

hours, during which crystals were deposited, the solution was filtered hot. The filtrate was evaporated gradually with filtration of the solution from the crystals from time to time. The results were as follows: Fraction I, 0.675 g., m. p. 292–293°; fraction II, 0.320 g., m. p. 210° (not sharp); fraction III, 0.280 g., m. p. 210° (not sharp); fraction IV, 0.300 g., m. p. 210° (not sharp); fraction V, 0.250 g., m. p. 195° (not sharp); fraction VI, 0.260 g., m. p. 190° (not sharp).

Fraction I was recrystallized from glacial acetic acid, m. p. 292–293° (cor.).

Anal. Calcd. for $C_{22}H_{22}N_2O_4Cl_2S_2$: C, 51.46; H, 4.32; N, 5.46. Found: C, 51.49; H, 4.28; N, 5.67.

Fraction V was refractionated and the more soluble part crystallized thrice from ethanol, m. p. 203–204° (cor.).

Anal. Calcd. for $C_{22}H_{22}N_2O_4Cl_2S_2$: C, 51.46; H, 4.32; N, 5.46. Found: C, 51.62; H, 4.52; N, 5.53.

This lower-melting isomer after melting solidified at 205–206° and melted again at 290–292°. A larger quantity of product heated for one hour above its melting point was then recrystallized from glacial acetic acid and proved to be the higher melting form. To observe satisfactorily the melting point of the lower-melting form, it

was found desirable to preheat the bath to 195° and introduce the melting point tube with only a small quantity of product present.

Summary

1. *N*-Carboxymethyl-*o*-benzenesulfonamidotoluene could not be resolved. *Cis* and *trans* isomers could not be obtained from *N,N'*-dimethyl-2,4-dibzenesulfonamido-*m*-xylene, *N,N'*-dimethyl-2,6-dibzenesulfonamido-*m*-xylene, and *N,N'*-dimethyl-2,5-dibzenesulfonamido-*p*-xylene. It appears that merely one methyl group in the benzene ring *ortho* to the amino group is inadequate to restrict the C–N rotation when the nitrogen atom is substituted with the groups indicated.

2. *N,N'*-Dimethyl-2,5-dibzenesulfonamido-3,6-dichloro-*p*-xylene was obtained in *cis* and *trans* forms.

URBANA, ILLINOIS

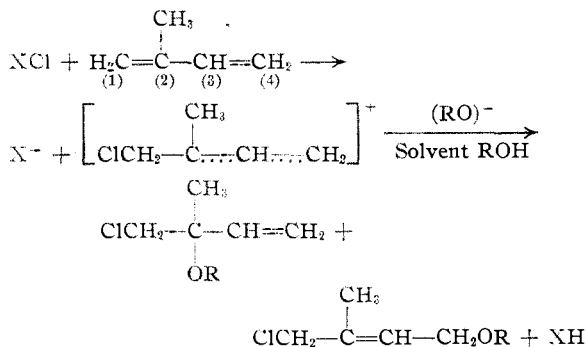
RECEIVED MARCH 17, 1950

[CONTRIBUTION FROM THE DIVISION OF ORGANIC CHEMISTRY OF THE ORTHO RESEARCH FOUNDATION]

The Reaction of Isoprene with *t*-Butyl Hypochlorite in Hydroxylic Solvents

BY WILLIAM OROSHNIK AND ROBERT A. MALLORY

According to the prevailing ionic theory, the hypochlorination of isoprene would be expected to proceed by electrophilic initiation at carbon-1, as follows^{1,2}



The intermediate carbonium ion can react at either carbon-2 or carbon-4, producing a pair of isomers. The literature, however, is at variance as to whether a 1,4-adduct can actually be obtained. Petrov,³ who observed only 1,2-adducts, questioned the validity of the claim of Ingold and Smith⁴ that the 1,4-bromohydrin can be obtained in this reaction. An isoprene chlorohydrin obtained through the action of *t*-butyl hypochlorite and water has been described in a German patent. Although no indication was made as to its struc-

ture, comparison with the product obtained in the present work showed it to be a 1,2-adduct.

The present work was prompted by a need for the 1,4-chlorohydrin of isoprene in a synthesis of vitamin A.⁶ The hypochlorination method used was the elegant one discovered by Harford⁷ and extended by Irwin and Hennion⁸ wherein *t*-butyl hypochlorite is added to a solution of olefin in a reactive solvent. It was found in the present study that this reagent reacted smoothly with isoprene in glacial acetic acid to give two easily-fractionated isomers, which were shown to be 1,2- and 1,4-adducts by the reactions shown.

The non-allylic nature of the chlorine in I, its facile rearrangement to IV, and its conversion to III, left no doubt as to its structure. In establishing the structure of the 1,4-isomer, the terminal character of the chlorine and acetoxy groups was first demonstrated by conversion to the diacetate V, and thence to tiglic aldehyde.⁹ Catalytic dehalogenation of IV, followed by hydrogenation, gave isoamyl acetate, thereby establishing the exact position of the acetoxy group in IV. Although VI analyzed very poorly, the alcohol obtained from it by alcoholysis gave the correct derivatives for prenol.¹⁰ Conclusive confirmation of the structure of IV was furnished by the excellent yield of chloroacetone upon ozonolysis.

