solution stood overnight and the solid which was now pale yellow was filtered and washed with water and then pentane to yield 0.63 g (100%), mp 143–170°. Three recrystallizations from methanol gave pale yellow crystals, mp 167–170° (lit.[5] 167°).

The nmr spectrum is discussed above. An infrared spectrum showed peaks at λ_{max} 5.95, 6.28, 6.87–6.97 (d), 8.0 and 10.63–11.37 μ (t).

The other isomer (**7**) may be prepared by the methods of Toji,[16] Barnett, Cook, and Matthews,[6] or by treatment of 4,5-dichloro-10-methoxy-9-anthrone (**8**) with hydriodic acid in acetic acid as described previously.

4,5-Dichloro-10-methoxy-9-anthrone (8).—The reaction was carried out under nitrogen and the reagents used were deoxygenated as in the preparation of 4,5-dichloro-9-methoxyanthracene (**17**).

To a boiling solution of 3 g (7.48 mmol) of dimethyl 4,5-dichloro-10-methoxy-9-anthryl phosphate (**5**) in 50 ml of 2-propanol was added 50 ml of 10% sodium hydroxide solution. The mixture immediately turned dark red and gradually became yellow after 20 hr of refluxing. The hot solution was acidified with concentrated hydrochloric acid; 2.02 g (100%) of **8**, mp 127–133°, was removed by filtration, washed with water and then pentane. Treatment with Norit and several recrystallizations from acetone gave white, diamond-shaped crystals melting at 134–136° (lit.[8] 136°): nmr ($CDCl_3$), 8.1–8.01 (q, 2, *peri* protons), 7.8–7.2 (m, 4), 6.4 (s, 1, H-10), and 2.96 ppm (s, 3, OCH_3); ir, 6.0 6.3 (sh), 6.35 (sh), 7.5–7.94 (t), 9.38–9.5 (d), and 13.37–13.78 (d). After standing overnight in a closed container, the crystals turned pink but there was no change in the nmr or infrared spectra or in the melting point.

(10-Keto-9,10-dihydro-9-anthryl)succinic acid (14).—A solution of 2.9 g (6.7 mmol) of 9-methoxy-10-dimethylphosphato-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride (**13**) in 15 ml of hydriodic acid and 30 ml of glacial acetic acid was refluxed for 15 hr. When the product was isolated following the procedure for compound **6**, 1.68 g (81%) of **14**, mp 190–195° dec was obtained. Recrystallization from acetone–petroleum ether gave colorless crystals melting at 196–198° dec (lit.[12] 194.3–195.3°). The acid was identified by comparison with an authentic sample prepared from 9-methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride.[12]

(4,5-Dichloro-10-keto-9,10-dihydro-9-anthryl)succinic Acid (16).—Hydriodic acid in acetic acid converted 1.34 g (2.69 mmol) of 1,8-dichloro-9-methoxy-10-dimethylphosphato-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride (**15**) into 0.84 g (72%) of acid **16**, mp 220–260° dec. After two recrystallizations, white crystals were obtained which turned yellow at 240° and melted at 260° dec.

Anal. Calcd for $C_{18}H_{12}Cl_2O_5$: C, 57.01; H, 3.19. Found: C, 56.97; H, 3.15.

An infrared spectrum showed peaks at λ_{max} 3.4 (broad s), 5.83–5.94 (d), 6.03 (sh), 6.87–7.07 (t), 7.77 and 8.05 μ.

(1,8-Dichloro-10-keto-9,10-dihydro-9-anthryl)succinic Acid (19).—The procedure was previously described. Cleavage of 2.16 g (5.76 mmol) of 1,8-dichloro-10-methoxy-9,10-dihydro-9,10-ethanoanthracene-11-12-dicarboxylic anhydride (**18**) gave 1.37 g (65%) of pale yellow crystals, mp 230–245° dec. The analytical sample melted at 245–255° dec.

Anal. Calcd for $C_{18}H_{12}Cl_2O_5$: C, 57.01; H, 3.19. Found: C, 57.30; H, 3.39.

An infrared spectrum showed peaks at λ_{max} 3.2 (broad s), 5.55 (sh), 5.85–5.95 (d), 6.25, 6.3 (sh), 6.9, 7.65, 8.8 and 13.5 μ.

3-(4,5-Dichloro-10-keto-9,10-dihydro-9-anthryl)propionic Acid (21).—From a hydriodic acid cleavage as before, a quantitative yield of acid **21**, mp 200–205° dec, was obtained from 0.37 g (0.748 mmol) of 1,8-dichloro-9-methoxy-10-dimethylphosphato-9,10-dihydro-9,10-ethanoanthracene-12-carboxylic acid (**20**). The analytical sample melted at 204–206° dec.

Anal. Calcd for $C_{17}H_{12}Cl_2O_3$: C, 60.91; H, 3.61. Found: C, 60.83; H, 3.53.

An infrared spectrum showed peaks at λ_{max} 3.43 (broad m), 5.88–5.93 (d), 6.27–6.35 (d), 6.88–7.12 (t), 8.04–8.15 (d), 10.58–10.97 (t), and 12.45–12.72 μ (t).

3-(1,8-Dichloro-9-keto-9,10-dihydro-10-anthryl)propionic Acid (23).—A solution of 0.65 g (1.97 mmol) of 1,8-dichloro-10-methoxy-9,10-dihydro-9,10-ethanoanthracene-12-carboxylic acid (**22a**) or the cyano derivative (**22b**) in 5 ml of hydriodic acid and 10 ml of glacial acetic acid was refluxed for 2.5 hr. The same open acid (**23**) was obtained from both starting materials in quantitative yield and the analytical sample melted at 175–178°.

Anal. Calcd for $C_{17}H_{12}Cl_2O_3$: C, 60.91; H, 3.61. Found: C, 61.06; H, 3.64.

