in butadiene and that step 2 is not rate determining. Based on the results shown in Table III, from mole ratios of 1:1 to 3:1 the reaction is dependent on the concentration of bromotrichloromethane. However, it is difficult to draw any conclusion about the dependence on bromotrichloromethane at higher mole ratios. For a great change in mole ratio from 3:1 to 46:1 only results in a 30% change in the absolute concentration of bromotrichloromethane.

Acknowledgment.—The writers wish to express their appreciation to Mr. Stanley E. Polchlopek for obtaining the infrared and Raman spectra, to Mr. John Koren and Mr. R. G. Schmitt for advice regarding the analyses in the near infrared, to Mr. John W. Zulsa for carrying out certain experiments in dosimetry, to Mr. N. B. Colthup for advice on the interpretation of the infrared spectra, and to Dr. L. A. Siegel for helpful discussions on dosimetry.

Addition Reactions Induced by Ionizing Radiation. II. Bromotrichloromethane to Isoprene and 2,3-Dimethylbutadiene

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For comparison with the previously reported[1] addition of bromotrichloromethane to butadiene induced by ionizing radiation, similar reactions involving isoprene and 2,3-dimethylbutadiene have been investigated. In the isoprene reaction using three moles of bromotrichloromethane to isoprene, the 1:1 adduct was shown to contain products resulting from 72% 1,4-addition, 26% 4,1-addition, and a small amount of 1,2- and 4,3-additions. In the 2,3-dimethylbutadiene reaction, in all mole ratios studied, the product obtained was exclusively the 1:1 adduct resulting from 1,4-addition. The kinetics of the reaction were investigated over the temperature range 25 to 40°; the dose rate ranged from $(1.4 \text{ to } 6.3) \times 10^3$ rads min.$^{-1}$; and the mole ratio of bromotrichloromethane:diene was varied from 1:2 to 19:1. It was observed that 2,3-dimethylbutadiene was the most reactive among the three dienes. The activation energies were 3.96 kcal. mole^{-1} for isoprene and 3.09 kcal. mole^{-1} for 2,3-dimethylbutadiene. The G values (molecules of diene consumed/100 e.v. absorbed) ranged from 450–1000 for isoprene and 1000–3650 for 2,3-dimethylbutadiene. The dose rate dependences were: for isoprene, rate $\propto$ dose rate$^{0.53}$; G $\propto$ dose rate$^{-0.48}$; for 2,3-dimethylbutadiene, rate $\propto$ dose rate$^{0.58}$; G $\propto$ dose rate$^{-0.42}$. In the cases of both isoprene and 2,3-dimethylbutadiene, the reactions are zero order in the diene over the entire range of mole ratios investigated.

The addition reaction of bromotrichloromethane to butadiene induced by ionizing radiation has been found to yield primarily the 1,4-*trans* adduct.[1] This investigation deals with the same type of reaction involving some substituted butadienes—2-methylbutadiene (isoprene) and 2,3-dimethylbutadiene. One of our purposes was to study the modes of addition of bromotrichloromethane to these dienes induced by ionizing radiation in the vicinity of room temperature. In the case of 2,3-dimethylbutadiene 1,2- and 1,4-additions similar to those described for the butadiene reaction[1] are possible, while in the case of isoprene all 1,2-, 1,4-, 4,1-, and 4,3-additions leading to various products are possible. Another purpose was that of comparing the reactions involving the unsubstituted and substituted butadienes from a kinetic point of view. It was hoped that these findings would help us to understand more clearly the mechanisms of the described reactions.

Experimental

Materials.—Research grade isoprene of Phillips Petroleum Co. was employed. Both 2,3-dimethylbutadiene and bromotrichloromethane were supplied by Eastman Kodak Co. and purified by fractionation shortly before use.

The radiation source, dosimetry, and other experimental procedures were similar to those described for the butadiene reaction.[1]

Gas-liquid chromatographic analyses were carried out using a Podbielniak Co. instrument, Model 9580. A 12-ft. column packed with 15% w./w. Hy-Vac silicone grease on 60/80-mesh Chromosorb-W solid support was used. The column temperature was 166°, and the helium gas pressure was 15 p.s.i.g.

N.m.r. spectra were obtained with a Varian V4300B high-resolution spectrometer at 40 Mc. in carbon tetrachloride solution with tetramethylsilane as an internal standard.

Identification of Products. Bromotrichloromethane–Isoprene Reaction.—Similarly to the bromotrichloromethane–butadiene reactions,[1] the bromotrichloromethane–isoprene reactions produced both the 1:1 adduct [$C_6H_8Cl_3Br$, b.p. 49.0–54.3° (0.025 mm.)] and the 1:2 adduct [$C_{11}H_{16}Cl_3Br$, b.p. 90° (0.075 mm.)].

