increased in temperature (formation of intermediate), started to reflux, turned a bright yellow, and finally became homogeneous. The mixture was gently refluxed for 10 h. An NMR spectrum of the solution indicated mainly neopentyl thiocyanate (plus some neopentyl isothiocyanate) and neopentyl chloride as the reaction products. A solid had formed during the reaction; the solid was filtered and washed with pentane, and the pentane was added to the filtrate. The solvent was removed at 25–38 °C under water aspirator vacuum by using a rotary evaporator. When the mixture was concentrated, much of the triphenylphosphine oxide formerly in solution was precipitated by the addition of pentane. The solid which was formed was filtered and then triturated with pentane; the pentane extracts were combined, dried, and further distilled to concentrate the organic layer. This whole procedure was repeated and the final concentrated liquid distilled under vacuum. The final product (2.3 g, 0.018 mol, 21.7% yield) had a boiling point of 62 °C at 12 torr. Its purity was >99% by GLC (105–190 °C, temperature programmed at 24 °C/min). Anal. Calcd for $C_6H_{11}NS$: C, 55.77; H, 8.58; N, 10.84; S, 24.81. Found: C, 55.52; H, 8.58; N, 10.79; S, 24.58. NMR analysis by relative peak heights indicated a 90/10 mixture of neopentyl thiocyanate ($(CH_3)_3C$, δ 1.07; $CH_2SC{\equiv}N$, δ 2.93) and neopentyl isothiocyanate ($(CH_3)_3C$, δ 1.03; $CH_2N{=}C{=}S$, δ 3.17). Infrared (neat) clearly indicated absorptions at 2960 (CH alkane), 2150 (sharp, $SC{\equiv}N$), and 2080 cm^{-1} (br, $N{=}C{=}S$, small peak). These results are still consistent with the 90/10 thiocyanate/isothiocyanate mixture. Mass spectral analysis showed a parent peak (M) of m/e 129, an M - 15 peak at m/e 114, and m/e 72 (CH_2SCN), 71 (C_5H_{11}), 58 (SCN), 57 (C_4H_9), 55 (C_4H_7), 43 (C_3H_7), 41 (C_3H_5), 29 (C_2H_5), and 27 (HCN). The mass spectral analysis is consistent with both neopentyl thiocyanate and neopentyl isothiocyanate.

Acknowledgment is made to the East Tennessee State Research Advisory Council for financial assistance, to Mrs. Susan Campbell for her aid in the drawings and preparation of the manuscript, and to Dr. J. L. Miller for his valuable discussions. B.F. acknowledges the assistance of Dr. Frank C. Spencer of New York University School of Medicine, without whose aid this manuscript could never have been written.

Registry No. 1, 66085-08-3; 3, 69626-79-5; 4, 25343-65-1; neopentyl alcohol, 75-84-3; (*R*)-(+)-2-octanol, 5978-70-1; (*S*)-(−)-2-chlorooctane, 16844-08-9.

Models for the Ion-Pair Cluster Mechanism in Nucleophilic Substitution Reactions

Socorro Ramos and William Rosen*

Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881

Received April 1, 1981

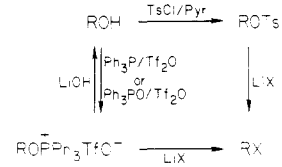
Several bis(alkoxytriphenylphosphonium) salts have been prepared. When sterically constrained, as close neighbors, the leaving groups of these cations react rapidly at room temperature with negative nucleophiles to produce the expected substitution product. When sterically unconstrained, these types of functional groups behave as if they were mono(alkoxytriphenylphosphonium) salts, substituting very slowly or not at all at room temperature. The ion-pair cluster mechanism is discussed in light of these results.