Upon extension of the reaction to the homolo-

(1) P. D. Bartlett and D. S. Tarbell, *THIS JOURNAL*, **58**, 466 (1936); G. Williams, *Trans. Far. Soc.*, **37**, 749 (1941).

(2) P. D. B. de la Mare, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, **18** (1948).

(3) A. Petrov, *J. Gen. Chem. (U. S. S. R.)*, **13**, [6] 481 (1943).

(4) C. K. Ingold and H. G. Smith, *J. Chem. Soc.*, 2752 (1931).

(5) German Patent 590,432.

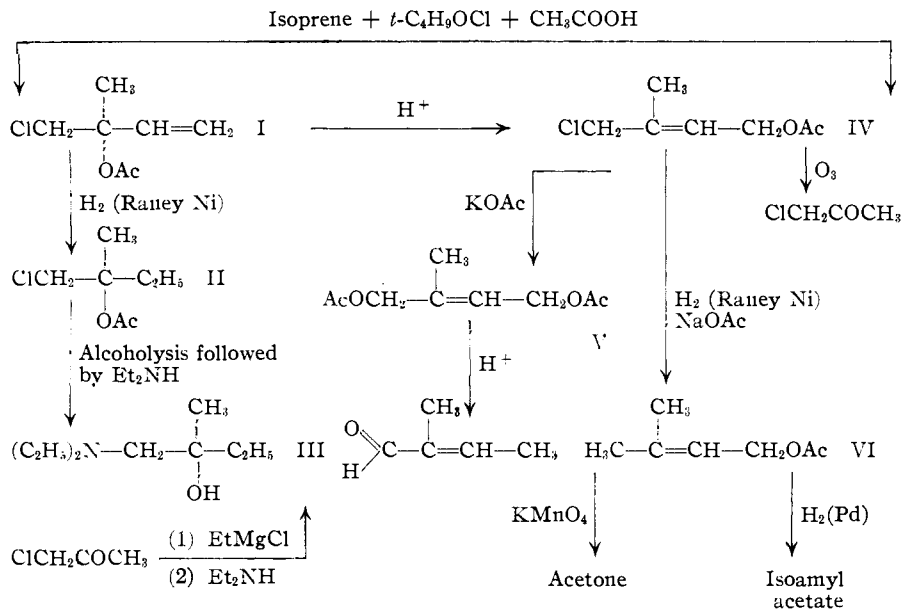
(6) W. Oroshnik, *THIS JOURNAL*, **67**, 1627 (1945).

(7) C. G. Harford, U. S. Patent 2,054,814, 2,107,789, 2,207,983.

(8) C. F. Irwin and G. F. Hennion, *THIS JOURNAL*, **63**, 858 (1941).

(9) A. F. Shepard and J. R. Johnson, *ibid.*, **64**, 4388 (1932).

(10) The name prenol has been suggested for γ,γ -dimethylallyl alcohol by E. Späth and J. Bruck to indicate its derivation from isoprene: *Ber.*, **71**, 2709 (1938).



butanol, and a product C₉H₁₇ClO, giving the same 149° isothioureapicrate, was indeed obtained. However, in addition, a small quantity of an isomeric picrate of m. p. 160° was isolated from the mother liquors of the derivatization. Its infrared spectrum indicated that it was derived from 1-chloro-2-methyl-4-*t*-butoxybutene-2, the "normal" 1,4-adduct of isoprene. This was confirmed as follows: ether fission of C₉H₁₇ClO with acetic anhydride gave *t*-butyl acetate and a

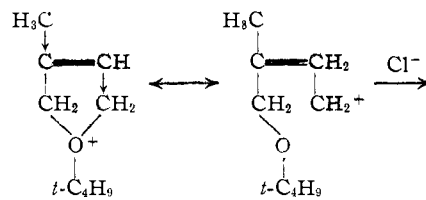
gous series of carboxylic acids, it was found that although the expected isomers were obtained, their yield increasingly diminished as one went up in the series, while a new and unexpected allylic chloride appeared in increasing proportions. First observed in small quantities in acetic acid, it actually constituted the major product in butyric and isobutyric acids. The nature of this product will be discussed below.

The hypochlorination of isoprene in methanol also gave 1,2- and 1,4-adducts. The former proved to be quite inert and could not be rearranged to any other isomeric form as in the case of the acetate I. In spite of its allylic-ether structure, it failed to react at room temperature with acetic anhydride containing anhydrous ferric chloride, although its hydrogenated analog reacted spontaneously to give the corresponding acetate. Conversion of the latter to III demonstrated the structure of the 1,2-adduct. The structure of the 1,4-isomer was shown by ozonolysis to chloroacetone and dehalogenation to methyl prenyl ether. Similar hypochlorinations in ethanol, propanol, isopropyl alcohol and *n*-butanol likewise gave the 1,2- and 1,4-isomers, in yields comparable to those obtained in methanol. In no instance was the allylic by-product obtained above with the carboxylic acids, detected. In water, however, this compound was formed in major proportion along with the two isomeric chlorohydrins. Phenol gave complex side reactions, and no well-defined products were obtained.

