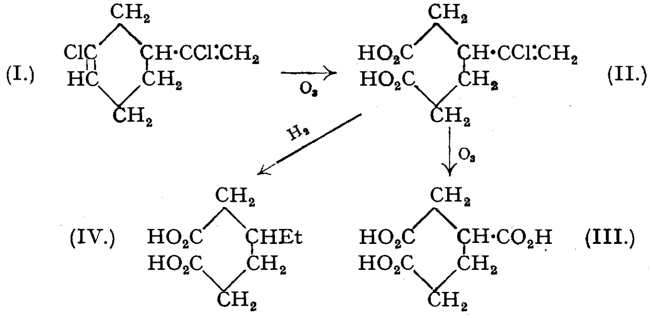
37. 3-*Chloro*-1-α-*chlorovinyl*-Δ^3-cyclo*hexene, and* 1 : 5-*Dichloro*-$\Delta^{1:5}$-cyclo*octadiene.*

By J. G. T. Brown, J. D. Rose, and J. L. Simonsen.

The two dimers formed when chloroprene is kept either as such or in a solvent (Carothers, Williams, Collins, and Kirby, *J. Amer. Chem. Soc.*, 1931, **53**, 4211; Carothers, Kirby, and Collins, *ibid.*, 1933, **55**, 791) have been shown to have the structures represented by (I) and (V).

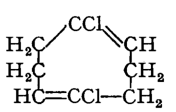
During his investigations on chloroprene, Carothers and his collaborators (*locc. cit.*) observed the formation of a " β-polymer " when chloroprene was kept alone or in a solvent. This polymer can be separated into two fractions, b. p. 92—93°/27 mm. and 114 –118°/27 mm. The structure of these polymers was not determined, but, having a quantity available, we have undertaken this, for it seemed that a knowledge of their structure might throw some further light in the mechanism of polymerisation.

Fractionation of the oil remaining after the removal of the monomer and some xylene gave two fractions having approximately the same b. p.'s as those obtained by Carothers. The b. p. and the analytical data indicated that they consisted essentially of two dimers, $C_8H_{10}Cl_2$, although neither was obtained quite pure. The lower-boiling dimer has been shown to be 3-*chloro*-1-α-*chlorovinyl*-Δ^3-cyclo*hexene* (I). It yields on ozonolysis a crystalline *acid*, $C_8H_{11}O_4Cl$, m. p. 152—154°, which must be 3-α-*chlorovinyladipic acid* (II), since on ozonolysis it gives in theoretical yield butane-αβδ-tricarboxylic acid (III). The inertness of ethylenic linkages to the action of ozone has been previously recorded (Escott and Linstead, J., 1930, 914; Penfold, Ramage, and Simonsen, J., 1939, 1499).

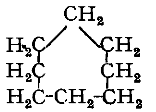


On catalytic hydrogenation the chloro-acid gives 3-*ethyladipic acid* (IV), m. p. 47—48°. This acid appears to be new, and attempts to prepare it from β-acetyladipic acid failed, for this acid is not reduced by the Clemmensen method or by the action of sodium ethoxide on its semicarbazone or hydrazone. The liquid lactone, prepared by reduction of the keto-acid with sodium amalgam, also resists further reduction by hydriodic acid. Similar instances of the stability of keto-acids have been observed by Birch and Robinson (J., 1942, 485). The acid is not identical with α-ethyladipic acid, m. p. 49°, for which a simple method of preparation from ethyl 1-ethyl*cyclo*pentan-2-one-1-carboxylate is described. On catalytic hydrogenation 3-chloro-1-α-chlorovinyl-Δ^3-*cyclo*hexene gives ethyl*cyclo*hexene.

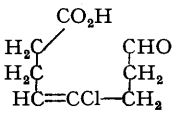
Although the formation of this chloro*cyclo*hexene derivative was anticipated, since it is a simple adduct of the Diels–Alder type, yet that of the higher-boiling dimer, found to be 1 : 5-*dichloro*-$\Delta^{1:5}$-cyclo*octadiene* (V), was unexpected, since there is no recorded case of cyclisation by head-to-tail union in this manner. The assignment of a *cyclo*octadiene structure to this dimer is based upon the following considerations. It contains two ethylene linkages, since it absorbs 4 molecules of hydrogen on catalytic hydrogenation to yield *cyclo*octane (VI). The identity of this hydrocarbon with that prepared by Willstätter *et al.* (*Ber.*, 1908, **41**, 1480; 1910, **43**, 1076) and by Zelinsky and Freimann (*ibid.*, 1930, **63**, 1480) was established by its oxidation to suberic acid by nitric acid.