The reactions leading to the formation of tetracovalent phosphorus moieties are numerous.[1] In several of these reactions, alkoxyphosphonium salts have been implicated as important intermediates rather than stable entities. This is particularly true in those reactions where an alcohol functionality is transformed to another function by the use of a phosphine(ite) in conjunction with different reagents. Examples are the Michaelis–Arbusov reaction,[2] the Lee reaction,[3] and the DEAD reaction.[4] Recently, Hendrickson and Schwartzman have shown that some of the suspected alkoxytriphenylphosphonium intermediates from these reactions can be easily prepared as relatively stable compounds when the anion is the trifluoromethanesulfonyl (triflate) group.[5] As a result, we have been able to prepare several bis(alkoxytriphenylphosphonium) systems[6] which shed considerable light on the mechanism of nucleophilic substitution in these important reactions.

The nucleophilic substitution mechanism is one of the most important concepts in chemistry. Recently, several variations of this important concept have been proposed to explain the results obtained in the Lee reaction.[7] One of these variations proposes an unusual clustering process involving ion pairs, and it is to this mechanism that we address ourselves in this report.

The clustering of molecular entities is a phenomenon of increasing import.[8] It is becoming recognized by chemists as an area of study which should help to bridge the gap that exists between the chemistry of monomolecular units and polymolecular moieties. This may be nowhere more true than in reactions leading to nucleophilic

Scheme I.[a,b] Cycle of Reactions Used To Verify the Integrity for the Carbon Skeletons of the Alkoxytriphenylphosphonium Salts Studied



[a] See Table I for the alkyl groups. [b] X = Cl, Br, or I; R = alkyl; Ph = phenyl; Ts = *p*-toluenesulfonyl; Pyr = pyridine.

(1) Kirby, A. J.; Warren, S. G. "The Organic Chemistry of Phosphorus"; Elsevier: New York, 1967.
(2) Harvey, R. G.; LeSombre, E. G. *Top. Phosphorus Chem.* **1964**, *1*, 58.
(3) Appel, R. *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 801.
(4) Mitsunobu, O. *Synthesis* **1981**, 1.
(5) Hendrickson, J. B.; Schwartzman, S. M. *Tetrahedron Lett.* **1975**, 277. See also: Aaberg, A.; Gramstad, T.; Husebye, S. *Ibid.* **1979**, 2263.
(6) Ramos, S.; Rosen, W. *Tetrahedron Lett.* **1981**, 35.
(7) Jones, L. A.; Sumner, C. E., Jr.; Franzus, B.; Huang, T. T.-S.; Snyder, E. I. *J. Org. Chem.* **1978**, *43*, 2821.
(8) See for examples: Kenney-Wallace, G. A. *Acc. Chem. Res.* **1978**, *11*, 434. Geoffroy, G. L. *Ibid.* **1980**, *13*, 469.

0022-3263/81/1946-3530$01.25/0

Table I. Pertinent NMR Data and Approximate Bromide Reaction Times

alkyl groups (R)[a]	^{1}H NMR chemical shift (α-CH), δ[b] OH	$O^+PPh_3TfO^-$	^{31}P NMR[c]	reaction time,[d] h (X = Br)
	3.85 (dd)	4.50 (p, J = 6)	−62	3.0
	3.75 (m)	4.35 (p, J = 6)	−61	2.5[e]
	3.50 (m)	4.30 (m, J = 4)	−56 −57	3.0 ~72.0
1,6-hexanediyl	3.70 (m)	4.50 (q, J = 5)	−60	>96
neopentyl	3.30 (s)	3.95 (d, J = 4)	−57	>48
isobutyl	3.80 (d)	4.05 (m, J = 6)		>72
sec-butyl	3.85 (sx)	4.65 (m, J = 6)		>48
l-(−)-menthyl	3.45 (m)	4.50 (m, J = 5)	−60	~48[f]

