J. Husbands, T. R. B. Mitchell, and J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans. 1*, 596 (1974); M. Guilotti, R. Ugo, and S. Collonna, *J. Chem. Soc. C*, 2652 (1971).
(5) E. Malunowicz and S. Tyrlik, *J. Organomet. Chem.*, **72**, 269 (1974).
(6) J. C. Orr, M. Mersereau, and A. Sanford, *Chem. Commun.*, 162 (1962).
(7) Y. Sasson, P. Albin, and J. Blum, *Tetrahedron Lett.*, 833 (1974).
(8) E. L. Eliel, T. W. Doyle, R. O. Hutchins, and E. C. Gilbert, *Org. Synth.*, **50**, 13 (1970).
(9) K. Ohno and J. Tsuji, *J. Am. Chem. Soc.*, **90**, 99 (1968); M. C. Baired, C. J. Nyman, and G. Wilkinson, *J. Chem. Soc. A*, 348 (1968); H. M. Walborsky and L. E. Allen, *J. Am. Chem. Soc.*, **93**, 5465 (1971); R. E. Ireland and G. Pfister, *Tetrahedron Lett.*, 2145 (1969); H. M. Walborsky and L. E. Allen, *ibid.*, 823 (1970).
(10) T. Nishiguchi and K. Fukuzumi, *J. Am. Chem. Soc.*, **96**, 1893 (1974).
(11) T. Nishiguchi, K. Tachi, and K. Fukuzumi, *J. Org. Chem.*, **40**, 237, 240 (1975).
(12) H. Imai, T. Nishiguchi, and K. Fukuzumi, *J. Org. Chem.*, **39**, 1622 (1974); H. Imai, T. Nishiguchi, M. Kobayashi, and K. Fukuzumi, *Bull. Chem. Soc. Jpn.*, **48**, 1585 (1975).
(13) J. Trocha-Grimshaw and H. B. Henbest, *Chem. Commun.*, 544 (1967); Y. Sasson and J. Blum, *Tetrahedron Lett.*, 2167 (1971); J. Blum, Y. Sasson, and S. Iflah, *ibid.*, 1015 (1972); H. B. Henbest and J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans. 1*, 601 (1974).
(14) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1959, p 181.
(15) P. R. Hitch, S. K. Gondal, and C. T. Sears, *Chem. Commun.*, 777 (1971).
(16) J. Chatt and B. L. Shaw, *Chem. Ind. (London)*, 931 (1960); 290 (1961); J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962); H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
(17) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 2947 (1970).
(18) P. S. Hallman, B. R. MacGarvey, and G. Wilkinson, *J. Chem. Soc. A*, 3143 (1968).
(19) T. A. Stephenson and G. Wilkinson, *J. Chem. Soc. A*, 2660 (1968).
(20) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
(21) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 96 (1970).
(22) H. B. Charman, *J. Chem. Soc. B*, 548 (1970); 629 (1967); J. Chatt and B. L. Shaw, *J. Chem. Soc. A*, 1437 (1966).
(23) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958); *J. Inorg. Nucl. Chem.*, **8**, 137 (1958).
(24) M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 693 (1962); J. Chatt and B. L. Shaw, *ibid.*, 285 (1961).
(25) J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1622 (1939).
(26) K. A. Jensen, *Z. Anorg. Allg. Chem.*, **229**, 225 (1936).

Free-Radical and Hydrogen Bromide Inhibition in the Dark Reaction of Bromine with the 1,2-Dimethylcyclopropanes

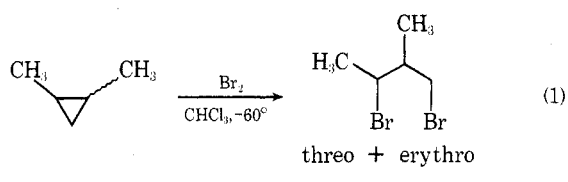
Joseph B. Lambert*[1a] and Keiji Kobayashi[1b]