Anal. (1:1 adduct). Calcd. for $C_6H_8Cl_3Br$: C, 27.05; H, 3.03; Cl, 31.81; Br, 23.89. Found: C, 27.58; H, 3.51. (1:2 adduct). Calcd. for $C_{11}H_{16}Cl_3Br$: C, 39.49; H, 4.82; Cl, 31.81; Br, 23.89. Found: C, 39.33; H, 4.70.

However, the 1:2 adduct was obtained only in cases where the initial concentration of isoprene was high (1:1 mole ratio) or when the mixture was exposed to radiation for a long time; it was also formed in smaller amounts in comparison with the corresponding butadiene reactions.[1]

The 1:1 adduct (I) formed in the addition reaction of bromotrichloromethane to isoprene (3:1 mole ratio) induced by X-rays (dose rate: 6×10^3 rads min.$^{-1}$) was shown by infrared and Raman spectroscopy to contain less than 5% terminal double bond resulting from either 1,2-addition or 4,3-addition. The vibrational spectra showed conclusively the presence of —CH_2Br and —CCl_3 groups as major components. In addition, the cleanness of the Raman spectrum indicated that the 1:1 adduct contained either a single compound or else a mixture of compounds whose structures were such as to yield identical spectra for the several components. However, these methods were unable to distinguish between *cis* and *trans* structures with regard to the locations of the H atom and —CH_3 group on the residual double bond. Also, the amounts of 1,4- and 4,1-addition products could not be ascertained. A gas-liquid chromatograph of I showed two minor peaks, 0.5 and 1.5%, before two major peaks, 26.1 and 71.9%. The n.m.r. spectrum of I showed a mixture of the 1,4- and 4,1-adduct with the component possessing a doublet at lower field being present in greater concentration. The compound Br—CH_2—CH=C(CH_3)—CH_2—CCl_3 would be the more abundant component if the H resonances on the methylene adjacent to the Br atom appear at a lower field than those on the methylene adjacent to the —CCl_3 group. A preliminary look at the models Br—CH_3 and Cl_3C—CH_3 showed that the difference was very slight and possibly in the reverse order. Another approach was

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[1] C. S. Hsia Chen and R. F. Stamm, *J. Org. Chem.*, **28**, 1580 (1963).

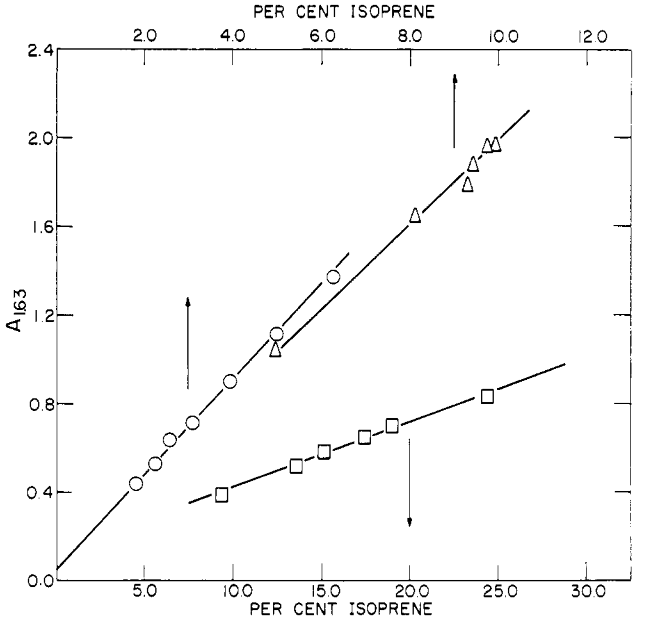

Fig. 1.—Standardization of isoprene solutions in bromotrichloromethane. ○: 10-mm. cell; geometrical slit = 0.12 mm.; $A_{1.63}$ = 0.2175 (% C_5H_8) + 0.04100. Δ: 10-mm. cell; copper screen, T = 0.1; slit = 1.2 mm.; $A_{1.63}$ = 0.1886 (% C_5H_8) + 0.066. □: 2-mm. cell; slit = 0.12 mm.; $A_{1.63}$ = 0.02927 (% C_5H_8) + 0.1322.