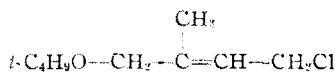
The above-mentioned allylic chloride by-product yielded an isoprene 1,4-dihalide with hot hydrobromic acid and also gave an isothioureapicrate, m. p. 149°, whose analysis showed the parent compound to have the formula C₉H₁₇ClO. Since this suggested a chloro-*t*-butoxy-adduct of isoprene, the hypochlorination was performed in *t*-

chloro-acetoxy mixture which likewise furnished two isomeric isothioureapicrates. That formed in lesser quantity was, in fact, identical with the one obtained from the acetate IV. Catalytic dehalogenation of the chloro-acetoxy mixture, followed by hydrolysis, gave a mixture of alcohols consisting chiefly of 2-methylbutene-2-ol-1, tiglyl alcohol. This established the structure of the predominant isomer in C₉H₁₇ClO as 1-*t*-butoxy-2-methyl-4-chlorobutene-2. It was subsequently found that this isomer results almost exclusively upon direct reaction of *t*-butyl hypochlorite with isoprene in the absence of solvent.

This "abnormal" addition to isoprene opens to speculation some possible competing mechanisms. The ionic mechanism shown above predicts the appearance of chlorine predominantly at carbon-1 and hence is untenable here. However, if one may assume an initial attack by the *t*-butyl hypochlorite at its oxygen atom rather than its chlorine, it is possible to formulate a cyclic oxonium salt through an electron-sharing process similar to that involved in the formation of the cyclic sulfone from isoprene and sulfur dioxide.¹¹ The vinylogous electron-repelling effect of the 2-methyl group in this cyclic ion would tend to bring about a ring-opening shift of the bonding electron-pair from carbon-4 to the oxygen, leaving the former with a residual positive charge.

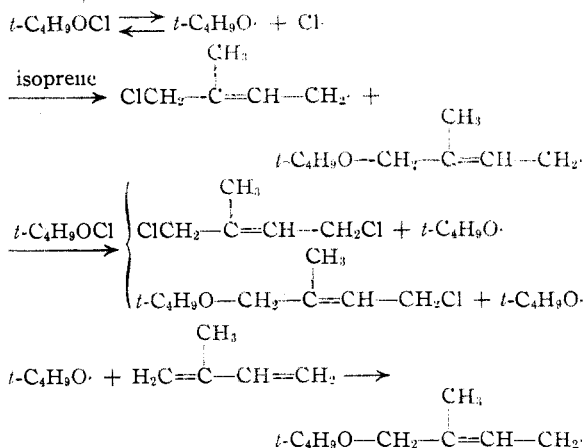


(11) C. M. Suter, "Organic Chemistry of Sulfur," John Wiley & Sons, Inc., New York, N. Y., 1944, p. 729.

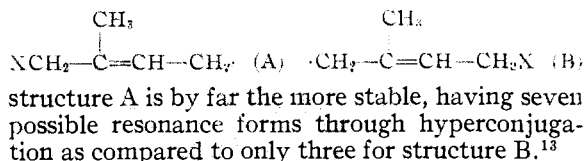


The explanation for the absence of the "abnormal" reaction in the primary and secondary alcohols would then be in terms of stronger competition for the electron pair of oxygen by the available protons; *i. e.*, solvation of the *t*-butyl hypochlorite in such solvents by hydrogen bonding.

It has been shown that reactions of "positive halogen" compounds might be explained in many cases by a free radical mechanism,¹² initiation resulting from the homopolar dissociation of the reagent. Such a mechanism might equally explain the formation of the above "abnormal" adduct.



Initial attack upon isoprene by the free radicals at carbon-1 is postulated here, for, of the two possible intermediates A and B, resulting from attack at carbon-1 or carbon-4



The free radical mechanism as shown above predicts the formation of some isoprene 1,4-dichloride. This compound was indeed identified in the foreruns, by conversion to isoprene 1,4-diisothioureapicrate.

Experimental

Hypochlorination of Isoprene.—The procedure used was essentially the same in all cases. One mole of *t*-butyl hypochlorite¹⁴ was added during two hours to a well-stirred solution of 1.25 moles of isoprene¹⁵ dissolved in six moles of the reacting solvent. The reaction mixture was then poured into a large volume of water and extracted

(12) W. A. Waters, "Chemistry of Free Radicals," Oxford University Press, London, England, 2nd edition, 1948, p. 252.

(13) A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 2nd edition, 1949, pp. 505, 529.

(14) Prepared by the method of F. D. Chattaway, and O. G. Backerberg, *J. Chem. Soc.*, 2999 (1923).

(15) The isoprene used was a commercial product obtained from Newport Industries. It was always redistilled before use and had an isoprene content of 95%.

with ether or petroleum ether. After neutralizing with aqueous bicarbonate and drying over anhydrous potassium carbonate, the solution was distilled. In the alcohol reactions troublesome labile halides were formed as impurities which decomposed during distillation. These were effectively removed before distillation by stirring the petroleum ether concentrate with anhydrous potassium carbonate at 70° for eight hours. The results are summarized in Table I. For characterization, the 1,4-adducts were converted into isothioureapicrates by the method of Brown and Campbell.¹⁶ This derivatization failed with the 1,2-adducts. The results are summarized in Table II.