(V.)



(VI.)



(VII.)

The position of the two ethylenic linkages was proved by ozonolysis of the chloride to succinic acid, obtained in a 76·7% yield of that required for the formation of 2 mols. of the acid from one of the chloride. A further product of the ozonolysis was an aldehydo-acid, probably (VII), isolated as its 2 : 4-*dinitrophenylhydrazone*, $C_{14}H_{15}O_6N_4Cl$, m. p. 119°.

Experimental

22 Kg. of the still residue remaining after the removal of monomeric chloroprene were fractionated under diminished pressure (3—4 mm.), and after removal of the xylene the following fractions were obtained: (1) low-boiling xylene mixture (94 g.), (2) b. p. 66—70° (450 g.), (3) b. p. 84—85° (320 g.), (4) b. p. 95—104° (75 g.). Fractions (2) and (3) were refractionated to yield 3-*chloro*-1-α-*chlorovinyl*-Δ^3-cyclo*hexene*, b. p. 66—67°/4 mm., and 105°/20 mm., $d_{25°}^{25°}$ 1·1533—

1·168, $n_{\mathrm{D}}^{24^\circ}$ 1·51565, $[R_L]_{\mathrm{D}}$ 46·4; calc., 45·74 (Found: C, 55·45; H, 5·75; Cl, 38·9. $C_8H_{10}Cl_2$ requires C, 54·25; H, 5·65; Cl, 40·1%), and 1 : 5-*dichloro*-$\Delta^{1:5}$-cyclo*octadiene*, b. p. 84—85°/2 mm., 126°/18 mm., $d_{25^\circ}^{25^\circ}$ 1·174, $n_{\mathrm{D}}^{25^\circ}$ 1·5260, $[R_L]_{\mathrm{D}}$ 46·28 (Found : C, 57·7; H, 6·3; Cl, 35·1%). On distillation both fractions decomposed slightly with evolution of hydrogen chloride, and this is reflected in the analytical data.

3-Chloro-1-α-chlorovinyl-Δ^3-*cyclo*hexene is a colourless oil having a somewhat acrid odour and becoming brown on keeping, Its absorption spectrum has been examined by Dr. A. E. Gillam, of the University of Manchester, to whom we are indebted for the following report : "The absorption spectrum shows rising absorption at wave-lengths longer than 2240 A. The only selective absorption must therefore have its maximum below these wave-lengths. From the intensity of absorption at the limit reached (2240 A., $\varepsilon = 1820$) it can be safely inferred that a conjugated system of double bonds is absent." Attempts to eliminate hydrogen chloride by digestion with sodium methoxide or diethylaminoethanol were unsuccessful, although some dehalogenation did occur with the latter reagent. The polymer did not react with either maleic anhydride or α-naphthaquinone. In chloroform solution addition of bromine took place readily, a crystalline *tetrabromide* remaining on evaporation of the solvent. This separated from ligroin (b. p. 40—60°) in large, well-formed prisms, m. p. 146—147°, softening at 144° (Found : AgCl + AgBr, 207. $C_8H_{10}Cl_2Br_4$ requires AgCl + AgBr, 208%).

Hydrogenation of 3-*Chloro*-1-α-*chlorovinyl*-Δ^3-cyclo*hexene*.—*Ethyl*cyclo*hexane*. On catalytic hydrogenation the absorption of hydrogen (4 mols.) was never complete, owing probably to poisoning of the catalyst by the hydrogen chloride formed. (It was later found that if this was absorbed by sodium acetate added initially, hydrogenation was complete.) In two micro-estimations using acetic acid as solvent and an Adams catalyst, the absorption was 2·35 c.c. and 4·14 c.c. in place of 3·17 and 4·83 c.c., respectively. In a macro-experiment with the polymer (13·34 g.), the hydrogen absorption was 6·26 l. (Calc. for $4H_2$: 6·76 l.). The hydrocarbon, ethyl*cyclo*hexane, isolated from the acetic acid solution, after neutralisation with sodium carbonate, by extraction with ether, had b. p. 130—131°/768 mm., $d_{25^\circ}^{25^\circ}$ 0·784, $n_{\mathrm{D}}^{25^\circ}$ 1·432 (Found : C, 85·45; H, 14·4. Calc. for C_8H_{16} : C, 85·7; H, 14·3%).

