and 230 ml. of acetone was heated to reflux for twelve hours. At the conclusion of this period the product was isolated as described above. Methallyl 3-(trifluoromethyl)-phenyl ether was obtained as a colorless liquid (b.p. 73° at 4 mm.), $n^{20}_{\rm D}$ 1.4578. The yield was 54 g. representing a quantitative conversion.

Anal. Calcd. for $C_{11}H_{11}F_3O$: C, 61.1; H, 5.09. Found: C, 61.3; H, 5.14.

2-Allyl-5-(trifluoromethyl)-phenol.—Samples of allyl 3-(trifluoromethyl)-phenyl ether were heated at reflux temperature under an atmosphere of carbon dioxide. After the heating period had been concluded, the material was dissolved in ether and extracted with excess 20% sodium hydroxide solution. Acidification of the basic extracts liberated 2-allyl-5-(trifluoromethyl)-phenol, which was taken up in ether and the solution dried with Drierite. After removal of the ether at atmospheric pressure, colorless 2-allyl-5-(trifluoromethyl)-phenol, $n^{20}_{\rm D}$ 1.4802, was obtained by distillation at reduced pressure (b.p. 73–75° at 4 mm.). Unreacted allyl 3-(trifluoromethyl)-phenyl ether was recovered by distillation of the non-acidic material remaining after basic extraction of the ether solution of the reaction mixture. Yields and conversions for different heating periods are summarized in Table I.

TABLE I

Run	Reflux hr.	Ether, g.	Recovery, g.	Phenol, g.	Yield, %	Conv., %
1	5	22.0	9.2	9.0	70	41
2	7	16.7	5.0	8.8	75	54
3	9	21.6	5.4	12.8	76	59
4	15	10	...	7.5	75	75

Anal. Calcd. for $C_{10}H_9F_3O$: C, 59.4; H, 4.46. Found: C, 59.4; H, 4.20.

2-Propyl-5-(trifluoromethyl)-phenol.—2-Allyl-5-(trifluoromethyl)-phenol was hydrogenated at room temperature in a Maxted semi-micro hydrogenator[10] (5.6 g. 0.027 mole). 2-Allyl-5-(trifluoromethyl)-phenol was dissolved in 20 ml. of absolute ethanol and 2 g. of "activated" Raney nickel catalyst[11] was added. Hydrogen uptake required two hours and ceased when a quantitative amount had been absorbed. After filtration of the catalyst and removal of the ethanol at reduced pressure, colorless 2-propyl-5-(trifluoromethyl)-phenol, $n^{20}_{\rm D}$ 1.4668, was distilled (b.p. 80–82 at 4 mm.). The yield was 4.7 g. (82%).

Anal. Calcd. for $C_{10}H_{11}F_3O$: C, 58.8; H, 5.39. Found: C, 58.7; H, 5.39.

2-Allyl-5-(trifluoromethyl)-anisole.—A solution of 6.7 g. (0.12 mole) of potassium hydroxide in 16 ml. of water was poured into a mixture of 7.75 g. (0.038 mole) of 2-allyl-5-(trifluoromethyl)-phenol, 11.2 g. (0.089 mole) of methyl sulfate and 15 ml. of methanol which had been cooled to 0°. After the exothermic reaction had subsided and the solution had cooled, the organic phase was removed, diluted with ether, and dried. After removal of the ether at atmospheric pressure, 6.9 g. (83% yield) of 2-allyl-5-(trifluoromethyl)-anisole, $n^{20}_{\rm D}$ 1.4702, distilled under reduced pressure (b.p. 71–73° at 4 mm.).

Anal. Calcd. for $C_{11}H_{11}F_3O$: C, 61.1; H, 5.09. Found: C, 61.4; H, 4.79.

2-Propyl-5-(trifluoromethyl)-anisole.—2-Propyl-5-(trifluoromethyl)-anisole was prepared in 92% yield by methylation of the phenol. This ether, a colorless liquid, $n^{20}_{\rm D}$ 1.4591, was distilled under reduced pressure (b.p. 72–73° at 4 mm.).

Anal. Calcd. for $C_{11}H_{13}F_3O$: C, 60.55; H, 5.96. Found: C, 60.55; H, 5.81.

2-Bromo-5-(trifluoromethyl)-anisole.—Methylation of 2-bromo-5-(trifluoromethyl)-phenol[2] gave a 60% yield of 2-bromo-5-(trifluoromethyl)-anisole, a colorless oil, $n^{20}_{\rm D}$ 1.4589 (b.p. 66–67° at 3 mm.).

