

A CONTRIBUTION TO PROBLEMS OF DIELS-ALDER REACTION OF PERCHLORO-1,3-BUTADIENE AND ITS DERIVATIVES

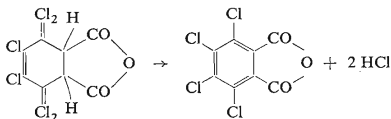
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In accord with the theoretical presumptions it has been proved that the synthesis of hexachloro- Δ^4 -tetrahydrophthalic anhydride *via* Diels-Alder addition reaction from hexachloro-1,3-butadiene and maleic anhydride by action of enhanced temperatures and free-radical initiators is not feasible. The analogous reaction with 1-ethoxypentachloro-1,3-butadiene has given negative results, too. In the both cases maleic anhydride undergoes homopolymerization reaction to give decarboxylated polymers with cyclopentanone structure. Perchlorinated dienes do not take part in the reaction and behave as inert solvents.

Polyhalogenated phthalic acids *e.g.* tetrachlorophthalic acid or hexachloro-3,6-endomethylene- Δ^4 -tetrahydrophthalic acid are important monomers with retardation effect to burning. The anhydride of the abovementioned hexachloro-acid can be obtained easily in a high yield by heating hexachlorocyclopentadiene with maleic anhydride¹. In contrast to this the sterical requirements for an analogous very attractive synthesis of hexachloro- Δ^4 -tetrahydrophthalic acid (*I*) from maleic anhydride (*II*) and hexachloro-1,3-butadiene (*III*) are not fulfilled²⁻⁴. It was, therefore, surprising that the publications⁵⁻⁷ described the synthesis of *I* from *II* and *III* (in an almost theoretical yield) in the presence of azo-bis(isobutyronitril) or α -cumenyl hydrogen peroxide; the product was identified⁶ by its chlorine content and molecular weight. Theoretical objections were raised⁸ against these results. The existence of *I* also must be questionable (especially so at an enhanced temperature) due to the instability of the presumed halogenocyclohexenedicarboxylic acid structure which has a high tendency towards β -elimination reactions. Tetrachlorophthalic acid resp. its anhydride could be stable final products after elimination of 2 hydrogen chloride molecules under the conditions mentioned.



As the hexachloro- Δ^4 -tetrahydrophthalic anhydride could not be prepared⁹ according to the method described⁵⁻⁷, the respective reaction and the analogous

one using 1-ethoxypentachloro-1,4-butadiene were submitted to a further study which is described in the present paper.

EXPERIMENTAL

Raw materials. Maleic anhydride (*II*) (Montecatini, Milano) of 98.8% purity, determined alkalimetrically and polarographically. Hexachloro-1,3-butadiene (*III*), technical product, was purified by a modified procedure¹⁰ viz. repeated shaking with 10% aqueous NaSH until the disappearance of a reddish colouration of the extract (99.5% according to GLC); b.p. 211°C, n_D^{20} 1.5552, d_4^{20} 1.6822. 1-Ethoxypentachloro-1,3-butadiene (*IV*) was prepared according to ref.¹¹, b.p. 98.5–99.5°C/8 Torr, n_D^{20} 1.5283 (99% according to GLC a mixture of *cis* and *trans* isomers in the ratio 10 : 1). The initiators azo-bis(isobutyronitril), tert-butyl perbenzoate (91.5%; its additions to reaction mixtures were corrected to 100%), and tert-butyl peroxide (98%) were technical products. The further chemicals used were of c.p. purity grade, nitrogen gas was of the quality used in bulb production.

Procedures. A mixture of 10 mmol *II*, 40 mmol perchlorinated diene *III* or *IV*, and 5% initiator (by wt. with respect to the both reactants or only to *II*) was heated at 125°C under a reflux condenser and with introducing nitrogen gas under the surface of the reaction mixture. The reaction was accompanied by elimination of CO₂ and HCl, the mixture turned black, and a tarry to resinous polymer substances separated. The reaction product was extracted three times with a threefold volume of hot water, and the overall content of maleic and fumaric acids was determined polarographically¹² in the solution after filtration.

The dicarboxylic acids were examined in the extracts by means of paper chromatography (Whatman No 1; descending arrangement); acid elution system was prepared by 16 h standing of a mixture benzene–acetic acid–water 2 : 2 : 1 and taking the upper layer; the samples of 100 to 400 µg of investigated acids or 25–50 µg of standards (maleic, fumaric, tetrachlorophthalic and hexachloro-3,6-endomethylene- Δ^4 -tetrahydrophthalic acids) were separated and their spots made visible with bromocresol green.

The mass-balance experiments were initiated with azo-bis(isobutyronitril) (with addition of 0.1% iodine by wt. in the case of *III*) and the acid gas evolved was absorbed in 0.5M-NaOH, whereafter the amounts of CO₂ and HCl were determined alkalimetrically and argentometrically resp. The residual content of carboxylic acid groups was determined both in the aqueous extracts and in the separated polymeric portions by means of direct titrimetry or by saponification with an excess of 0.1M-NaOH. Besides that, chlorides were determined in the extracts argentometrically after saponification.