An infrared spectrum showed peaks at λ_{max} 3.4 (broad m), 5.75 (sh), 5.83–5.97 (d), 6.26, 6.85–9.4 (t), 7.6–8.0 (m), 8.8, 10.48 and 12.72–13.70 μ (t).

Registry No.—**5**, 16622-38-1; **8**, 16622-39-2; **12**, 16622-40-5; **13**, 16622-41-6; **15**, 16622-42-7; **16**, 16622-43-8; **18**, 16622-44-9; **19**, 16622-45-0; **20**, 16622-46-1; **21**, 16622-47-2; **22a**, 16622-48-3; **22b**, 16622-49-4; **23**, 16622-50-7.

Isoprene Chlorination

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The chlorination of isoprene does not appear to be a free-radical chain reaction either in the liquid or the gas phase at low temperatures. A mixture of substitution and addition products is obtained regardless of phase; somewhat more 1-chloro-2-methylbutadiene and less 1,4-dichloride were obtained in the gas phase. Dichlorides were obtained in greater yield when the chlorination was carried out in the presence of chloride ion.

Isoprene has been chlorinated in both liquid[1–4] and gas phase[4–7] to give products of substitution and addition. Because isoprene resembles both butadiene and isobutylene one might expect a common mechanism; however, in a recent study[8] Poutsma favors a radical mechanism for the chlorination of undiluted butadiene in the liquid phase. Isobutylene has been shown to undergo polar chlorination in the liquid phase.[9] Using *t*-butyl hypochlorite rather than chlorine, Oroshnik and Mallory[10] found that with undiluted isoprene in the liquid phase the orientation of 1,4 addition is that typical of a radical mechanism.

In Table I are shown true product yields obtained by chlorination below room temperature in neat liquid isoprene and in the gas phase at 100°. The liquid-phase results are corrected in that the addition products of hydrogen chloride are considered as recoverable isoprene. The conversion was complete with respect to

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(1) W. J. Jones and H. G. Williams, *J. Chem. Soc.*, 829 (1934).

(2) D. V. Tischenko, A. Abramova, and E. Yorzhemskaya, *Zh. Obshch. Khim.*, **27**, 227 (1957).

(3) E. G. E. Hawkins and M. D. Philpot, *J. Chem. Soc.*, 3204 (1962).

(4) L. F. Hatch and J. L. A. Rodriguez, University of Texas.

(5) G. H. Morey and R. F. Taylor, U. S. Patent 2,453,089; Commercial Solvents, 1948.

(6) M. B. Berenbaum, U. S. Patent 2,937,125 (Thiokol) (1960).

(7) K. M. Taylor, U. S. Patent 3,202,721 (Monsanto) (1965).

(8) M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966).

(9) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **70**, 3364 (1948).

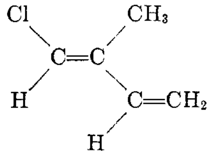
(10) W. Oroshnik and R. A. Mallory, *ibid.*, **72**, 4608 (1950).

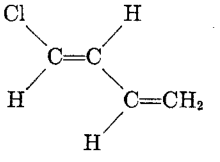
TABLE I[a]
BATCH LIQUID PHASE *vs.* CONTINUOUS VAPOR PHASE CHLORINATIONS

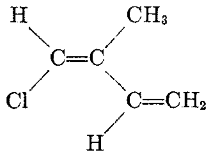
Phase	Temp, °C	2-Chloro-methyl	1-Chloro-2-methyl	Dichlorides 1,2	3,4	*cis*-1,4	*trans*-1,4	Hydro-chlorides[b]
Liquid	−20	42.5	8.0	5.7	0.2	4.6	33.3	15.2
Liquid	8	41.2	9.0	6.7	1.3	4.0	34.4	5.1
Liquid[c]	8	45.1	9.7	6.1	0.4	4.0	31.6	3.7
Liquid	20	44.1	7.3	5.5	2.7	4.1	33.6	4.8
Vapor	100	36.4	30.1	6.5	0.8	3.8	17.4	0.7
Vapor[d]	100	38.2	32.3	7.0	0.5	3.4	15.5	0.3
Vapor[e]	100	33.2	25.0	6.8	0.7	5.4	24.3	Trace

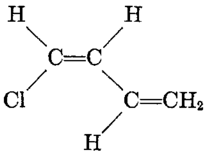
[a] Nitrogen sweep used in all vapor experiments; ratio isoprene to chlorine = 2.5; ratio nitrogen to chlorine = 30. Ratio isoprene to chlorine = 6 in liquid phase chlorinations. [b] Considered as recoverable isoprene. [c] With oxygen, ratio O_2/Cl_2 = 0.25. [d] With oxygen, ratio O_2/Cl_2 = 3. [e] With nitric oxide, ratio Cl_2/NO = 6.

chlorine and the mole ratio of isoprene to chlorine was 2.5 or higher. The substitution products consist of 2-chloromethylbutadiene and 1-chloro-2-methylbutadiene. The *cis* and *trans* isomers of 1-chloro-2-methylbutadiene were obtained in a ratio slightly richer (52%) in that isomer (II) in which methyl and chlorine have *trans* relationship. This was the case in the liquid chlorination at −20° and vapor phase chlorination at 100°. Isomer I is structurally related to *trans*-1-chlorobutadiene and, like it,[11] could be removed selectively from a mixture of isomers by reaction with maleic anhydride.


