1,2- and 1,4-Dibromides from Cyclopentadiene

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The addition of bromine to cyclopentadiene has been examined because of an interest in the cyclopentadiene dibromides as allylic isomers. In the present work, the following isomeric dibromides have been obtained: (i) dibromide A, m.p. 45°, cis-3,5-dibromocyclopentene, previously thought to be the trans isomer; (ii) dibromide B, in impure form, b.p. 53–54° (2 mm.), trans-3,5-dibromocyclopentene, previously thought to be the cis isomer; (iii) a new dibromide C, m.p. 15°, trans-3,4-dibromocyclopentene. The cis-1,4-addition product is an important direct product of bromine addition to cyclopentadiene. The dibromides have been converted to glycols, and the structure and configuration of these have been elucidated. Further, dibromide C has been converted to trans-3,4-bis-dimethylaminocyclopentene. Also, the three dibromides have been shown to display comparable reactivities in solvolysis and in elimination induced by sodium iodide. The confusion in the assignment of configuration to the dibromoglutaric and dihydroxyglutaric acids is cleared up by the present work. Further, the implications of the present findings for the interpretation of the mechanisms of addition of bromine to cyclopentadiene and substitution reactions of the derived dibromides are discussed.

Historical

The bromination of cyclopentadiene in petroleum ether was originally studied by Kraemer and Spilker,[2] who isolated a dibromide A melting at 40°, which they assumed without proof to be a 3,4-dibromocyclopentene (III).

In Thiele's careful study,[3] cyclopentadiene was brominated in chloroform solution, and the reaction mixture was repeatedly fractionally distilled. In this way he obtained two main fractions, b.p. 53–

(1) UCLA Research Associate, 1950–1952.
(2) G. Kraemer and A. Spilker, Ber., 29, 552 (1896).
(3) J. Thiele, Ann., 314, 300 (1900).

54° (2 mm.) and 72–75° (2 mm.). The higher-boiling fraction crystallized on standing to the dibromide A, m.p. 45°. Thiele gave the trans-3,5 structure I to this dibromide and assigned the cis-3,5-configuration II to the major constituent (B) of the lower-boiling fraction. The evidence for these assignments involved permanganate oxidation of each of the dibromides to a crystalline dibromocyclopentanediol. These were cleaved by chromic acid to isomeric dibromoglutaric acids. Treatment of each of the dibromoglutaric acids with zinc and acetic acid gave glutaric, not glutaconic, acid. Thiele stated that the acid, m.p. 142°, was the dl-isomer and that the acid, m.p. 170°, was meso. If this were true, the crystalline dibromide A must have been trans-3,5-dibromocyclopentane (I) and the liquid must have contained the cis-3,5-isomer II. Thiele, however, offered no experimental evidence pertaining to the stereochemistry of the dibromoglutaric acids.

Apparently in the belief that Thiele had established the configuration of the dibromoglutaric acids by relating them to known dibromocyclopentenes, Ingold[4] accepted the dl-configuration for the 142° acid. Ingold observed that this acid was hydrolyzed by 2 N sodium carbonate solution to a dihydroxyglutaric acid which melted with loss of water at 120–130°, resolidified as the lactone, and melted at 170°. On the reasonable assumption that conversion of dibromoglutaric acid to dihydroxyglutaric acid would involve an even number (0 or 2) of Walden inversions, the dl-designation was given to the dihydroxyglutaric acid. Actually, this acid had been assigned the meso configuration in the work of Kiliani and Mathes[5] and of Nef,[6] but Ingold contended that the earlier workers were mistaken.

Similarly, Ingold found that the dibromoglutaric acid, m.p. 170°, gave rise to a dihydroxyglutaric acid, m.p. 162°, to which he assigned the meso configuration. This acid has been encountered only as a dextrorotatory form, α 3.9°, m.p. 125°,[5] and as a levorotatory form, $\alpha^{20}D$ −2.614°, m.p. 135°,[6] the dl-form being unknown. The configurational relationships so far discussed are summarized in Table I.

From the foregoing considerations, either Thiele's assignment of configurations to the dibromocyclo-
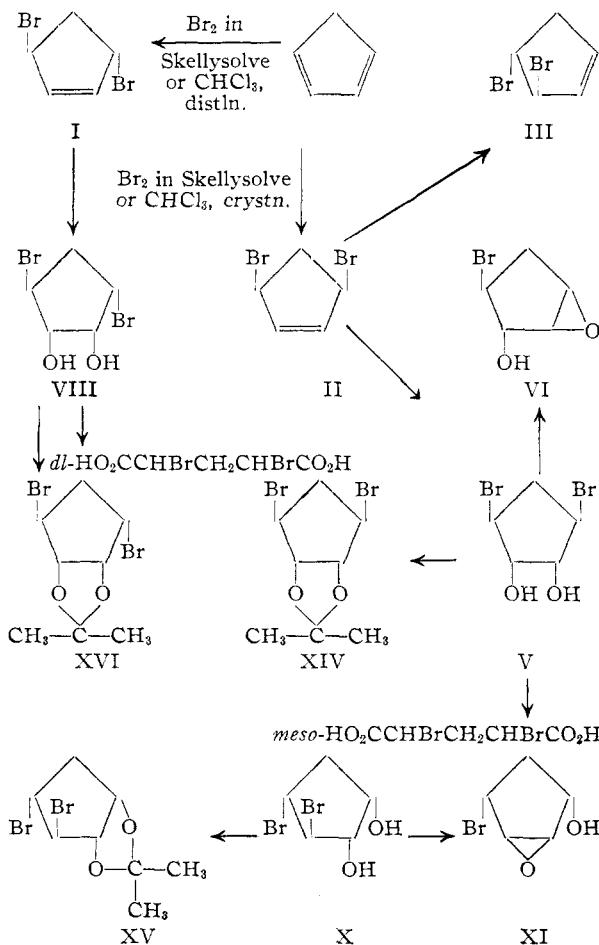
(4) C. K. Ingold, J. Chem. Soc., 119, 312 (1921).
(5) H. Kiliani and O. Mathes, Ber., 40, 1238 (1907).
(6) J. U. Nef, Ann., 376, 22, 49 (1910).

