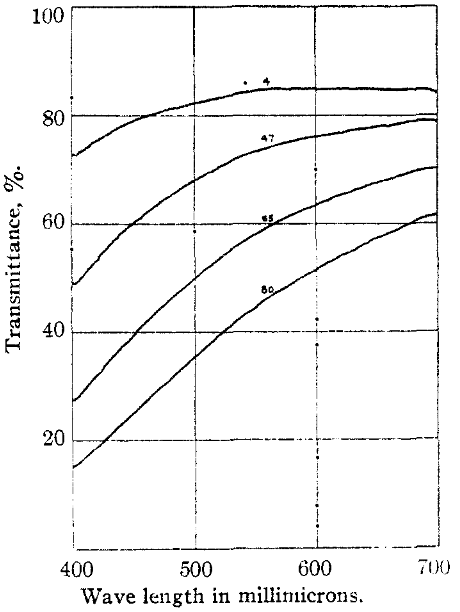

Fig. 1.—Transmittance of silicic acid gel mixtures as a function of wave length and age of sol.

four, forty-seven, sixty-five and eighty minutes after mixing, as indicated on the curve. The gel set in seventy-five minutes.

These transmittance curves are smooth, indicating no particularly strong absorption in any band. The curve of the mixture four minutes old shows the start of loss of the radiation of shorter wave length. This tendency increases with the age of the sol, until at age eighty minutes, which is five minutes after the gel has set, transmittance of radiation of 4000 Å. is only 0.15, while that of radiation 7000 Å. is 0.63 compared to a maximum of about 0.85 at the start, as shown on the four-minute curve. These results are probably due to the preferential scattering of radiation of smaller wave length. This scattering has been studied carefully by several investigators and the results reported.[6]

Summary

A study has been made of the effects of radiation upon the time of set of silicic acid gels, produced by mixing solutions of sodium silicate and acetic acid. Great care was taken that no measurable temperature change was produced by the radiation. Radiations from a Mazda lamp, a capillary mercury arc and an iron spark were used.

No significant effects of these types of radiation on the time of set were found.

A series of curves obtained with the Recording Spectrophotometer, showing the per cent. radiation transmitted by the sol are also given. The effect of age of the sol upon light transmitted is shown.

[6] Prasad, Mehta and Desai, *J. Phys. Chem.*, **36**, 1324 (1932).

SCHENECTADY, N. Y. RECEIVED NOVEMBER 8, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Diolefins from Allylic Chlorides. II

BY ALBERT L. HENNE AND HENRY H. CHANAN

We have shown[1] that two molecules of butadiene hydrochloride react with magnesium in ether to give a mixture of 1,5-diolefins, the composition of which remains the same whether the primary form of the halide, its secondary form, or the equilibrated mixture of both forms is used as the starting material. These results were in agreement with some of Young's observations[2] on allylic equilibria.

This method of synthesizing 1,5-diolefins is now extended to five allylic chlorides grouped in a variety of pairs. Allyl and methallyl chlorides which exist in only one form ($CH_2=CHCH_2Cl$ and $CH_2=C(CH_3)CH_2Cl$) were purchased. Piperylene hydrochloride which also exists in only one form ($CH_3CHClCH=CHCH_3$) was made by adding dry hydrogen chloride to commercial piperylene. Butadiene and isoprene hydrochlorides were made similarly from commercial butadiene or isoprene; they both exist in two forms, namely, $CH_3CHClCH=CH_2 \rightleftarrows CH_3CH=CHCH_2Cl$; and $(CH_3)_2C=CHCH_2Cl \rightleftarrows (CH_3)_2CClCH=CH_2$. All materials were supplied to us by a Research project of the American Petroleum Institute, directed here by Dr. C. E. Boord.

Experimentally, the condensations were carried out substantially as previously[1] described. Two different allylic chlorides were mixed in equimolecular proportion, and the mixture was added to magnesium turnings covered with dry ether. After completing the condensation and working up the products, a hydrocarbon fraction was obtained which amounted to about 35% of the quantity possible if pure allylic halides had been used and had condensed completely. It was, however, found more expedient to use the extremely impure materials obtained from a stream of hydrogen chloride through the commercial dienes and to discard from the condensation products all impurities, unreacted halides and resinified materials. From thirty to fifty moles

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[1] Henne, Chanan and Turk, THIS JOURNAL, **63**, 3474 (1941).