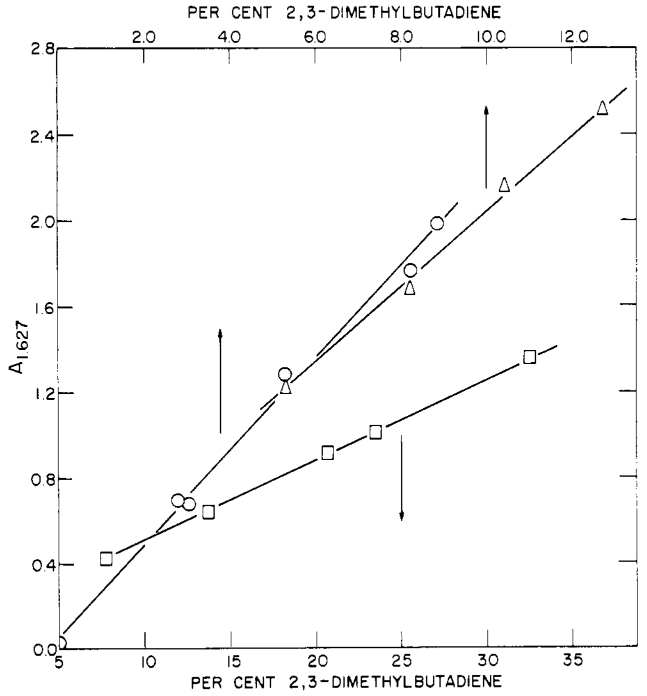

Fig. 2.—Standardization of 2,3-dimethylbutadiene solution in bromotrichloromethane. ○: 10-mm. cell; geometrical slit = 0.12 mm.; $A_{1.627}$ = 0.2162 (% C_6H_{10}) + 0.0542. Δ: 10-mm. cell; copper screen, T = 0.1; slit = 1.2 mm.; $A_{1.627}$ = 0.1776 (% C_6H_{10}) + 0.3013. □: 2-mm. cell; slit = 0.12 mm.; $A_{1.627}$ = 0.03785 (% C_6H_{10}) + 0.1400.

then taken. Work by Hatch, *et al.*,[2] has shown that by using lithium aluminum hydride, the bromide in a compound such as $BrCH_2—CH═CH—CH_3$ can be replaced by hydrogen in greater than 95% yield with the double bond remaining intact. Thus, the 1:1 adduct (I) was treated with lithium aluminum hydride under mild conditions favoring replacement of Br in preference to the less reactive Cl. An 86% (or higher) yield of the reduced product (II) was obtained. The results in gas-liquid chromatography showed that II was a mixture of three fractions in the relative amounts of A, 1.0%, B, 22.4%, and C, 76.6%. Fraction C, had a slightly unsymmetrical peak which could not be resolved. Approximately 20 μl. each of fractions B and C were trapped from the gas chromatograph by employing 20 or more passes. N.m.r. spectra of fractions B and C were examined. Fraction C gave a spectrum corresponding roughly to three parts $CH_3—CH═C(CH_3)—CH_2—CCl_3$, derived from $BrCH_2—CH═C(CH_3)—CH_2—CCl_3$, and one part $CH_3—C(CH_3)═CH—CH_2—CCl_3$. The spectrum of fraction B corresponded to $CH_3—CH═C(CH_3)—CH_2—CHCl_2$ derived from $CH_3—CH═C(CH_3)—CH_2—CCl_3$ also, where, aside from the Br atom, one Cl atom was also replaced by H. The gross identity of fraction B was verified by mass spectrometry. Therefore, over-all, II was composed of (76.6 × $^3/_4$) + 22.4 = 79.9% of the products derived from the 1,4-addition product and 20.1% from the 4,1-addition product. Since the yield from the lithium aluminum hydride reduction was 86%, and since II contained 80% of products which were derived from the 1,4-addition compound, therefore, in I the largest fraction, 71.9%, must be the 1,4-addition compound, and the lesser fraction, 26.1%, the 4,1-addition product. The remaining minor fractions totaling 2% could be the 1,2- and 4,3-addition compounds or other impurities.

Bromotrichloromethane–2,3-Dimethylbutadiene Reaction.—Unlike the butadiene and isoprene reactions, the addition of bromotrichloromethane to 2,3-dimethylbutadiene yielded only the 1:1 adduct even at 100% conversion. Infrared and Raman spectroscopy established that the 1:1 adduct has the 1,4-configuration, $Cl_3C—CH_2—C(CH_3)═C(CH_3)—CH_2Br$, a clear liquid, b.p. 74° (0.2 mm.).