Ozonolysis of 3-*Chloro*-1-α-*chlorovinyl*-Δ^3-cyclo*hexene*.—3-α-*Chlorovinyladipic acid*. The polymer (4·5 c.c.) in methyl acetate (50 c.c.) was ozonised at 0°, the issuing gases containing only traces of formaldehyde. After removal of the solvent under diminished pressure, the residual gum was mixed with water (10 c.c.) and gently warmed, the ozonide decomposing with considerable violence. The decomposition was completed by heating on the water-bath for 1 hour, the aqueous solution, which contained ionic chlorine, being evaporated. The residual oil (3·8 g.) crystallised, and after trituration with formic acid, the acid was collected and crystallised from this solvent. The *chloro-acid* separated in leaflets or bayonet-shaped needles, m. p. 152—154°, softening at 135° (Found : C, 46·3; H, 5·5; Cl, 16·9. $C_8H_{11}O_4Cl$ requires C, 46·5; H, 5·3; Cl, 17·1%). The *di*-p-*phenylphenacyl* ester crystallised from alcohol in small plates, m. p. 54—55° (Found : C, 72·3; H, 5·4. $C_{36}H_{31}O_6Cl$ requires C, 72·7; H, 5·2%).

The chloro-acid (1 g.) in methyl acetate (25 c.c.) was ozonised at 0°. The gummy ozonide, remaining after removal of the solvent, was decomposed with water (5 c.c.). Evaporation gave an oil (1 g.), which solidified. The acid crystallised from methyl acetate or acetone in rosettes of prisms, m. p. 121—122°, both alone and in admixture with butane-αβδ-tricarboxylic acid (Found : C, 44·1; H, 5·2. Calc. for $C_7H_{10}O_6$: C, 44·1; H, 5·3%).

Hydrogenation of 3-α-*Chlorovinyladipic Acid*.—3-*Ethyladipic acid*. In two micro-hydrogenations the acid absorbed 1·44 and 1·58 c.c. of hydrogen (Calc. for $2H_2$: 1·3 and 1·62 c.c., respectively). The acid (0·5 g.) was hydrogenated in alcohol by means of a palladium–norit catalyst; owing to an accident the volume of gas absorbed was not measured. After addition of alkali to the filtered solution, the alcohol was evaporated, and the acid isolated from the acidified solution by ether in the usual manner. 3-*Ethyladipic acid* crystallised from ether–ligroin (b. p. 40—60°) in needles, m. p. 47—49° (Found : C, 54·9; H, 7·9. $C_8H_{14}O_4$ requires C, 55·0; H, 8·0%). The *di*-p-*phenylphenacyl* ester crystallised from alcohol as a powder, seen under the microscope to consist of small prisms, m. p. 100—101° (Found : C, 76·4; H, 6·1. $C_{35}H_{32}O_6$ requires C, 76·1; H, 6·0%).

Ethyl 1-*ethyl*cyclo*pentan*-2-*one*-1-*carboxylate*. The *ester*, prepared by treating ethyl sodio*cyclo*pentan-2-one-1-carboxylate with ethyl iodide in benzene solution, had b. p. 115°/13 mm. (Found : C, 65·5; H, 8·6. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%). By digestion with alcohol containing sodium (1%) for 2 hours, *ethyl* α-*ethyladipate*, b. p. 133°/13 mm., was obtained (Found : C, 62·8; H, 9·5. $C_{12}H_{22}O_4$ requires C, 62·6; H, 9·5%). which on hydrolysis with hydrochloric acid gave α-ethyladipic acid, m. p. 47—49°. The *di*-p-*phenyphenacyl* ester crystallised from alcohol in balls of soft needles, m. p. 118—120°, depressed to 93° in admixture with the corresponding derivative of the β-ethyl acid (Found : C, 75·9 : H, 6·1%).

