g. of starting material. Then the column was eluted with eleven 100-ml. portions of 10% benzene-10% petroleum ether. Evaporation of the solvents

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gave 4 g. of crude starting material. Next the column was eluted with nine 100-ml. portions of 50% benzene-50% petroleum ether. Evaporation of these fractions gave 1.6 g. of white crystals which after recrystallization from ether melted at 183–184° (0.48 g.).

Anal. Calcd. for $C_{24}H_{16}$: C, 94.70; H, 5.30; mol. wt., 304. Found: C, 95.08; H, 5.63; mol. wt., 298.

Triphenylene. Santowax (crude 1,2-diphenylbenzene), 23 g., was dissolved in 78 g. of thiophene-free benzene and this solution was then passed over 10 ml. of chromia on alumina catalyst at 625° during the course of 215 min. The catalyst activity as indicated by the rate of hydrogen evolution was almost constant during the course of the run. The benzene was evaporated from the condensate and the white solid remaining was crystallized from 320 ml. of ethanol. Crude triphenylene (2.6 g.) m. p. 182–193° was obtained. This material was again crystallized from ethanol to give 2 g. of pure triphenylene m.p. 197–198°. No melting point depression was observed when a mixed melting point was made with triphenylene as prepared above and an authentic sample.

A number of variations of the above procedure were tried in attempts to improve the yield. Temperatures of 500 to 650° at various space velocities were investigated without success, however.

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Chlorosulfonation of Ethyl Chloride

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The photochemical reaction of hydrocarbons with sulfur dioxide and chlorine to yield alkanesulfonyl chlorides (the Reed reaction)[1] has received much technical investigation as a step in the preparation of synthetic detergents and in the modification of polyethylene. It is considered[2,3] to be a radical chain process involving the propagating steps

$$\mathrm{Cl\cdot} + \mathrm{RH} \longrightarrow \mathrm{HCl} + \mathrm{R\cdot} \qquad (1)$$

$$\mathrm{R\cdot} + \mathrm{SO_2} \longrightarrow \mathrm{RSO_2\cdot} \qquad (2)$$

$$\mathrm{RSO_2\cdot} + \mathrm{Cl_2} \longrightarrow \mathrm{RSO_2Cl} + \mathrm{Cl\cdot} \qquad (3)$$

in which (2) competes with chlorination,

$$\mathrm{R\cdot} + \mathrm{Cl_2} \longrightarrow \mathrm{RCl} + \mathrm{Cl\cdot} \qquad (4)$$

and, in fact, alkyl chlorides are often obtained as by-products.

The sulfochlorination of small molecules has received relatively little study, although Asinger and co-workers have studied the reaction of propane,[4] butane,[5] and isobutane,[6] and Helberger, Manecke and Fischer[7] have investigated the reaction of propyl and higher chlorides.

The reaction attracted our attention as a possible route to derivatives of 2-substituted ethanesulfonic acids, and we find in fact that 2-chloroethanesulfonyl chloride can be prepared in reasonable yield by this route.

Trials of various experimental conditions indicated that the best yields are obtained under strong illumination by the slow introduction of chlorine into a mixture of sulfur dioxide and ethyl chloride, allowed to reflux under a Dry Ice-condenser. Typical results appear in Table I, and it is evident that various additives had a deleterious effect on the process, as did attempts to generate chlorine and sulfur dioxide *in situ* from SO_2Cl_2 and pyridine.[2,8]

TABLE I

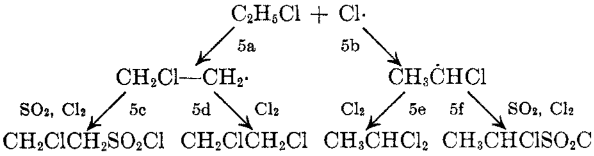
Sulfochlorination of Ethyl Chloride

Reactants (Moles)			Time of Cl_2 Addn. (hr.)	Yield (% [a])	
EtCl	SO_2	Cl_2		$C_2H_4SO_2Cl_2$	$C_2H_4Cl_2$
1.0	2.34	1.31	3.5	26.6	18.2
4.0	9.37	4.0	11	31.8	28.3
6.0	14.0	6.0	8	35.0	25.5
7.5	14.0	6.0	4	12.0	—
2.12[b]	4.7[b]	2.0[b]	1.5	13	17
2.5[c]	4.7[c]	2.0[c]	1.5	Trace	56
7.5[d]	13.0[d]	6.0[d]	4	2	7.7
1.0[e]	0.5 (SO_2Cl_2)[e]		—	5.2	35.9

[a] Based on Cl_2 added. [b] 10 cc. water added. [c] 0.5 cc. C_2H_5SH added. [d] 1 cc. pyridine added. [e] 0.5 cc. pyridine added.

The sulfonyl chloride obtained was identified as the 2-chloro isomer by its physical constants, and by conversion to known derivatives by reaction with aniline and with thiourea, and none of the lower-boiling 1-chloro isomer was detected on fractional distillation. The best yield was 35%, based on Cl_2, or 58% based on organic products isolated. The difference probably represents SO_2Cl_2 formed by reaction between SO_2 and chlorine, and considerable quantities were actually detected during product work-up. The dichloroethane produced was chiefly 1,1-dichloroethane, containing a small amount (<7%) of 1,2-dichloroethane.

Aside from any possible synthetic utility, the sulfochlorination of ethyl chloride has some interesting features, since the products arise from a rather complicated set of competitive radical reactions shown in Equation 5.



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