TABLE I

RELATIONSHIPS AMONG THE CYCLOPENTADIENE DIBROMIDES AND DERIVED MATERIALS

Dibromide	A	B	C
M.p., °C.	45		15
B.p.	72–75°	53–54°	56°
	(2 mm.)	(2 mm.)	(2 mm.)
Structure	3,5	3,5	3,4
Configuration { Thiele[3]	trans	cis	
{ Present	cis	trans	trans
Dibromoglycol, m.p., °C.	75.5[a,c,d,e]	76–77[a,i,j]	87[f,g,h]
Configuration	V	VIII	
Dibromoglutaric acid, m.p., °C.	142	170	
Configuration { Thiele[3]	dl	meso	
{ Present	meso	dl	
Dihydroxyglutaric acid, m.p., °C.	170[b]	162	
Configuration { Ingold[4]	dl	meso	
{ Kiliani[5] and	meso	dl	
{ present			

[a] Mixed m.p. depressed. [b] M.p. of the lactone after loss of water and resolidification. [c] M.p. of di-p-nitrobenzoate, 159°. [d] M.p. of acetonide, 27.2°. [e] M.p. of derived mono-epoxide, m.p. 53.5°. [f] M.p. of di-p-nitrobenzoate, 165–165.5°. [g] M.p. of acetonide, 48–50°. [h] M.p. of derived mono-epoxide, 64.0–65.4°. [i] M.p. of di-p-nitrobenzoate, 145–147°. [j] M.p. of acetonide, 72.5–73.5°.

pentenes is incorrect, or else an odd number of Walden inversions occurs during the hydrolysis of the dibromoglutaric acids. Subsequent workers[7–13] have overlooked this contradiction and have accepted Thiele's assignments.

As regards other isomers, Farmer and Scott,[7] in the belief that isomerization upon distillation of an initially formed 3,4-dibromide (III) led to the mixture of isomers encountered by Thiele, endeavored unsuccessfully to isolate a 3,4-dibromocyclopentene. They isolated glutaconic acid from successive permanganate and chromic acid oxidation of dibromocyclopentene mixtures, followed by debromination. The 3,4-dibromide was therefore indicated as one component of the mixtures.

With respect to isomerization, Blomquist and Mayes[8] discovered that slow distillation of the crystalline dibromide A converted it to a liquid, b.p. 54–55° (2 mm.), which they assumed consisted mainly of dibromide B.

Because cyclopentadiene dibromides were of interest as allylic systems, the addition of bromine to cyclopentadiene and the nature and behavior of the derived dibromides were studied recently in these laboratories. The results of this study are presented and discussed in the present manuscript.

Results and Configurations

Dibromocyclopentenes.—The crystalline dibromide A was obtained conveniently by the bromination of cyclopentadiene in petroleum ether b.p. 28–38° at −30 to −40°. Bromination of cyclopentadiene in chloroform at −35°, in contrast to petroleum ether, formed no semi-crystalline precipitate. However, after the chloroform had been

(7) E. H. Farmer and W. D. Scott, *J. Chem. Soc.*, 172 (1929).
(8) A. T. Blomquist and W. G. Mayes, *J. Org. Chem.*, **10**, 134 (1954).
(9) A. C. Cope, L. L. Estes, Jr., J. R. Emery and A. C. Haven, Jr., THIS JOURNAL, **73**, 1199 (1951).
(10) E. B. Reid and J. F. Yost, *ibid.*, **72**, 1807 (1950).
(11) G. W. Barber and J. English, Jr., *ibid.*, **73**, 746 (1951).
(12) L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4035 (1952).
(13) R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *ibid.*, 1803 (1953).

pumped off, the oily residue could be crystallized from petroleum ether b.p. 30–60° to give a 34% yield of A, m.p. 45°.[14] The dipole moment of dibromide A was found to be 3.40 D in dioxane solution.[15] Since the calculated value for trans-3,5-dibromocyclopentene (I) is less than 1 D, it becomes clear that dibromide A is actually cis-3,5-dibromocyclopentene (II). The new assignment of configuration is in accord with the general rule that the isomer with the higher boiling point should have the higher dipole moment.

Distillation of crystalline cis-3,5-dibromocyclopentene, A, through a helix-filled column at 2 mm. pressure, according to the instructions of Blomquist and Mayes[8] proceeded smoothly to give a liquid dibromide, b.p. 56° (2 mm.). Crystallization of the product from petroleum ether b.p. 30–60° at low temperature gave a 25% yield of a crystalline dibromocyclopentene, C, m.p. 15°. Permanganate oxidation of this dibromide gave a 68% yield of a new crystalline dibromocyclopentanediol, m.p. 87°. The dipole moment of C in dioxane was 1.37 D,[15] very close to that of trans-1,2-dibromocyclopentane, 1.51 D. C is therefore trans-3,4-dibromocyclopentene (III).

Thiele[3] and Farmer and Scott,[7] have been the only workers to offer evidence, based on oxidation studies, that the liquid, b.p. 54° (2 mm.), which they prepared actually contained dibromide B. In endeavoring to repeat their procedure, we found it impossible to fractionate the bromination mixtures through a helix-filled column, because the latter decomposed much too quickly. The dibromide mixtures could, however, be distilled through a Vigreux head at 2 mm. pressure. In several experiments permanganate oxidation of each fraction separately showed that the first fraction consisted mainly of trans-3,4-dibromocyclopentene, C, while the later fractions gave increasing yields of a dibromocyclopentanediol, m.p. 75°. The melting point of this diol, and that of its di-p-nitrobenzoate, agreed with those reported by Thiele[3] for the derivatives obtained from dibromide B. Therefore, trans-3,5-dibromocyclopentene was increasingly predominant in the late fractions of these distillations.

In later experiments, however, the final fraction consisted of almost pure trans-3,4-dibromocyclopentene, and the above experiments leading to trans-3,5-dibromocyclopentene as the final fraction were not uniformly reproducible. In one even more erratic experiment, crystalline cis-3,5-dibromocyclopentene, m.p. 45°, was isolated from the final distillation fraction. The reason for this irreproducibility may be the presence in varying amounts of hydrogen bromide, tar (carbon) and possibly peroxides. In almost all cases, however, the dibromocyclopentanediol, m.p. 75°, derived from trans-3,5-dibromocyclopentene, could be obtained by the oxidation of intermediate fractions, even though attempts to crystallize the dibromocyclopentene fractions themselves were of no avail.