Anal. Calcd. for $C_7H_{10}Cl_3Br$: C, 29.98; H, 3.59. Found: C, 30.28; H, 3.60

Results

Kinetics.—The results on the standardization of isoprene of different concentration ranges with regard to absorbance [log (I^0/I)] at 1.63 μ are represented in Fig. 1. Similarly, the results on the standardization of 2,3-dimethylbutadiene are represented in Fig. 2. In all these cases Beer's law is followed. In Fig. 3, the results on very concentrated solutions of 2,3-dimethylbutadiene in bromotrichloromethane are shown (30–50%). It is seen that Beer's law is no longer followed and that a curve is obtained. This curve was used graphically for determining the C_6H_{10} concentration in the reaction where the mole ratio was 1:2. (Mole ratio, unless specified otherwise, refers to bromotrichloromethanediene.)

Typical kinetic plots for X-ray induced bromotrichloromethane–isoprene and bromotrichloromethane–2,3-dimethylbutadiene reactions are shown in Fig. 4 and 5, respectively. In both figures all the plots are

TABLE I

DATA FOR ADDITION OF BROMOTRICHLOROMETHANE TO ISOPRENE

Mole ratio $BrCCl_3:C_5H_8$	Temperature, °C. ± 0.2	Dose rate[a] rads min.$^{-1}$	Rate × 10^3, moles kg.$^{-1}$ min.$^{-1}$	G values[b]
2.90:1	25	1454	1.46	969
2.99:1	25	3807	2.30	883
2.98:1	25	5896	3.10	507
3.04:1	32.5	5798	3.60	556
3.18:1	40	5650	4.88	833
1.03:1	25	5235	2.82	520
2.05:1	25	5699	2.70	456
6.19:1	25	6097	3.65	577
8.36:1	25	6154	3.75	564
17.95:1	25	6257	3.46	525

[a] Dose rate calculated from the composition of the system based on Fe^{+2}–Fe^{+3} dosimetry under the same conditions. Filtration, 1 mm. of aluminum + 1 mm. of copper. [b] Molecules of isoprene reacted per 100 e.v. absorbed.

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[2] L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Am. Chem. Soc.*, **81**, 5943 (1959).

Table II

Data for Addition of Bromotrichloromethane to 2,3-Dimethylbutadiene

Mole ratio $BrCCl_3:C_6H_{10}$	Temperature, °C. ± 0.2	Dose rate[a] rads min.$^{-1}$	Rate × 10^3, moles kg.$^{-1}$ min.$^{-1}$	G value[b]
2.93:1	25	1423	5.39	3653
3.20:1	25	3611	7.33	1957
2.99:1	25	5749	12.88	2160
2.91:1	32.5	5896	14.32	2381
2.93:1	40	5778	18.63	2737
1:2.06	25	4347	4.80	1065
0.99:1	25	5020	11.17	2146
4.25:1	25	5904	1[illegible].67	2074
6.08:1	25	6043	13.54	2161
10.63:1	25	6160	15.23	2384
11.06:1	25	6106	16.23	2559
11.22:1	25	6158	16.19	2537
18.72:1	25	6223	15.41	2388

[a] Dose rate calculated from the composition of the system based on Fe^{+2}–Fe^{+3} dosimetry under the same conditions. Filtration, 1 mm. of aluminum + 1 mm. of copper. [b] Molecules of 2,3-dimethylbutadiene reacted per 100 e.v. absorbed.

essentially linear. The kinetic data concerning various experimental conditions are recorded in Table I for isoprene and in Table II for 2,3-dimethylbutadiene. When employing a mole ratio of 3:1 for isoprene at 25°, it was found that the rate was proportional to the 0.53 power of the dose rate ($k \alpha I^{0.53}$), and the G value was inversely proportional to the 0.48 power of the dose rate ($G \alpha I^{-0.48}$). For 2,3-dimethylbutadiene, the rate was proportional to the 0.58 power of the dose rate ($k \alpha I^{0.58}$), while the G value was inversely proportional to the 0.42 power of the dose rate ($G \alpha I^{-0.42}$). Figure 6 represents the dependence of rates on the mole fractions of bromotrichloromethane at 25° for both isoprene and 2,3-dimethylbutadiene. It shows that maximum rates are in the neighborhood of 0.8–0.9 mole fraction of bromotrichloromethane. Figure 7 shows the Arrhenius plots involving temperatures of 25, 32.5, and 40°. An activation energy of 3.96 kcal. mole^{-1} was calculated for the addition to isoprene, and 3.09 kcal. mole^{-1} for that to 2,3-dimethylbutadiene.