[a] Alkyl groups used in study. See Scheme I for definitions of other symbols. [b] The POCH coupling constants are in hertz. [c] Resonance in parts per million downfield from external 80% H_3PO_4. Current practice would list downfield shifts as positive. [d] The one-phase method, using LiBr, was the standard technique employed. Solubility of LiBr in acetone is ~4 g/10 mL. Saturated solutions of anhydrous LiBr in acetone were employed in this study. [e] Using the two-phase method with LiCl and a catalytic quantity of LiOH produced a 4:3 mixture of the dichloride and the diol in an 85% yield. [f] Completed reaction time with LiCl instead of LiBr.

substitution.[9] If the Lee reaction is an example of one that involves a clustering of the molecular units prior to nucleophilic attack,[7] then it is of utmost urgency to better understand the processes leading to these results. Before that is done, however, some experimental observations on the possible existence of nucleophilic substitution clustering mechanisms must be presented. We believe we have systems that allow for such observations, and thus we present our qualitative results at this time.

Results

The alkoxytriphenylphosphonium triflates that were prepared and studied are listed in Table I. All were prepared from the corresponding alcohols as previously described.[5,6] They were most easily characterized by their NMR spectra, details of which are also presented in Table I. Most of the alkoxytriphenylphosphonium triflates could be reconverted to the original alcohol by treatment with LiOH (see Scheme I), thus proving that the integrity of the carbon skeleton had been maintained. The exception was (−)-menthoxytriphenylphosphonium triflate which yielded (+)-neomenthol on reaction with LiOH.[6] All the alkoxytriphenylphosphonium triflates were assumed to be ionic as indicated by the ^{31}P NMR data.[10]

As indicated in Table I, the bis(alkoxytriphenylphosphonium triflates) reacted differently toward negative nucleophiles such as bromide ion than did the alkoxytriphenylphosphonium triflates. The difference was most apparent when one considered the amount of time necessary to complete the nucleophilic substitution reaction at room temperature (see Table I). Bis(oxyphosphonium) salts constrained to the same spatial arrangement required approximately 3 h for completion of the reaction. Unconstrained bis(oxyphosphonium) salts reacted like the monooxyphosphonium examples, either very slowly to produce the substitution product or by simple exchange of the anion. The results can be summarized by the following examples.

(1) *cis*-Cyclobut-3-ene-1,2-diylbis[(methyleneoxy)triphenylphosphonium triflate] reacted rapidly with bromide ion (reaction complete in less than three hours at room temperature[6]) to yield *cis*-1,2-(bromomethyl)-3-cyclobutene.

(2) Hexane-1,6-diylbis[oxytriphenylphosphonium triflate] reacted with bromide ion by simple exchange to produce hexane-1,6-diylbis(oxytriphenylphosphonium bromide) as the sole product even after 4 days contact at room temperature with excess LiBr.

(3) L-(−)-(Menthyloxy)triphenylphosphonium triflate reacted slowly with chloride ion to yield (+)-neomenthyl chloride[11] (reaction complete within 48 h).

(4) Isobutoxytriphenylphosphonium triflate reacted with bromide ion to produce, by exchange, isobutoxytriphenylphosphonium bromide.

(5) *cis*-Cyclobutane-1,2-diylbis[(methyleneoxy)triphenylphosphonium triflate] reacted with mixtures of negative nucleophiles to produce mixtures of substitution products, i.e., when chloride and hydroxide ions were present, the product mixture consisted mainly, but not solely, of *cis*-1,2-(chloromethyl)- and *cis*-1,2-(hydroxymethyl)cyclobutane (see Table I, footnote *e*).

(6) As noted previously[6], the bis(oxyphosphonium triflate) of 1,2,2-trimethyl-1,3-bis(hydroxymethyl)cyclopentane reacted in two stages with negative nucleophiles.[12]

Discussion

The mechanism for the reaction of alkoxyphosphonium ions with negative nucleophiles has been a matter of some discussion for several years now. Three different proposals have been enumerated: (1) a $_\sigma2_s + _\sigma2_a$ pericyclic mechanism;[13] (2) an ion-pair four-center mechanism;[14] (3) an ion-pair cluster mechanism.[7]