Proof of the Structure of the 1,2-Adducts

Hydrogenation of the 1,2-Adducts: (a) 1-Chloro-2-methyl-2-acetoxybutane (II).—A solution of 65.0 g. (0.4 mole) of the acetate I in 200 ml. of methanol containing 30 g. of calcium carbonate and 3.0 g. of Raney nickel was shaken in a Parr apparatus under hydrogen at an initial pressure of 45 lb. Absorption ceased abruptly when 0.41 mole of hydrogen had been absorbed. The mixture was filtered and worked up with water and ether. After drying with anhydrous potassium carbonate, distillation yielded 52 g. (79%) of product at 60–63° (11 mm.), n_D^{20} 1.4312.

Anal. Calcd. for $\text{C}_7\text{H}_{13}\text{ClO}_2$: Cl, 21.54. Found: Cl, 21.66; 21.59.

(b) 1-Chloro-2-methyl-2-methoxybutane.—The methoxy analog of I was reduced in the same way as above. The yield was 86%, b. p. 67–68° (55 mm.), n_D^{20} 1.4313.

Anal. Calcd. for $\text{C}_8\text{H}_{15}\text{ClO}$: C, 52.74; H, 9.59; Cl, 25.95. Found: C, 52.98; H, 9.60; Cl, 25.88, 25.78.

The reduction product was converted into II in the following manner: 25.3 g. of the methoxy compound was dissolved in 75 ml. of acetic anhydride. On adding 0.2–0.5 g. of anhydrous ferric chloride, a mild exothermic reaction set in, the temperature rising to 50° before dropping again. The opaque red-brown solution was then warmed at 50–60° for one hour, cooled, and worked up with water and ether, the excess acetic anhydride being removed by 6–8 successive washes with 10% brine and a final wash with bicarbonate solution. Distillation yielded 16.8 g. (55%) of product, b. p. 65–68° (15 mm.), n_D^{20} 1.4308.

Anal. Calcd. for $\text{C}_7\text{H}_{13}\text{ClO}_2$: C, 51.07; H, 7.96; Cl, 21.54. Found: C, 51.44, 51.44; H, 8.02, 7.86; Cl, 21.10, 21.18.

This acetate yielded compound III after alcoholysis and diethylamination as described below.

Alcoholysis of II: 1-Chloro-2-methylbutanol-2.—A solution of 49 g. of the acetate II, prepared from I, in 250 ml. of methanol containing one drop of concentrated hydrochloric acid was slowly distilled during eight hours through a 12" Vigreux column at such a rate that 50–70 ml. of distillate was collected. After standing overnight the remaining solution was neutralized with a little anhydrous potassium carbonate, filtered and distilled, yielding 22 g. of product, b. p. 74–78° (62 mm.), n_D^{20} 1.4421.

The same chlorohydrin was also prepared as follows: to a solution of ethylmagnesium chloride prepared from 52.4 g. of magnesium in 2000 ml. of ether was added 185.6 g. of chloroacetone at –30°. After hydrolysis with dilute acid and working up in the usual manner there were obtained 186 g. of chlorohydrin b. p. 80–81° (73 mm.), n_D^{20} 1.4442.

1-Diethylamino-2-methylbutanol-2 (III).—A solution of 10.8 g. of the chlorohydrin obtained from the alcoholysis of II, 20 g. of diethylamine and 20 ml. of 95% ethanol was heated in a pressure bottle for four hours at 100°. On cooling, the dark brown solution solidified to a crystalline mush. After adding twice the volume of 20% potassium hydroxide, extracting with ether, and drying over potassium carbonate, distillation yielded 9.8 g. (70%) of amine, b. p. 72–74° (15 mm.), n_D^{20} 1.4341.

Anal. Calcd. for $\text{C}_9\text{H}_{21}\text{NO}$: N, 8.79. Found: N, 8.75, 8.54.

(16) E. L. Brown and N. Campbell, *J. Chem. Soc.*, 1691 (1937).