(14) Blomquist and Mayes[8] had claimed that use of chloroform as solvent led to the predominant formation of isomer B. However, they distilled the reaction mixture, undoubtedly causing isomerization of the initially formed isomer A.
(15) W. D. Kumler, A. C. Huitric and H. K. Hall, Jr., THIS JOURNAL, **78**, 4345 (1956).

Dibromocyclopentanediols.—It was anticipated that the hydroxyl groups in each of the three dibromocyclopentanediols would be *cis* to each other. This was verified by the formation of a cyclic acetonide from each diol.

Bartlett[16] showed that the reaction of *trans*-chlorohydrins with alkali gave epoxides quantitatively at room temperature, while *cis*-chlorohydrins formed ketones on heating. Each of the three diols under study consumed one equivalent of alkali to form an epoxide, two of which were isolated. 2,4-Dinitrophenylhydrazine gave no precipitate with the titrated solutions, demonstrating the absence of ketonic products.

These facts shed no further light on the structures of the parent dibromocyclopentenes, but exclude structures IV and IX for the diols derived from *cis*-3,5-dibromocyclopentene (II) and *trans*-3,4-dibromocyclopentene (III), respectively. Instead,

Br Br Br
OH HO OH
Br OH
IV IX
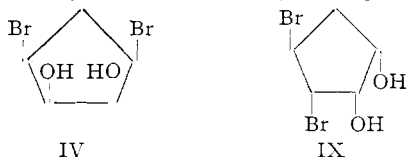
the facts support structures V and X for these diols and VIII for the diol from dibromide I.[17] It may be noted that, wherever there is a choice, permanganate hydroxylation places two hydroxyl groups on the less hindered side of the ring.

That the bromine atoms are vicinal in the dibromocyclopentanediol X, m.p. 87°, was confirmed by its smooth debromination by zinc in ethanol to give *cis*-3,4-cyclopentenediol (XII) in 47.1% yield. This proved identical with an authentic sample of this glycol, which was synthesized by the method of Criegee.[18]

Kinetic Studies.—The rates of elimination and solvolysis reactions of the dibromocyclopentenes were measured. Potassium iodide in methanol was not a suitable reagent for the dibromocyclopentenes because methanolysis competed with elimination. Sodium iodide in absolute ethyl acetate was found to give conveniently measurable rates. The results are summarized in Table II. Solvolysis in 80% ethanol at 25° proceeded at a convenient rate, the results being summarized in Table III.

Discussion

Bromination of Cyclopentadiene.—Summarizing our experience in the preparation of isomeric cyclopentadiene dibromides, the solid 3,5-dibromide A is obtainable without difficulty; the 3,4-dibromide C, the product of 1,2-addition which Farmer and Scott[7] could not isolate and which has to our knowledge not been reported previously, can be prepared by distillation of isomer A. The 3,5-dibromide B has been obtained only in impure form by distillation of crude bromination mixtures; however, its presence must be confirmed in each sample by oxidation with permanganate.

(16) P. D. Bartlett, THIS JOURNAL, **57**, 224 (1935).

(17) A corroborating detail is that the formation of the acetonide from diol VIII, which is unique in possessing a bromine *cis* to hydroxyl, requires more vigorous conditions than for the other diols.

(18) (a) R. Criegee, *Ann.*, **481**, 263 (1930); (b) R. Criegee and H. Beucker, *ibid.*, **541**, 224 (1939).

TABLE II

RATES OF REACTION OF DIBROMOCYCLOPENTENES WITH SODIUM IODIDE IN ETHYL ACETATE AT 25.00°

| Dibromo-cyclo-pentene	(NaI), $10^2 M$	(RBr$_2$), $10^3 M$	(NaI)/(RBr$_2$)	$10^3 k_2$, l. mole^{-1} sec.$^{-1}$
cis-3,5-	5.78	10.0	5.78	8.88
cis-3,5-	5.78	9.67	5.98	9.58
cis-3,5-	5.78	6.87	8.42	10.4
cis-3,5-	5.93	4.98	11.9	12.0
trans-3,4-	5.78	9.27	6.24	7.38

TABLE III

INITIAL RATES OF SOLVOLYSIS OF DIBROMOCYCLOPENTENES IN 80% AQUEOUS ETHANOL AT 25.00°

Compound	Concn., $10^3 M$	$10^6 k_1$, sec.$^{-1}$
cis-3,5-Dibromocyclopentene	12.9	3.78
cis-3,5-Dibromocyclopentene	8.95	3.85
trans-3,4-Dibromocyclopentene	9.07	1.15
trans-3,5-Dibromocyclopentene (impure)		3.13

In the present work, we observed no consistent support for the statement of Blomquist and Mayes[8] that rapid addition of bromine to cyclopentadiene in chloroform favors formation of dibromide B while slow addition in petroleum ether favors A. A similar report has been made by Farmer and Scott[7] that the change from hexane to chloroform reduces the content of 1,2- and increases the content of 1,4-addition product, at the same time reducing the content of solid 1,4-addition product. In our hands, comparable amounts of crystalline dibromide A were isolated from either petroleum ether or chloroform. Because of the greater solubility of dibromide A in chloroform, it does not precipitate from chloroform, as it does from petroleum ether.

The present work does not disclose the exact composition of the cyclopentadiene dibromide mixtures from kinetic control of the addition reactions. However, it is clear from the experimental results that the solid 3,5-dibromide A is an important direct product in both petroleum ether and chloroform. The fact that dibromide A is the *cis*-1,4-addition product is of interest in connection with possible mechanisms of addition. Without any information on the kinetics of the addition reaction leading to this dibromide, it is not possible to decide the order of the reaction with respect to bromine. However, the types of permissible mechanisms may be illustrated as though the order of the reaction with respect to bromine were unity. On this basis, *cis*-dibromide A can be conceived to arise either from: (i) a mechanism involving a bromo-carbonium bromide ion pair and collapse of this to dibromide A or (ii) a concerted 1,4-addition of a bromine molecule to yield dibromide A directly.[19]

Br Br⊖ Br
H H
Br (ii) ⟵ (i) ⟶ ⊕
Br₂ Br₂
H
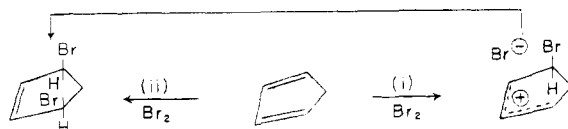
With acyclic 1,3-dienes, 1,4-addition may conceivably lead to either a *cis* or *trans* arrangement about the newly created central double bond. It is

(19) H. Eyring, A. Sherman and G. Kimball, *J. Chem. Phys.*, **1**, 586 (1933).

worthwhile for clarity to notice what stereochemical results are expected from the above mechanisms (i) and (ii). While mechanism (ii) would be expected to lead to cis-1,4-product, mechanism (i) could lead either to trans- or cis-1,4-product, depending on the rotational position about the 2,3-single bond in the reacting diene. The absence of cis-1,4-product from addition of bromine[20] and chlorine[21] to 1,3-butadiene can be taken as evidence, not strong, however, against mechanism (ii) for cyclopentadiene.