Aneja and co-workers[13] first proposed the $_\sigma2_s + _\sigma2_a$, thermal, pericyclic mechanism in their work on cholesterol and *i*-cholesterol. The active intermediate was depicted as a phosphorane in a trigonal-bipyramidal or square-pyramidal structure, with the two reacting groups (alkoxide and halide) occupying apical and equatorial positions. The symmetry-allowed $_\sigma2_s + _\sigma2_a$ process would occur during the concerted, suprafacial breaking of the phosphorus–halide and carbon–oxygen bonds, thus forming the carbon–halide and phosphorus–oxygen bonds of the products.[7] The inversion of configuration and small isotope effect observed in the formation of the products would thus be accountable. This mechanism does not, however, explain the apparent dependence of rate on back-side hindrance of the alkoxide moiety.[7]

The four-center, nonconcerted mechanism proposed by Snyder and Weiss[14] involved a tight ion pair where the phosphorus–halide bond breaks prior to the cleavage of the carbon–oxygen bond. In order to rationalize the predominant back-side attack, however, it was necessary to

(9) Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789.
(10) Hudson, H. R.; Rees, R. G.; Weeks, J. E. *J. Chem. Soc., Perkin Trans. 1* **1974**, 982.
(11) Kato, A.; Ueda, H.; Hashimoto, Y. *Agric. Biol. Chem.* **1970**, *34*, 1843.
(12) Erikson, G. W.; Fry, J. L. *J. Org. Chem.* **1980**, *45*, 970.
(13) Aneja, R.; Davies, A. P.; Knaggs, J. A. *Tetrahedron Lett*, **1974** 67.
(14) Weiss, R. G.; Snyder, E. I. *J. Org. Chem.* **1970**, *35*, 1627.

place the halide ion in a particular location with respect to the cation in the tight ion pair, and thus the model became energetically untenable.

Recognizing that the artificial spatial positioning of a halide ion in a tight ion pair is energetically unsatisfactory, Franzus and co-workers[7] modified the picture somewhat and proposed the ion-pair cluster mechanism. In this model, the ion pairs are postulated to exist as two- or three-dimensional clusters such that the "positive phosphorus in one ion pair is in part electrically neutralized by a negative chloride from (an) other ion pair(s)" and vice versa. This model would, therefore, predict that prior to nucleophilic substitution, two or more ion pairs must associate or cluster together.

The data presented in Table I seem to substantiate this last mechanism. That is, when alkoxytriphenylphosphonium ions are forced to cluster, i.e., sterically and molecularly constrained as close neighbors, the energetics for nucleophilic substitution are greatly lowered, and reactions with negative nucleophiles occur with great facility. If, however, alkoxytriphenylphosphonium ions are molecularly attached to one another but unconstrained sterically or they are molecularly unattached, then the energetics for bringing the two positively charged entities together become formidable, and subsequent substitution reactions of an S_N2 type become less likely. As a consequence, the ion-pair cluster mechanism appears to explain all observations made thus far on systems where alkoxytriphenylphosphonium ions have been the postulated or proven intermediate. Whether this unusual mechanism is specific to these systems or more generally applicable to other nucleophilic substitution reactions will have to await future observations.