TABLE I
 SUMMARY OF *t*-BUTYL HYPOCHLORITE REACTIONS IN DIFFERENT SOLVENTS

Solvent	Temp. of addn., °C.	Product	Yield, %	°C.	B. p. Mm.	n_D^{20}	Carbon, %			Hydrogen, %			Chlorine, %		
							Calcd.	Found	Found	Calcd.	Found	Found	Calcd.	Found	Found
Formic acid	10-15	1, 2	28	61-63	12	1.4528	48.50	48.58	48.60	6.10	6.39	23.86	23.90	23.95	
		1, 4	32	82-85	14	1.4675		50.40 ^b	50.15		6.70	6.58		23.56	23.49
Acetic acid	10-15	1, 2	20	60-63	10	1.4457	51.70	51.76	51.90	6.82	7.01	21.81	21.96	21.90	
		1, 4	32	90-92	10	1.4654		51.98	51.88		6.83	6.87		21.72	22.00
		A.A. ^c	5	80-85	10	1.4530									
Propionic acid	25-30	1, 2	15	61-64	5	1.4456	54.39	54.97	55.00	7.42	7.65	20.07	20.22	20.45	
		1, 4	18	91-95	5	1.4652		54.43	54.12		7.71	7.59		21.06	20.94
		A.A. ^c	22	74-77	5	1.4570									
<i>n</i> -Butyric acid	25-30	1, 2	^d				56.69			7.93		18.60			
		1, 4 ^e	14	110-112	10	1.4636		56.72	56.72		7.93	8.03		19.80	19.85
		A.A. ^c	30	81-85	10	1.4538									
Isobutyric acid	25-30	1, 2	^d				56.69			7.93		18.60			
		1, 4 ^e	7	108-112	14	1.4639		55.69	55.80		8.03	7.69		20.58	20.71
		A.A. ^c	35	85-89	14	1.4532									
Water ^f	10-15	1, 2	17	71-73	55	1.4583	49.80	50.42	50.17	7.52	7.63	29.41	28.99	29.07	
		1, 4	3	68-71	1.5	1.4880		49.88	50.21		7.49	7.56		30.47	30.35
		A.A. ^c	25	73-78	5	1.4588									
Methanol ^g	0-10	1, 2	27	68-69	55	1.4432	53.53	53.40	53.46	8.24	8.45	26.34	26.27	26.44	
		1, 4	19	89-91	55	1.4595		53.39	53.46		8.47	8.45		26.41	26.27
Ethanol ^h	0-10	1, 2	27	74-77	55	1.4395	56.56	56.52	56.44	8.81	8.94	23.86	23.78	23.95	
		1, 4	18	69-71	10	1.4575		56.27	56.31		8.57	8.67		23.84	24.17
<i>n</i> -Propanol ^h	25-30	1, 2	28	62-64	15	1.4414	59.07	60.12	59.51	9.30	9.30	21.80	21.74	21.81	
		1, 4	16	84.5-87.5	13	1.4564		59.43	59.50		9.29	9.39		21.62	21.63
Isopropyl alc. ^h	25-30	1, 2	17	56-58	15	1.4379	59.07	58.84	58.84	9.30	9.51	21.80	22.38	22.37	
		1, 4	19	82-84	16	1.4542		59.37	59.18		9.37	9.47		21.93	22.03
<i>n</i> -Butanol ^h	30	1, 2	18	76-78.5	12	1.4437	61.17	61.18	61.10	9.70	9.76	20.07	20.20	19.94	
		1, 4	16	101-102.5	12	1.4574		60.96	61.37		9.80	9.88		20.22	20.26

^a The yields represented are not those of analytically pure product but with a purity of 95% or more, which could be used without further purification for usual laboratory syntheses. ^b The boiling range, and the high carbon and hydrogen and somewhat low chlorine values, strongly suggest contamination with the "abnormal" adduct A.A. The product, nevertheless, gave a 40% yield of chloroacetone upon ozonolysis. ^c This refers to the mixture of 4,1- and 1,4-chloro-*t*-butoxy adducts of isoprene. A typical analysis was C, 59.24; H, 9.08; Cl, 19.65, and repeated fractionations brought no significant change. All products A.A. gave the same derivatives. See Experimental part under "Abnormal Addition to Isoprene." ^d This isomer could not be isolated. ^e Although this product gave a reasonable analysis, it was actually highly impure as indicated by the poor yields of chloroacetone from ozonolysis and of isothiurea picrate. ^f The 1,4-chlorohydrin is unstable, darkening and becoming acidic within two days at room temperature. ^g Five grams of *p*-toluenesulfonic acid monohydrate per mole was used as a catalyst.

 TABLE II
 S-ALKYLISOTHIUREA PICRATES FROM THE 1,4-ADDUCTS

Compound ^a	M. p., °C.	Carbon, %			Hydrogen, %			Nitrogen, %		
		Calcd.	Found	Found	Calcd.	Found	Found	Calcd.	Found	Found
Acetate	132-132.5	38.98	39.28	39.19	3.97	4.19	4.00	16.24	16.54	16.40
Propionate	139.5-141.5	40.45	40.32	40.45	4.30	4.40	4.35	15.73	15.99	15.66
Butyrate	107.-107.7	41.83	41.88	42.05	4.61	4.46	4.41	15.24	15.32	15.50
Isobutyrate	115-117	41.83	42.02	41.98	4.61	4.88	4.64	15.24	15.14	15.16
Hydroxy	180.5-183	37.01	37.08	37.00	3.88	3.98	3.93	17.99	17.86	17.75
Methoxy	177-178	38.71	38.81	38.99	4.24	4.33	4.24	17.36	17.42	17.44
Ethoxy	161-162	40.28	40.46	40.53	4.59	4.71	4.68	16.78	16.70	16.70
<i>n</i> -Propoxy	135.7-137.3	41.76	42.12	41.89	4.91	4.91	5.13	16.23	16.39	16.49
Isopropoxy	138-139	41.76	41.87	41.77	4.91	4.78	4.88	16.23	16.32	16.38
<i>n</i> -Butoxy	117-119	43.14	43.53	43.24	5.20	5.32	5.24	15.72	15.97	16.02

^a The formate underwent alcoholysis during its formation and yielded the derivative of the 1,4-chlorohydrin.

