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.

[1] M. Marcel Oswald, *Ann. chim.*, **6**, 32 (1914).

METALLURGICAL LABORATORY
FACULTY OF SCIENCE
KYOTO UNIVERSITY
KYOTO, JAPAN

RECEIVED JULY 16, 1950

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.), $n^{20}\mathrm{D}$ 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

---

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

[1a] D. S. Tarbell, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 29–47.

[2] E. T. McBee and E. Rapkin, THIS JOURNAL, **73**, 1325 (1951).

[3] L. Claisen and O. Eisleb, *Ann.*, **401**, 57 (1913).

[4] Q. R. Bartz, R. F. Miller and R. Adams, THIS JOURNAL, **57**, 371 (1935).

[5] C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

[6] H. B. Watson, *Ann. Repts. Chem. Soc.*, **1939**, 206.

[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).