It is now clear that the configurations of dibromides A and B are the reverse of those which have been traditionally accepted. Therefore, the configurations of the dibromoglutaric acids employed by Thiele[3] and Ingold[4] must be reversed.[21a] Contrary to the latter, the configurations assigned to the dihydroxyglutaric acids by Kiliani and Mathes[5] and by Nef[6] are therefore correct. These configurational relationships are summarized in Table I.

Reactions of the Dibromocyclopentenes.—There are serious implications of the present findings for the interpretation of substitution reactions reported in the literature, starting with either solid or liquid cyclopentadiene dibromides. In the case of the solid dibromide A, we have merely to consider the effect of the reversal of configuration on the interpretation. In the case of the liquid dibromide, the situation is less clear. Although it is clear from the work of Thiele[3] and Farmer and Scott[7] that careful fractionation is necessary to isolate a sample of dibromide oxidizable to diol VIII, later workers have accepted any dibromide fraction boiling near 55° (2 mm.) as dibromide B. Since trans-3,4-dibromocyclopentene, C, boils at about this temperature, the liquid fractions used by most investigators were almost certainly mixtures of B and C. This renders some of the results of earlier workers difficult to interpret.

On the basis of the present results, the configurations of the two 1,3-cyclopentanediols reported by Owen and Smith in a valuable recent article[12] should be reversed. These investigators prepared the glycols by treatment of the dibromides A and B with tetraethylammonium acetate in acetone, conditions favorable to SN2 substitution, and subsequent saponification and hydrogenation. The diol, m.p. 40°, should be labeled cis and the isomer, m.p. 30–32°, should be labeled trans. The identity of the di-p-toluenesulfonate prepared from dibromide A and silver toluenesulfonate still requires proof.

Cope and co-workers[9] showed that the reaction of both the crystalline dibromide A and a liquid di-

bromide, b.p. 55° (2 mm.), with dimethylamine in benzene led to the exclusive formation of trans-3,4-bis-dimethylaminocyclopentene. In the present work, we have found that trans-3,4-dibromocyclopentene, C, gives an identical yield of the same final product. These results still leave an uncertainty regarding the exact behavior of dibromide B in this reaction. The situation is somewhat similar in the case of reaction of the cyclopentadiene dibromides with sodiomalonic ester to yield ethyl bicyclo[3.1.0]hex-2-ene-6,6-dicarboxylate.[13] A liquid dibromide gave the bicyclic product in only approximately half the yield obtained from the solid dibromide A, but it is not clear whether the low yield is to be associated with the presence of dibromide B or C.

For the reactions of 3,5-dibromocyclopentene with dimethylamine or sodiomalonic ester, respectively, Cope and co-workers[9] and Linstead and co-workers[13] suggested mechanisms based on successive SN2 and internal SN2' displacement.[22] With dibromide A, now known to be cis, such a mechanism requires the displacing group for the internal SN2' process to attack trans to the leaving bromine anion. While there is evidence that cis displacement[23] by a secondary amine in SN2' is preferred when a choice exists, it is not clear how strong is the argument against the trans internal SN2' displacements required above. However, other mechanisms are conceivable, especially for the reaction of the dibromide with dimethylamine. An example is SN2 followed by SN2'. For the reaction of dibromide C with dimethylamine, several mechanisms seem possible, such as: (i) SN2', SN2'; (ii) SN2', internal SN2', immonium ion opening; (iii) SN2, SN2.

Reactivities.—The few measurements of solvolytic reactivities of the three cyclopentadiene dibromides A, B and C showed these isomers were of comparable reactivity. As is clear from Table III, the cis- and trans-3,5-dibromides are quite similar in rate of solvolysis and ca. 3 times as reactive as the trans-3,4-dibromide in 80% ethanol. The level of reactivity of these materials is about what would be anticipated for an allylic cyclopentenyl bromide with a second halogen atom resisting[24] ionization of the first one.

In elimination of bromine by sodium iodide in ethyl acetate, the cis-3,5-dibromocyclopentene is very reactive, as is clear from Table II. The trans-3,4-dibromocyclopentene is not quite as reactive. The opposite order of reactivity was reported by Farmer, Laurence and Thorpe[25] for the butadiene dibromides. The 1,2-dibromide was observed to liberate iodine from potassium iodide in acetic acid faster than the 1,4-dibromide. Whether the present results have any bearing on the question of the relative rates of 1,2[26] and 1,4-conjugative[27] E2

(20) (a) J. Thiele, Ann., **308**, 334 (1899); (b) C. Prevost, Ann. chim., [10] **10**, 113, 356 (1928); (c) A. Valette, ibid., [12], **3**, 644 (1948); (d) K. Mislow, THIS JOURNAL, **75**, 2512 (1953).

(21) K. Mislow and H. M. Hellman, ibid., **73**, 244 (1951).

(21a) ADDED IN PROOF.—Since the completion of this manuscript, it has come to our attention that Schotte has presented evidence confirming our reassignment of configuration to the dibromoglutaric acids [L. Schotte, Acta Chem. Scand., **8**, 130 (1954)]. He found that the reaction of sodium disulfide with the dibromoglutaric acid, m.p. 169–170°, led to 1,2-bithiolane-3,5-dicarboxylic acid. This was shown to be the dl-isomer by resolution into the dextro- and levorotatory forms with brucine. Arguments similar to those we have applied above to the reaction of the dibromoacids with hydroxyl ion indicate that the starting acid, m.p. 169–170°, is the dl-isomer. Infrared evidence supporting this conclusion has also been given by Schotte [Arkiv för Kemi, **9**, 423 (1956)].