Discussion

From the results obtained for the bromotrichloromethane–isoprene system, it is seen that addition of the trichloromethyl radical ($\dot{C}Cl_3$) is more favorable (3:1) at the end nearest to the methyl group (position 1). Presuming that the initiation is $BrCCl_3 \rightarrow \dot{B}r + \dot{C}Cl_3$, this is expected since $\dot{C}Cl_3$ is an "acceptor-type"[3] radical which preferentially attacks double bonds with electron-donating groups in the propagation step. In the displacement step the polar factor is also more favorable. This is also shown by the relative reaction rates obtained for the addition of bromotrichloromethane to butadiene, isoprene, and 2,3-dimethylbutadiene. For example, at 3:1 mole ratio, 25°, and a dose rate of 6 × 10^3 rads min.$^{-1}$, the ratios in rates are

$$C_4H_6:C_5H_8:C_6H_{10} = 1:1.27:5.28$$

In the rate *vs.* mole fraction of bromotrichloromethane plots (Fig. 8), in the cases of both isoprene and 2,3-dimethylbutadiene, as well as in that of butadiene,[1] the maxima lie in the region of 0.7–0.9 mole fraction of bromotrichloromethane (especially in the case of 2,3-dimethylbutadiene); this is in agreement with the idea of radical reactivities.[3] Since the radicals derived from the dienes are relatively stable due to resonance, these remain as the major radical species in the systems up to a high mole fraction of bromotrichloromethane. Among these three dienes, the steepest rise and highest maximum yield is observed with 2,3-dimethylbutadiene. This may result from the greatest reactivity of this diene in the present "donor–acceptor" type reaction.

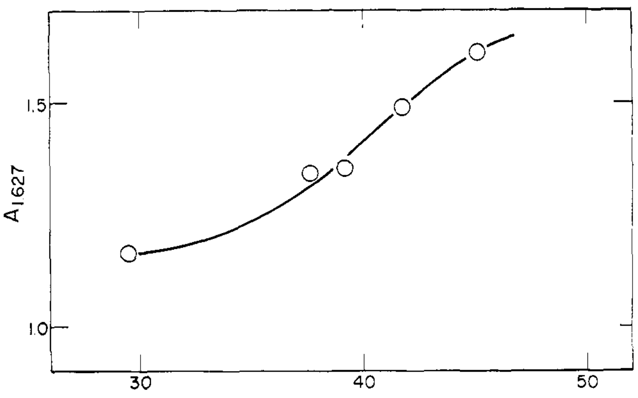

Fig. 3.—Standardization of concentrated 2,3-dimethylbutadiene in bromotrichloromethane; 2-mm. cell; slit = 0.12 mm.

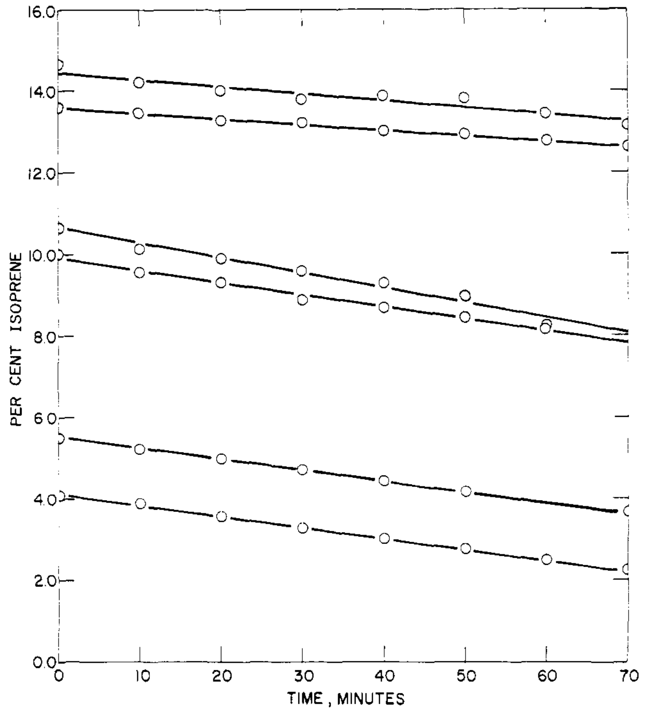

Fig. 4.—Some typical plots in reaction kinetics between isoprene and bromotrichloromethane as expressed in disappearance of isoprene.

In all kinetic runs reported, the conditions were chosen so that the 1:1 adduct was the only product. Therefore, the rates pertain to reactions on p. 1588. The stepwise, free radical reaction schemes for the addition reactions of these dienes are similar to that represented for butadiene.[1] The results from the kinetic studies show that the rates and G values are in the order of butadiene < isoprene < 2,3-dimethylbutadiene

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(3) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chap. 6.