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received September 15, 1975

All detectable dibromide products and most of the tribromide products have been identified in the reaction of *cis*- and *trans*-1,2-dimethylcyclopropane with bromine in chloroform. The uncatalyzed reaction is close to 50% complete after 3 h at 0°. The addition of ferric bromide accelerates the reaction slightly but perturbs the product distribution to only a small extent, the main result being an increase in the proportion of the homovicinal dibromides (6) at the expense of some of the vicinal dibromides. Free-radical inhibition by either molecular oxygen or isoamyl nitrite has a similar effect on the product distribution. Suppression of the HBr in solution by the addition of NBS also enhances the proportion of the homovicinal dibromides. Some of the vicinal dibromides must therefore come from an addition–elimination–addition pathway, and the homovicinal dibromides 6 are indicated to be the primary electrophilic products. Nonstereospecific production of the homovicinal dibromides 6 in the identical ratio of 4:1 from both isomers is consistent with open carbonium ion intermediates.

Skell and co-workers[2] have recently found that a significant part of the products from the dark reaction of bromine with alkyl-substituted cyclopropanes results from attack by HBr rather than Br_2 on the ring. Opening of the ring by protonation, followed by loss of a proton, gives an alkene, which yields a vicinal dibromide on addition of Br_2. These authors found that this pathway may be suppressed by carrying out the reaction in the presence of *N*-bromosuccinimide.[2] We had previously reported that the major products from the uncatalyzed bromination of *cis*- and *trans*-1,2-dimethylcyclopropane included *threo*- and *erythro*-1,3-dibromo-2-methylbutane (eq 1).[3] The absence of stereospecificity in the formation of these materials was interpreted in terms of open carbonium ion intermediates.[3] The reaction was carried out at low temperatures in the dark in order to minimize free-radical reactions. The conclusions reported previously would be unfounded if the products resulted either from a free-radical or an HBr-mediated pathway. The present paper is a report of the results of electrophilic catalysis (added ferric bromide), free-radical inhibition (molecular oxygen and isoamyl nitrite), and HBr inhibition (NBS) on the reaction of Br_2 with the dimethylcyclopropanes, in order to provide firm evidence for the electrophilic nature of the reaction and to determine which products arise from direct addition of Br_2 and which from the addition of Br_2 to alkenes that arose from initial attack of HBr. Absolute yields have been measured. We have been able to identify several more minor dibromide products, and the structures of two of the previously reported[3] minor dibromides are corrected. We have tentatively determined the structures of the major tribromide products. With the knowledge of the structures of essentially all dibromide and tribromide products and with the assurance that the reaction is indeed electrophilic in nature, we are able to construct a reasonable material balance of carbonium-ion pathways. The results of these experiments confirm the original conclusions regarding the mechanism of the addition of Br_2 to cyclopropanes.[3]

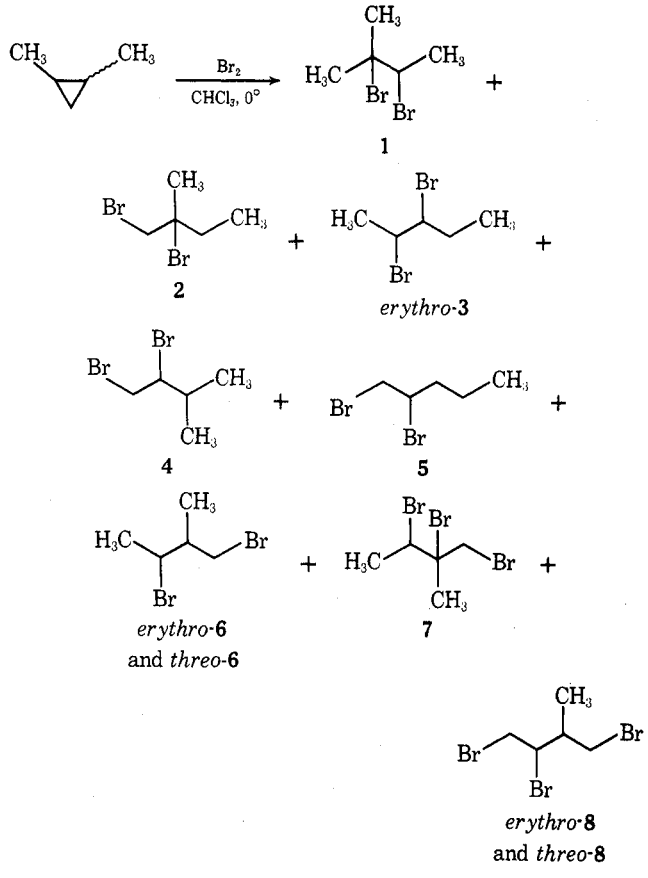


threo + erythro (1)