(22) (a) R. E. Kepner, S. Winstein and W. G. Young, THIS JOURNAL, **71**, 115 (1949); (b) W. G. Young, I. D. Webb and H. L. Goering, ibid., **73**, 1076 (1951).

(23) G. Stork and W. N. White, ibid., **75**, 4119 (1953).

(24) S. Winstein and E. Grunwald, ibid., **70**, 828 (1948).

(25) E. H. Farmer, C. D. Laurence and J. F. Thorpe, J. Chem. Soc., 729 (1928).

(26) S. Winstein, D. Pressman and W. G. Young, THIS JOURNAL, **61**, 1645 (1939).

(27) S. J. Cristol, W. Barasch and C. H. Treman, ibid., **77**, 583 (1955).

elimination of bromine from the cyclopentadiene dibromides is not clear without more indication whether substitution[28] of bromide by iodide precedes elimination.[29]

Experimental Part

Preparation of cis-3,5-Dibromocyclopentene in Petroleum Ether.—To a solution of 116.2 g. (1.76 moles) of freshly distilled cyclopentadiene in 88 ml. of purified petroleum ether, b.p. 35–60° maintained at −25 to −35°, was added over 20 minutes with stirring a solution of 282 g. (1.76 moles) of bromine in 200 ml. of petroleum ether b.p. 35–60°. A semi-crystalline white precipitate appeared as the addition proceeded. The last bit of bromine solution was not added if a permanent orange color had already appeared. Pyridine, 12 ml., was added with stirring and the mixture was brought to 0°. A solution of 12 ml. of acetic acid and 15 g. of calcium chloride in 90 ml. of water was added with stirring. Two liquid phases resulted. The organic layer was separated and chilled overnight in Dry Ice. The solid white mass was quickly transferred to a previously chilled Buchner funnel, a rubber dam applied and the aspirator vacuum turned on. After most of the oily material had passed through but before discoloration of the remaining solid material commenced, the slightly oily white solid, 133.9 g., was recrystallized once from petroleum ether b.p. 60–70°. This yielded 77.7 g. (19.5%) of cis-3,5-dibromocyclopentene,[30] m.p. 45°.

Preparation of cis-3,5-Dibromocyclopentene in Chloroform.—A solution of 73.5 g. (1.11 moles) of cyclopentadiene in 56 ml. of chloroform was brominated in 10 minutes with stirring at −35° with a solution of 170 g. (1.06 moles) of bromine in 110 ml. of chloroform. No precipitate was observed. Pyridine, 10 ml., was added and the solution was brought to 0°. It was shaken with a solution of 5 ml. of acetic acid and 5 g. of sodium chloride in 50 ml. of water, separated, and dried over potassium carbonate. Most of the chloroform was removed by submitting the solution to the aspirator vacuum while keeping the flask in an ice–water-bath, and the remainder was removed by pumping down to 3 mm. The wine-colored residue was left in Dry Ice to crystallize. It was drained on a funnel as above to give 72.6 g. of oily white crystals. The filtrate, 237 g., was diluted with 175 ml. of petroleum ether b.p. 35–60° and brought to boiling. The clear supernatant liquid was decanted from a black oil and allowed to crystallize in Dry Ice. From this was obtained 34.9 g. of solid material. Recrystallization of the combined solids from petroleum ether b.p. 35–60° gave 85.0 g. (34.3%) of crystalline cis-3,5-dibromocyclopentene, m.p. 45°, mixed m.p. with the product obtained above, 45°.

Preparation of Glycol V.—Three liters of 95% ethanol was chilled to −30°. To this was added 60.0 g. (0.266 mole) of cis-3,5-dibromocyclopentene, m.p. 45°, dissolved in 100 ml. of chloroform at −50°. A solution of 64.0 g. of potassium permanganate and 128 g. of magnesium sulfate heptahydrate in 1280 ml. of water was added rapidly with vigorous stirring, keeping the temperature below −30°. The mixture was stirred for an additional 30 minutes and was allowed then to warm to 0°. Sulfur dioxide was passed in until the solution was colorless and the ethanol was removed by means of the aspirator vacuum, keeping the temperature of the solution below 30°. The remaining liquid, 1300 ml., was extracted continuously with ether for 24 hr. The extract was dried with sodium sulfate, the ether was removed and the slightly oily crystalline material was crystallized once from methylene chloride–petroleum ether b.p. 30–60°. There was obtained 47.2 g. (68.4%) of white crystals of V, m.p. 75° (reported[3] m.p. 75.5°). Several attempts to prepare a di-p-nitrobenzoate by the procedure

of Shriner and Fuson[31] failed. However, when 2,6-lutidine was used in place of pyridine, a good yield was obtained. It melted at 158.9° after one crystallization from absolute ethanol (reported[3] m.p. 158–159°).

Preparation of Acetonide XIV.—A solution of 9.00 g. (0.0346 mole) of glycol V, m.p. 75°, in 150 ml. of dry acetone was shaken with 5.00 g. of dry copper sulfate for 60 hr. at room temperature. The copper sulfate was filtered and washed with 20 ml. of acetone. The acetone was removed from the combined filtrates and 30 ml. of water and 30 ml. of methylene chloride were added. After vigorous shaking the organic layer was separated. The water layer was extracted once with 30 ml. of methylene chloride and discarded. The combined organic layers were dried over magnesium sulfate and the solvents were removed. The residue was crystallized from petroleum ether b.p. 30–60° to give 8.70 g. (83.8%) of nicely crystalline material, m.p. 27.2°.

Anal. Calcd. for $C_8H_{12}O_2Br$: C, 32.02; H, 4.03. Found: C, 31.77; H, 4.14.

Chromic Acid Oxidation of Glycol V.—This oxidation, according to the directions of Thiele,[3] gave in 45% yield, after crystallization from toluene, the meso-α,α'-dibromoglutaric acid, m.p. 139° (reported[13] m.p. 142°).

Preparation of Epoxide VI.—A solution was prepared from 6.50 g. (0.025 mole) of glycol V and 1.00 g. (0.025 mole) of sodium hydroxide in 35 ml. of water. After continuous extraction with ether for 1 hr., the extract was dried with sodium sulfate, evaporated and distilled from a small Claisen flask with a wide sidearm. This gave 3.32 g. (74.2%) of material, b.p. 108° (3 mm.). The analytical sample, after two recrystallizations from chloroform–petroleum ether b.p. 30–60° melted at 53.2–53.7°.