[2] Young, *ibid.*, **54**, 404 (1932); **58**, 104, 289, 441 (1936); **59**, 2051 2441 (1937); **60**, 847, 900 (1938).

TABLE I

CONDENSATION RESULTS OF EQUIMOLECULAR MIXTURES

Reacting chlorides	Molecular proportions and molecular percentages of condensed dienes					Total number of groups		
Allyl chloride and piperylene HCl	AA	PP	AP			A	P	
	1	4.8	15.3			17.3	24.9	
	4.7%	22.7%	72.5%					
Methallyl chloride and piperylene	MM	PP	MP			M	P	
	1	6	10			12	22	
	5.8%	35.4%	58.7%					
Butadiene HCl and piperylene HCl	B^2B^2	B^1B^2	B^1P	PP	B^2P	P	B^2	B^1
	1	13.2	21.3	22.0	29.3	94.6	44.5	34.5
	1.2%	15.2%	24.5%	25.3%	33.8%			
Allyl chloride and isoprene HCl	AI^3	I^1I^1	I^1I^3	AA	AI^1	A	I^1	I^3
	1	2.1	2.8	2.8	12.5	19.1	19.5	3.8
	4.7%	10.0%	13.2%	13.2%	58.9%			
Methallyl chloride and isoprene HCl	I^1I^3	I^1I^1	MI^3	MM	MI^1	M	I^1	I^3
	1	1.2	2.1	8.6	11.7	31	14.9	3.1
	4.0%	5.0%	8.5%	35.0%	47.5%			
Butadiene HCl and isoprene HCl	B^2B^2	I^1I^1	I^1I^3	B^1B^1	B^1I^3	B^1	B^2	
	1	5.6	8.2	11.3	13.1	92.1	89.3	
	0.65%	3.6%	5.3%	7.2%	8.4%			
	B^1B^2	B^1I^1	B^2I^1			I^1	I^3	
	28.2	28.2	59.1			106.7	21.3	
	18.3%	18.3%	38.3%					

of each halide was used to secure a quantity of hydrocarbons ample for adequate separation. Before subjecting them to repeated distillations through a 30-plate, helix-packed, total reflux-partial take-off, adiabatic column, the hydrocarbons were treated with sodium in liquid ammonia[3] until the disappearance of the Beilstein flame test indicated that they were free of halides. For physical measurements, only the centers of the distillation fractions were used. In the following list of results, the percentages of the various compounds refer only to the distilled product.

Experimental Results

Let each chloride be designated by its initial with a superscript (when needed) to denote a primary, secondary or tertiary isomer when two allylic isomers are possible. Thus A, M and P will designate allyl chloride, methallyl chloride and piperylene hydrochloride, while B^1 or B^2 will designate the two forms of butadiene hydrochloride, and I^1 or I^3 those of isoprene hydrochloride.

The results of the condensations are represented in Table I, where the relative amounts of the dienes obtained by condensation are given on a molar basis.

Quite a number of possible combinations were absent. In line with our previous observation[1] condensations between different molecules predominated over condensations between two identical molecules or two forms of the same molecule. In the fourth, fifth and sixth pairs, the ratio of the total number of I^1 groups to the total number of I^3 groups was consistently close to $I^1:I^3 = 5:1$. For the butadiene group, the ratio $B^1:B^2$ proved to be about 4:5 in the third pair, and about 1:1 in the sixth pair. In our preceding paper it had been found close to unity in the condensation of butadiene hydrochloride on itself, while it was about 5:3 in the condensation of butadiene hydrochloride with allyl chloride. The experimental data do not permit more precise generalizations.

The observed physical properties of the hydrocarbons, and the analyses of the new compounds, together with the symbols representing the diolefins appear in Table II.

Identifications

Most of the diolefins were new compounds. They were first analyzed as reported in the table, then hydrogenated to the corresponding paraffins to establish their carbon skeleton. Most of these paraffins were known. Where the paraffins were new compounds, it proved possible to show that their physical constants were measurably different from possible alternate formulas. Finally the position of the double bonds was determined by ozone oxidation, using procedures previously described.[4,5] In the following paragraphs, the observed data refer to the freezing point, the corrected boiling point at 760 mm, the density d^{20}_4 and the refractive index n^{20}_D, in that order.

B reduced to 4-methylheptane,[6] glass, 117.6°, 0.7042, 1.3980. Ozonization gave formaldehyde, acetic acid and methylsuccinic acid, m. p. 110–

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(3) Lebeau, *Bull. soc. chim.*, (3) **33**, 1089 (1905). Practical details will be published soon.

