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The Synthesis of γ-3,4,5,6-Tetrachlorocyclohexene (γ-BTC) by Means of a Diels-Alder Reaction

Kiichi SHINODA
Nishiki Research Laboratory of Kureha Chemical Industry Co., Ltd.,
Nishiki-machi, Iwaki-shi, Fukushima 974

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γ-3,4,5,6-Tetrachlorocyclohexene (γ-BTC) was synthesized in a yield of 14—30% by a Diels-Alder reaction between *trans,trans*-1,4-dichloro-1,3-butadiene and *trans*-dichloroethylene. The *s-cis* requirement and stereochemical relationships consistent with Alder's rule are shown. Antioxidants are effective in this reaction.

Orloff *et al.*[1,2] isolated 3,4,5,6-tetrachlorocyclohexene (benzene tetrachloride, BTC) isomers and clarified their conformations and their relationships with 1,2,3,4,5,6-hexachlorocyclohexane (BHC) isomers. By Orloff's method, however, the yield of γ-BTC is very low and the isolation procedure is very laborious. Kurihara *et al.*[3] obtained γ-BTC from α-BTC, which is the main product in Orloff's method, through several routes.

In this report, the synthesis of γ-BTC by a Diels-Alder reaction between 1,4-dichloro-1,3-butadiene (I) and 1,2-dichloroethylene (II) will be described.

Results and Discussion

Each isomer of 1,4-dichloro-1,3-butadiene, which had been prepared[4-6] by the dechlorination of 1,3,4,4-tetrachlorobutene, was reacted in a small bomb with *trans*-dichloroethylene (IIa), under the conditions below: temperature, 150 °C; time, 30 hr; molar ratio, I/IIa=1/20.

The results are shown in Table 1. γ-BTC was obtained in the reactions of *trans,trans*-I (Ia), *trans,cis*-I (Ib) and an isomer mixture of I with IIa. None of the BTC could be obtained by the reaction of *cis,cis*-I (Ic) with IIa. γ-BTC was identified by IR, its mp (87—88 °C, Orloff *et al.*,[2] mp 88.2—88.8 °C), and by photochlorination to BHC. As has already been clarified by Orloff *et al.*,[2] γ-BTC formed α, γ, and δ-BHC upon photochlorination.

Stereochemical Relationships. It has been illustrated in many cases that, in Diels-Alder reactions, dienes

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[1] G. Calingeart, M. E. Griffing, E. R. Kerr, A. J. Kolka, and H. D. Orloff, *J. Amer. Chem. Soc.*, **73**, 5224 (1951).

[2] H. D. Orloff, A. J. Kolka, G. Calingaert, M. E. Griffing, and E. R. Kerr, *ibid.*, **75**, 4243 (1953).

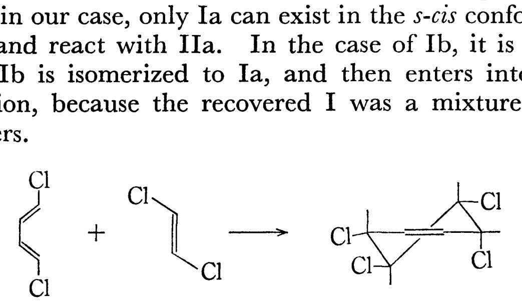
[3] N. Kurihara, Y. Sanemitsu, T. Kimura, M. Kobayashi, and M. Nakajima, *Agr. Biol. Chem. Jap.*, **34**, 784 (1970).

[4] R. Criegee, W. Hörauf, and W. D. Schellenberg, *Chem. Ber.*, **86**, 126 (1953).

[5] H. G. Viehe and E. Franchimont, *ibid.*, **97**, 602 (1964).

[6] P. D. Batlett and G. E. H. Wallbillich, *J. Amer. Chem. Soc.*, **91**, 409 (1969).

must take the cisoid conformation.[7] It is probable that, in our case, only Ia can exist in the *s-cis* conformation and react with IIa. In the case of Ib, it is clear that Ib is isomerized to Ia, and then enters into the reaction, because the recovered I was a mixture of I isomers.