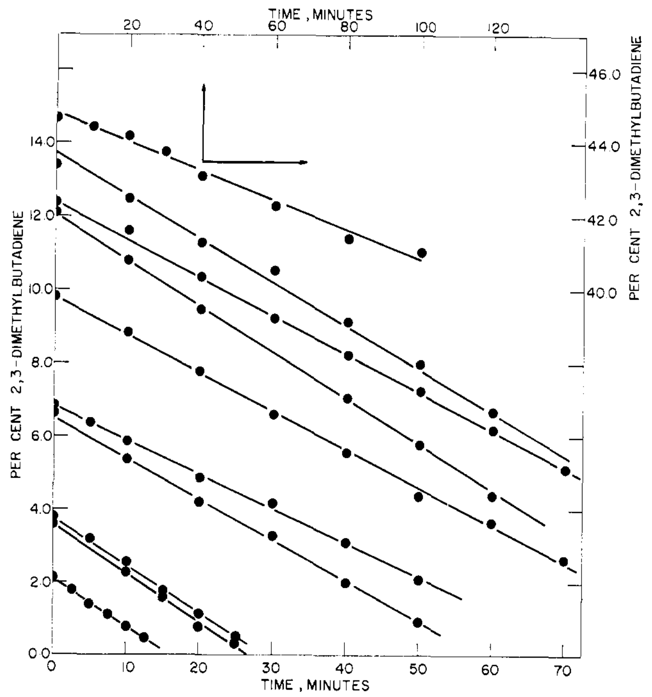


Fig. 5.—Some typical plots in reaction kinetics between 2,3-dimethylbutadiene and bromotrichloromethane as expressed in disappearance of 2,3-dimethylbutadiene *vs.* time. The scales on top and right of the graph belong to the uppermost plot.

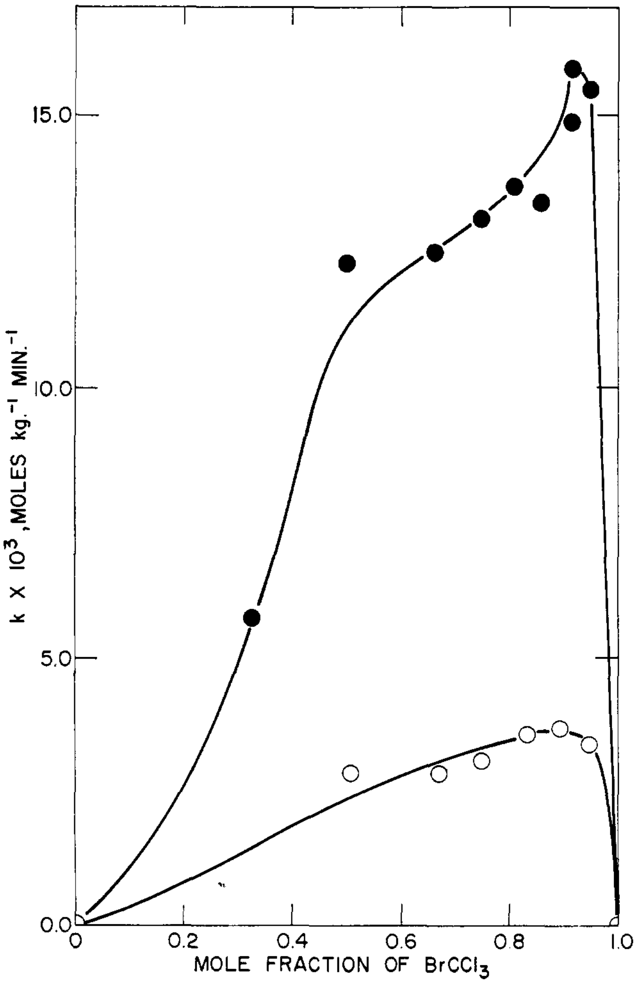


Fig. 6.—Dependence of rate on the mole fraction of bromotrichloromethane at 25°. ○, Isoprene; ●, 2,3-dimethylbutadiene.