Results

The addition of bromine to *cis*- and *trans*-1,2-dimethylcyclopropane in chloroform was carried out at progressively higher temperatures beginning at −60°, always in the dark. The effect of temperature on the dibromide product distribution was found to be very small. Each dibromide product was collected by preparative gas chromatography and identified by comparison of its spectral and chromatographic properties with those of authentic materials. The tribromides were collected by gas chromatography and identified

Scheme I



by their spectroscopic properties. The structure proof of 8 is still considered tentative. The product identities are given in Scheme I (in order of increasing VPC retention time) and the product distributions in Table I. The extent of conversion was measured by direct examination of the NMR spectrum of the crude product mixture. The integral of the high-field cyclopropylmethylene resonances in the starting material was easily compared to that of the remainder of the spectrum. Conversion after 3 h reached about 50% at 0°. Two of the minor components were previously reported to be *meso*- and *dl*-2,4-dibromopentane,[3] by comparison of retention times only. Isolation of these components proved that the materials in fact were *erythro*-2,3-dibromopentane (*erythro*-**3**, coincident with the *dl* retention time) and 1,2-dibromopentane (**5**, coincident with the meso retention time). The retention time of *threo*-2,3-dibromopentane (*threo*-**3**) coincided with that of another product, 1,2-dibromo-3-methylbutane (**4**). Examination of the NMR spectrum of collected **4** revealed small resonances attributable to *threo*-**3**. The latter material therefore most likely comprises an additional, but very minor, product. The tribromide products were not observed in the original study,[3] since they do not survive Carbowax. The materials, however, were clearly evident on silicone columns. The reactions were all carried out at least three times with good reproducibility.

To promote the opening of the cyclopropane ring, ferric bromide was added to the reaction mixture as an electrophilic catalyst. To inhibit free-radical reactions, molecular oxygen and isoamyl nitrite were added in separate reactions. To decrease side reactions caused by the presence of HBr, the reaction was also carried out with added NBS.[2] The results of these studies are given in Table II for the trans isomer.[4]

Discussion

The question of the stereochemistry of the reaction has been dealt with in the previous paper.[3] The observation that both cyclopropanes give the same erythro/threo ratio of about 4/1 (the actual stereoisomers were not individually identified) indicates that the reaction must pass through the same open carbonium ion in both cases. The homobromonium ion would have led to opposite stereochemical results for the two isomers. These conclusions are further confirmed by the near constancy of the erythro/threo ratio when the reaction is carried out in the presence of the various additives (Table II).

The question of the polar or radical nature of the intermediates can be answered by examination of the effect on product distribution of added electrophilic catalysts and free-radical inhibitors. Ferric bromide accelerates the reaction slightly, but has little effect on the product distribution, the main result being an increase in the homovicinal dibromides (**6**) at the expense of certain vicinal dibromides (**3–5**). Introduction of molecular oxygen or isoamyl nitrite produces a similar result, but to a somewhat greater extent. The total amount of **6** (both isomers) increases from 50% without any additives to 63% in the presence of $FeBr_3$, and to 78% with oxygen. Thus 1,3-dibromo-2-methylbutane (**6**) in its two forms is clearly the predominant product of the

Table I
Normalized Product Distribution from the Bromination of Dimethylcyclopropane[a]

Isomer	1	2	*erythro*-3	4[b]	5	*erythro*-6[c]	*threo*-6	7	*erythro*-8[c]	*threo*-8	Other tribromides	Total convn
Trans	5	5	1	22	4	7	28	6	12	8	2	47
Cis	7	22	2	8	3	4	16	19	10	6	3	49