A similar preparation from 25 g. of authentic 1-chloro-2-methylbutanol-2 prepared as above yielded 24.5 g. (76%) of amine, b. p. 72-74° (15 mm.), n_D^{20} 1.4342.

The amine was also prepared from the 1,2-chlorohydrin (see Table I). From 38.3 g. of the chlorohydrin, after hydrogenation followed by diethylamination in the usual manner, there was obtained 23.8 g. (47.5% over-all), b. p. 71-72° (14 mm.), n_D^{20} 1.4338.

A picrate was obtained from each of these three specimens of amine by warming 1 ml. with 1.3 g. of dry picric acid in benzene. After precipitation with isopropyl ether and recrystallization from normal butyl chloride, each

picrate melted at 88.5-89° and mixed melting points showed no depression.

Anal. Calcd. for C₁₅H₂₄N₄O₈: C, 46.39; H, 6.23; N, 14.43. Found: C, 46.61, 46.32; H, 6.28, 6.25; N, 14.32, 14.23.

Rearrangement of 1-Chloro-2-methyl-2-acetoxybutene-3 (I→IV).—The chloro compound (55.5 g.) was dissolved in 190 ml. of glacial acetic acid containing 1.25 g. of sulfuric acid and 1.25 g. of CuSO₄·H₂O, and the solution allowed to stand at room temperature for three to four days. After working up with water and ether there were obtained 8.3 g. (15%) of unchanged I, and 42.5 g. (77%)

of IV, b. p. 91–93° (10 mm.), n_D^{20} 1.4658, isothiurea picrate m. p. 130°. Compound I is recovered completely unchanged if the catalyst is absent.

Proof of the Structure of the 1,4-Adducts

1,4-Diacetoxy-2-methylbutene-2.—A mixture of 40.0 g. of 1-chloro-2-methyl-4-acetoxybutene-2 (IV), 150 ml. of glacial acetic acid and 100 g. of anhydrous potassium acetate was stirred at 110° for six hours. After working up with water and ether, distillation yielded 39 g. (81%) of the diacetate, b. p. 124–126° (15 mm.), n_D^{20} 1.4495.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.89, 57.63; H, 7.77, 7.55.

An authentic sample prepared according to the method of Shepard and Johnson⁹ from isoprene dibromide and potassium acetate had b. p. 122–125° (15 mm.) and n_D^{20} 1.4485.

The hydrolysis and rearrangement of the diacetate was accomplished by warming 0.5 g. of the compound in a mixture of 2 ml. methanol and 0.5 ml. concentrated hydrochloric acid at 45° for fifteen minutes. After neutralization with alkali, addition of semicarbazide hydrochloride produced a copious precipitate of tiglic aldehyde semicarbazone; yield 65%, m. p. 214–216° (from 50% methanol). An authentic specimen also melted at 214–216° and a mixed melting point showed no depression. The melting point of this semicarbazone apparently varies with the method of determination, Shepard and Johnson⁹ reporting 200–208° in a capillary and 232° on a Maquenne block, while Grignard and Abelmann have reported 225°. ¹⁷

Dehalogenation of the 1,4-Adducts. (a) **Dehalogenation of 1-Chloro-2-methyl-4-acetoxybutene-2 (IV → VI).**—A mixture of 80 g. of the chloro compound, 120 g. of anhydrous sodium acetate, 200 ml. of methanol and 5.0 g. of Raney nickel was shaken under hydrogen in a Parr apparatus at an initial pressure of 50 lb. After four hours 0.51 mole of hydrogen had been absorbed and the rate of hydrogen uptake markedly decreased. The mixture was worked up in the usual manner and yielded 39 g. (62%) of product, b. p. 83–88° (90 mm.), n_D^{20} 1.4274.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 63.44; H, 9.58.

Alcoholysis of the above acetate was carried out in the usual manner but omitting the acid catalyst. The alcohol was obtained in 80% yield, b. p. 79–81° (75 mm.), n_D^{20} 1.4384.

Anal. Calcd. for $C_8H_{10}O$: C, 69.72; H, 11.70. Found: C, 68.63; H, 12.06.

Repeated refractionations of both the alcohol and acetate failed to yield products that analyzed any better. Nevertheless, both, upon wet permanganate oxidation, gave considerable quantities of acetone. The alcohol yielded a *p*-bromophenylurethan, m. p. 72.5–73.5°, and a *p*-nitrobenzoate, m. p. 59.5–60.5°, neither of which depressed the melting points of the corresponding derivatives of prenil, below. The authentic prenil was prepared from isoprene hydrochloride¹⁸ as follows: one mole of the chloride and two moles of anhydrous potassium acetate were heated with stirring in 600 ml. of glacial acetic acid at 60–70° for two hours. Working up in the usual manner yielded 52.7 g. of prenil acetate, b. p. 84–87° (75 mm.), n_D^{20} 1.4294.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.34, 65.53; H, 9.35, 9.46.

The prenil obtained by methanolysis of this acetate had b. p. 80–82° (75 mm.), n_D^{20} 1.4434.

Anal. Calcd. for $C_8H_{10}O$: C, 69.72; H, 11.70. Found: C, 69.51, 69.55; H, 11.65, 11.75.