Ia IIa γ-BTC

According to Alder's rule,[7,8] the chlorine atoms at the 4,5-position of BTC produced from Ia and IIa must be *trans* (aa or ee) to each other, while those of 3,6 must be *cis* (ae). Therefore, the BTC have to be γ ($\overline{\overline{\text{HH}}}$ aeee$\rightleftarrows\overline{\overline{\text{HH}}}$ eaaa). Our results shown in Table 1 are consistent with Alder's rule.

Table 1. Diels-Alder reaction of 1,4-dichloro-1,3-butadiene isomers (I) with *trans*-dichloroethylene (IIa)
Temp. 150 °C, 30 hr, Molar ratio I/IIa = 1/20

I isomer	Product	Yield %	Recovered I			
			%	Ia	Ib	Ic
trans, trans(Ia)[a]	γ-BTC	14.3	36.3	24.9	48.8	26.3
trans,cis (Ib)[a]	γ-BTC	0.03	41.6	4.9	90.0	5.1
cis,cis (Ic)[a]	no BTC	0			4.2	95.8
Isomer mixture[b] Ia:Ib:Ic= 18.1:46.4:25.5	γ-BTC	16.8[c]	58.5	13.3	48.2	38.3

a) The amounts used were Ia 1.12 g, Ib 1.23 g, and Ic 1.23 g, respectively.
b) The amount used was 4.1 g. Molar ratio I/IIa was 1/5.
c) The yield is based on Ia charged initially.

Effects of Antioxidants and Temperature. The reaction mixture, after the excess II and the unreacted I had been removed, was generally reddish-brown in color. This colored material seemed to be the decomposition product of I. In order to suppress the decomposition of I, the effect of the antioxidants was examined. The results are shown in Table 2. The effect of the antioxidants was obvious; the effective ones were *p*-phenylenediamine and *p*-aminophenol.

Table 2. Diels-Alder reaction of *trans,trans*-1,4-dichloro-1,3-butadiene (Ia) with *trans*-dichloroethylene (IIa). Effect of antioxidants and temperature
Molar ratio Ia/IIa = 1/20

Antioxidants[a]	Atmosphere	Temp. (°C)	Time (hr)	γ-BTC Yield (%)
Hydroquinone	air	150	30	19.3
1,3,5-Trinitrobenzene	air	150	30	19.1
p-Phenylenediamine	air	150	30	31.1
None	N_2	150	30	18.3
p-Aminophenol	N_2	150	30	30.9
None	N_2	200	14	3.2
p-Phenylenediamine	N_2	200	14	Trace
Lauryl disulfide	N_2	200	14	15.7

a) The amounts used were 1.0 mol % *vs.* Ia.

Effect of Friedel-Crafts Catalysts. There have been reports[9,10] that, in some cases, Friedel-Crafts-type metal halides function as catalysts in Diels-Alder reactions. We tried several metal halides—anhydrous $AlCl_3$, $FeCl_3$, $TiCl_4$, and $SnCl_4$, but no BTC was obtained because of the decomposition-promoting property of metal halides.

Experimental

All the melting points are uncorrected. The IR spectra were recorded with a Nihonbunko DS-301 or a Shimadzu IR-27 spectrophotometer.

1,3,4,4-Tetrachlorobutene (IV).[11,12] *cis*-Dichloroethylene (IIb) (700 g) was refluxed for 80 hr, with 1.0 g of benzoyl peroxide being added every 5 hr. The reaction mixture was then subjected to distillation at reduced pressure, and a fraction boiling at 79—85 °C/15 mmHg was collected. The yield was 28.9%, based on the IIb used.

Similarly, IV was prepared from IIa. The yield was 5.3%. The IV obtained consisted of 39% *trans*- and 61% *cis*-isomer.