The sample of the polymeric product was prepared in an analogous way according to the abovedescribed procedure in the presence of 5% by wt. tert-butyl perbenzoate (calculated for the mixture *II* and *III* in the molar ratio 4 : 1) by heating at 125°C for 14 h (after diluting the mixture with toluene in the ratio 5 : 1 by wt.). After a threefold extraction of the reaction mixture with benzene the polymeric product of the interaction of *II* and tert-butyl perbenzoate was obtained in the yield of 110% (calculated for the starting substance *II*) or 70% (calculated for the both reactants); the product showed only a slight positive test for chlorine. After precipitation of the acetone solution with benzene a yellow-brown powder was isolated in a 56% yield (with respect to initial *II*). It contained 1.24% chlorine, its overall acid number (*x*) 560.2 mg KOH/g corresponded to the saponification number 567.5 mg KOH/g (15 min heating with 0.5M-KOH on water bath) with respect to the slight positive test for chlorides in the saponified solution. For the sake of estimation of the content of anhydride groups, the partial acid number (*y*) was determined by titrimetry with 0.1M-CH₃ONa. The value 472.4 mg KOH/g found corresponded

to the free and anhydride-bound carboxylic groups in the ratio $(x - 2(x - y)) : 2(x - y)$ i.e. to the values 68.6 and 31.4% respectively.

RESULTS AND DISCUSSION

From the values of Table I it can be seen that the extent of the reaction taking place by heating maleic anhydride (II) with hexachloro-1,3-butadiene (III) or 1-ethoxypentachloro-1,3-butadiene (IV) in the presence of radical initiators depends on both the kind and concentration of the initiator and, to some extent, on the type of the perchlorinated diene. Besides the decrease of II a significant decrease of saponifiable carboxylic acid groups was observed, too, which was due to direct elimination of CO₂ gas (only a smaller part) and mainly to an internal rebuilding of anhydride carboxylic groups:

The diene used	III	IV
The reacted portion of anhydride II (%)	55.4	33.6
Decarboxylation of the reacted II (%)		
— total	32.9	61.8
— as CO ₂ in evolved gas	14.8	16.7
Eliminated HCl (mol % with respect to diene)		
— in the evolved gas	1.5	2.7
— in the saponified extract	0.9	1.7

TABLE I

Reaction of Maleic Anhydride (II) in Medium of Hexachloro-1,3-butadiene (III) or 1-Ethoxypentachloro-1,3-butadiene (IV)

Initiators (In): tert-butyl perbenzoate (V), azo-bis(isobutyronitril) (VI), tert-butyl peroxide (VII); m_{In} and m'_{In} are the amounts of initiator in % by wt. calculated for the sum (diene + II) and II alone resp.

Diene	Diene/II mol/mol	In	m_{In}	m'_{In}	Temp. °C	Time h	Consumption of II, %
III	4	V	4.9	60	125	12	84.3
III	4	V	4.9	60	125	4	65.0
III	4	VI	4.8	58	125	4	37.0
III	4	VII	4.8	58	125	4	14.3
IV	4	V	4.6	58	80	5.5	40.4
IV	4	VI	4.8	60	125	8	33.6
III	4	VI ^a	0.42	5	120	15	13.6
IV	4	VI ^a	0.43	5	120	15	13.8
III	11	VI	0.036	5	120	4	22.3
III	0.27	V	3.1	5.6	120	6	14.3
IV	0.27	V	2.8	5.2	120	6	10.6
—	—	V	3.8	3.8	120	6	12.9

^a Recrystallized from ethanol.

The neutralization characteristics of the polymer isolated, which had the total acid number about 560 mg KOH/g (as compared to the theoretical value 1145 mg KOH/g in the case of polymaleic anhydride) from which two thirds were due to carboxylic acid groups and one third was due to anhydride groups, indicate that it is a highly decarboxylated product of homopolymerization of the anhydride *II*. This conclusion agrees with a formerly published work¹³ in which the polymer was ascribed a complicated poly(carboxycyclopentanone) structure. A quite insignificant chlorine content in the resinous polycarboxylic products suggests that the dienes *III* resp. *IV* do not take part in their formation. Also the slight extent of HCl elimination during both the proper reaction and the alkaline hydrolysis of aqueous extracts of the reaction products (Table I) indicate that the both perchlorinated dienes (*IV* rather more than *III*) undergo only negligible side reactions under the conditions given.

The non-participation of the dienes *III* and *IV* in the reaction with *II* was confirmed also by the results of paper chromatography of the aqueous extracts. In the case of the reaction initiated by azo-bis(isobutyronitril) only the presence of maleic acid (R_F 0.05) was established. In the case of the use of tert-butyl perbenzoate two further acids were found in small concentrations, but their R_F values (0.77 and 0.90) were out of the region of polychlorophthalic acids (tetrachlorophthalic acid R_F 0.35; hexachloro-3,6-endomethylene- Δ^4 -tetrahydrophthalic acid R_F 0.66). The acids found, which are obviously the products of interaction of the initiator with *II*, could be isolated in the form of a white crystalline solid sparingly soluble in water. After two recrystallizations from water they melted constantly at 161°C (corr.); the substance had the neutralization equivalent 522 mg KOH/g, it did not contain any chlorine, it did not decolourize aqueous $KMnO_4$ solution, and it separated on paper chromatogram into two spots having the abovementioned R_F values. These observations also confirm that the products of the reactions of *II* are of macromolecular polycarboxylic acid type.

In conclusion it can be stated that hexachloro-1,3-butadiene does not react with maleic anhydride even in the presence of free radical initiators, which stands in contrast to papers⁵⁻⁷ but agrees with theoretical arguments in ref.⁸ The abovementioned diene as well as 1-ethoxypentachloro-1,3-butadiene behave practically as inert solvents.

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