(4) Henne and Hill, *ibid.*, **65**, 752 (1943).

(5) Henne and Perilstein, *ibid.*, **65**, 2183 (1943).

(6) In agreement with information from the American Petroleum Institute.

TABLE II

PHYSICAL CONSTANTS AND ANALYSES

	Name	Symbol	F. p., °C.	B. p., cor., °C.	d^{20}_4	$n^{20}D$	% C Calcd.	% C Found	% H Calcd.	% H Found	Other refs.
A	$CH_2=CHCH_2CH_2CH=CH_2$	AA			Known[1]						
B	$CH_2=CHCH_2CH(CH_3)CH=CHCH_3$	AP	Glass	110.3	0.7282	1.4231					*a, b*
C	$CH_3CH=CHCH(CH_3)CH(CH_3)CH=CHCH_3$	PP	− 64.8	153.3	.7662	1.4392					*b*
D	$CH_2=C(CH_3)CH_2CH_2C(CH_3)=CH_2$	MM			Known[1]						
E	$CH_2C(CH_3)CH_2CH(CH_3)CH=CHCH_3$	MP	Glass	132.1	0.7457	1.4312	87.0	87.0	13.0	13.2	
F	$CH_2=CHCH(CH_3)CH(CH_3)CH=CH_2$	B^1B^1			Known[1]						
G	$CH_2=CHCH(CH_3)CH_2CH=CHCH_3$	B^1B^2			Known[1]						
H	$CH_2=CHCH(CH_3)CH(CH_3)CH=CHCH_3$	B^2P	Glass	129.8	0.7462	1.4312	87.0	87.0	13.0	12.9	*a*
I	$CH_2=CHC(CH_3)_2CH_2CH=CH_2$	AI^3	Glass	101.6	.7249	1.4160	87.2	87.0	12.8	13.1	
J	$CH_2=CHCH_2CH_2CH=C(CH_3)CH_3$	AI^1	Glass	119.1	.7406	1.4316	87.2	87.0	12.8	13.0	
K	$CH_2=CHC(CH_3)_2CH_2CH=C(CH_3)CH_3$	I^1I^3	Glass	149.7	.7657	1.4391	86.9	86.9	13.1	13.0	
L	$CH_3C(CH_3)=CHCH_2CH_2CH=C(CH_3)CH_3$	I^1I^1	−74.4	168.6	.7755	1.4478	86.9	87.0	13.1	13.2	*c, d*
M	$CH_2=C(CH_3)CH_2C(CH_3)_2CH=CH_2$	MI^3	Glass	126.3	.7500	1.4288	87.0	86.8	13.0	13.2	
N	$CH_2=C(CH_3)CH_2CH_2CH=C(CH_3)CH_3$	MI^1	−102.7	141.9	.7560	1.4389	87.0	87.1	13.0	13.1	*e, f*
O	$CH_3CH=CHCH_2CH_2CH=CHCH_3$	B^1B^1			Known[1]						
P	$CH_2=CHCH(CH_3)CH_2CH=C(CH_3)CH_3$	B^2I^1	Glass	134.6	0.7491	1.4330	87.0	87.2	13.0	13.0	
Q	$CH_3C(CH_3)=CHCH_2CH_2CH=CHCH_3$	B^1I^1	Not isolated from K				Separated as paraffin				
R	$CH_2=CHC(CH_3)_2CH_2CH=CHCH_3$	B^1I^3	Not isolated from O				Separated as paraffin				
S	$CH_3CH_2CH_2CH(CH_3)CH(CH_3)CH_2CH_2CH_3$		Glass	162.4	0.7446	1.4178					
T	$CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_2CH_3$		Glass	140.1	.7314	1.4108					
U	$CH_3CH_2C(CH_3)_2CH_2CH_2CH(CH_3)CH_3$		Glass	152.8	.7336	1.4123					

[a] Slotterbeck, Ph.D. Dissertation. O. S. U. (1936). [b] Mulliken, Wakeman and Gerry, THIS JOURNAL, **57**, 1605 (1935). [c] Kresterisky, *J. Russ. Phys.-Chem. Soc.*, **46**, 904 (1914). [d] Petrov, *J. Gen. Chem.* (U. S. S. R.), **9, 2129** (1939). [e] Harries and Weil, *Ber.*, **37**, 846 (1904). [f] Escourrou, *Bull. soc. chim.*, [4] **39,** 1249 (1926).

