thermal motion of the boron and hydrogen atoms could be attempted.

KNOLLS RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY, N. Y. RECEIVED NOVEMBER 16, 1950

Preparation of Silver Colloid

BY GENTARO MATSUMURA

Finely pulverized magnesium oxide (5 g.) was kneaded with dilute aqueous silver nitrate solution (0.01 *N*, 5 cc.) crushed to a fine powder after drying at room temperature in desiccator, put into a graphite crucible and kept at 1010° for thirty minutes in a nichrome resistor furnace. Since it is well known that silver nitrate undergoes thermal decomposition at about 320° with the formation of silver nitrite and simultaneously the nitrite is further decomposed into metallic silver at that temperature,[1] on this heat-treatment finely dispersed crystals of silver nitrate are probably transformed into finely divided liquid silver droplets. After cooling, the reaction product was treated with excess of dilute acetic acid to dissolve magnesium oxide, filtered through filter paper and subjected to electrodialysis, giving a gray-pink colloidal solution of silver.

Spectral analysis showed that the particles of this colloidal solution consisted of metallic silver contaminated with a trace of magnesium.

I wish to express thanks to Prof. K. Iwase and Dr. K. Ogawa for continued advice and to Prof. R. Goto and Dr. N. Koizumi for performing the electrodialyses.

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Claisen Rearrangement of Allyl 3-(Trifluoromethyl)-phenyl Ether

BY E. T. MCBEE AND EDWARD RAPKIN[1]

An extensive survey of the literature[1a] reveals that little has been reported on Claisen rearrangement of negatively meta-substituted allyl phenyl ethers. The purpose of the investigation described in this paper was to determine the course of substitution when allyl 3-(trifluoromethyl)-phenyl ether and its homologs were made to undergo the Claisen rearrangement.

In agreement with previous observations,[2] the trifluoromethyl group appears to have a marked deactivating effect toward substitution in the phenol nucleus. Consequently, it was necessary to heat allyl 3-(trifluoromethyl)-phenyl ether for fifteen hours at reflux to achieve the same conversion in the Claisen rearrangement that can be obtained in one hour of heating allyl 3-methylphenyl ether.[3] Whereas it is usual for a methallyl ether to rearrange more rapidly than the corresponding allyl ether,[4] under similar reaction conditions methallyl 3-(trifluoromethyl)-phenyl ether did not give evidence of rearrangement during a twelve-hour reflux period.

Claisen rearrangement of allyl 3-(trifluoromethyl)-phenyl ether gives 2-allyl-5-(trifluoromethyl)-phenol. The structure of this material was demonstrated by conversion to 2-allyl-5-(trifluoromethyl)-anisole and subsequent oxidation to 2-methoxy-4-(trifluoromethyl)-benzoic acid. Synthesis of this acid was independently accomplished from 2-bromo-5-(trifluoromethyl)-anisole by halogen–metal interconversion with butyl lithium and carbonation of the resultant 2-methoxy-4-(trifluoromethyl)-phenyl lithium. Also oxidation of 2-propyl-5-(trifluoromethyl)-anisole, obtained by hydrogenation of the allylphenol followed by methylation of the product gave 2-methoxy-4-(trifluoromethyl)-benzoic acid.

Similar mechanisms for the Claisen rearrangement of allyl phenyl ether have been advanced in slightly different form by several investigators.[5,6,7] An essential step of the proposed mechanism involves the transfer of an electron pair from a carbon atom of the aromatic nucleus to the γ-carbon of the allyl group. On this basis it is reasonable to expect that allyl attack should occur at the carbon atom of highest electron density ortho to the allyloxy grouping. In the case of ethers of 3-(trifluoromethyl)-phenol, carbon atom 6 should have a much greater electron density than carbon atom 2 since the trifluoromethyl group is strongly electronegative. Therefore, the formation of 2-allyl-5-(trifluoromethyl)-phenol on heating allyl 3-(trifluoromethyl)-phenyl ether is in conformity with logical predictions which can be made on the basis of the postulated mechanism for the Claisen rearrangement.

Experimental[8]

Allyl 3-(Trifluoromethyl)-phenyl Ether.—A mixture of 35 g. (0.25 mole) of potassium carbonate, 30 g. (0.25 mole) of allyl bromide, 40.5 g. (0.25 mole) of 3-(trifluoromethyl)-phenol,[9] and 200 ml. of acetone was heated at reflux temperature for twelve hours. During this period a heavy precipitate of potassium bromide formed. At the conclusion of the reaction period, water was added until the inorganic salts dissolved. The upper organic layer was removed and the aqueous phase extracted with ether. The combined organic solutions were extracted with 10% sodium hydroxide solution and dried with Drierite. After removal of the ether at atmospheric pressure, the residual yellow oil was distilled at reduced pressure to yield 41 g. of colorless allyl 3-(trifluoromethyl)-phenyl ether (b.p. 62.4–62.8° at 4 mm.), n^{20}_{D} 1.4562. Acidification of the sodium hydroxide extract gave 3 g. of unreacted 3-(trifluoromethyl)-phenol. The conversion to allyl 3-(trifluoromethyl)-phenyl ether was 80% and the yield was 86%.

Anal. Calcd. for $C_{10}H_9F_3O$: C, 59.4; H, 4.46. Found: C, 59.4; H, 4.74.

Methallyl 3-(Trifluoromethyl)-phenyl Ether.—A mixture of 35 g. (0.25 mole) of potassium carbonate, 42 g. (0.25 mole) of potassium iodide, 23 g. (0.25 mole) of methallyl chloride, 41 g. (0.25 mole) of 3-(trifluoromethyl)-phenol

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[1] This paper contains material abstracted from the doctoral thesis of Edward Rapkin.

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[7] A. C. Cope and E. M. Hardy, THIS JOURNAL, **62**, 441 (1940).

[8] Microanalyses by Dr. H. Galbraith,

[9] F. Swarts, *Bull. sci. acad. roy. Belg.*, **113**, 241 (1913).

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.), $n^{20}\mathrm{D}$ 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, $n^{20}\mathrm{D}$ 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, $n^{20}\mathrm{D}$ 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, $n^{20}\mathrm{D}$ 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, $n^{20}\mathrm{D}$ 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, $n^{20}\mathrm{D}$ 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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[1] Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

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