Anal. Calcd. for $C_5H_7O_2Br$: C, 33.54; H, 3.94. Found: C, 33.58; H, 3.92.

This compound failed to give a precipitate with 2,4-dinitrophenylhydrazine solution[31b] on standing for 3 days at 0°. A p-nitrobenzoate[31a] melted at 120.5–121.5°.

Anal. Calcd. for $C_{12}H_{10}O_5BrN$: C, 43.92; H, 3.07. Found: C, 44.20; H, 3.03.

Preparation of trans-3,4-Dibromocyclopentene.—cis-3,5-Dibromocyclopentene, 88.6 g. (0.392 mole), and a few crystals of 1,3,5-trinitrobenzene were charged to a 1.5 × 90 cm. column packed with glass helices. The condenser was chilled by ice–water and the receiver was kept in Dry Ice–acetone. A liquid nitrogen trap was placed in the vacuum line to condense the considerable amount of hydrogen bromide which was evolved. The charge was distilled at 2 mm. pressure over a 5 hr. period, the pot temperature rising from 104–110°, while the head temperature remained in the range 50–58°. The distillate, 51.6 g., crystallized nicely in the chilled receiver and the last material to distil crystallized even in the condenser. To the distillate was added 20 ml. of petroleum ether b.p. 30–60° and the mixture was crystallized in Dry Ice, transferred to a chilled Buchner funnel and allowed to drain in the deep freeze[32] (4°). There remained on the filter 26.0 g. of crystalline dibromide III, m.p. 8–9°. One recrystallization from petroleum ether b.p. 30–60° gave 22.4 g. (25.3%) of trans-3,4-dibromocyclopentene, m.p. 12–13°, $n^{25}D$ 1.5737. An analytical sample, prepared by several recrystallizations from petroleum ether b.p. 30–60° melted at 15°.

Anal. Calcd. for $C_5H_6Br_2$: C, 26.52; H, 2.67. Found: C, 26.40; H, 2.61.

Preparation of Dibromocyclopentanediol X.—Permanganate oxidation, exactly as described for the cis-3,5-isomer, of 39.0 g. of freshly recrystallized trans-3,4-dibromocyclopentene, m.p. 12–13°, gave a first crop of white crystals, 27.0 g., m.p. 84.2–84.8°, and a second crop, 3.7 g., m.p. 81–83°, combined yield of glycol X 68.5%. An analytical sample melted at 86–87°.

Anal. Calcd. for $C_5H_8O_2Br_2$: C, 23.06; H, 3.10. Found: C, 22.96; H, 3.28.

A di-p-nitrobenzoate, prepared as above using 2,6-

(28) (a) J. Hine and W. H. Brader, Jr., THIS JOURNAL, **77**, 361 (1955); (b) W. M. Schubert, B. S. Rabinovitch, N. R. Larson and V. A. Sims, ibid., **74**, 4590 (1952).

(29) With trans-1,4-dibromo-2-butene, sodium iodide in ethyl acetate yields sodium bromide and a colorless solution of organic iodide. The latter subsequently yields butadiene and iodine. Potassium iodide in acetone, on the other hand, gives iodine immediately [H. K. Hall, Jr., unpublished work].

(30) This compound was quite unstable even when carefully purified and could not be stored in the ice-box overnight without discoloration. It could be kept for several months, however, packed in Dry Ice.

(31) (a) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 137; (b) p. 143.

(32) In later work the technique of Miller and Noyes [THIS JOURNAL, **73**, 2376 (1951)] was used and found to be very convenient.

lutidine, melted at 165–165.5° after one recrystallization from absolute alcohol.

Anal. Calcd. for $C_{19}H_{14}O_8N_2Br_2$: C, 40.88; H, 2.53. Found: C, 40.50; H, 2.64.

Oxidation of Diol X.—Oxidation with chromic acid gave only sirupy materials which could not be crystallized. Attempts to purify these by regeneration from the sodium salt were unsuccessful. Periodic acid cleaved the glycol to a dialdehyde, isolated as its crude 2,4-dinitrophenylhydrazone, in 90% yield. This derivative decomposed on attempted purification. Neither nitric acid nor 30% hydrogen peroxide gave a crystalline product from the dialdehyde, while the action of nitric acid on the diol X itself gave no isolable products.

Preparation of Acetonide XV.—The acetonide XV was prepared from 3.70 g. (0.0142 mole) of glycol X, m.p. 84–85°, 3.5 g. of dry copper sulfate and 30 ml. of dry acetone by shaking at room temperature for 18 hr. Working up as described above gave 0.20 g. of unreacted diol and 2.86 g. of crude acetonide. This was sublimed at 2 mm. pressure and crystallized twice from petroleum ether b.p. 30–60° to give 2.13 g. (50.0%) of white crystals, m.p. 48.0–49.7°.

Anal. Calcd. for $C_8H_{12}O_2Br_2$: C, 32.02; H, 4.03. Found: C, 32.15; H, 4.10.

Debromination of Diol X.—A solution of 7.31 g. (0.028 mole) of diol X in 35 ml. of ethanol was added over 10 minutes with stirring to a refluxing mixture of 10.0 g. of freshly activated zinc powder and 25 ml. of ethanol. After five minutes additional stirring, 15 ml. of saturated sodium carbonate solution was added. The mixture was cooled and the zinc was filtered, washed twice with 10-ml. portions of ethanol and discarded. Alcohol and water were removed by means of the aspirator vacuum, and the sirupy residue was taken up in 20 ml. of chloroform. After drying with sodium sulfate, the chloroform was removed and the residue was distilled from a small Claisen flask to give 1.38 g. (47.1%) of colorless *cis*-3,4-cyclopentenediol, b.p. 84° (2 mm.), $n^{25}D$ 1.4958. A di-*p*-nitrobenzoate melted at 114.6–115.0°.

Anal. Calcd. for $C_{19}H_{14}O_8N_2$: C, 57.29; H, 3.54. Found: C, 57.26; H, 3.62.

A monophenylurethan melted at 123.0–123.4°. *Anal.* Calcd. for $C_{12}H_{13}O_3N$: C, 65.74; H, 5.98. Found: C, 65.41; H, 6.16.