111°. **C** reduced to a new paraffin (**S** in table) measurably different from the possible known isomers. Ozonization gave acetaldehyde, acetic acid and a dicarboxylic acid m. p. 178–190° with a molecular weight of 147.4. This acid was regarded as a mixture of *dl*- and α,β-dimethylsuccinic acid. The pure *meso*-acid is said to melt[7] at 198° and 208° with decomposition, while the *dl*-mixture melts[7] at 127°; they can be separated by treatment with a benzene–ether mixture, in which the *dl*-form is more soluble than the *meso*-form. This treatment was applied to the dicarboxylic acid, and raised the m. p. to 188–189.5°. Further purification was deemed not to be indispensable, in view of the fact that the isomeric diacids melt much lower, *i. e.*, ethylsuccinic acid at 100°, and α,α-dimethylsuccinic at 141°. **E** reduced to 2,4-dimethylheptane,[8] glass, 133.1°, 0.7153, 1.4031. Ozonization gave formaldehyde, acetic acid and a keto-acid whose semicarbazone had m. p. 178° and analyzed correctly for $C_7H_{13}N_3O_3$ (calcd. C, 44.9; H, 7.0; N, 22.4. Found: C, 44.9; H, 7.0; N, 22.3). The keto acid was interpreted as being α-methyl-γ-ketovaleric acid, whose semicarbazone is said to melt[9] at 191° and also at 181°. **H** reduced to a new paraffin (**T** in table) measurably different from the known isomers. Ozonization gave formaldehyde, acetic acid and α,β-dimethylsuccinic acid m. p. 190° (*cf.* compound **C**) **I** reduced to 3,3-dimethylhexane,[6] glass, 112.2°, 0.7096, 1.4000. Ozonization gave formaldehyde and α,α-dimethylsuccinic acid m. p. 139°. **J** reduced to 2-methylheptane.[6] −109.6°, 117.6°, 0.6978, 1.3950. Ozonization gave formaldehyde, acetone with a 2,4-dinitrophenylhydrazone m. p. 125° and succinic acid m. p. 186°. **K** reduced to a new paraffin (**U** in table) measurably different from the known possible isomers. Ozonization gave formaldehyde and α,α-dimethylsuccinic acid m. p. 141°. **L** reduced to 2,7-dimethyloctane,[10] −50.7°; 160.0°; 0.7250; 1,4087. Ozonization gave acetone detected by the nitroprusside test, and succinic acid m. 187°. **M** reduced to 2,4,4-trimethylhexane,[11] −117.7°, 130.8°, 0.7231, 1.4068. Ozonization gave formaldehyde and α,α-dimethyl-γ-ketovaleric acid, with a semicarbazone, m. p. 196°. **N** reduced to 2,6-dimethylheptane,[12] −103.6°, 135.2°, 0.7102, 1.4009. Ozonization gave formaldehyde, acetone (color test) and levulinic acid with a semicarbazone m. p. 184.5° (calcd., N, 24.2. Found: N, 23.9). **P** reduced to 2.5-dimethylheptane,[13] glass, 136.2°, 0.7175, 1.4042. Ozonization gave formaldehyde, acetone (color test) and methylsuccinic acid, m. 110°. **Q** could not be isolated from **K**. The mixture was hydrogenated and the paraffins were separated. The paraffin ratio was taken to represent the diolefin ratio in the mixture. **R** could not be isolated from **O**. This ratio was computed from the relative quantities of paraffins, after hydrogenation.

Summary

Five allylic chlorides have been condensed in six different pairs to give a series of 1,5-diolefins, which were purified sufficiently to permit the listing of their physical properties and the determination of their relative abundance.

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(7) Heilbron, "Dictionary of Organic Compounds."

(8) Richards and Shipley, THIS JOURNAL, **38**, 996 (1916).

(9) Béhal, *Bull. soc. chim.*, [3] **25**, 245 (1904); also Baker and Laufer, *J. Chem. Soc.*, 1312 (1937).

(10) Calingaert, THIS JOURNAL, **58**, 636 (1936).

(11) Mosher, Ph.D. Dissertation, Pennsylvania State College, 1940.

(12) White, *J. Research Natl. Bur. Standards*, **22**, 317 (1939).

(13) Clarke and Beggs, THIS JOURNAL, **34**, 54 (1912).