1-chloro-*cis*-2-methylbutadiene (I)


trans-1-chlorobutadiene


1-chloro-*trans*-2-methylbutadiene (II)


cis-1-chlorobutadiene

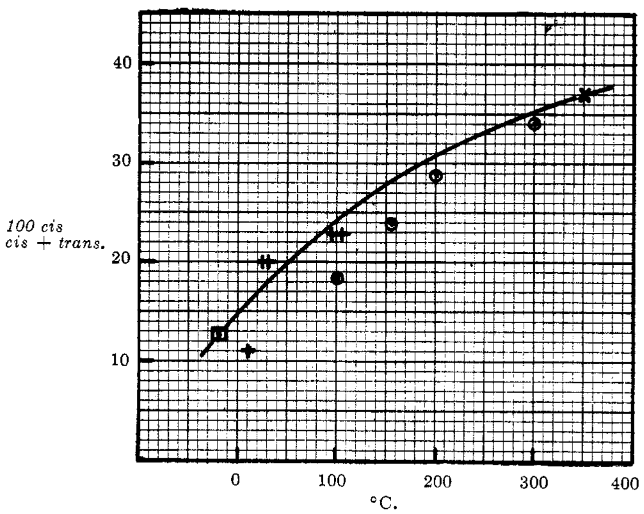


Figure 1.—Ratio of isoprene 1,4-dichlorides derived as follows: ×, rearrangement of 1,2-dichloride; ⊙, gas phase chlorination of isoprene; +, liquid phase chlorination of neat isoprene; ⊟ 2-years' storage of mixture rich in *cis*-1,4-dichloride; ++, treatment of mixture rich in *trans*-1,4-dichloride (considerable by-product formation).

In liquid phase chlorinations in a nonpolar medium the ratio of yields of 2-chloromethylbutadiene and 1-chloro-2-methylbutadiene was of the magnitude of 5; however, as shown in Table II the ratio dropped when the solvent was aqueous *t*-butyl alcohol or 2,6-lutidine or when a quaternary ammonium chloride was dissolved in the isoprene. Under these conditions the yields of dichlorides, and especially that of the 1,2-dichloride, were increased. It is assumed that the effect of the polar solvents was to provide chloride ion from dissolved or combined hydrochloric acid. That the chloride ion participated in addition implies an ionic mechanism, at least in the polar solvents. The greater reduction in yield of 2-chloromethylbutadiene than of 1-chloro-2-methylbutadiene can be rationalized in terms of a common intermediate by assuming that chloride ion, as a stronger base than hydrogen chloride, tended to remove the more acidic proton from the chlorine-bearing carbon. Dehydrohalogenation of the 1,2-dichloride does not occur under the conditions of chlorination; however, dehydrohalogenation with sodium hydroxide at 60° gives 4.2 times as much 1-chloro-2-methylbutadiene as 2-chloromethylbutadiene.

In the absence of chloride ion the greater electron-supplying effect of the methyl group tends to favor the formation of 2-chloromethylbutadiene as it does the formation of methallyl chloride in the chlorination of isobutylene.[9]

The addition of drying agents or ground glass to a liquid-phase chlorination had little effect. There was a minor product change when the Saran vapor phase reactor was packed with glass. Under these conditions some 7% conversion occurred to additional dichlorides, normally obtained in smaller amount.

To establish which products, if any, were not primary ones, several attempts were made to isomerize one to another. Under the conditions of chlorination there was no isomerization; however, the dichlorides could be interconverted by long standing or treatment with zinc chloride. As shown in Figure 1 the mole percentage of *cis* isomer of the 1,4-dichloride increased with increasing temperature, whether the mixture was one obtained directly by chlorination or by isomerization.

Under the conditions of short contact time and excess isoprene neither the monochloro substitution products nor the dichlorides underwent to an appreciable extent further reaction with chlorine or hydrogen chloride. The hydrochlorides did compete with isoprene in addition of hydrogen chloride. There was an indication that the addition of hydrogen chloride to isoprene in the liquid phase was slower than chlorination. Thus the use of a nitrogen sweep to remove hydrogen chloride (or alternatively a partial covolatilization of the isoprene and hydrogen chloride) minimized the formation of addition products of hydrogen chloride to isoprene. As the temperature was increased, relatively more of that hydrogen chloride adduct which did form had the 1,4 structure. Hydrochlorides were not formed in the gas phase reaction.

An attempt was made to obtain product ratios at incomplete consumption of chlorine. In these experi-

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[11] A. S. Onishchenko and N. I. Aronova, *Dokl. Akad. Nauk SSSR*, **132**, 138 (1960).

TABLE II

LIQUID PHASE BATCH CHLORINATION WITH VARIOUS ADDITIVES

Additive[a]	Temp, °C	2-Chloromethylbutadiene	1-Chloro-2-methylbutadiene	Dichlorides			
				1,2	3,4	*cis*-1,4	*trans*-1,4
Neopentane	−20	39.4	8.4	6.0	0.4	4.6	38.3
(Heptyl)$_4$NCl[b]	−20	9.8	4.0	43.2	3.4	3.9	28.5
t-Butyl alcohol[c]	−20	14.1	10.1	18.2	2.0	2.0	20.2
2,6-Lutidine	−20	10.3	5.1	27.5	2.3	3.6	50.8
Chloroform	−20	38.4	~15.2	6.8	2.1	2.1	27.9
Ground glass	−20	38.1	10.5	5.9	0.7	5.3	31.2
Calcium hydroxide	−20	38.6	8.5	5.8	0.7	5.6	35.7
Sodium sulfate	−20	39.9	9.2	5.5	0.9	<4.8	33.5
Carbon disulfide	−78	37.5	11.9	7.2	~0.7	3.2	38.2
Benzene	5	37.0	14.7	8.4	3.0	3.1	29.0
Cyclohexane	5	37.0	10.2	7.6	~0.7	3.1	33.6

[a] Solvents were used in equal volume with isoprene; solids were added at 2% of isoprene weight and chlorination conducted with agitation. Yields corrected for hydrochloride formation. [b] 10% by weight of isoprene. [c] Containing 10% water.

ments in the gas phase an on-stream mass spectrometer was used. Because of the problems associated with electrode corrosion by chlorine, it was not possible to distinguish isomers or establish *K* values, but the addition and substitution products were clearly resolved and could be qualitatively compared. These experiments were conducted under vacuum and at several temperatures. It was concluded that the ratio of substitution to addition did not change much with change in temperature between room temperature and 100° in gas phase chlorination.