Synthesis of *cis*-3,4-Cyclopentenediol.—Acetic anhydride, 20 ml., was added to 700 ml. of benzene which had been distilled from lead tetraacetate. The solution was heated to 70°, and 683 g. (1.54 moles) of freshly crystallized lead tetraacetate was introduced. Then a solution of 60 g. (0.91 mole) of freshly distilled cyclopentadiene and 3 ml. of acetic anhydride in 75 ml. of purified benzene was added over 1.5 hr. at 70°. The reaction mixture was cooled, and the precipitated salts were filtered, washed with 100 ml. of benzene, and discarded. The combined benzene extracts were washed with two 200-ml. portions of water and then with two 500-ml. portions of 5% sodium carbonate solution, during which carbon dioxide was evolved. The organic layer was dried over magnesium sulfate, and the benzene was distilled through a Vigreux head. After removal of the remaining benzene by use of the aspirator vacuum, the heavy oil, 157 g., was dissolved cautiously, with chilling in ice, in a solution of 100 g. (1.75 moles) of potassium hydroxide in 75 ml. of water. Enough water was then added to the dark mixture to dissolve the precipitated salts, and the solution was extracted continuously for 3 days with methylene chloride. The methylene chloride extract was dried, evaporated and the residue was distilled from a small Claisen flask with a wide sidearm. There was obtained 28.3 g. (31.1%) of glycol, b.p. 70–80° (1.5 mm.), $n^{25}D$ 1.4938.

Preparation of the Acetonide XIII of *cis*-3,4-Cyclopentenediol.—The above glycol, 5.00 g. (0.050 mole), was shaken for 36 hr. with 100 ml. of dry acetone and 5.00 g. of dry copper sulfate at room temperature. The copper sulfate was filtered and washed, and most of the acetone was distilled through a small column. To the residue was added 10 ml. of water and 15 ml. of methylene chloride. After thorough shaking, the water layer was separated, extracted twice more with 15-ml. portions of methylene chloride and discarded. The combined organic layers were dried with magnesium sulfate and the solvent was removed through a small column. The residue, on distillation from a small Claisen flask, gave 5.12 g. (0.0365 mole) of *cis*-3,4-cyclo-

pentenediol acetonide, b.p. 148°, $n^{25}D$ 1.4453. This compound absorbed oxygen readily from the air, as shown by the liberation of iodine from potassium iodide solution, and gave unsatisfactory analyses.

Hydrolysis of *cis*-3,4-Cyclopentenediol Acetonide (XIII).—A mixture of 10.00 g. (0.0715 mole) of acetonide XIII, 17.7 g. of copper sulfate pentahydrate and 55 ml. of water was shaken at room temperature for 14 days. The unreacted acetonide was removed by adding petroleum ether b.p. 30–60° and separating the two layers. Distillation of the organic layer gave 2.56 g. of acetonide. Continuous extraction of the water layer with methylene chloride for 3 days, and working up as before, gave 1.22 g. of pure *cis*-3,4-cyclopentenediol, b. p. 82° (2 mm.), $n^{25}D$ 1.4957. A monophenylurethan melted at 120.8–122.0°, mixed m.p. with monophenylurethan of the debromination product, 119.5–120.5°. A di-*p*-nitrobenzoate melted at 114.0–115.5°, mixed m.p. with di-*p*-nitrobenzoate of the debromination product, 114.5–115.2°.

Preparation of Epoxide XI.—The reaction was carried out as before, using 6.5 g. (0.0084 mole) of glycol X and 1.0 g. of sodium hydroxide in 35 ml. of water. After 15 minutes, the mixture was extracted continuously with ether for 4 hr. The solution was dried over sodium sulfate and distilled to give 2.99 g. (66.8%) of epoxide XI, b.p. 136° (3 mm.), solidifying in the receiver to waxy hygroscopic white crystals. After two crystallizations from chloroform-petroleum ether b.p. 30–60° it melted at 64.0–65.4°.

Anal. Calcd. for $C_5H_7O_2Br$: C, 33.54; H, 3.94. Found: C, 33.60; H, 3.86.

A phenylurethan melted at 142.5–143.5°. *Anal.* Calcd. for $C_{12}H_{12}O_3NBr$: C, 48.34; H, 4.06. Found: C, 48.31; H, 4.18.

Preparation of Impure *trans*-3,5-Dibromocyclopentene.—A solution of 171.5 g. (2.57 moles) of cyclopentadiene in 130 ml. of pure chloroform was brominated over 20 minutes at −40° with 400 g. (2.50 moles) of bromine in 366 ml. of chloroform. After 1 hr. at −80°, the solution was treated with 8 ml. of pyridine, warmed to 0° and washed with a mixture of 100 ml. of water and 15 ml. of acetic acid. One-half of this solution was dried over calcium chloride and distilled through a Claisen head at aspirator pressure over 2.5 hr. Redistillation of the green liquid gave 270 g. of crude dibromocyclopentenes which were distilled through a Vigreux head at 1.5 mm. The receiver was chilled in Dry Ice-acetone, and a liquid nitrogen trap was used to condense hydrogen bromide. The dibromide fractions were drained as before in the deep freeze and oxidized with permanganate with the results shown in the right-hand column. The

Fr.	Head temp., °C.	Time, min.	Crude, wt., g.	Wt. after crystn. in Dry Ice, g.	Yield of cryst. glycol, g.	(formula) %
1	46	30	10.9	Non-cryst.		
2	47	80	25.1	17.1	2.20	11.2 (X)
3	48	120	22.6	7.6	0.75	8.6 (VIII)
4	48	225	33.3	20.0	2.26	9.8 (VIII)
5	31	345	15.0	11.0	3.80	30.0 (VIII)

dibromocyclopentanediol VIII melted at 74.8–76.8° (reported[3] m.p. 76–77°) and was noticeably more hygroscopic than V.

Anal. Calcd. for $C_5H_8Br_2O_2$: C, 23.06; H, 3.10. Found: C, 22.81; H, 3.20.

A di-*p*-nitrobenzoate, prepared using 2,6-lutidine, melted at 145.2–147° (reported[3] m.p. 142°). Each of the three dibromocyclopentanediols V, VIII and X depressed the melting point of the other two isomers, as did their di-*p*-nitrobenzoates.

The above experiment was repeated, keeping all conditions as nearly the same as possible. The last dibromocyclopentene fraction, crystallized from petroleum ether b.p. 30–60° in Dry Ice-acetone, gave 4.0 g. of crystalline material (0.38%). Oxidation with permanganate gave 2.25 g. (48.8%) of VIII, m.p. 75°, and 1.54 g. of sirupy material.