Anal. Calcd. for $C_8H_6BrF_3O$: C, 37.6; H, 2.35. Found: C, 37.35; H, 2.42.

2-Methoxy-4-(trifluoromethyl)-benzoic Acid. A.—A mixture of 6.1 g. (0.028 mole) of 2-allyl-5-(trifluoromethyl)-anisole, 26 g. (0.177 mole) of potassium permanganate, one pellet of potassium hydroxide and 300 ml. of water was refluxed vigorously for ten hours. By the end of this period the permanganate had been decolorized completely. The manganese dioxide was filtered off and washed with distilled water. The combined colorless filtrates were acidified to give a copious white precipitate of 2-methoxy-4-(trifluoromethyl)-benzoic acid. The crude dried material weighed 5.4 g. and melted at 124–127°. Recrystallization from ethanol–water solution gave a white crystalline solid, m.p. 129–130°. The yield of crude material was 87.5%.

B.—Oxidation of 2-propyl-5-(trifluoromethyl)-anisole by the above procedure gave a 72% yield of 2-methoxy-4-(trifluoromethyl)-benzoic acid.

C.—An ether solution of butyl lithium prepared from 0.42 g. (0.06 mole) of lithium[12] was added dropwise to a stirred solution of 6.14 g. (0.024 mole) of 2-bromo-5-(trifluoromethyl)-anisole in 100 ml. of anhydrous ether. The mixture was heated at reflux for three hours, then carbonated by the addition of excess Dry Ice. After hydrolysis with dilute hydrochloric acid the ether solution was extracted with base. Acidification of the basic extract gave 3.6 g. of 2-methoxy-4-(trifluoromethyl)-benzoic acid (yield 64%). The melting point of a recrystallized sample was 129–130°. Mixed melting point determinations with material obtained by methods A and B showed no depression.

Anal. Calcd. for $C_9H_7F_3O_3$: C, 49.1; H, 3.18. Found: C, 49.1; H, 3.18.

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The Composition of So-Called *cis*-Diiodoethylene

BY SIDNEY I. MILLER[1] AND RICHARD M. NOYES

The accepted method for preparing the *cis* isomer of 1,2-diiodoethylene involves fractional crystallization of a mixture of the *cis* and *trans* isomers. If such a mixture is frozen to Dry Ice temperatures and is allowed to warm while it is centrifuged in a sintered glass funnel, one obtains a solid melting at about 72° and a liquid freezing below room temperature. Repeated treatments of the liquid result in a material freezing sharply at −13.5°. The solid residue always melts very close to 72° even when only a few crystals are obtained; it is obviously pure *trans*-diiodoethylene and not a solid solution. The liquid phase must therefore be a eutectic mixture rather than a pure substance.

Chavanne and Vos[2] tried without success to fractionate the eutectic mixture by distillation and by partial solubility and concluded that it was identical with the *cis* isomer. This interpretation requires the implausible assumption that solid *trans*-diiodoethylene is virtually insoluble in the liquid *cis* isomer at −13.5° and yet is quite soluble at slightly higher temperatures. Nevertheless, this eutectic liquid is the "*cis*-diiodoethylene" of all subsequent studies. Later measurements[3] have shown that the vapor pressures of the pure *trans*

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[3] R. M. Noyes, Wm. A. Noyes and H. Steinmetz, THIS JOURNAL, **72**, 33 (1950).

isomer and of the eutectic mixture are nearly the same, and the curves appear actually to cross to about 100 mm. and 120°; therefore, fractional distillation at reduced pressure could not be expected to be efficient.

In connection with some studies of elimination reactions we have obtained or reinterpreted kinetic, spectroscopic and phase equilibrium data all of which indicate that the eutectic material contains about 20% of the *trans* isomer.

Kinetic Evidence.—We have found that a solution of the eutectic material in methanol will react at 25° with only 75 to 80% of a stoichiometric quantity of methoxide ion. Among other products, the final solution contains diiodoacetylene and *trans*-diiodoethylene, identified by chemical analysis and infrared absorption spectrum. The pure *trans* isomer does not react with methoxide ion under these conditions.

At elevated temperatures in methanol *trans*-diiodoethylene undergoes an elimination reaction with sodium iodide. Under the same conditions the eutectic mixture undergoes a similar but slower reaction, and kinetic measurements suggest that only about 20% of the material is reactive.