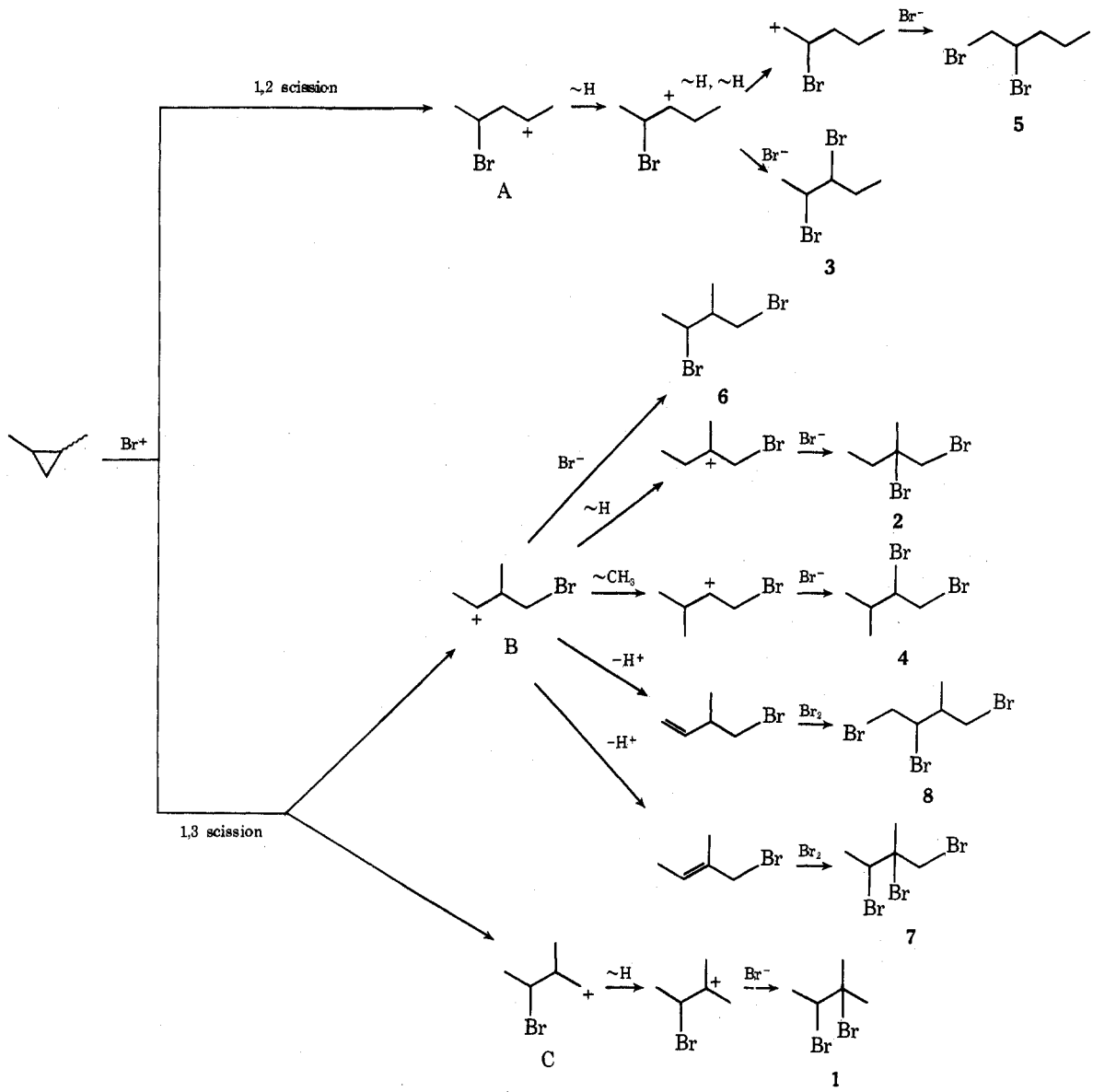
[a] At 0° for 3 h in $CHCl_3$; yields in percent. [b] Also includes a small amount of *threo*-3. [c] Isomers separated but not identified.

Table II
Normalized Yields of Dibromides from the Trans Isomer with Various Added Reagents[a]

Added reagent	1	2	*erythro*-3	4	5	*erythro*-6	*threo*-6
None	7	7	1	30	5	10	40
$FeBr_3$	7	10	–	17	3	16	47
NBS	4	8	1	20	3	13	51
O_2	–	6	–	9	7	21	57
i-AmONO	–	8	–	16	11	13	52

[a] At 0° for 3 h in $CHCl_3$; yields in percent.