Repetitions of this experiment gave different results for the final fraction. A typical distillation was

Fraction	Head	Time, min.	Weight, g.
1	48°	165	32.5
2	51	235	21.5
3	49	425	17.0
4	30	650	5.8

Fraction 4 was almost pure *trans*-3,4-dibromocyclopentene, as shown by its melting point, after crystallization from petroleum ether fl.p. 30–60° and mixed melting point with authentic material. Nevertheless, fractions 2 and 3 were combined and oxidized with permanganate to give a 20.3% yield of crystalline VIII, m.p. 75°. Fraction 1 gave only sirupy material.

In still another attempt, 185 g. of charge, which had been stored for 2 weeks at −80°, gave the results

Frac-tion	Head	Time, min.	Wt., g.	Yield of crystalline dibromocyclo-pentanediol, %
1	50°	60	17.0	
2	53	125	30.3	8.5
3	57	200	11.5	14.2
4	34	375	5.1	10.6

This was the only run out of the many studied in which oxidation of the intermediate fractions gave the dibromo-cyclopentanediol X, m.p. 86–87°, from all fractions. The infrared spectrum of fraction 3 was also observed to be identical with that of dibromide III.

Preparation of the Acetonide XVI.—The conditions with which the other two acetonides were prepared led only to recovery of unchanged VIII. The dibromocyclopentanediol VIII, 2.50 g (0.0096 mole), was dissolved in a solution prepared by carefully adding 10 ml. of concentrated sulfuric acid dropwise to 10 ml. of ice-cold acetone. The mixture was swirled, poured into 200 ml. of water, and a crystalline precipitate appeared. Petroleum ether b.p. 30–60°, 25 ml., was added. The precipitate dissolved in the upper layer, which was separated, dried and evaporated. After one crystallization there was obtained 2.40 g. (83.3%) of crystalline XVI, m.p. 72.5–73.5°, melting 50–55° when mixed with starting material.

Anal. Calcd. for $C_8H_{12}O_2Br_2$: C, 32.02; H, 4.08. Found: C, 32.74; H, 4.25.

Titrations of the Dibromocyclopentanediols.—The diols, 0.3 g., were weighed into flasks and dissolved in 25 ml. of methanol. Standard 0.16 N sodium hydroxide, 10 cc., was pipetted in and the solution was allowed to stand for 5 or for 15 minutes, either time giving the same results for each isomer. Standard 0.14 N sulfuric acid, 5.1 ml., was pipetted in and the solution titrated with 0.04 N sodium hydroxide to a brom cresol purple end-point; the calculated equivalent weight is 260.

Dibromocyclo-pentanediol	Equiv. wt.	Equiv. wt. after 3 days over P_2O_5 under vacuum
V	260, 260	
VIII	276, 276	261
X	271, 271	271

The diol X seems to be more hygroscopic than the other two compounds. The reaction mixtures were tested after each titration with a freshly prepared solution of 2,4-dinitro-phenylhydrazine. In no case was a precipitate observed.

Reaction of *trans*-3,4-Dibromocyclopentene with Di-methylamine.—This reaction was carried out as described by Cope, *et al.*,[9] using 12.5 g. (0.0553 mole) of freshly crystal-lized dibromide, a solution of 35.8 g. of dimethylamine in 250 ml. of dry benzene and a reaction time of 2 days. This gave rise to 5.70 g. (67.2%) of *trans*-3,4-bis-dimethylamino-cyclopentene, b.p. 72° (8 mm.), n^{25}D 1.4679. A picrate melted at 182.0–184.0° (reported[9] m.p. 182.6–183.5°), and a mixed melting point with material prepared[9] from *cis*-3,5-dibromocyclopentene was not depressed.

Rate Measurements.—Solvents were prepared as follows: acetone and methanol were fractionated over Drier-ite through a 30-plate column, boiling points 56.1 and 64.2°, respectively. Ethyl acetate was fractionated through the same column from phosphorus pentoxide, b.p. 76.1°. Commercial absolute ethanol was dried with magnesium and distilled.

For the elimination rates the dibromide was weighed into a 50-ml. volumetric flask and made up to the mark with pure ethyl acetate. Sodium iodide, a weighed amount, was dissolved in ethyl acetate by shaking overnight, a saturated solution being about 0.06 M. The reaction was performed in a glass-stoppered flask, into which 40 cc. of freshly pre-pared dibromide solution and 120 cc. of iodide solution, both thermostated to 25.00°, were pipetted. Aliquots of 5 ml. were pipetted into a separatory funnel containing 5 ml. of of 0.02 N standard sodium thiosulfate solution and 35 ml. of pure petroleum ether b.p. 30–60°. The mixture was shaken and the aqueous layer was separated. The organic layer was shaken with 10 ml. of water. The combined water layers were titrated with 0.02 N iodine–potassium iodide solution, no indicator being used.

The results of the iodide reactions were handled by the equation of Dillon.[33] In all cases the second-order rate constant was steady within a run, but the values obtained for various runs did not agree well. Since a saturated solution of sodium iodide in ethyl acetate is only about 0.08 M and since the iodide concentration must be six or more times that of the dibromide in order to avoid perturbing effects caused by the tri-iodide ion, the concentration of the di-bromide could not be varied greatly to determine whether this effect was real. Other solvents tested included metha-nol, in which solvolysis was found to compete with elimina-tion, and acetone and dimethylformamide, in which the rates were much too fast to measure.

Solvolysis rates were determined by the method of Brown and Fletcher.[34] The initial instantaneous rate con-stants for solvolysis of the first bromine atom in 80% aqueous ethanol were obtained as follows: The titers for each point were divided by one-half the infinity titer to obtain values for the "fraction of the first bromine" to be solvolyzed. Values of log $1/(1 − x)$ were plotted *versus* time and extra-polated to zero time (the points plotted were those ob-tained from 3 to 15 minutes after mixing the reactants). The slope of the line was read with a tangent meter and the rate constant calculated.

Attempts to measure the kinetics of acetolysis of *cis*-3,5-dibromocyclopentene were unsuccessful because the dibro-mide decomposed in this solvent to give a dark colored prod-uct and the rate of formation of bromide ion was very er-ratic.

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(33) R. T. Dillon, This Journal, **54**, 952 (1932).

(34) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).