The reaction went quite well in the dark in both phases and did not seem to depend upon adventitious peroxidic impurities. Purification of the isoprene had no effect nor did addition of peroxide. No inhibitor was found. Oxygen and nitric oxide were ineffective in either phase and bromotrichloromethane and triphenylmethane were ineffective in the liquid phase.

Confirming evidence for the absence of a radical-chain mechanism was found in a competitive chlorination of a mixture of isoprene and ethylene. Except when ultraviolet irradiation was used the ethylene was not attacked either in the liquid or gas phase. As pointed out by Poutsma, chlorine atoms show essentially no discrimination between dienes and olefins.[9]

We conclude therefore that the mechanism operating in the chlorination of isoprene in the dark at 100°, or below, is not a free-radical chain reaction even in the vapor phase. Such an interpretation is not entirely new. Rust and Vaughan[12] found that in the low temperature (below 300°) chlorination of ethylene in the gas phase the ratio of substitution to addition could be increased by increasing reactant pressure and that the former but not the latter could be completely inhibited by oxygen. Propylene showed a similar but less pronounced effect. They concluded that in the case of olefins chlorine addition at low temperatures in the vapor phase can occur by a nonchain reaction in addition to the chain reaction which is produced by free-radical sources.

Inasmuch as the products are not rearranged, any thermodynamic control in the formation of *cis* and *trans* 1,4-addition products must be established in the transition state, and it is tempting to suggest that this state has the form of a π complex. Some evidence exists for the formation of complexes between iodine and aromatic hydrocarbons in the gas phase.[13] The effect of temperature on the proportion of *cis* isomer is consistent with—and may be related to—the expected effect of temperature on the proportion of cisoid isomer in isoprene.

The rate of chlorination of isoprene is inconveniently fast in concentrated solution for kinetic study even at −78°. Kinetic measurements can be made at room temperature at a chlorine concentration of 10^{-3} *M* which is inconveniently dilute for quantitative vapor phase chromatography.

The rate was followed by disappearance of chlorine absorption at 332 mμ and the half-life was approximately 3 hr. The rate was not changed by raising the ratio of isoprene to chlorine from 2 to 4 but was highly dependent on chlorine concentration. At 10^{-2} *M* chlorine the half-life was less than 5 min. As shown in Figure 3 the rate was essentially first order in chlorine and subject to pronounced acceleration by intermittent illumination after the addition of *t*-butyl hypochlorite.[13a]

The liquid phase butoxylation of isoprene with *t*-butyl hypochlorite appears to have some free-radical character. Tiglaldehyde and tiglic acid were detected as products, presumably derived from the abnormal substitution product 1-butoxy-2-methylbutadiene which was not itself isolated. 2-Chloromethylbutadiene and 1-chloro-2-methylbutadiene were produced also presumably by concurrent polar mechanism.

Experimental Section

The products of chlorination were analyzed by glpc using matched 9-ft columns (0.375 in. o.d.; 10% FFAP (fatty acid ester of a polyglycol, from Wilkins Instruments on 60–80 mesh acid-washed DMCS treated Chromosorb P) with the temperature programmed at 10°/min from 70 to 170°. The lined injection port temperature was 130°. The carrier gas was helium at a flow rate of 50 cc/min with detection by thermal conductivity. The instrument employed was a Model 1520 manufactured by the Aerograph Co. A typical curve of a liquid phase chlorination product with ethylene dichloride added is shown in Figure 2.

By this schedule the hydrochlorides were evolved below the temperature at which they broke down. The hydrochlorides could be readily converted to 3-hydroxy-3-methyl-1-butene[14] by shaking with dilute sodium hydroxide solution; however, this compound appeared from the column at the same time as isomer

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(12) F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, **5**, 472 (1940).

(13) F. T. Lang and R. L. Strong, *J. Amer. Chem. Soc.*, **87**, 2345 (1965).

(13a) NOTE ADDED IN PROOF.—It was discovered later that this catalytic effect could be duplicated by injection of a trace of hydrogen chloride; neither illumination nor *t*-butyl hypochlorite was needed.

(14) A. J. Ultee, *Rec. Trav. Chim. Pays Bas*, **68**, 483 (1949).

II. Several chromatographs of hydrochlorides were made isothermally using a column made with 15% polyethylene glycol on acid-washed Chromosorb. It was not satisfactory. At 100° the amounts of eluted hydrochlorides were much lower than at 80°. The other products were stable on either column. The high-temperature program was especially necessary to elute all of the 1,4-dichlorides.

Peak identification was done by mass, infrared, and nmr spectroscopy after separation of relatively pure components by fractional distillation and collection of fractions from the gas chromatograph.

The tabulations of yields of various products were calculated from area percentages from the gas chromatographs without the use of response factors. It was felt that although such corrections would be desirable they would have little effect on the mechanistic interpretations. Relative response factors were determined, however, for several components and are shown in Table III.

Table III

Relative Response Factors Thermal Conductivity Detector (Helium Carrier Gas)

Compound	Relative weight response	Relative molar response
Isoprene	1.23	0.82
trans-1-Chloroisoprene	0.99	0.99
cis-1-Chloroisoprene	0.95	0.95
4-Chloro-2-methyl-2-butene	1.09	1.09
2-Chloromethylbutadiene	1.00	1.00
1,2-Dichloro-2-methyl-3-butene	0.82	1.09
1,4-Dichloro-2-methyl-2-butene	0.77	1.04
Carbon tetrachloride	0.7	1.05
Nitromethane	1.1	0.65
Benzene	1.15	0.87

The identification of the geometric isomers of 1-chloromethylbutadiene was based on nmr spectroscopy and reaction with maleic anhydride. The first isomer to appear in glpc was the isomer removed. A comparison with 1-chlorobutadiene was made. For both the isoprene and butadiene derivatives that isomer which reacted with maleic anhydride had a chemical shift of the single 3-hydrogen of 6.25 ppm, as with isoprene itself, whereas the other isomer had a chemical shift of 6.95 *vs.* TMS. As is the case in butadiene itself[15] the nmr line of the hydrogen in position 1 (*trans* to vinyl) of isomer II was located upfield (0.13 ppm) from and broader than that of isomer I.

