328. *Experiments in the* cyclo*Butane Series. Part II.*[1]

By F. B. Kipping and J. J. Wren.

Perkin's bromination of *cis-cyclo*butane-1 : 2-dicarboxylic anhydride has been re-investigated, together with debromination of the products. Experiments directed to the synthesis of tetrahydroanemonin from *cyclo*butene-1 : 2-dicarboxylic acid are described.

In Part I[1] preliminary experiments towards an unambiguous synthesis of anemonin were described. This paper deals with experiments directed to a synthesis of tetrahydroanemonin, which presumably has the same carbon skeleton as anemonin, but in which that skeleton is apparently more stable; for example, basic reagents cleave the *cyclo*butane ring of anemonin, but the tetrahydro-compound undergoes reversible basic hydrolysis.[2] Synthesis would confirm the structure of anemonin and show whether the spirolactone groupings are *cis-* or *trans*-related to one another. It has recently been realised that, whereas in the *cyclo*butyl anion[3] and radical[4] the ring is stable, in the *cyclo*butyl cation it is not[4, 5] and consequently any reaction which involves generation of a *cyclo*butyl cation yields a mixture of products and is therefore unsuitable for an unambiguous synthesis. It seemed, therefore, that the crucial step in the synthesis of tetrahydroanemonin should be the stereospecific hydroxylation of an appropriate 1 : 2-disubstituted *cyclo*butene and that Perkin's *cyclo*butene-1 : 2-dicarboxylic acid[6] would be a suitable starting material.

---

[1] Alberman and Kipping, *J.*, 1951, 779.

[2] Asahina and Fujita, *Acta Phytochim.* (*Japan*), 1922, **1**, 1.

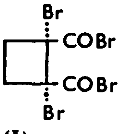
[3] Hamlin and Biermacher, *J. Amer. Chem. Soc.*, 1955, **77**, 6376.

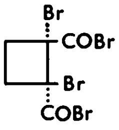
[4] Roberts and Mazur, *ibid.*, 1951, **73**, 3542.

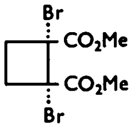
[5] Dewar, *Ann. Reports*, 1951, **47**, 120; Roberts and Mazur, *J.*, *Amer. Chem. Soc.*, 1951, **73**, 2509; Roberts and Chambers, *ibid.*, p. 5034; Roberts and Simmons, *ibid.*, p. 5487; Applequist and Roberts, *ibid.*, 1956, **78**, 874.

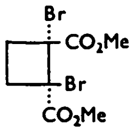
[6] Perkin, *J.*, 1894, 950.

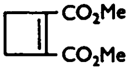
Bromination of *cis-cyclo*butane-1 : 2-dicarboxylic anhydride afforded a mixture of *cis-* (I) and *trans*-1 : 2-dibromo*cyclo*butane-1 : 2-dicarbonyl bromide (II). Solvolysis of this mixture, with silver acetate in 1 : 1 acetic acid–acetic anhydride, gave a complex mixture, from which neither the *cis-* nor the *trans*-tetra-acetoxy-derivative could be isolated; this confirmed the unsuitability of reactions involving *cyclo*butyl cations. Water converted the acid bromide mixture into a product from which *cis*-1 : 2-dibromo*cyclo*butane-1 : 2-dicarboxylic anhydride was obtained by distillation, and from it the corresponding acid as described by Perkin; the *trans*-acid sublimed from the residue after distillation. Treatment of the acid bromide mixture with methanol and subsequent crystallisation afforded Perkin's crystalline dimethyl 1 : 2-dibromo*cyclo*butane-1 : 2-dicarboxylate, which has now been shown to be the *trans*-isomeride (IV). Perkin therefore isolated the *cis*-acid but the *trans*-ester. The *cis*-ester (III) was obtained from the mother-liquor, for the first time in crystalline form. A number of attempts to hydrolyse the esters to the respective acids, and also to prepare them from the acids gave inhomogeneous products, presumably owing to solvolysis of their labile tertiary bromine atoms.


(I)


(II)


(III)


(IV)


(V)

Boiling ethanolic potassium iodide smoothly debrominated the *trans*-dibromide (IV), giving dimethyl *cyclo*butene-1 : 2-dicarboxylate (V), but it had no action on the *cis*-dibromide (III) which liberated no iodine from potassium iodide even in boiling butan-1-ol, and although some reaction occurred in boiling diethylene glycol or in methanol at 225° the products were mixtures. Preferred *trans*-elimination of bromine from vicinal dibromides in the presence of iodide ion is well known,[7] and therefore provides strong evidence for the configurations here assigned to the isomeric dibromides. In passing, it is interesting that Ellingboe and Fuson [8] apparently assigned the wrong configurations to the isomeric 1 : 2-dibenzoyl-1 : 2-dibromo*cyclo*butanes; the higher-melting isomeride (m. p. 155—156°) was called the *trans*, yet it was debrominated in the presence of iodide ion much less readily than the other (m. p. 111—112°). Both eventually yielded 1 : 2-dibenzoyl*cyclo*butene which gave, as would be expected, *cis*-1 : 2-dibenzoyl*cyclo*butane when it was catalytically hydrogenated, but when brominated (which should give *trans*-addition) gave the lower-melting dibromide. Modern knowledge of these reactions thus shows that the lower-melting dibromide must be the *trans*-isomeride.