The *p*-bromophenylurethan melted at 72.5–73.5° (from ligroin).

Anal. Calcd. for $C_{12}H_{14}BrNO_2$: C, 50.72; H, 4.97; N, 4.93. Found: C, 50.87, 50.86; H, 4.79, 5.01; N, 4.90, 4.82.

(17) V. Grignard and P. Abelmann, *Bull. soc. chim.*, [4] **7**, 644 (1910).

(18) W. J. Jones and H. W. T. Cherley, *J. Chem. Soc.*, 892 (1946).

The *p*-nitrobenzoate melted at 60.5–61° (from ligroin).

Anal. Calcd. for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.55, 61.58; H, 5.46, 5.66; N, 5.85, 6.04.

Hydrogenation of VI to isoamyl acetate was carried out in ethyl acetate with 10% palladium-charcoal. From 21.0 g. of VI and 1.0 g. of catalyst there was obtained 11.3 g. of isoamyl acetate, b. p. 140–142°, n_D^{20} 1.4003. This was identified after hydrolysis, by conversion to the α -naphthylurethan m. p. 63–64.5° and the *p*-nitrophenylurethan m. p. 102–103°. Mixed melting points with authentic specimens showed no depression.

(b) **Dehalogenation of 1-chloro-2-methyl-4-methoxybutene-2** was carried out as described under (a). The yield was 68%, b. p. 102–104.5°, n_D^{20} 1.4119.

Anal. Calcd. for $C_8H_{14}O$: C, 71.95; H, 12.08. Found: C, 71.93; H, 11.71.

Wet permanganate oxidation produced considerable acetone.

Authentic methyl prenyl ether was obtained in 42% yield from isoprene hydrochloride and two equivalents of sodium methoxide in refluxing methanol: b. p. 103–105°, n_D^{20} 1.4128.

Ozonolysis.—Five grams of IV in 125 ml. of carbon tetrachloride was ozonized using the apparatus of Henne and Perilstein.¹⁹ The solution was then concentrated under vacuum at room temperature, 100 ml. of distilled water added and the mixture stirred for 2.5 hours at 85°. After cooling and saturating with sodium chloride, it was extracted eight times with 25-ml. portions of methylene dichloride, the combined extracts dried with anhydrous magnesium sulfate and concentrated *in vacuo* at room temperature. The concentrate was made up to 50 ml. with methanol and then treated with 50 ml. of a methanolic solution of 5 g. of 2,4-dinitrophenylhydrazine and 5 ml. concentrated hydrochloric acid. The solution crystallized to a slurry within a few seconds; yield 3.6 g. (43%) of chloroacetone 2,4-dinitrophenylhydrazone, m. p. 121–124°. On recrystallization from methanol it had m. p. 122–124.5°. A specimen prepared from authentic chloroacetone had m. p. 125–126° (from methanol) and showed no depression when mixed with the above sample.

By the same procedure, a 48% yield of chloroacetone was obtained from 1-chloro-2-methyl-4-methoxybutene-2.

To determine the maximum possible yield of chloroacetone obtainable by the above procedure a blank was run, in which 3 g. of pure chloroacetone was stirred at 85° for 2.5 hours in 100 ml. of 0.5% H_2O_2 . Upon working up the solution as described above, only 53% of the chloroacetone was recovered as its 2,4-dinitrophenylhydrazone.

The "Abnormal" Addition to Isoprene

(a) In *t*-Butanol.—A solution of one liter of isoprene in three liters of *t*-butanol was treated with 796 g. of *t*-butyl hypochlorite during six hours at 25°. The excess isoprene and solvent were then removed under vacuum. Subsequent fractionation yielded 441 g. of product b. p. 70–78° (6–7 mm.), n_D^{20} 1.4580. A redistilled sample boiled at 53–55° (1.2 mm.), n_D^{20} 1.4573.

Anal. Calcd. for $C_9H_{17}ClO$: C, 61.18; H, 9.70; Cl, 20.07. Found: C, 60.74, 60.53; H, 9.49, 9.47; Cl, 20.57, 20.70.

A 5-g. sample yielded 9.5 g. of isothiurea picrate. Upon fractional crystallization from 40% ethanol, this was separated into 3.7 g. of a picrate m. p. 148.5–149.5° and 2.3 g. of a more soluble picrate m. p. 159.5–161°. Although the two picrates analyzed alike, a mixture of the two melted at 132–135°. The higher melting picrate was shown by infrared analysis to belong to the homologous series of picrates derived from the 1,4-chloro-alkoxy adducts (Table II).

Anal. Calcd. for $C_{16}H_{23}N_2O_8S$: C, 43.14; H, 5.20; N, 15.72. Found: C, 43.25, 43.19; H, 5.06, 5.19; N, 15.76, 16.08.

(19) Albert L. Henne and W. L. Perilstein, *This Journal*, **65**, 2183 (1943).