After the reported procedure[16] *cis*- and *trans*-1-chlorobutadiene were prepared in approximately equal amounts by the pyrolysis of 1,4-dichloro-2-butene, and the *cis* isomer, by reaction with caustic. They were not separable on the glpc column used in the isoprene work but at 50° on a column containing di-2-ethylhexyl sebacate the *cis* isomer appeared first. The ratio of peak heights of *cis* to *trans* was 0.9. As reported,[11] the *trans* isomer was found to be removable by reaction at 80° for 0.5 hr with maleic anhydride.

A minor by-product of high-temperature chlorination was found to be 3-chloro-2-methylbutadiene.[17] The nmr spectrum showed the CH_3 singlet at 1.95 ppm, and $=CH_2$ multiple peaks at 5.0–5.6 ppm. There was no absorption in the 6.09–6.25-ppm range to indicate Cl—CH=. The mass spectrum was that of a monochlorinated isoprene. The elution time in glpc was after the 1,2-hydrochloride, and before the 1-chloro-2-methylbutadiene. Another isomer having a slightly higher retention time was a small component of liquid phase chlorinations and was assumed to be 4-chloro-2-methylbutadiene.

Rearrangement of the Dichlorides of Isoprene.—Samples (1.0 μl) of the 1,2-dichloride (93.1% purity) were injected into a heated length of 0.0625-in. tubing attached to the glpc column and operated at various temperatures. The contact time was very short but at 250° there was essentially no change. At 350° there was 22% rearrangement. Half of the rearrangement was to the *trans*-1,4-dichloride; 6.5% of the *cis*-1,4-dichloride and 2% of the 3,4-dichloride were formed.

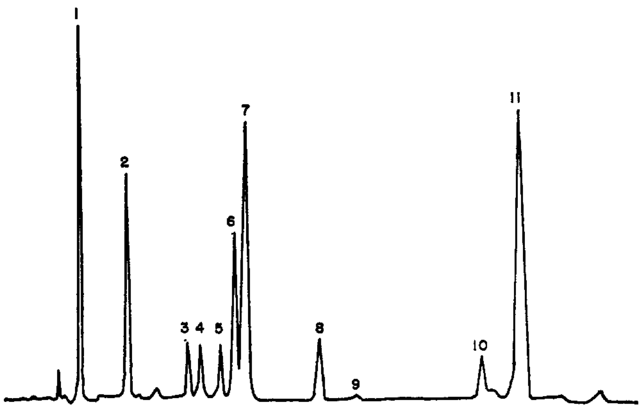

Figure 2.—The order of appearance of FFAP-packed glpc column of isoprene chlorination products plus added ethylene dichloride is as follows (attenuation values are in parentheses): 1, isoprene (128); 2, 1,2-hydrochloride (4); 3, *cis*-1-chloro-2-methylbutadiene (4); 4, *trans*-1-chloro-2-methylbutadiene (4); 5, 1,4-hydrochloride (4); 6, ethylene dichloride; 7, 2-chloromethylbutadiene (8); 8, 1,2-dichloride (4); 9, 3,4-dichloride; 10, *cis*-1,4-dichloride (4); 11, *trans*-1,4-dichloride (4).

A sample (10 ml) of the 1,2-dichloride (93.4% purity) was injected into the Saran gas phase chlorinator and exposed to chlorine at 100°. The injection was accomplished by preheating the dichloride to 100° and sparging the nitrogen through it. The ratio of chlorine to dichloride was 0.8 and the ratio of nitrogen to chlorine was 90. The product was condensed in a sulfite scrubber and analyzed by glpc. No significant change was observed in it.

A sample of the 1,4-dichloride which was 94.2% *trans*- and 2.4% *cis*-1,4-dichloride was saturated with zinc chloride and left at room temperature for 148 hr. The *cis* percentage increased to 17.1 and then dropped to 14.5 after 172 hr whereas the *trans* percentage decreased steadily to 62.6. Some of the 1,2- and 3,4-dichlorides formed.

Another sample was saturated with zinc chloride and heated at 100°. Within 10 min the concentration of the *cis* isomer had reached 22.6% and went no higher, although the 1,4 isomer continued to disappear on prolonged heating. There was first an increase and then decrease of the 1,2- and 3,4-dichlorides.

Secondary Reactions.—Chlorine was bubbled through 2-chloromethylbutadiene of 94% purity at 0°. There was a 5% conversion in 5 min to a variety of chlorinated products whereas the chlorination of isoprene went to completion in less than 0.5 min. The concentration of 1-chloro-2-methylbutadiene was reduced from 1 to 0.6%.

2-Chloromethylbutadiene was saturated with hydrogen chloride at 0° for 1 hr. There was a 3% conversion to a mixture of isoprene 1,2- and 1,4-dichlorides. In contrast isoprene saturated with hydrogen chloride at −20° underwent 16% addition in 2 min to mixed hydrochlorides (51.5% 1,2-hydrochloride; 38.6% 1,4-hydrochloride). 1-Chloro-2-methylbutadiene in a nickel vessel at room temperature was treated with hydrogen chloride at 100 psi for 21 hr. There was 13.7% conversion to a dichloride different from those obtained from isoprene and chlorine.