Scheme II



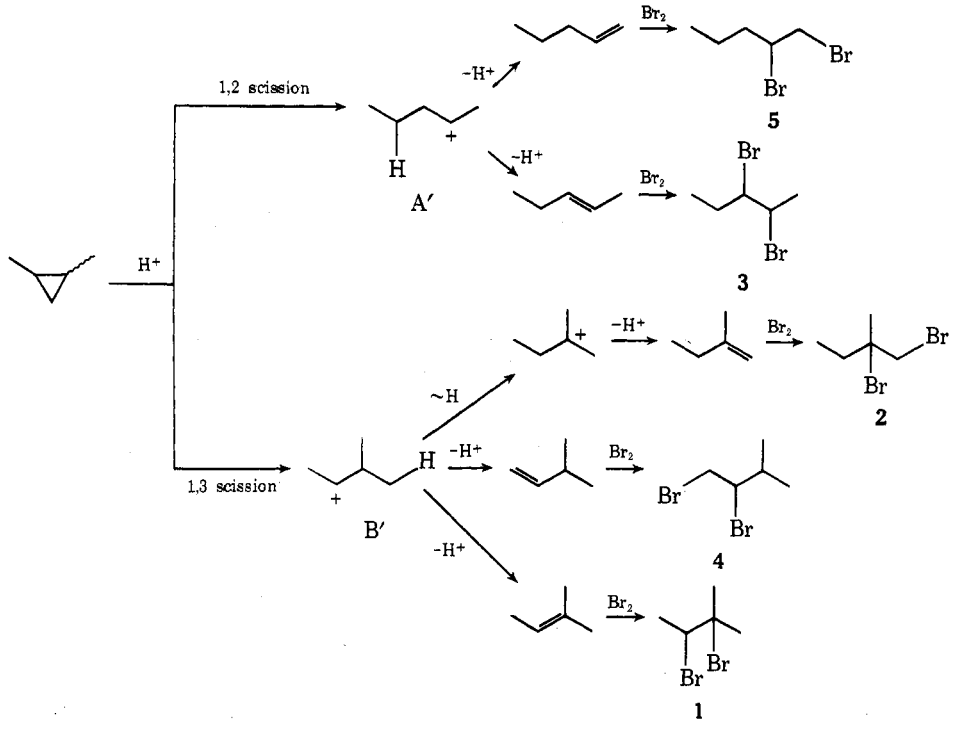
electrophilic pathway, so that the original stereochemical conclusions are indeed valid for the polar reaction. Scheme II depicts possible pathways for the production of all the observed materials, utilizing only open carbonium ions. The scheme is intended to be entirely illustrative, since it leaves out many important details, such as the collapse of α-bromocarbonium ions to three-membered bromonium ions. The tribromides are presumed to come from the addition of bromine to alkenes formed by loss of a proton from the initial bromocarbonium ion.[2]

As Skell et al. have pointed out,[2] there are several drawbacks to a scheme of this sort, e.g., the use of primary carbonium ions and methyl shifts. Thus, it is entirely unreasonable to expect that **5** could emanate from the indicated path in Scheme II. Although ion A is likely to undergo a hydride shift, the resulting cation probably collapses to a bromonium ion and ultimately gives **3**, rather than undergoing further hydride shifts to the primary carbonium ion that gives **5**. Likewise, **4** must come from ion B via a methyl shift, and **1** must result from ring opening to the primary carbonium ion C. Thus, although there are reasonable paths to **2**, **3**, and **6**, Scheme II is unlikely for **4** and not at all plausible for the production of **1** or **5**.

