cis- and *trans*-1-Halobutadienes and Their Relation to Diene Synthesis

1960

SovietRxiv

Abstract

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Chemistry

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cis- and *trans*-1-Halobutadienes and Their Relation to Diene Synthesis

(Presented by Academician B. A. Kazanskii, January 8, 1960)

In a number of papers ($^{1-4}$) it was reported that 1-chlorobutadiene-1,3 does not enter into diene synthesis. This behavior was explained by the stabilizing influence of the chlorine atom at C_1 in the intermediate carbonium system (I), which, because of this, is incapable of ring closure (^{5}).

(I) (II) (IIa) (III) (IIIa) (IV)

However, the ability of 1-substituted butadienes to undergo diene-synthesis reactions also depends on their geometrical isomerism. It is known that the *cis*-isomers (II, $R = CH_3$, C_6H_5, CN etc.), whose structure hinders their conversion into the cisoid conformation (IIa), do not enter into this addition reaction, whereas the *trans*-dienes (III), for which facile conversion into the cisoid conformation (IIIa) required for diene synthesis may take place, give normal adducts in good yield ($^{6-11}$). From the fact that 1-chloro-2-methyl- (^{12,13}), 1-chloro-3-methyl- (^{14}), and 1,4-dichlorobutadienes (^{15}) react readily with maleic anhydride, it must likewise be concluded that these dienes are *trans*-isomers. Until now nothing has been known about the geometrical isomerism of 1-halobutadienes, and it could only be assumed that their *trans*-isomers (III, $R = \mathrm{Cl}$, Br) should enter into the diene-synthesis reaction, whereas the *cis*-isomers (II, $R = \mathrm{Cl}$, Br) would not be capable of this reaction.

We have established that 1-chlorobutadiene, obtained by dehydrochlorination of 1,4-dichlorobutene-2 (^{2,3,16}), is a mixture of *cis*- and *trans*-isomers in a ratio of approximately 9 : 1, which cannot be separated on a column at 25 theoretical plates. On interaction of this mixture with maleic anhydride (50–55°, 12 hr), a normal diene-synthesis product is formed in up to 10% yield; its structure was proved by dehydrogenation to phthalic anhydride. This fact undoubtedly shows that the initial mixture contains about 10% *trans*-1-chlorobutadiene, which forms the adduct. The *cis*-isomer remaining after isolation of the adduct, in accordance with its configuration, is in fact incapable of entering into diene synthesis. However, in the presence of iodine, *cis*-1-chlorobutadiene is converted comparatively readily into the *trans*-isomer, giving an equilibrium mixture of *cis*- and *trans*-forms, similarly to what occurs in the case of *cis*-piperylene (^{17}). As a result, when a mixture of *cis*-1-chlorobutadiene with maleic anhydride is heated in the presence of iodine, gradual formation of the adduct corresponding to the *trans*-isomer takes place, the yield of which may reach 80%. Such conversion of *cis*-1-chlorobutadiene into the *trans*-form also occurs at room temperature, but the reaction rate is then low. Were ⋯

the Raman spectra of cis- and mixtures of cis- and trans-isomers of 1-chlorobutadiene-1,3 were recorded and studied ([18]). Similarly, 1-bromobutadiene-1,3, obtained by dehydrobromination of 1,4-dibromobutene-2 ([3,19]), is a mixture of cis- and trans-isomers ($II + III,\ R = \mathrm{Br}$) in a ratio of approximately 14 : 1, which was proved by condensation of the trans-isomer with maleic anhydride and isolation of the cis-isomer. Under the influence of iodine, cis-1-bromobutadiene is also isomerized to the trans-form, which gives an adduct with maleic anhydride that, already under the experimental conditions (∼ 70°, 100 hr), splits off hydrogen bromide and adds a new molecule of maleic anhydride, giving a bis-anhydride of composition $C_{12}H_8O_6$.

Experimental Part

1-Chlorobutadiene-1,3 ($II{+}III,\ R = \mathrm{Cl}$), obtained from 1,4-dichlorobutene, had the following constants: b.p. 66—67° at 760 mm, n_D^{20} 1.4712; d_4^{20} 0.9537. MR found 25.93. $C_4H_5Cl,\ F_2$, calculated 24.61. $\lambda = 232,\ \varepsilon = 17400$.