A mixture of the hydrochlorides and monochloro substitution products of isoprene was treated with hydrogen chloride for 1 hr at 0°. The hydrochlorides reacted preferentially. None of the dichlorides added hydrogen chloride when treated for 1 hr at 0°.

Chlorination in Polar Solvents.—Into a solution of isoprene (100 ml) in 2,6-lutidine (57 ml) stirred at −25° was bubbled chlorine (35.5 g) mixed with air. The vessel was equipped with a condenser chilled with Dry Ice. A yellow precipitate of lutidine hydrochloride formed. The liquid product was washed with water and the glpc analysis of Table II made on it.

In another experiment 2,6-lutidine (57 ml) was dissolved in isoprene (200 ml) and chlorine (35.5 g) introduced at 30°. The amount of chloride ion which formed was 0.088 equiv; of this only a small part (0.005 equiv) was present as a quaternary ammonium chloride resulting from alkylation of the lutidine.

In a Teflon-coated reactor at −20°, isoprene (0.3 mol) was dissolved in an equal volume of aqueous *t*-butyl alcohol solution (10:1 *t*-BuOH/H_2O). Chlorine (0.05 mol) was bubbled into

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[16] L. J. Hughes, French Patent 1,326,120 (Monsanto) (1963).

[17] G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *J. Amer. Chem. Soc.*, **72**, 3542 (1950).

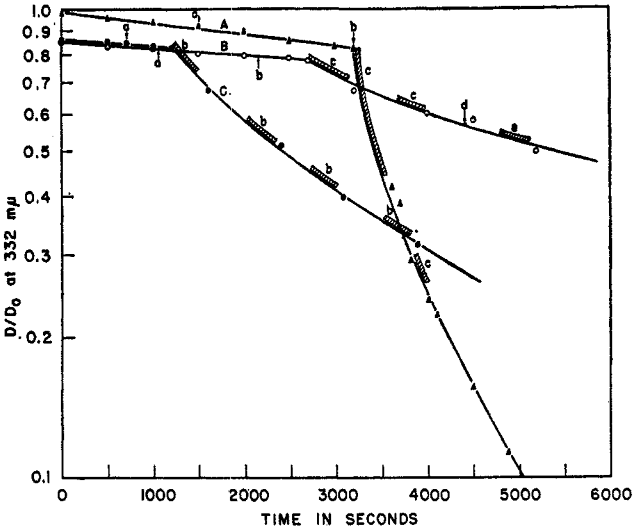

Figure 3.—Reaction of chlorine (0.026 mmol) (0.029 in curve A) and isoprene (0.050 mmol) in carbon tetrachloride (30 ml) under nitrogen; cross-hatched areas represent illumination (3660 Å): (A) at point a additional isoprene added (0.05 mmol), at point b *t*-butyl hypochlorite added (1% of isoprene); (B) at point a air injected (4.8 ml); at point b *t*-butyl hypochlorite added (1% isoprene); at point d additional isoprene added (0.05 mmol); (C) at point a *t*-butyl hypochlorite (1% of isoprene).

this over a period of 33 sec. The product was purged with nitrogen for 15 min.

Tetraheptylammonium chloride (2.04 g) was dissolved in isoprene (0.3 mol, 20.43 g). Chlorine (0.05 mol) was bubbled into this at −20° for a period of 33 sec. The product was purged with nitrogen to remove hydrogen chloride.

Liquid Phase Chlorination.—For batch chlorinations in the liquid phase a Teflon-coated glass reactor of 75-ml capacity was equipped with a condenser containing Dry Ice. The gas inlet tube was also Teflon coated as was the cold finger. The outlet was connected to a cold trap, and in most of the work no precautions were taken to exclude moisture. The liquid volume in the chlorinator was 30 ml, and agitation was only that caused by the gas sparger. The external cooling bath was incapable of preventing a rise in temperature of several degrees during chlorination, especially because the chlorine was added rapidly. The difficulty was minimized by keeping the mole ratios of chlorine to isoprene low.

Isoprene (20.43 g, 0.3 mol) was chilled to −20° and chlorine (0.05 mol) introduced during the period of 33 sec. There was no chlorine in the exit gas. After chlorination the product was purged with nitrogen to remove hydrogen chloride; yield 20.98 g. By glpc the product contained (on an area per cent basis) 79.0% isoprene, 2.2% 1,2-hydrochloride, 0.7% *cis*-1-chloro-2-methylbutadiene, 0.7% *trans*-1-chloro-2-methylbutadiene, 1.0% 1,4-hydrochloride, 7.4% 2-chloromethylbutadiene, 1.0% 1,2-dichloride, 0.03% 3,4-dichloride, 0.8% *cis*-1,4-dichloride, 5.8% *trans*-1,4-dichloride, and six unidentified peaks amounting to a total of 0.9%. The yield of 2-chloromethylbutadiene corrected for hydrochlorides and isoprene was 42.5%.

An experiment was made using isoprene presaturated with about 3% triphenylmethane. The amount of recovered isoprene was 72.2%, and the yield of 2-chloromethylbutadiene was 44.2%. The product composition was essentially the same as without the triphenylmethane.

Reaction of Isoprene with *t*-Butyl Hypochlorite.—Reaction of the premixed ingredients at low temperatures was not controllable. Isoprene (0.68 g, 0.01 mol) and *t*-butyl hypochlorite (1.09 g, 0.01 mol) were mixed at 10°. After 10 min most of the contents were suddenly expelled. The residue contained chlorination products. The ratio of 2-chloromethylbutadiene to 1-chloro-2-methylbutadiene was 4. Although delayed, a similar uncontrolled reaction occurred even when the vessel was kept in the dark.

