1,5-dichloro-2-pentyl methyl ether, 10.6 g (26%) of 4,5-dichloro-1-pentyl methyl ether, and 3.7 g (13%) of 2-chloromethyltetrahydrofuran: bp 75–77° (28 Torr) [lit.[10] 55–56° (20 Torr)]. The isomeric ethers were separable analytically on a DC-550 gas chromatographic column and were identified by their spectra.

1,5-Dichloro-2-pentyl methyl ether: bp 103° (19 Torr); nmr (CCl_4) δ 3.38 (s, 3, CH_3O), 3.2–3.6 (m, 5, $ClCH_2CH$ and $ClCH_2$), and 1.5–2.1 (m, 4, $CH_2CH_2CH_2Cl$).

Anal. Calcd for $C_6H_{12}OCl_2$: C, 42.14; H, 7.04. Found: C, 42.14; H, 7.04.

4,5-Dichloro-1-pentyl methyl ether: bp 95–100° (19 Torr); nmr (CCl_4) δ 3.27 (s, 3, CH_3O), 3.36 (t, 2, OCH_2), 1.4–2.6 (m, 4, $CH_2CH_2CH_2O$), 3.4–3.9 (m, 2, $ClCH_2$), and 3.8–4.2 (m, 1, CH).

Anal. Calcd for $C_6H_{12}OCl_2$: C, 42.14; H, 7.04. Found: C, 42.33; H, 7.05.

That 2-chloromethyltetrahydrofuran was not arising from the dichloro compounds during distillation was evidenced by its sharp disappearance from distillation fractions early in the distillation.

4,5-Dibromo-1-pentyl Methyl Ether.—5-Methoxy-1-pentene (20.0 g, 0.20 mol) and bromine (30 g, 0.187 mol) were allowed to react in carbon tetrachloride (100 ml) in subdued light. Because of the pyrolytic instability of 1,5-dibromo-2-pentyl methyl ether, the only compounds isolated in pure form by slow distillation were 2-bromomethyltetrahydrofuran, bp 60–61° (14 Torr) [lit.[10] bp 63.5–64° (17 Torr)], and 4,5-dibromo-1-pentyl methyl ether: bp 105° (7 Torr) [lit.[8,9] bp for "$CH_2BrCHBr(CH_2)_3OCH_3$," 100° (8 Torr)]; nmr (CCl_4) δ 3.9–4.3 (m, 1, CH), 3.4–3.9 (m, 2, $BrCH_2$), 3.36 (t, 2, CH_2O), 3.27 (s, 3, CH_3O), and 1.2–2.4 (m, 4, $CH_2CH_2CH_2O$).

Registry No.—2-Chloro-1-propyl methyl ether, 5390-71-6; 2-bromo-1-propyl methyl ether, 22461-48-9; 2-iodo-1-propyl methyl ether, 22461-49-0; 3-chloro-1-butyl methyl ether, 3565-66-0; 4-chloro-1-pentyl methyl ether, 22461-51-4; 4-bromo-1-pentyl methyl ether, 4457-68-5; 5-bromo-2-pentyl methyl ether, 3706-57-8; 1,5-dichloro-2-pentyl methyl ether, 22434-10-2; 4,5-dichloro-1-pentyl methyl ether, 22461-54-7.

(10) G. Eglinton, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2873 (1952).

Stereoselective Addition of Bromine to 2-Buten-2-yl Tosylates. Formolysis of *erythro*-2,3-Dibromo-2-butyl Tosylate[1a]

PAUL E. PETERSON AND JOSEPH M. INDELICATO[1b]

Department of Chemistry, St. Louis University, St. Louis, Missouri 63156

Received July 14, 1969

It is widely recognized that the electrophilic addition of bromine to olefins proceeds *via* an intermediate bromonium ion, or its equivalent, to give *trans* adducts. This cyclic intermediate was first postulated by Roberts and Kimball[2] and later observed in the nmr studies of Olah and Bollinger.[3] Olefins which can form highly stabilized cations are less prone to form bridged cations, and they may give mixtures of stereoisomeric products.[4]

Of particular interest to this study is the stereochemistry of the addition of bromine to olefins containing an sp^2-hybridized bond to an atom other than hydrogen or carbon. Lemieux has demonstrated that bromination of dihydropyran and related compounds occurs *via* a stabilized oxonium ion, and that this reaction yields significant amounts of the *cis*- as well as the *trans*-dibromide.[5] Stevens has shown that bromine-82 adds to 1-bromocyclohexene with *trans* stereospecificity.[6]