Experimental Section

General Methods. Proton nuclear magnetic resonance (NMR) spectra were recorded either on a Varian EM-360 or a Brucker 270-MHz instrument at Yale University. Carbon-13 NMR spectra were recorded on a Varian CFT-20 multinuclear instrument. Phosphorus-31 NMR spectra were obtained by using the 60-MHZ JEOL-FT instrument at Northeastern University. Solutions in $CDCl_3$ or acetone-d_6 were generally prepared as concentrated (~10%) as needed to easily observe all signals. Infrared spectra were obtained by using a Beckman Acculab TM4 spectrometer. Optical rotation measurements were obtained on a Perkin-Elmer 141 polarimeter using the Na D line. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. High-performance liquid chromatography (HPLC) or thin-layer chromatography (TLC) were oftentimes used to separate complex reaction mixtures. For the HPLC work, a homemade apparatus was built by using a Rheodyne syringe loading sample injector with a 20-μL sample loop, a Milton Bay Instruments minipump (500 psig), a Chromatec UV detector, and a Waters Associates μCN column. For the TLC work, Eastman TLC sheets made with silica gel impregnated with fluorescent indicator (No. 6060) were cut in strips, developed, and visualized by using UV light. Chloroform was the eluent in both systems. When necessary, thick-layer chromatography was utilized to preparatively separate some of the mixtures. Precoated plates made with silica gel of 1500-μm thickness were used. In most situations, however, column chromatography was sufficient to separate the components of the reaction mixtures. Silica gel (SilicAR cc-7) from Mallinckrodt was used as the stationary phase. Chloroform was again the starting eluent with increasing percentages of acetone as needed. All reactions were performed under a blanket of dry nitrogen gas. Elemental analyses were performed by Micro-Analysis, Inc.

Preparation of *cis*-1,2-Bis(hydroxymethyl)-3-cyclobutene. This material was prepared by the lithium aluminum hydride reduction of *cis*-cyclobutene-3,4-dicarboxylic anhydride[15] as reported by others.[16] Conversion to the ditosylate by utilizing *p*-toluenesulfonyl chloride and pyridine was easily accomplished; mp 62–63 °C (lit.[17] mp 66–67 °C).

Preparation of *cis*-1,2-Bis(halomethyl)-3-cyclobutenes. *cis*-1,2-Bis[(tosyloxy)methyl]-3-cyclobutene and excess lithium halide were mixed with anhydrous acetone in a round-bottomed flask. The mixture was refluxed until TLC indicated that the reaction had been completed. After the mixture cooled, the solids were removed by filtration, and water was added. The aqueous mixture was extracted three times with ether, and the combined organic extracts were dried over anhydrous $MgSO_4$. The dried organic layer was filtered and the solvent evaporated, leaving a yellow, residual oil in quantitative yield.

Chloride: IR (neat) 3100, 3000, 2900, 1450, 1300, 1260, 760, 740, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.25 (s, 2 H), 3.05–3.80 (m, 6 H). Anal. Calcd for $C_6H_6Cl_2$: C, 47.71; H, 5.34. Found: C, 47.63; H, 5.31.

Bromide: IR (neat) 2980–2860, 1450, 1270, 1230, 780, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.23 (s, 2 H), 3.20–3.65 (m, 6 H). Anal. Calcd for $C_6H_8Br_2$: C, 30.03; H, 3.36. Found: C, 30.11; H, 3.48.

Preparation of *cis*-1,2-Bis(hydroxymethyl)cyclobutane. *cis*-1,2-Bis(hydroxymethyl)-3-cyclobutene (0.5 g, 4.4 mmol) was dissolved in 50 mL of anhydrous ethyl acetate. To this mixture was added ~10 mg of 10% Pd/C, and the mixture was then blanketed with hydrogen gas in an atmospheric pressure hydrogenator. After stirring was commenced, a total of 98 mL of H_2 gas was absorbed. The mixture was filtered through Celite and the solvent removed by evaporation to yield quantitatively the desired material: IR (neat) 3400, 3000–2800, 1500, 1090, 1030 cm^{-1} NMR ($CDCl_3$) δ 4.25 (s, 2 H), 3.35–4.10 (m, 4 H), 2.35–3.0 (br m, 2 H), 1.1–2.35 (m, 4 H). The ditosylate derivative could be prepared as above: mp 48–50 °C.

Preparation of *cis*-1,2-Bis(halomethyl)cyclobutane. The dichloride, dibromide, and diiodide could be prepared quantitatively from the ditosylate as described above.

Chloride: ^1H NMR ($CDCl_3$) δ 3.5–3.8 (m, 4 H), 2.6–3.2 (m, 2 H), 1.5–2.2 (m, 4 H).