Isoprene (0.02 mol) was refluxed and *t*-butyl hypochlorite (0.02 mol) added through the condenser over the period of 15 min. Carbonyl- and hydroxyl-containing compounds were formed, one of which was identified by mass spectrometry as tigylaldehyde. In addition, 2-chloromethylbutadiene and 1-chloro-2-methylbutadiene were formed, but none of the abnormal 1,2 adduct.

Chlorination of Isoprene at High Dilution in Carbon Tetrachloride.—Carbon tetrachloride (30 ml) in a 10-cm uv cell was purged with nitrogen to remove oxygen. Chlorine (0.026 mmol) dissolved in carbon tetrachloride, isoprene (0.05 mmol), and *t*-butyl hypochlorite (1% of isoprene, by weight) were added. The disappearance of the chlorine band at 332 mμ was followed at room temperature on a Cary spectrophotometer, Model 15. The reaction was catalyzed by intermittent light exposure (3600-mμ band) with a Bausch & Lomb high intensity monochromator at 10^{16} photons/sec (curve C, Figure 3). Absorption was incomplete. Variations of the above basic procedure (curves A and B, Figure 3) were used with the addition of more isoprene (0.05 mmole) and air (4.8 cc) and catalysis by monochromatic light at the 3660-mμ line.

Vapor Phase Chlorination of Isoprene.—Small-scale vapor phase chlorination of isoprene was carried out in a downflow cocurrent fashion in a 4-ft glass column (20 mm i.d.) containing a full length thermocouple well (6 mm o.d.).

In later experiments a 4 ft × 0.625 in. i.d. Saran pipe was substituted for the glass column and the thermocouple well was omitted. The product distribution was not changed by packing this reactor with glass, except that the minor dichlorides amounted to 7%.

A steam jacket surrounded the column. The gas mixture used in a particular reaction was monitored through flow meters and preheated in a coil by means of steam. Isoprene vapor was sparged into the column with nitrogen from a reservoir kept at room temperature. The chlorine also was diluted with nitrogen and the ratio of nitrogen to isoprene was kept at 30 to prevent condensation. The product gas was passed through a solution of sodium sulfite (12%) and sodium hydroxide (4%) containing antifoaming agent (Dow Corning Antifoam A).

To show that this procedure was adequate to prevent any liquid phase chlorination some isoprene was placed in the scrubber and chlorine passed through the column. Less than 1% chlorination occurred. 2-Chloromethylbutadiene was shown to be stable under the conditions of the scrubber and only slowly chlorinated in the column.

A mixture of isoprene and ethylene was chlorinated using the Saran column heated with steam at atmospheric pressure. The ethylene was passed through the chilled isoprene and into the reactor where it was mixed with chlorine which was diluted with nitrogen. In the first experiment the isoprene was chilled to zero, and the flow was 0.006 *vs.* 0.016 m min^{-1} ethylene. In the second it was chilled to −10° and the flow rate was 0.005 *vs.* 0.023 m min^{-1} ethylene. The chlorine flow rate was half the isoprene flow rate, and the nitrogen flow was 3 l. min^{-1}. In the first experiment the isoprene was 44% converted and in the second 53%, but no ethylene dichloride was detected. The product ratios were similar to those of Table II for gas phase chlorination. The yields were 32% 1-chloro-2-methylbutadiene (44% *cis*), 37% 2-chloromethylbutadiene, and 27% dichlorides (25% *1,2*; 1.8% *3,4*; 12% *cis*-1,4).

Vacuum Chlorination of Ethylene-Isoprene Mixture.—A mixture of 2 vol of ethylene and 1 vol of isoprene was introduced through one orifice and chlorine through another into an evacuated glass vessel 24 cm long consisting of the annular space between a water-cooled core (5 cm o.d.) and a jacket (8 cm i.d.). The pressure was maintained at 3 mm. Chlorine was introduced at half the rate of the hydrocarbon mixture. Immediately downstream from the reactor was an orifice leading to a modified Consolidated Electrodynamics cycloidal mass spectrometer. Some unreacted chlorine entered the mass spectrometer. The substitution and addition products of isoprene fell into two separate groups but were not resolved within these groups. No ethylene dichloride was observed when the chlorination was conducted without ultraviolet illumination. When the vessel was irradiated with a 450-W medium pressure Hanovia lamp, ethylene dichloride was formed. Owing to the heat of the lamp the temperature rose from 17 to 23° and the amount of isoprene chlorination increased. The free chlorine disappeared. When the lamp was turned off the chlorine reappeared and the ethylene dichloride disappeared (the disappearance was delayed owing to some retention in the mass spectrometer). When the reactor was heated to 50° without illumination, no ethylene dichloride was formed and free chlorine was still observed.

For the purpose of collecting a glpc sample a different reactor was used. Into 75 ft of Saran tubing (0.375-in. i.d.) was introduced at 2 mm pressure the 2:1 ethylene–isoprene mixture, and chlorine at the ratio of 5 mol % of the isoprene. The gas flow was 3×10^{-4} mol/min. The product was condensed with liquid nitrogen, and no chlorine was visible. Ethylene dichloride is resolvable from 2-chloromethylbutadiene, although it appears close to it, and none was observed. The actual conversions were 1,2-hydrocloride, 1.4%; 1-chloro-*cis*-2-methylbutadiene, 0.3%; 1-chloro-*trans*-2-methylbutadiene, 0.4%; 2-chloromethylbutadiene, 0.8%; 1,2-dichloride, 0.5%; *cis*-1,4-dichloride, 0.09%; *trans*-1,4-dichloride, 0.9%.

Registry No.—Isoprene, 78-79-5.

Acknowledgment.—We acknowledge with appreciation the assistance of C. Bredeweg, The Dow Chemical Co., and of Professor Lewis Hatch who sent us the M.S. thesis of J. L. A. Rodrigues, University of Texas (1965), on the vapor phase reaction between chlorine and dienes.