A solution of 25 g. of the above chloride mixture in 75 ml. of acetic anhydride was treated with 0.1–0.2 g. of anhydrous ferric chloride. There was an immediate mild exothermic reaction lasting a few minutes. The mixture was kept below 60° by intermittent immersion in cold water, and then was maintained at 50–60° for one hour. The solution was then evaporated under vacuum to two thirds its volume, condensing the volatiles in a Dry-Ice trap. This condensate was fractionated atmospherically and yielded *t*-butyl acetate, b. p. 95–97°, n_D^{20} 1.3838, d_4^{20} 0.876. The literature gives constants for *t*-butyl acetate: b. p. 97.8°, n_D^{25} 1.3840, d_4^{25} 0.8620.²⁰

The remainder of the reaction mixture was worked up with petroleum ether and water, washing several times with the latter to remove excess acetic anhydride. Distillation gave 13.6 g. of acetate (59%), b. p. 91–96° (10 mm.), n_D^{24} 1.4633.

Anal. Calcd. for $C_7H_{11}ClO_2$: C, 51.70; H, 6.80; Cl, 21.81. Found: C, 52.03, 52.11; H, 6.82, 6.93; Cl, 20.87, 21.17.

From 5.0 g. of this chloro-acetoxy compound there was obtained 11.3 g. of crude isothioureia picrate. Fractional crystallization starting with 70% methanol and ending with 50% methanol yielded 3.8 g. of a picrate, m. p. 160–162°, and 1.6 g. of a more soluble picrate m. p. 131–132°. The latter did not depress the melting point of that from IV (see Table II). Both picrates gave the same elementary analysis.

Anal. Calcd. for $C_{14}H_{17}N_3O_9S$: C, 38.98; H, 3.97; N, 16.24. Found: C, 39.10, 39.34; H, 4.14, 3.98; N, 16.29, 16.31.

A methanolic solution of 17.0 g. of the above chloro-acetoxy mixture was catalytically dehalogenated in the same manner as described above. The crude acetate obtained was hydrolyzed with a very slight excess of methanolic sodium hydroxide at room temperature. The yield was 6.1 g. of alcohol, collected at 80–88° (100 mm.), n_D^{22} 1.4346. It yielded a *p*-nitrophenylurethan m. p. 112.5–113.5° and a *p*-bromophenylurethan m. p. 97–98°, neither of which depressed the melting points of the corresponding derivatives of tiglyl alcohol. Authentic tiglyl alcohol was prepared by the Meerwein–Ponndorf reduction of tiglic aldehyde using aluminum isopropoxide. The yield of product collected at 139–145°, n_D^{20} 1.4420, was 37%.

Anal. Calcd. for $C_9H_{10}O$: C, 69.72; H, 11.70. Found: C, 69.95, 69.86; H, 11.53, 11.62.

The *p*-nitrophenylurethan melted at 112.5–113.5° (from ligroin).

Anal. Calcd. for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.41, 57.42; H, 5.54, 5.61; N, 11.09, 11.13.

(20) J. F. Norris and G. W. Rigby, *THIS JOURNAL*, **54**, 2088 (1932).

The *p*-bromophenylurethan melted at 100.5–101.5° (from ligroin).

Anal. Calcd. for $C_{12}H_{14}BrNO_2$: C, 50.72; H, 4.97; N, 4.93. Found: C, 50.86, 50.63; H, 4.80, 4.94; N, 5.03, 5.08.

(b) **In the Absence of Solvent.**—Two moles of *t*-butyl hypochlorite were added with stirring, to one liter of isoprene at 32–34° during ninety minutes. The reaction mixture gave a negative test for acetone and for free acid. It was then distilled directly, giving 206 g. of product b. p. 57–65° (2.2 mm.). Upon refractionation there was obtained 164 g. of product, b. p. 54–55° (1.5 mm.), n_D^{23} 1.4568.

Anal. Calcd. for $C_9H_{17}ClO$: C, 61.18; H, 9.70; Cl, 20.07. Found: C, 60.68; 60.64; H, 9.86, 9.53; Cl, 20.19, 20.32.

A 10-g. sample yielded 21 g. of isothioureia picrate which upon fractional crystallization gave 16 g. of 149° picrate and only 0.8 g. of 156–158° picrate. These were identical with the corresponding salts obtained under (a).

The foreruns gave a small yield of picrate, m. p. 226–227°, which did not depress the melting point of that obtained from isoprene 1,4-dibromide (m. p. 229.5–230°). The same compound was also obtained from the foreruns from (a).

Anal. Calcd. for $C_{16}H_{20}N_4S_2O_{14}$: C, 33.73; H, 2.98; N, 20.71. Found: C, 33.89, 33.89; H, 2.96, 2.86; N, 20.65, 20.81.

All melting points were determined on a Fisher–Johns melting point block, heating at the rate of 2° per minute.

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Summary

1. Isoprene reacts with *t*-butyl hypochlorite in hydroxylic solvents to give 1,2- and 1,4-adducts.
2. Orientation of the addenda follows the same course as other electrophilic additions to isoprene.
3. As the hydroxylic nature of the solvent diminishes, it plays a progressively lesser role in the reaction, and *t*-butyl hypochlorite then apparently adds directly to isoprene. Under such conditions the orientation of the chlorine and alkoxy groups is the reverse of that in the electrophilic additions.
4. Two alternative mechanisms have been suggested to account for the “abnormal” addition.

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