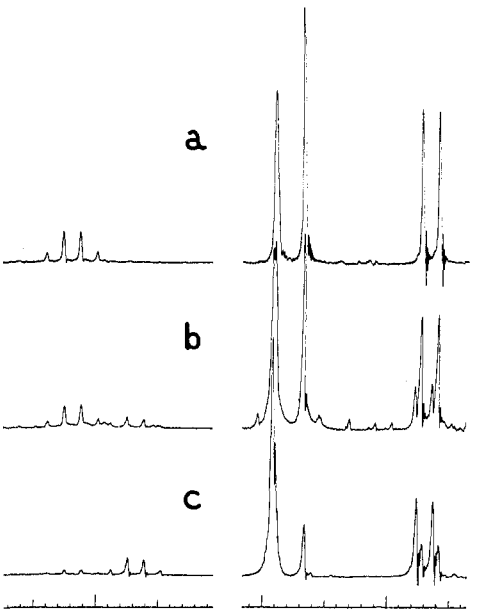


Figure 1.—Nmr spectrum (CCl_4): (a) crystallized *erythro*-2,3-dibromo-2-butyl tosylate; (b) mixture of *erythro* and *threo* diastereosmers from the addition of bromine to *trans*-2-buten-2-yl tosylate; (c) mixture of diastereosmers from the addition of bromine to the *cis* isomer.

In the present study, the stereochemistry of the addition of bromine in carbon tetrachloride to 2-buten-2-yl tosylates was determined.[7] The nmr spectra (Figure 1) of the products of the addition to the *cis* and *trans* isomers, indicate some stereoselectivity in the addition to the double bond (Scheme I). The lack of complete stereospecificity can be interpreted in terms of stabilized oxonium ions **2** and **3** which may be formed directly or from **1** and **4** in competition with attack of bromide ion. The stereochemical assignment is based on the assumption of a preponderance of *trans* addition. The products of the addition of bromine to 1-cyclohexen-1-yl tosylate proved to be so unstable that they could not be identified.

The α,β-dibromo tosylates are of some interest as solvolytic substrates which may undergo solvolysis with α- or β-bromine assistance or with both. Accordingly, the crystalline **6** was dissolved in formic acid containing sodium formate and was found to have undergone rapid formolysis to give 3-bromo-2-butanone (eq 1).

$$6 \xrightarrow[HCOONa]{HCOOH} CH_3CHBrC(=O)CH_3 \qquad (1)$$

Information concerning the role of β-bromine in solvolyses was available from an unpublished study of

(1) (a) We acknowledge partial support of the purchase of a Varian HA-100D nmr spectrometer through National Science Foundation Grant GP-8510. (b) NSF Graduate Trainee, 1966–1969.

(2) I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, **59**, 947 (1937).

(3) G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967).

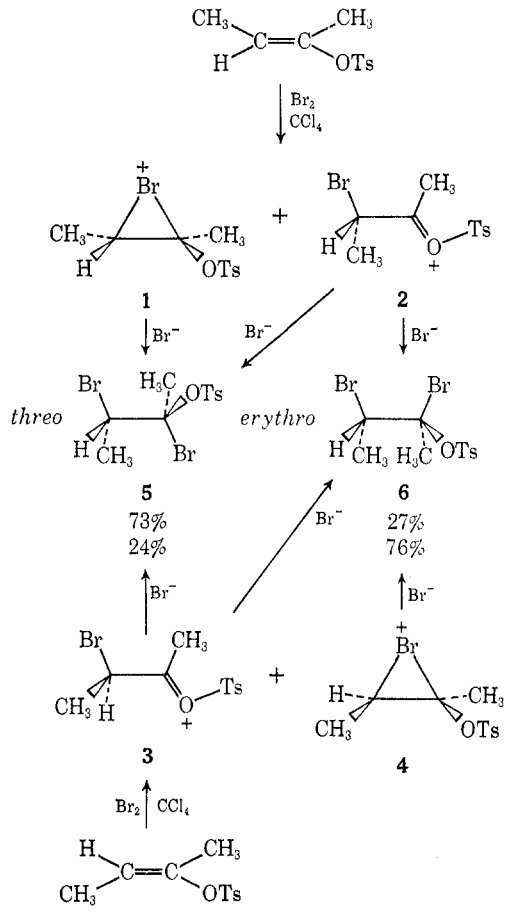
(4) (a) R. C. Fahey and H. J. Schneider, *ibid.*, **90**, 4429 (1968); (b) J. H. Rolston and K. Yates, *ibid.*, **91**, 1469 (1969); (c) J. H. Rolston and K. Yates, *ibid.*, **91**, 1477 (1969).

(5) (a) R. U. Lemieux and B. Fraser-Reid, *Can. J. Chem.*, **42**, 532 (1964); (b) R. U. Lemieux and B. Fraser-Reid, *ibid.*, **43**, 1460 (1965).

(6) C. L. Stevens and J. A. Valicenti, *J. Amer. Chem. Soc.*, **87**, 838 (1965).

(7) For the preparation and stereochemical assignments of the vinyl tosylates, see P. E. Peterson and J. M. Indelicato, *ibid.*, **90**, 6515 (1968).

SCHEME I



the formolysis of *trans*- and *cis*-2-bromocyclohexyl brosylate. In the case of the *trans* isomer where β-bromine assistance is possible, the rate of formolysis relative to that of the parent cyclohexyl brosylate was decreased by a factor of 2.8. In the case of the *cis* isomer where β-bromine assistance is impossible, the inductive effect of the bromine decreased the reaction rate by a factor of 8500.[8] On the other hand, the effect of an α-bromine in the case of the solvolysis of some benzhydryl dibromides was to speed up solvolysis.[9] Based on an estimate that the half-life for the reaction (eq 1) was less than 6 min, the solvolysis of the α,β-dibromo tosylate **6** is faster than that of 2-butyl tosylate by at least a factor of 35.[10] The cited literature suggests that both α- and β-bromine assistance occur in the formolysis of **6**.