Thermal Decomposition of *o*-Azidoazobenzenes. I. *o,o'*-Diazidoazobenzene[1]

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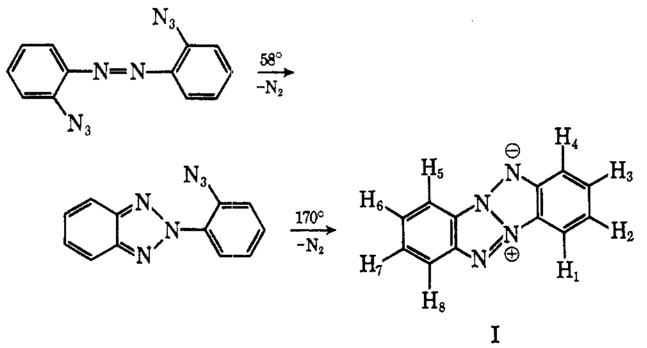
Thermal decomposition of 2-(2-azidophenyl)-5-methylbenzotriazole has been found to give a mixture of 2-methyl- and 3-methyl-5,6H-dibenzo[*b,f*]-1,3a,4,6a-tetraazopentalenes. Each of these products was prepared separately by decomposition of 2-(2-azido-5-methylphenyl)benzotriazole and 2-(2-azido-4-methylphenyl)benzotriazole, respectively. The results of an nmr study on the parent 5,6H-dibenzo[*b,f*]-1,3a,4,6a-tetraazopentalene as well as the 2-methyl and 3-methyl derivatives is presented. The chemical shifts were found to be consistant with electron distribution calculations of Chia and Simmons[5d] and with the observations of Carboni, *et al.*,[5d] on orientation effects in electrophilic substitution reactions.

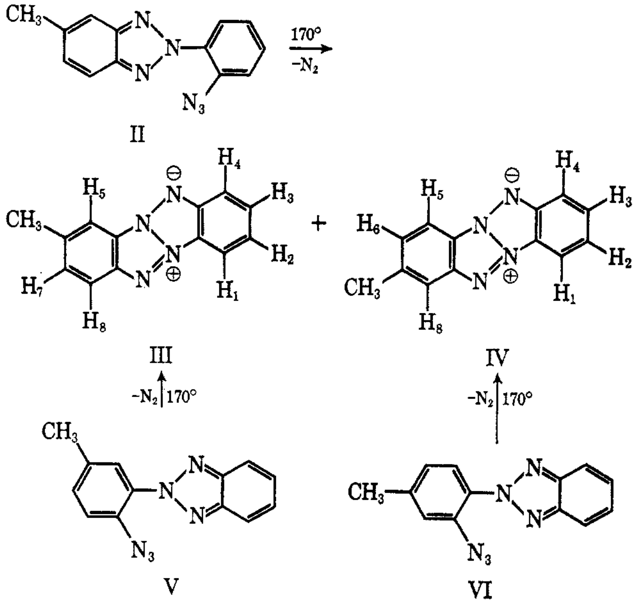
The thermal decomposition of *o,o'*-diazidoazobenzene has been shown to proceed by stepwise loss of nitrogen to give 5,6H-dibenzo[*b,f*]-1,3a,4,6a-tetrazopentalene (I).[2,3] A preliminary report of an X-ray study of I described it as having two different N–N bond distances and as probably being planar.[4] In recent work, chemical evidence for structure I was presented and alternate methods of synthesis were described.[5]



I

In a further investigation of this interesting aromatic system, we prepared 2-(2-azidophenyl)-5-methylbenzotriazole (II) and studied the decomposition in decalin at 170° (Scheme I). A yellow solid was obtained, mp 184–185°. Because of the sharpness of the melting point, this solid was initially felt to be a single compound. However, in order to be certain, the two possible products, III and IV, were independently synthesized. Compound III was prepared by thermal decomposition of 2-(2-azido-5-methylphenyl)benzotriazole (V) and compound IV was prepared by thermal decomposition of 2-(2-azido-4-methylphenyl)benzotriazole (VI). The syntheses of V and VI were accomplished by condensation of 2-azidoaniline with the corresponding nitroso compound in acetic acid to give the substituted 2-azido-2'-nitroazobenzene. The azo compound was not isolated but was decomposed during the work-up of the reaction mixture to give the substituted 2-(2-nitrophenyl)benzotriazole. The nitro group was reduced with iron and acetic acid to the amine. Diazotization of the amine followed by treatment of the diazonium salt solution with sodium azide gave the sub-

SCHEME I



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[1] (a) Acknowledgment is made to the donors to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) This work was taken in part from the M.A. Thesis of John G. Stephanie.

[2] (a) R. A. Carboni and J. E. Castle, *J. Amer. Chem. Soc.*, **84**, 2453 (1962); (b) R. A. Carboni, U. S. Patent 2,904,544 (Sept 1959); (c) R. A. Carboni, U. S. Patent Reissue 25,238 (Sept 1962).

[3] Other names that have been used include 5,11-dehydrobenzotriazole-[2,1-*a*]benzotriazole, dibenzo[*c,g*]-1,2,5,6-tetraazocine, 5H,11H-benzotriazolo[2,1-*a*]benzotriazol-6-ium salt, and dibenzo[2,3;4,5]-1,3a,4,6a-tetraazopentalene.

[4] M. E. Burke, R. A. Sparks, and K. N. Trueblood, *Acta Cryst.*, **16**, A64 (1963).

[5] (a) R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *J. Amer. Chem. Soc.*, **89**, 2618 (1967); (b) R. A. Carboni, J. C. Kauer, W. R. Hatchard, and R. J. Harder, *ibid.*, 2626 (1967); (c) J. C. Kauer and R. A. Carboni, *ibid.*, 2633 (1967); (d) Y. T. Chia and H. E. Simmons, *ibid.*, 2638 (1967); R. J. Harder, R. A. Carboni, and J. E. Castle, *ibid.*, 2643 (1967).