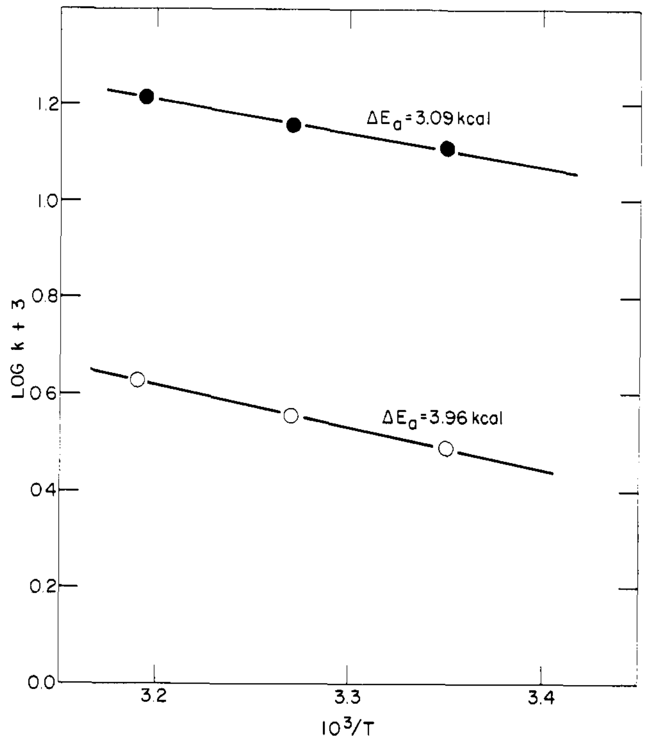
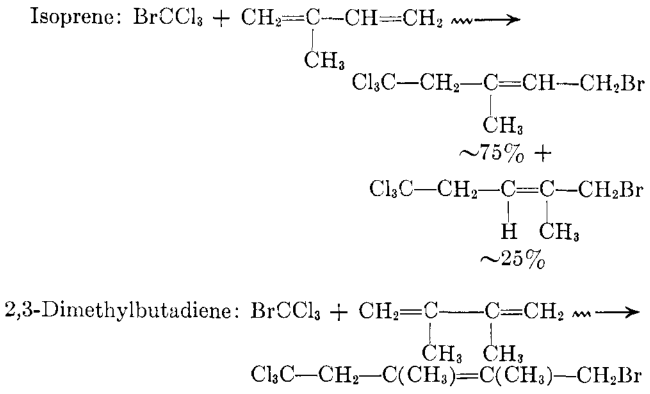


Fig. 7.—Arrhenius plot of addition of bromotrichloromethane to diene. Mole ratio, 3:1, dose rate, 6 × 10^3 rads $min.^{-1}$. ●, 2,3-Dimethylbutadiene; ○, isoprene.



Isoprene: $BrCCl_3 + CH_2{=}C(CH_3){-}CH{=}CH_2 \rightsquigarrow Cl_3C{-}CH_2{-}C(CH_3){=}CH{-}CH_2Br$ ~75% + $Cl_3C{-}CH_2{-}C(H){=}C(CH_3){-}CH_2Br$ ~25%

2,3-Dimethylbutadiene: $BrCCl_3 + CH_2{=}C(CH_3){-}C(CH_3){=}CH_2 \rightsquigarrow Cl_3C{-}CH_2{-}C(CH_3){=}C(CH_3){-}CH_2Br$

and that the activation energies are in the order of butadiene > isoprene > 2,3-dimethylbutadiene. Also, based on the dose rate dependence, the extent of allylic degradative chain transfer is in the order of 2,3-dimethylbutadiene > isoprene > butadiene. All these observations are in accordance with the structural features of these three dienes. The 2,3-dimethylbutadiene having two electron-donating groups which also carry six allylic hydrogens, is expected to be the most reactive, and the one capable of the highest allylic chain transfer among the three. However, the allylic chain transfer is not extensive in any case as is shown by the nearly square root dependence on the dose rate in all three cases. It is conceivable that considerable attack on allylic hydrogens could have taken place, but the resulting radicals were able to attack the reactive bromotrichloromethane and still propagate the chain.

The linear plots obtained for concentrations of diene *vs.* time (Fig. 4 and 5) indicate that the reactions are zero order in the diene. Table III represents the de-

TABLE III

DEPENDENCE OF RATE ON THE CONCENTRATION OF BROMOTRICHLOROMETHANE[a]

Diene	Mole ratio $BrCCl_3$:diene	$[BrCCl_3]$, moles kg.$^{-1}$	Rate × 10^3, moles kg.$^{-1}$ min.$^{-1}$
Isoprene	1.03:1	2.98	2.84
	2.05:1	4.30	2.74
	2.98:1	4.54	3.09
	6.19:1	4.78	3.58
	8.36:1	4.84	3.66
	17.95:1	4.96	3.34
2,3-Dimethylbutadiene	1:2.06	2.79	5.74
	0.99:1	3.56	12.29
	2.99:1	4.43	13.10
	4.25:1	4.60	12.70
	6.08:1	4.72	13.38
	10.63:1	4.85	14.88
	11.06:1	4.86	15.95
	11.22:1	4.86	15.83
	18.72:1	4.93	14.97

