Figure 1.—Semilogarithmic plot of ln (C_0/C) vs. reciprocal of injection block absolute temperature for cis-stilbene isomerization.

several hours after devising a suitable product analysis. For the analytical separations 0.125 in. × 5 ft packed columns were used: for the stilbenes, 5% SE-30, on 60/80 Chromosorb W; for the allyl phenyl ether system, 2% xylenyl phosphate, on 80/100 Chromosorb G; for the norbornene system, 15% Apiezon L, on 60/80 Chromosorb W.

Figure 1 is a semilogarithmic plot of ln (C_0/C) vs. the reciprocal of the absolute temperature of the injection block for the isomerization of cis-stilbene. The activation energy obtained from the slope of this plot is 42.6 ∓ 1.0 kcal mol^{-1} (lit.[3] 42.8 kcal mol^{-1}). Similarly the activation energy for the Diels–Alder retrogression of norbornene was found to be 41.3 ∓ 1.5 kcal mol^{-1} (lit.[4] 42.8 ∓ 0.6 kcal mol^{-1}), and that for the Claisen rearrangement of allyl phenyl ether was found to be 33.2 ∓ 1.5 kcal mol^{-1} (lit.[5] 32.2 kcal mol^{-1} in Carbitol).

Several notes of caution should be given. Owing to the nature of the logarithmic function the spread of experimental points is expected to be greater at low rather than at high conversions under conditions of equal precision in temperature measurement, flow rate regulation, sample introduction, and analysis. Nonlinearity, however, is also observed at very high temperatures, where appreciable back reaction becomes evident for cis-stilbene or, in the case of the Claisen rearrangement of allyl phenyl ether, where a concurrent reaction with a greater temperature coefficient becomes important. In the allyl phenyl ether reaction at high temperatures cleavage to phenol competes favorably with ortho rearrangement and is the preferred reaction above 380° at a helium flow rate of 6 cc min^{-1} with the particular block geometry of our instrument. The activation energy given in the case of allyl phenyl ether is that for its disappearance, determined from the linear, lower temperature portion of the plot analogous to Figure 1.

An increase in flow rate from 10 to 14 cc min^{-1} did not afford an experimentally significant difference (>1.0 kcal mol^{-1}) in activation energy for the cis-stilbene isomerization, although it decreased the extent of reaction.

(3) G. B. Kistiakowsky and W. R. Smith, J. Amer. Chem. Soc., 56, 638 (1934).
(4) W. C. Herndon, W. B. Cooper, and M. J. Chambers, J. Phys. Chem., 68, 2016 (1964).
(5) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, J. Amer Chem. Soc., 80, 3271 (1958).

On a Supposed Preparation of α-Chloroanisole

MAURICE SHAMMA, LUDVIK NOVAK, AND MICHAEL G. KELLY

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Because of a need for α-chloroanisole (chloromethyl phenyl ether) in connection with some synthetic work in progress, we had a chance to repeat the most recent preparation for this compound given in the literature.[1] Following the instructions given in ref 1, anisole in methylene chloride solution was brought to reflux temperature, and sulfuryl chloride was added dropwise, exactly as specified. The product was distilled and exhibited the physical constants quoted, namely, bp 74–77° (13 mm) and n^{25}D 1.5342.

To our surprise, however, the product was insensitive to silver nitrate solution and did not react with benzyldimethylamine.[2] The nmr spectrum in CDCl$_3$ solution clearly showed two doublets centered at δ 6.78 and 7.31 ($J = 10$ cps), characteristic of an aromatic AB system. It therefore appeared probable that our product was p-chloroanisole rather than the expected α-chloroanisole. The preparation was repeated four times with identical results, so that aromatic chlorination always occurred. Spectral (nmr and ir) comparison of the synthetic material with an authentic sample (Eastman Distillation Products) of p-chloroanisole indicated the two compounds to be essentially identical, but gas chromatography showed our product to be only 90% pure, as specifically stated in the preparation given.[1]

Aromatic chlorination by means of sulfuryl chloride is not unusual, and has been amply recorded in the literature.[3] It is claimed that the procedure utilized in ref 1 is that of Bordwell and Pitt. These authors prepared a number of α-chloromethyl sulfides by this procedure, but it was never suggested that the method could be extended to prepare α-chloromethyl ethers.[4]

It is easy to see in retrospect how p-chloroanisole could be mistaken for α-chloroanisole. Besides having identical elemental analyses, the two compounds possess very close boiling points and refractive indices as indicated in Table I.

TABLE I

	Bp, °C (mm)	nD
p-Chloroanisole	90–92 (18)	1.5351 at 20°
α-Chloroanisole	88–90 (15)	1.5362 at 20°

In conclusion, therefore, the best method for preparing α-chloroanisole is still that used by Schollkopf and coworkers.[5] The supposed preparation of α-chloroanisole given in ref 1 is at best a procedure for obtaining slightly impure p-chloroanisole.

Registry No.—α-Chloroanisole, 6707-01-3; p-chloroanisole, 623-12-1.

(1) C. S. Davis and G. S. Lougheed, Org. Syn., 47, 23 (1967).
(2) H. J. Barber and M. B. Green, J. Appl. Chem., 115 (1954).
(3) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, N. Y., 1967, p 1128.
(4) F. G. Bordwell and B. M. Pitt, J. Amer. Chem. Soc., 77, 572 (1955).
(5) U. Schollkopf, A. Lerch, and J. Paust, Chem. Ber., 96, 2266 (1963).