Bromide: ^1H NMR ($CDCl_3$) δ 3.3–3.8 (m, 4 H), 3.1–3.7 (m, 2 H), 1.6–2.4 (m, 4 H).

Iodide: ^1H NMR ($CDCl_3$) δ 2.9–3.7 (m, 6 H), 1.6–2.3 (m, 4 H).

Preparation of (+)-(1*R*,3*S*)-1,2,2-Trimethyl-1,3-bis(hydroxymethyl)cyclopentane. D-Camphoric acid was reduced with lithium aluminum hydride according to the procedure described by Klein and Johnson[18] to give the desired white solid: 89% yield; mp 132–134 °C (lit.[18] mp 133–134 °C; $[\alpha]^{25}_D$ + 61° ($CHCl_3$).

General Procedure for the Preparation of Alkoxytriphenylphosphonium Triflates. Triphenylphosphine (2.0 g, 0.76 mmol) was dissolved in 10 mL of anhydrous CH_2Cl_2 in a three-necked, 50-mL, round-bottomed flask fitted with serum cap, nitrogen inlet, and addition funnel. After the apparatus was thoroughly flushed with N_2, the mixture was cooled to −20 °C and magnetic stirring was commenced. A solution of 0.1 mmol of alcohol dissolved in 15 mL of CH_2Cl_2 was then added via the addition funnel and the temperature allowed to reequilibrate. Triflic anhydride (0.6 mL) was added via a syringe, and the solution was stirred at −20 °C for 1.5 h. The mixture was poured into a cooled, 25-mL, saturated, aqueous solution of $NaHCO_3$, the layers quickly separated, and the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated, and the resultant oil was column chromatographed. Elution was always begun with pure $CHCl_3$ and continued until all the excess triphenylphosphine had been eluted. Most of the triphenylphosphine oxide could be eluted next by using 9:1 $CHCl_3$–acetone. The alkoxytriphenylphosphonium triflate, usually contaminated with some triphenylphosphine oxide, was then eluted with chloroform–acetone mixtures or pure acetone. It was never possible to completely rid the alkoxytriphenylphosphonium triflate of triphenylphosphine oxide. In point of fact, a small amount of triphenylphosphine oxide seemed necessary to stabilize the salt against further decomposition; i.e., if the salt was purified by direct

(15) Bloomfield, J. J.; Owsley, D. C. "Organic Photochemical Synthesis"; Srinivasan, R. Ed.; Wiley: New York, 1976, Vol. II, p 36.

(16) Brauman, J. I.; Archie, W. C., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 4262.

(17) Winter, R. E. K. *Tetrahedron Lett.* **1965**, 1207.

(18) Johnson, T. H.; Klein, K. C. *J. Org. Chem.* **1979**, *44*, 461.

collection from an HPLC column, reinjection of the sample always showed contamination by triphenylphosphine oxide. Consequently, integrations of the ^1H NMR spectra of these materials were always high in the aromatic region. The same substances could be obtained by using the procedures delineated by Hendrickson and Schwartzman.[5,19]

Physical Data for Alkoxytriphenylphosphonium Triflates. ***cis*-Cyclobut-3-ene-1,2-diylbis[(methyleneoxy)triphenylphosphonium triflate]**: fluffy, glasslike solid (decomposes at 37 °C) when evacuated in partial vacuum; IR (neat) 3040, 3000 (m), 1590 (m), 1480 (m), 1430 (s), 1260 (vs), 1220, 1150 (s), 1030, (m), 990, 750 (s), 690 (s), 640 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–8.1 (m, 32 H), 6.0 (s, 2 H), 4.2–4.8 (p, 4 H), 3.2–3.6 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 137.73 (s), 136.50 (d, J = 0.11 Hz), 133.46 (d, J = 0.58 Hz), 131.30 (d, J = 0.68 Hz), 118.59 (d, J = 5.33 Hz), 71.65 (d, J = 0.43 Hz), 45.14 (d, J = 0.33 Hz), for ^{31}P NMR data, see Table I.