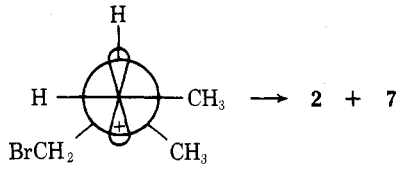
When alkenes are formed from the initial intermediates of Scheme II, a molecule of HBr is produced at the same time. As has been noted by Skell,[2] the HBr can protonate the starting cyclopropane to give a bromine-free carbonium ion. Attack of bromide on such an intermediate would produce a monobromide. A small amount (10% without NBS, a trace with NBS) has been found by Skell.[2b] The bromine-free carbonium ion, however, can also lose a proton to form an alkene, to which a molecule of Br_2 can add (Scheme III). The resulting dibromides have the same structures as those obtained from the direct pathway. Added *N*-bromosuccinimide reacts with any HBr formed and suppresses this pathway. The result of this experiment (Table II) is a decrease in the amounts of **1**, **4**, and **5**. These in fact are the products that must result from unfavorable pathways involving primary carbonium ions or methyl shifts in Scheme II. It is therefore likely that most, if not all, of these materials are formed via the HBr pathway of Scheme III, rather than from the direct Br_2 pathway. Our level of NBS was not sufficient to effect total suppression.

Because the amounts of **2** and **6** (and possibly **3**) increase or remain the same in the presence of NBS, we conclude that these materials are the result of initial ring opening by Br_2 rather than by HBr. Because there is still a very large amount of **4** remaining in the presence of NBS, some of this

Scheme III



material may indeed be formed from the methyl-shift pathway. The original attribution of the larger proportion of **2** in the reaction of the cis isomer than in that of the trans isomer to a steric effect on the hydride-shift process remains valid,[3] since **2** is a direct product. The conformation of the carbonium ion that leads to the hydride shift (**9**)



9

is obtained much more facilely from the cis than from the trans isomer.[3] It is interesting that this same ion can lead to the alkene that gives the tribromide **7**, which is also found in considerably larger amounts in the cis reaction mixture (Table I). The increased amounts of **2** and **7** bring about decreased amounts of the homovicinal dibromides **6** in the reaction of the cis isomer, since all three materials derive from the same initial carbonium ion, B (Scheme II).

In summary, the only products that are not suppressed by free-radical or HBr inhibitors are the homovicinal dibromides **6**, the vicinal dibromides **2** and **3**, and possibly some of **4**. These then are taken to be the primary products of the electrophilic addition reaction of Br_2. The identical erythro/threo ratio found for **6** in both the cis and the trans reaction mixtures substantiates the intermediacy of open carbonium ions.[3] The relative amounts of direct addition products (**6**) and rearrangement products (**2**) are controlled by conformational factors.[3] This result can be extended to the relative amounts of tribromide products (**7** vs. **8**). The presence of **3** and **5** indicates that there is possibly 5% of 1,2 scission, although the great predominance of the reaction mixture comes from 1,3 scission. No homovicinal dibromides are formed from 1,2 scission.

Experimental Section

Brominations. To a solution of 0.13 g (1.9 mmol) of 1,2-dimethylcyclopropane (Chemical Samples Co.) in 3 ml of $CHCl_3$, cooled to 0° in a dark room, was added a solution of 0.42 g (2.6 mmol) of Br_2 in 2 ml of $CHCl_3$. The reaction mixture was stirred for 3 h at 0° with the flask wrapped in aluminum foil. The reaction was stopped by the addition of dilute $Na_2S_2O_3$ solution. The organic layer was dried over $MgSO_4$, filtered, brought up to 10 ml in a volumetric flask, and analyzed by VPC on 11% Carbowax 20M on Chromosorb P (12 ft × 0.125 in.) at 110° with a flow rate of 40 ml/min. For the addition of molecular oxygen, the gas was bubbled into the solution by way of an inlet tube for 3 h at 0°. For the other additives, 0.102 g of NBS, 0.158 g of Fe, and the equivalent of 5% of isoamyl nitrite (based on Br_2) were used. For spectral and chromatographic comparisons, the vicinal dibromides **1–5** were prepared by the addition of bromine to the appropriate alkene. The homovicinal dibromides **6** were prepared as before.[3] Collection of all the dibromides was carried out on 10% Carbowax 20M on Chromosorb P 60–80 (12 ft × 0.25 in.) at 140° with a flow rate of 60 ml/min. Since tribromides were not observed under these conditions, they were collected using 4.8% Apiezon L on Chromosorb G 60–70 (6 ft × 0.25 in.) at 125° with a flow rate of 240 ml/min: NMR of **7** (CCl_4) δ 1.90 (d, 3 H), 1.97 (s, 3 H), 3.93 (s, 2 H), 4.54 (q, 1 H); NMR of **8** (first isomer) (CCl_4) δ 1.09 (d, 3 H), 2.49 (broad septet, 1 H), 3.39 (d, 2 H), 3.6–3.9 (m, 2 H), 4.65 (m, 1 H); NMR of **8** (second isomer) (CCl_4) δ 1.24 (d, 3 H), 2.53 (septet, 1 H), 3.48 (d, 2 H), 3.75–4.0 (m, 2 H), 4.27 (d of t, 1 H).