1 : 5-*Dichloro*-$\Delta^{1:5}$-cyclo*octadiene* is a colourless, mobile oil having a pleasant, terpene-like odour; it was somewhat unstable and darkened on keeping. The absorption spectrum as determined by Dr. A. E. Gillam shows only rising absorption at wave-lengths longer than 2240 A. There is an absorption band at 2650 A. ($\varepsilon = 80$). The intensity of the absorption at 2230 A. ($\varepsilon = 1140$) precludes the presence in the molecule of a conjugated system of double bonds. The presence of the band at 2650 A. is due probably to a small amount of a more strongly absorbing entity. The chloride did not react with either maleic anhydride or 1 : 4-naphthaquinone. In chloroform solution, bromine was rapidly absorbed but hydrogen bromide was vigorously evolved, and evaporation of the solvent left an oil.

Hydrogenation of the Chloride.—cyclo*Octane*. The chloride was hydrogenated in acetic acid solution by means of Adams's catalyst, but it was difficult to effect complete reduction. In three micro-hydrogenations the following results were obtained : 2·048, 6·722, and 7·017 mg. absorbed 0·71, 2·92, and 3·62 c.c., respectively, of hydrogen (Calc. for $4H_2$: 1·04, 3·4, 3·55 c.c.). On a larger scale, complete hydrogenation was only effected with considerable difficulty. The most satisfactory yield of hydrocarbon was obtained when an Adams catalyst was employed with acetic acid as the solvent with a hydrogen pressure of approx. 3 atm. After hydrogenation, the filtered acetic acid solution was neutralised with sodium carbonate, the hydrocarbon dissolved in ether, and the ether removed from the dried solution with the aid of a column. The *cyclo*octane prepared in this manner had b. p. 147—149°/743 mm., $d_{4^\circ}^{25^\circ}$ 0·831, $n_{\mathrm{D}}^{25^\circ}$ 1·4535 (Found : C, 85·5; H, 14·3. Calc. for C_8H_{16} : C, 85·7; H, 14·3%).

For oxidation to suberic acid, the hydrocarbon (1 g.) was mixed with nitric acid (*d* 1·42; 10 g.) and heated on the water-bath for 24 hours. On cooling, a crystalline solid separated, and was collected (0·4 g.); m. p. 133—135°, raised to 140—141° by crystallisation from water. The m. p. was unchanged in admixture with an authentic specimen of suberic acid (Found : C, 54·9; H, 7·9. Calc. for $C_8H_{14}O_4$: C, 55·1; H, 8·0%).

Ozonolysis of 1 : 5-*Dichloro*-$\Delta^{1:5}$-cyclo*octadiene*.—The chloride (5 c.c.) in methyl acetate (50 c.c.) was ozonised at 0°, the issuing gases being passed through water, in which only a trace of formaldehyde could be detected at the conclusion of the oxidation. After removal of the solvent under diminished pressure, the ozonide was mixed with water (10 c.c.) and tended to decompose with explosive violence. The decomposition was completed by warming on the water-bath for 0·5 hour. On cooling the aqueous solution, which contained ionic chlorine, a crystalline solid (3·5 g.) was deposited, which was identified as succinic acid by m. p. 187°, both alone and in admixture, and by the preparation of the di-*p*-bromophenacyl ester, m. p. 214—215°, crystallising from acetic acid in leaflets. The aqueous mother-liquor, from which the succinic acid had been separated, was concentrated, yielding a further quantity (1·2 g.) of the same acid. The filtrate was made alkaline with sodium carbonate, and oxidised at 0° with potassium permanganate (1%). Isolation of the organic acid from the filtered and concentrated alkaline solution by ether in the usual manner gave a further quantity of succinic acid (1·3 g.).

In one experiment the original aqueous filtrate from the succinic acid was mixed with aqueous 2 : 4-dinitrophenylhydrazine sulphate, a yellow 2 : 4-*dinitrophenylhydrazone* being deposited. This crystallised from alcohol in reddish-yellow needles, m. p. 119°, after softening at 115° (Found : C, 45·1; H, 4·3. $C_{14}H_{15}O_6N_4Cl$ requires C, 45·3; H, 4·0%), and was probably derived from the aldehydo-acid (VII).

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