Finally, it may be noted that the reaction of α,β-dibromo tosylates with formic acid may be of synthetic value, as it provides an alternative to a standard preparation of α-bromo ketones and aldehydes through the bromination of enol acetates.[11]

(8) (a) J. E. Duddey, Ph. D. Thesis, St. Louis University (1967). (b) These results may be compared with the acetolysis data from the literature: E. Grunwald, *J. Amer. Chem. Soc.*, **73**, 5458 (1951), and S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(9) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw Hill Book Co., New York, N. Y., 1962, p 102.

(10) P. E. Peterson, R. E. Kelley Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965).

(11) (a) E. R. H. Jones and D. J. Wluka, *J. Chem. Soc.*, 907 (1959); (b) P. Z. Bedoukian, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 127.

Experimental Section

Infrared spectra were determined on a Beckman Model IR-5A double-beam spectrophotometer. Gas chromatographic analysis was carried out on a Hewlett–Packard Model 5750 gas chromatograph. Nmr spectra were determined on a Varian Model HA-100D spectrometer.

Addition of Bromine to 2-Buten-2-yl Tosylates.—*trans*-2-Buten-2-yl tosylate (0.0358 g, 1.585×10^{-4} mol) was dissolved in 0.5 ml of CCl_4 and cooled in an ice bath. Bromine (0.025 g, 0.1585 mmol) was added and the mixture kept cold until the nmr spectrum was taken (2–5 min; *cf.* Figure 1): nmr (CCl_4) δ 1.83 and 1.85 (2d, J = 6 Hz, CH_3CHBr–), 2.34 and 2.46 (2s, $CH_3COTsBr$–), 2.45 (s, $CH_3C_6H_4$–), 4.59 and 4.34 (2q, J = 7 Hz, CH_3CHBr–), 7.72 (m, aromatic). To show that two peaks were present at δ 4.45 and 4.46, 20% benzene was added to the solution. The $CH_3C_6H_4$– peak was shifted upfield to δ 2.32 and the $CH_3COTsBr$– peak shifted upfield only to δ 2.43. The spectrum remained constant in the proportions of isomers after 36 hr at room temperature, indicating no interconversion of isomers. The addition to the *cis* isomer was carried out in a similar manner. The nmr spectrum showed that the minor component from the previously described addition reaction was now the predominant isomer present.

Isolation Experiment.—The *trans* isomer (0.0026 mol) was brominated. The solution was washed with distilled water and saturated NaCl solution and dried ($MgSO_4$). Removal of the solvent on a rotary evaporator yielded 91% of a mixture of diastereomers. Several crystallizations from hexane gave *erythro*-2,3-dibromo-2-butyl tosylate: mp 77.9–79.8; nmr (CCl_4) δ 1.83 (d, 3, J = 6 Hz, CH_3CHBr–), 2.34 (s, 3, $CH_3COTsBr$–), 2.45 (s, 3, $CH_3C_6H_4$–), 4.59 (q, 1, J = 7 Hz, CH_3CHBr–), 7.52 (m, 4, aromatic).

Anal. Calcd for $C_{11}H_{14}Br_2O_3S$: C, 34.22; H, 3.65. Found: C, 34.22; H, 3.65.

Formolysis of *erythro*-2,3-Dibromo-2-butyl Tosylate.—To a weighed quantity of dibromobutyl tosylate formic acid (0.125 M in sodium formate) was added to form a solution 0.1 M in tosylate. The tosylate was slow to dissolve, but did so after 10 min. At that time, nmr indicated that no starting material was present. The solution was neutralized with $NaHCO_3$ and extracted with CCl_4. The sole product of the reaction was identified by ir and nmr to be 3-bromo-2-butanone.

In a similar experiment, glpc of the reaction mixture, employing a base forecolumn,[12] indicated quantitative conversion into the bromo ketone.

Registry No.—Bromine, 7726-95-6; **5**, 22461-42-3; **6**, 22461-43-4.

(12) P. E. Peterson and E. Tao, *J. Org. Chem.*, **29**, 2322 (1964).

Quaternary Carbons by the Alkylation of Tertiary Halides with Aluminum Alkyls. A Model for Initiation and Termination in Cationic Polymerization

J. P. KENNEDY

Corporate Research Laboratories, Esso Research and Engineering Company, Linden, New Jersey 07036

Received May 30, 1969

The reactions of halo hydrocarbons with aluminum alkyls have been studied previously.[1] The best report in this field is by Miller,[1] who investigated the interaction between aluminum triethyl and a variety of halogen-containing hydrocarbons in ethyl ether at room or higher temperatures. Product analysis showed medium to high conversions into a variety of products

(1) D. B. Miller, *J. Org. Chem.*, **31**, 908 (1966), and references cited therein.