Acknowledgments. We are indebted to Professor P. S. Skell, The Pennsylvania State University, for valuable suggestions during the progress of this work.

Registry No.—**7**, 57513-16-3; *threo*-**8**, 57513-17-4; *erythro*-**8**, 57513-18-5; *cis*-1,2-dimethylcyclopropane, 930-18-7; *trans*-1,2-dimethylcyclopropane, 2402-06-4; Br_2, 7726-95-6; NBS, 128-08-5; O_2, 7782-44-7; *i*-AmONO, 110-46-3; $FeBr_3$, 10031-26-2.

References and Notes

(1) (a) This work was supported by the Chevron Research Co., by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant MPS72-05006). (b) Petroleum Research Fund Postdoctoral Fellow, 1973–1974, on leave of absence from the University of Tokyo.
(2) (a) J. C. Day, K. J. Shea, and P. S. Skell, *J. Am. Chem. Soc.*, **95**, 5089 (1974); (b) P.S. Skell, J. C. Day, and K. J. Shea, *Ibid.*, in press.
(3) J. B. Lambert and B. A. Iwanetz, *J. Org. Chem.*, **37**, 4082 (1972). We use the term "homovicinal" to describe these dibromides, since the carbon atoms bearing bromine are separated by one carbon atom.
(4) Parallel experiments were carried out on the previously studied[5] bromination of bicyclo[3.1.0]hexane. The main products of this reaction are 1,2-dibromocyclohexane and *cis*- and *trans*-1,3-dibromocyclohexane. The total conversion at 0° ranged from 20% (uncatalyzed) to 37%

(NBS). Conversion at −60° (uncatalyzed) was 10%. The effect of O_2, $FeBr_3$, i-AmONO, and NBS again was to depress the relative amount of the vicinal dibromide and to enhance the amount of the homovicinal dibromides slightly. The cis/trans ratio for the 1,3-dibromide remained constant at 2:3 under all conditions. We conclude that the reaction mechanism is not altered by free-radical or HBr inhibition or by electrophilic catalysis. The original conclusion that the reaction passes through open carbonium ions is not altered.[5]

(5) J. B. Lambert, R. D. H. Black, J. H. Shaw, and J. J. Papay, *J. Org. Chem.*, **35**, 3214 (1970).

Reaction of Tris(hydroxymethyl)phosphine with Substituted Ureas[1]

Armand B. Pepperman, Jr.,* Donald J. Daigle, and Sidney L. Vail

Southern Regional Research Center,[2a] New Orleans, Louisiana 70179

Received August 18, 1975

The reaction of tris(hydroxymethyl)phosphine with monosubstituted and unsymmetrically disubstituted ureas has been shown to produce tris(4-substituted ureidomethyl)phosphine oxides. The products were characterized by ir spectra, NMR spectra, and elemental analyses. The NMR spectrum for tris(4-phenylureidomethyl)phosphine oxide showed a triplet for the NH attached to the phosphorus methylene, appearing at a higher field than the NH attached to the phenyl ring, which demonstrated that the reactive nitrogen of the urea was the unsubstituted nitrogen. Reactions of several monosubstituted ureas with tris(hydroxymethyl)phosphine oxide failed to give any of the tris(4-substituted ureidomethyl)phosphine oxides, indicating that oxidation of phosphorus occurred after formation of the P–C–N bond.

Hydroxymethylphosphorus compounds condense readily with amines, amides, ureas, and other nitrogen-containing compounds to yield linear and branched polymers which are useful in flame-retarding cotton cellulose.[3-6] Monomeric products have been obtained when secondary amines were allowed to react with hydroxymethylphosphonium salts or tris(hydroxymethyl)phosphine.[7-10] Our general interest in flame retardants and hydroxyalkylphosphorus chemistry, coupled with recent interest in reactions of phosphorus compounds with ureas in the presence of aldehydes,[11-13] has prompted us to report on the reactions of tris(hydroxymethyl)phosphine with partially substituted ureas.