[a] Dose rate: isoprene, 5860 rads min.$^{-1}$; 2,3-dimethylbutadiene, 5920 rads min.$^{-1}$.

pendence of rate on the concentration of bromotrichloromethane when the rate in each case has been corrected to a common dose rate. It is seen that in the cases of both isoprene and 2,3-dimethylbutadiene, in the mole-ratio range of 1:1 to 18:1, the rates of disappearance of the dienes are essentially constant with variation in the mole ratio (within 25% variation), the maximum rates occurring at a mole ratio of 8:1 for isoprene and 11:1 for 2,3-dimethylbutadiene. However, the rate is much lower when a mole ratio of 1:2 is employed as indicated in the case of 2,3-dimethylbutadiene.

Acknowledgment.—The authors wish to express their appreciation to Mr. Stanley E. Polchlopek for obtaining the infrared and Raman spectra, to Dr. Robert F. Stamm and Mr. N. B. Colthup for advice on the interpretation of the Raman and infrared spectra, to Dr. Raymond Feinland for gas chromatographic analyses, and to Dr. John Lancaster for obtaining the n.m.r. spectra and interpreting them.

Potential Radiation-Protective Compounds. Synthesis of the Three Isomeric Three-Carbon Aminohydroxy Bunte Salts and Related Compounds[1]

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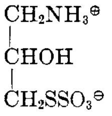
The isomeric internal Bunte salts, *S*-3-amino-2-hydroxypropylthiosulfuric acid (I), *S*-2-amino-1-(hydroxymethyl)ethylthiosulfuric acid (II), and *S*-2-amino-3-hydroxypropylthiosulfuric acid (III), have been prepared as the racemic forms. The last named has also been prepared in a levorotatory form. 3-Amino-2-bromo-1-propanol hydrobromide has been synthesized by the addition of hypobromous acid to the allylammonium ion; the isomeric 1-amino-3-bromo-2-propanol hydrobromide was a minor product of the addition. The acid hydrolysis of *N,O,S*-triacetyl-L-cysteinol probably proceeds *via* a thiazoline intermediate.

In recent years, Bunte salts,[2] *S*-alkyl thiosulfates, have been the subject of investigation in many laboratories. A Bunte salt related to glutathione, "S-sulfoglutathione", has been isolated from calf lens extracts.[3] Sulfite has been used to obtain soluble protein or peptide fractions from wool,[4] flour,[5] ribonuclease and insulin,[6] and from trypsinogen and α-chymotrypsinogen,[7] the cystine disulfide bonds are cleaved under mild conditions to form "S-sulfocysteinyl residues". The properties and potential uses of the "S-sulfocysteinyl residues" have been discussed by Swan.[8]

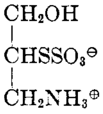
Several examples of Bunte salts containing amino or alkylamino groups were prepared by Bretschneider.[9] These, like the amino acids, are internal salts and the simplest compound of this type, *S*-2-aminoethylthiosulfuric acid, was found to have significant radiation-protective activity in mice. It was also 2.4 times less toxic than 2-aminoethanethiol (cysteamine) hydrochloride.[10] Other aminoalkyl thiosulfates have been prepared by Rosenthal and Citarel[11] who found that they were stable compounds which possessed significant anti-radiation activity. The low activity of 3-amino-1-propanethiol compared to the activity of *S*-3-aminopropylthiosulfuric acid[12] suggests that the protective activity of the Bunte salt is not, at least in this case, due to the formation of the thiol.

Aminoalkylthiosulfuric acids are, in general, stable, odorless, crystalline, water-soluble substances and are thus attractive potential anti-radiation drugs. This paper describes the synthesis of the three isomeric internal Bunte salts I, II, and III.



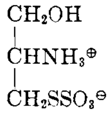
$CH_2NH_3^{\oplus}-CHOH-CH_2SSO_3^{\ominus}$

I



$CH_2OH-CHSSO_3^{\ominus}-CH_2NH_3^{\oplus}$

II



$CH_2OH-CHNH_3^{\oplus}-CH_2SSO_3^{\ominus}$

III

Bunte salts are prepared conveniently by the reaction of alkyl halides with thallous thiosulfate,[13] the insoluble thallous halide formed being removed easily from the reaction mixture. An aqueous solution of 1-

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