***cis*-Cyclobutane-1,2-diylbis[(methyleneoxy)triphenylphosphonium triflate]**: thick liquid; IR (neat) 3050, 2960–2900, 1580, 1440 (vs.), 1250, 1230, 1160, 1120, 1040, 1000, 920, 740, 700, 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–8.2 (m, 33 H), 4.2–4.5 (p, 4 H), 2.6–3.2 (m, 2 H), 1.5–2.4 (m, 4 H); for ^{31}P NMR data, see Table I.

Hexane-1,6-diylbis[oxytriphenylphosphonium triflate]: ^1H NMR ($CDCl_3$) δ 7.4–8.2 (m, 35 H), 4.2–4.8 (q, 4 H), 1.2–1.8 (m, 8 H).

1,2,2-Trimethylcyclopentane-1,3-diylbis[(methyleneoxy)triphenylphosphonium triflate]. This was prepared by the general procedure except that an excess of reagents was used, otherwise cyclic ether[12] was obtained: off-white, cottony solid when evacuated under partial vacuum; ^1H NMR ($CDCl_3$) δ 7.5–8.3 (m, 35 H), 4.0–2.7 (m, 4 H), 1.2–1.7 (m, 5 H), 1.15 (s, 3 H), 1.0 (s, 3 H), 0.65 (s, 3 H); for ^{31}P NMR data, see Table I.

Neopentoxytriphenylphosphonium triflate:[7] ^1H NMR ($CDCl_3$) δ 7.6–8.0 (m, 15 H), 3.9–4.0 (d, J = 2 H), 1.1 (s, 9 H).

Isobutoxytriphenylphosphonium triflate:[7] ^1H NMR ($CDCl_3$) δ 7.5–8.0 (m, 15 H), 3.97–4.15 (t, J = 6 Hz, 2 H, 1.6–2.5 (m, 1 H), 1.0 (d, J = 8 Hz, 6 H).

***sec*-Butoxytriphenylphosphonium triflate**: ^1H NMR ($CDCl_3$) δ 7.8–8.0 (m, 17 H), 4.4–4.9 (m, 1 H), 1.4–1.8 (m, 2 H), 1.3 (d, J = 6 Hz, 3 H), 0.5–0.8 (t, J = 6 Hz, 3 H).

General Procedures for Reacting Alkoxytriphenylphosphonium Triflates with Halides. Two-Phase Method. The alkoxytriphenylphosphonium triflate was dissolved in chloroform and shaken with a saturated solution of alkali metal halide in a separatory funnel. After several minutes, the layers were separated, the $CHCl_3$ layer was dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. Column chromatography yielded the alkyl halide when reaction had occurred.

One-Phase Method. The alkoxytriphenylphosphonium triflate was dissolved in anhydrous acetone, and an excess of the appropriate lithium halide was added. The mixture was stirred until TLC indicated the reaction was complete. The mixture was filtered and the solvent removed by rotary evaporation. Column chromatography yielded the alkyl halide.

Ion-Exchange Method. An acetone solution of the alkoxytriphenylphosphonium triflate was eluted through a column packed with Dowex resin of the appropriate halide ion. The elution was allowed to occur over approximately a 3-h period. The collected fraction was then evaporated and the alkyl halide purified by column chromatography.