The detailed kinetic evidence will be included in a paper concerned with the mechanism of these elimination reactions.

Spectroscopic Evidence.—Infrared absorption studies between 700 and 1300 cm.$^{-1}$ showed that all bands associated with *trans*-diiodoethylene were also observed in the eutectic mixture. Quantitative measurements on the band at 918 cm.$^{-1}$ with carbon tetrachloride solutions of the two materials gave 20.1, 20.5 and 20.6% of *trans* in the eutectic mixture used to prepare three different solutions. Some of these observations are illustrated in Fig. 1.

A methanol solution of the eutectic mixture was heated with sodium iodide, and the remaining diiodoethylene was isolated and analyzed by the same technique. It appeared to contain only about 15% of *trans* isomer.

Evidence from Phase Equilibria.—If A represents a pure substance which crystallizes without solid solutions, then for an equilibrium with an ideal solution we can write

$$-\ln N_{\mathrm{A}} = \frac{\Delta H(T_0 - T)}{RTT_0}$$

In this equation N_{A} is the mole fraction of A in the solution in equilibrium at temperature T with pure solid A, T_0 is the freezing point of pure A, and ΔH is the heat of fusion of pure solid A. This equation assumes that the solution is ideal and that ΔH is independent of temperature. Ordinarily this equation is used to calculate the freezing point depression of A; but if both T and N_{A} are measured, it permits a calculation of ΔH.

Latiers[4] reports the freezing points of several mixtures of *trans* and eutectic diiodoethylene. His data are in agreement with a smaller number of measurements by Chavanne and Vos.[2] We have used Latiers' data to calculate values of ΔH for the fusion of *trans*-diiodoethylene. If it is assumed that the eutectic is pure *cis*, calculated values of ΔH show a steady drift from 4470 cal./mole for a mixture containing 5.5% eutectic and freezing at 69° to 6170 cal./mole for a mixture containing 87.5% eutectic and freezing at 7.2°. If it is assumed that the eutectic contains 20.5% of *trans*, the calculated values of ΔH from these extreme concentrations are 3510 and 3540 cal./mole, respectively, and the values calculated for intermediate concentrations vary between the extremes of 3290 and 3690 cal./mole with little if any trend. We have also made rough freezing point measurements on a few mixtures prepared by adding small amounts of iodobenzene to pure *trans*-diiodoethylene. These measurements indicate that ΔH is between 3000 and 3500 cal./mole and is certainly less than 4000 cal./mole.

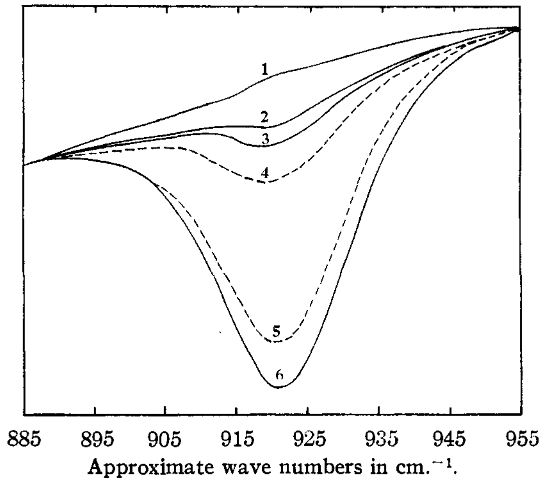

Fig. 1.—Infrared spectra of solutions of *trans* and eutectic diiodoethylene in carbon tetrachloride: 1, solvent alone; 2, 0.0057 g. *trans* per ml.; 3, 0.0107 g. *trans* per ml.; 4, 0.0830 g. eutectic per ml.; 5, 0.3083 g. eutectic per ml.; 6, 0.0824 g. *trans* per ml.

As a result of all the above evidence, we conclude that the "cis-diiodoethylene" of the literature is a eutectic mixture containing 20–21% of the *trans* isomer. Experiments are being undertaken to fractionate this material to obtain the pure *cis* isomer and to determine various properties to replace values now reported for the eutectic mixture.

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1,3-Bis-(*p*-methoxyphenyl)-cyclohexane

BY GEORGE P. MUELLER AND CARL B. HONAKER

Toward developing a series of diarylcycloalkanes bearing some structural relationship to the synthetic estrogens we have adapted the procedure involving dihydroresorcinol ethyl ether as an inter-