Anhydride of 3-chloro-Δ^4-cyclohexene-1,2-dicarboxylic acid ($IV,\ R = \mathrm{Cl}$). A mixture of 88.5 g (1 mole) of 1-chlorobutadiene and 33 g (0.3 mole) of maleic anhydride (+ hydroquinone) was left overnight at room temperature and then heated for 12 hr at 50—55°. The crystalline reaction product that separated was filtered off; 18.3 g (∼ 10%) of anhydride (IV) was obtained, which after recrystallization from a mixture of benzene with acetone had m.p. 130—131°.

Found %: C 51.42; H 3.78; Cl 19.24

$C_8H_7O_3Cl$. Calculated %: C 51.48; H 3.78; Cl 19.01.

Fusion of the adduct with sulfur (∼ 230°) until the evolution of hydrogen sulfide ceased led to the formation of phthalic anhydride with m.p. 130—131°, identical with an authentic sample.

cis-1-Chlorobutadiene-1,3 ($II,\ R = \mathrm{Cl}$). To the diene remaining after removal of the adduct, 5 g of maleic anhydride was added and the solution was heated at 50—55° for another 12 hr. No further formation of adduct was observed. The unreacted cis-1-chlorobutadiene was distilled on a column of 25 theoretical plates. 68 g (∼ 78%) of pure cis-diene (II) was obtained; b.p. 66.8—67°, n_D^{20} 1.4703; d_4^{20} 0.9553. MR found 25.86. $C_4H_5Cl,\ F_2$, calculated 24.61; $\lambda = 232,\ \varepsilon = 17400$.

Found %: C 54.31; H 5.74; Cl 40.05

C_4H_5Cl. Calculated %: C 54.26; H 5.70; Cl 40.05.

Isomerization of cis-1-chlorobutadiene (II) to the trans-isomer (III). 50 g of the pure cis-isomer, 1 g of iodine, and 50 ml of dry toluene were heated in an ampoule at 100° for 20 hr. After removal of the iodine with sodium thiosulfate, the mixture of isomers was distilled on a column (25 theoretical plates):

	b.p., °C	Amount, g	n_D^{20}	d_4^{20}
1st fraction	66.8–67	20.0	1.4703	–
2nd fraction	67.0–67.2	7.5	1.4720	0.9608
3rd fraction	67.2–67.5	4.2	1.4724	0.9608
4th fraction	67.5	2.4	1.4724	0.9608

To 5 ml of dry toluene were added 3.7 g of the 3rd fraction of the diene and 1 g of maleic anhydride (+ hydroquinone), after which the mixture was heated in an ampoule at 60° for 6 hr. 0.7 g of crystalline adduct (IV) was obtained, identical with that described above, with m.p. 130°.

Condensation of a mixture of cis- and trans-1-chlorobutadienes with maleic anhydride in the presence of iodine.
a) To a solution of 3.7 g of the original mixture of isomers of 1-chlorobutadiene and 4 g of maleic anhydride in 20 ml of benzene, 2% iodine and a small amount of

amount of hydroquinone, and the mixture was heated for 24 hours on a boiling water bath in a sealed ampoule. 5 g of adduct (IV) with m.p. 130° was obtained.

b) 1.7 g (0.02 mole) of 1-chlorobutadiene, 1.9 g (0.02 mole) of maleic anhydride, 2% iodine, and traces of hydroquinone were added to 10 ml of dry benzene, and this mixture was left in a sealed ampoule at room temperature for 6 months. The crystalline adduct that separated was isolated; 2.8 g (80%) of the above-described adduct (IV), m.p. 130.5°, was obtained.

1-Bromobutadiene-1,3 (II + III, R = –Br), obtained from 1,4-dibromobutene-2 (m.p. 53°), had the following constants: b.p. 47–48.2° at 161 mm, n_D^{20} 1.5112, d_4^{20} 1.3777. MR_D found 28.78. For C_4H_5Br, F_2, calculated 27.5.

Anhydride of 3-bromo-Δ^4-cyclohexene-1,2-dicarboxylic acid (IV, R = Br). A mixture of 56 g of the starting 1-bromobutadiene (II + III) and 5 g of maleic anhydride in the presence of hydroquinone was left at 25–30° for 5 days. The crystalline reaction product that separated was isolated; 7 g (~7%) of adduct (IV), with m.p. 107–109° with decomposition (from benzene), was obtained.