Results and Discussion

Monomeric products have been obtained from the reaction of tris(hydroxymethyl)phosphine (THP) with several monosubstituted ureas according to eq 1.

$$R_1NR_2CONH_2 + (HOCH_2)_3P \longrightarrow (R_1NR_2CONHCH_2)_3P{=}O \quad (1)$$
$$R_1 = CH_3, CH_3CH_2, CH_3(CH_2)_{11}, (CH_3)_3C, C_6H_5;$$
$$R_2 = H, R_1 = R_2 = C_6H_5$$

Only the phosphine oxides were isolated as oxidation of the phosphorus occurred at some stage of reaction or work-up. A similar reaction occurred when 1,1-diphenylurea was combined with THP. Yields of crude product varied widely and are summarized in Table I (see Experimental Section). No products were isolated from the reactions of THP with acetylurea, benzoylurea, 1,3-dibenzylurea, and 1,1-dimethylurea; rather, 75, 100, 45, and 75% of the starting ureas, respectively, were recovered. If the concentration of the reactants (THP plus substituted urea) was too low in the refluxing ethanol, then the starting urea was recovered in the dodecylurea (88%) and 1,1-diphenylurea (95%) examples. In both examples, concentrations of 16–20% of reactants were necessary before any product could be isolated. A similar dependence on concentration was noted in the *tert*-butylurea reaction, where, with only 4% of reactants, a dark yellow, intractable oil resulted, whereas raising the reactants concentration to 17% caused product to precipitate after refluxing for 16 h. However, even at the higher concentration, several other substituted ureas produced intractable oils from which no solid material could be recovered; among these were 1,3-dimethylurea, 1,3-diethylurea, allylthiourea, and *N*-methylethyleneurea.

The purified products were characterized by ir spectroscopy, NMR spectroscopy, and elemental analysis. The bonding in tris(4-phenylureidomethyl)phosphine oxide (**5**) was readily deduced from its NMR spectrum (Figure 1), which shows a triplet at 6.56 ppm which is assigned to the CH_2NH and integrates for three protons. The singlet at 8.81 ppm is assigned to the C_6H_5NH proton because of the deshielding effect of the phenyl group and integrates for three protons. The triplet for the higher field signal shows that the NH group bonded to the phosphorus methylene is the unsubstituted nitrogen, rather than the phenyl-substituted nitrogen. Such bonding obviously must exist in tris(4,4-diphenylureidomethyl)phosphine oxide (**6**), since one of the nitrogens is fully substituted. Based on steric considerations, one would expect tris(4-dodecylureidomethyl)phosphine oxide (**3**) and tris(4-*tert*-butylureidomethyl)phosphine oxide (**4**) to show similar bonding, since both *tert*-butyl and dodecyl are larger than phenyl. However, the steric bulk of methyl and ethyl is such that one cannot rule out the possibility of reaction occurring at either nitrogen. In fact, it may well occur at both nitrogens, but the products isolated indicate the presence of only one isomer. Clear-cut evidence for which nitrogen is involved in bonding to the methylene was not possible for all samples because the NMR spectra were obtained in D_2O, but bonding similar to **5** would be expected.

The reaction of THP with secondary amines yields the tris(aminomethyl)phosphines,[7-10] but the reactions of THP with substituted ureas yields the tris(ureidomethyl)phosphine oxides. Monitoring of the THP–urea reactions by NMR indicated that some oxidation of THP was occurring, because the doublet due to the methylene protons of THP (D_2O, δ 4.1, J = 5 Hz) was overlapped by another doublet (D_2O, δ 4.2, J = 3 Hz) which we believed resulted from tris(hydroxymethyl)phosphine oxide (THPO). The use of ^{31}P NMR also indicated the presence of THPO; thus the reaction pathway might consist of oxidation of THP to THPO and subsequent reaction of THPO with the urea to form the tris(ureidomethyl)phosphine oxide. This mechanism would involve loss of formaldehyde from THPO by a