Dechlorination of IV. Criegee's procedure[4] was followed, and a fraction boiling at 50—55 °C/50 mmHg was collected. The yield was 60—80%. The isomer ratio (Ia: Ib: Ic) was measured by glc (Shimadzu polyethylene glycol 6000). In general, the Ia: Ib: Ic ratio was 15: 50: 35.

Separation of 1,4-Dichloro-1,3-butadiene Isomers (Ia, Ib, and Ic). The separation of isomers was carried out by preparative glc; apparatus, Shimadzu GC-10A, using polyethylene glycol.

Ia, purified by sublimation at reduced pressure, has a mp of 36—37 °C (37—38 °C,[4] 38—39.6 °C[6]). Ib is a liquid (bp 53.0—55.0 °C/50 mmHg). Ic is also a liquid (bp 48.0—48.5 °C/50 mmHg). From 54.9 g of a mixture of I, pure Ia (1.5 g (after sublimation)), Ib (10.9 g), and Ic (8.4 g (after distillation)) were obtained.

In order to obtain only pure Ia from the isomer mixture, the mixture was cooled with dry ice–methanol, partially frozen, and then filtered under cooling with dry ice. The solid collected was purified by sublimation under reduced pressure. This Ia was pure enough for the reaction.

Diels-Alder Reaction between I and IIa. Usually IIa (19.4 g, 0.20 mol) was weighed in a 50 ml autoclave, and then the I isomer (1.23 g, 0.01 mol) was added, the solution was mixed well, and the autoclave was sealed. Then, the autoclave was placed in an oil bath kept at 150 or 200 °C. After the reaction, the excess IIa and unreacted I were removed by distillation under reduced pressure, first at about 100 mmHg and then 15 mmHg. The residue, usually a reddish brown solid with a little oily matter, was subjected to column chromatography. The column chromatography was carried out as follows: absorbent, activated alumina (Kanto Chemical, for chromatography); solvent, methanol or *n*-hexane; column dia., 15 mm; height of alumina layer, 50 mm. About 100 ml of the elute had been taken up, the solvent was removed under reduced pressure. The white solid thus obtained, a little yellowish in color, was found by

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[7] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).
[8] J. Sauer, *Angew. Chem. Int. Ed.*, **6**, 16 (1967).
[9] P. Yates and P. Eaton, *J. Amer. Chem. Soc.*, **82**, 4436 (1960).
[10] G. I. Fray and R. Robinson, *ibid.*, **83**, 249 (1961).
[11] C. E. Frank and A. U. Blackham, *ibid.*, **72**, 3283 (1950).
[12] K. E. Weale, *J. Chem. Soc.*, **1952**, 2223.

IR to be almost pure γ-BTC. The yields were calculated on the basis of the weights at this stage. After recrystallization from ethanol, mp was 87—88 °C.

Photochlorination of γ-BTC to BHC. Pure γ-BTC (0.44 g, 0.002 mol), chlorine (0.17 g, 0.0024 mol), and 10 ml of dry distilled carbon tetrachloride were charged in an ampoule (1.2 × 15 cm). The air in the ampoule and the carbon tetrachloride were then replaced by dry nitrogen. The ampoule was immersed in a methanol–dry ice bath kept at -10 ± 2 °C, and a 10 W blue fluorescent lamp (Mazda) was placed at a distance of 14 cm as the light source. The photochlorination was over within one hour.

After the reaction, the reaction mixture was subjected to steam distillation and a white solid (0.515 g, 88.9% as BHC) was obtained.

By IR the reaction product was found to consist of γ, α, and δ-BHC. The amount of each BHC isomer was determined by IR according to Milone.[13] The key bands for the isomers were α, 15.93; γ, 20.70; and δ, 17.65 μ. By our experiment, at −10 °C in carbon tetrachloride the produced BHC contained α, 37.6; γ, 56.0; and δ, 6.4%.

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13) M. Milone and E. Borello, *Gazz. Chim. Ital.*, **83**, 255 (1953); *Chem. Abstr.*, **47**, 12133 (1953).