Preparation of 1,2,2-Trimethyl-1,3-bis(bromomethyl)cyclopentane. Elution of 0.2 g of the appropriate dialkoxytriphenylphosphonium ditriflate over a bromide ion-exchange resin produced reaction at the normal primary carbon: ^1H NMR ($CDCl_3$) δ 7.2–8.3 (m, 18 H), 4.24–4.45 (dd, J = 6 Hz, 2 H), 3.0–3.7 (m, 2 H), 1.3–1.7 (m, 5 H), 1.15 (s, 3 H), 1.05 (s, 3 H), 0.7 (s, 3 H). Reaction of 0.1 g of this material with LiBr in anhydrous acetone for 3 days yielded 0.015 g of the desired dibromide: ^1H NMR ($CDCl_3$) δ 3.0–3.8 (m + s, 4 H), 1.4–2.0 (m, 5 H), 1.15 (s, 6 H), 0.95 (s, 3 H); see Table I for ^{31}P NMR data; $[\alpha]^{25}_D$ + 58° ($CDCl_3$). Anal. Calcd for $C_{10}H_{18}Br_2$: C, 40.30; H, 6.09. Found: C, 40.52; H, 5.99.

Acknowledgment. We thank the Research Corp. for their generous support of this research. We are deeply indebted to Dr. Dennis Owsley of Monsanto Corp. for a generous gift of *cis*-cyclobutene-3,4-dicarboxylic anhydride. S.R. thanks the American Hoechst Corp. for a fellowship.

Registry No. *cis*-1,2-Bis(hydroxymethyl)-3-cyclobutene, 77774-01-7; *cis*-1,2-bis[(tosyloxy)methyl]-3-cyclobutene, 1517-12-0; *cis*-1,2-bis(chloromethyl)-3-cyclobutene, 77774-02-8; *cis*-1,2-bis(bromomethyl)-3-cyclobutene, 77774-03-9; *cis*-1,2-bis(hydroxymethyl)cyclobutane, 54445-64-6; *cis*-1,2-bis[(tosyloxy)methyl]cyclobutane, 76497-45-5; *cis*-1,2-bis(chloromethyl)cyclobutane, 77774-04-0; *cis*-1,2-bis(bromomethyl)cyclobutane, 64811-90-1; *cis*-1,2-bis(iodomethyl)cyclobutane, 77774-05-1; (+)-(1*R*,3*S*)-1,2,2-trimethyl-1,3-bis(hydroxymethyl)cyclopentane, 68510-42-9; *cis*-cyclobut-3-ene-1,2-diylbis[(methyleneoxy)triphenylphosphonium triflate], 77774-07-3; *cis*-cyclobutane-1,2-diylbis[(methyleneoxy)triphenylphosphonium triflate], 77774-09-5; hexane-1,6-diylbis[oxytriphenylphosphonium triflate], 77774-11-9; (+)-(1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-diylbis[(methyleneoxy)triphenylphosphonium triflate], 77774-13-1; neopentoxytriphenylphosphonium triflate, 77774-14-2; isobutoxytriphenylphosphonium triflate, 77774-16-4; *sec*-butoxytriphenylphosphonium triflate, 77774-18-6; (+)-(1*R*,3*S*)-1,2,2-trimethyl-1,3-bis(bromomethyl)cyclopentane, 77774-19-7; *l*-(−)-(menthyloxy)triphenylphosphonium triflate, 77774-21-1.

(19) Schwartzman, S. M. *Ph.D. Dissertation*, Brandeis University, 1975.

Aromatic Substitution. 48.[1] Boron Trifluoride Catalyzed Nitration of Aromatics with Silver Nitrate in Acetonitrile Solution

George A. Olah,* Alexander P. Fung, Subhash C. Narang, and Judith A. Olah

Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90007

Received March 4, 1981

Benzene, alkylbenzenes, halobenzenes, and anisole were nitrated with silver nitrate/boron trifluoride in acetonitrile solution. Correlation of competitive rates with π- and σ-complex stabilities indicated that the transition state of highest energy lies relatively early on the reaction coordinate. Data indicate that nitrations occur via a polarized complex of the nitrating agent, with the catalyst undergoing nucleophilic displacement by the aromatic substrate.

Electrophilic nitration of aromatic hydrocarbons has been studied extensively. The nitrating agents commonly used are nitric acid in the presence of other acids, mixed nitric acid–carboxylic acid anhydrides, nitronium salts, and

0022-3263/81/1946-3533$01.25/0