Found, %: C 41.62; H 3.09; Br 34.16
$C_8H_7O_3Br$. Calculated, %: C 41.58; H 3.05; Br 34.16.

Fusion of this adduct with sulfur at 230—235° until evolution of hydrogen sulfide ceased led to phthalic anhydride with m.p. 130°, which gave no depression with an authentic sample.

cis-1-Bromobutadiene-1,3 (II, R = Br). The liquid mixture remaining after separation of the adduct was distilled with a dephlegmator, and after repeated distillation over sodium pure cis-1-bromobutadiene-1,3 (II) was obtained, with b.p. 47—48° at 161 mm; n_D^{20} 1.5100, d_4^{20} 1.3878. MR_D found 28.68; for C_4H_5Br, F calculated 27.50.

Found, %: C 36.32; H 3.84; Br 59.36
C_4H_5Br. Calculated, %: C 36.12; H 3.78; Br 60.09

Condensation of a mixture of cis- and trans-1-bromobutadienes with maleic anhydride in the presence of iodine. A mixture of 22 g (0.17 mole) of the starting 1-bromobutadiene, 18.6 g (0.17 mole) of maleic anhydride, and 0.4 g of iodine in 50 ml of dry benzene was heated in a sealed ampoule for 100 hours at 70°. 8.3 g of crystalline (crude) product was obtained, yield 37%. The substance is difficultly soluble in acetone and acetic anhydride and is a bis-anhydride of composition $C_{12}H_8O_6$, with m.p. 364°.

Found, %: C 58.20; H 3.46
$C_{12}H_8O_6$. Calculated, %: C 58.07; H 3.25

It is hydrolyzed by alkali as the anhydride of a tetrabasic acid.

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Received
2 I 1960

CITED LITERATURE

1. D. D. Coffman, W. H. Carothers, *J. Am. Chem. Soc.*, **55**, 2040 (1933).
2. A. A. Petrov, N. P. Sopov, *ZhOKh*, **15**, 981 (1945).
3. A. L. Klebanskii, R. M. Sorokina, Z. Ya. Khavin, *ZhOKh*, **17**, 235 (1947).
4. V. S. Miklashevskaya, A. A. Petrov, *ZhOKh*, **28**, 1125 (1958).
5. M. J. S. Dewar, *The Electronic Theory of Organic Chemistry*, Oxford, 1950, p. 152.
6. K. Alder, *Ann.*, **571**, 157 (1951).

7. K. Alder, M. Schumacher, in *Fortschritte der Chemie Organischer Naturstoffe*, **10**, 1 (1953).
8. D. Craig, *J. Am. Chem. Soc.*, **72**, 1678 (1950).
9. H. R. Snyder, J. M. Stewart, R. L. Myers, *J. Am. Chem. Soc.*, **71**, 1055 (1949).
10. O. Grummitt, E. Christoph, *J. Am. Chem. Soc.*, **71**, 4157 (1949); **73**, 3479 (1951).
11. H. R. Snyder, G. Poos, *J. Am. Chem. Soc.*, **72**, 4104 (1950).
12. D. V. Tishchenko, *ZhOKh*, **6**, 1131 (1936).
13. W. J. Jones, H. G. Williams, *J. Chem. Soc.*, **1939**, 829.
14. T. A. Favorskaya, *ZhOKh*, **9**, 386 (1939).
15. R. Criege, W. H. Orauf, W. D. Schellenberg, *Ber.*, **86**, 125 (1953).
16. J. E. Muskat, H. E. Northrup, *J. Am. Chem. Soc.*, **52**, 4043 (1931); Am. pat. 2038593 (1936); *Chem. Abstr.*, **30**, 3912 (1936); *Chem. Zbl.*, **2**, 3358 (1936).
17. R. L. Frank, R. D. Emmick, R. S. Johnson, *J. Am. Chem. Soc.*, **69**, 2313 (1947).
18. M. I. Shatenshtein, A. S. Onishchenko et al., *DAN*, **132**, No. 3 (1960).
19. A. A. Petrov, *ZhOKh*, **10**, 1887 (1940).

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