Although remarkably inactive towards iodide ions the *cis*-dibromide (III) was debrominated with zinc, but this change was accompanied by varying amounts of reduction, depending on the solvent employed, and in anhydrous methanol, for example, only the reduction product, dimethyl *trans-cyclo*butane-1 : 2-dicarboxylate, was formed. Kon and Nandi [9] treated a mixture of the diethyl esters corresponding with (III) and (IV) with zinc dust in boiling ethanol, which indeed appears to be the best solvent for debromination of the *cis*-isomeride (III), but they were apparently unaware that reduction occurs simultaneously with debromination and that the *trans*-isomeride in their mixture was probably unaffected; in our hands the *trans*-isomeride (IV) failed to react with zinc dust in boiling ethanol. Kon and Nandi mention that the same method was used on the dimethyl esters, but not whether dimethyl *cyclo*butene-1 : 2-dicarboxylate (V) was obtained crystalline; in fact it would appear that their liquid products were impure.

---

[7] Winstein, Pressman, and Young, *J. Amer. Chem. Soc.*, 1939, **61**, 1645; Alexander, " Ionic Organic Reactions," John Wiley and Sons, Inc., New York, 1950, p. 118; Cornubert and Rio, *Compt. rend.*, 1954, **238**, 867; Goering and Espy, *J. Amer. Chem. Soc.*, 1955, **77**, 5023; Barton, *Quart. Rev.*, 1956, **10**, 50.

[8] Ellingboe and Fuson, *J. Amer. Chem. Soc.*, 1934, **56**, 1774.

[9] Kon and Nandi, *J.*, 1933, 1628.

Conversion of the *cyclo*butene ester (V) into the *trans*-dibromo-compound (IV) provides comfirmatory evidence of the configurations assigned above, and the structure of *cyclo*butene-1 : 2-dicarboxylic acid, obtained by hydrolysis of the ester, was confirmed by catalytic hydrogenation to *cis-cyclo*butane-1 : 2-dicarboxylic acid. The *cyclo*butene acid was also reconverted into its dimethyl ester *via* the dicarbonyl chloride.

It has not been possible to prepare an anhydride of *cyclo*butene-1 : 2-dicarboxylic acid.[6, 10] When it was covered with acetyl chloride, the finely powdered acid did not dissolve until it was warmed and was then converted into the dicarbonyl chloride. Ethereal thionyl chloride and pyridine at 0° [11] also failed to convert it into the anhydride. When it was kept at 65° for nine days in pure acetic anhydride containing a trace of pyridine, or for shorter periods in boiling acetic anhydride or in a vacuum-sublimation apparatus at 200°, it was converted into rather involatile oils. These observations may be explained by assuming that too much ring strain would be present in the anhydride and also by Vogel's recent observation [12] that the ester (V) undergoes thermal cleavage to give dimethyl fulgenate (VI; R = Me) : he converted the ester (V) into the Diels–Alder adduct of dimethyl fulgenate with maleic anhydride. It was at first considered surprising that the literature apparently contains no reference to fulgenic acid (VI; R = H), its anhydride or its esters, but presumably these compounds would polymerise very readily, being both dienes and dienophils (a similar explanation has been advanced for the absence of derivatives of buta-1 : 3-diene-2-carboxylic acid from the literature [13]). Perkin obtained " a new acid " by the action of water on the oily product of heating the *cyclo*butene acid, and this was probably a polymeride of fulgenic acid.

trans-Hydroxylation of the *cyclo*butene acid was attempted in the hope of preparing the dihydroxy-dicarboxylic acid which might, with suitable protection of the hydroxyl groups, be twice bishomologated by the Arndt–Eistert procedure to give an acid which would lactonise to tetrahydroanemonin or its geometrical isomeride. Organic peroxides, the conventional reagents for *trans*-hydroxylation of olefinic double bonds, are unsuitable for αβ-unsaturated acids,[14] but maleic acid has been successfully *trans*-hydroxylated by using aqueous hydrogen peroxide in the presence of pertungstic acid.[15] This method was therefore applied to the *cyclo*butene acid, but only succinic acid was formed. A similar cleavage of the *cyclo*butane ring was observed by Wille,[16] who converted the ester (V) into dimethyl 1 : 4-dioxoadipate with hydrogen peroxide and osmium tetroxide.

Application of the Arndt–Eistert synthesis to the *cyclo*butene acid was next investigated. Although carboxylic acids containing isolated double bonds can be successfully homologated [17, 18] considerable difficulties arise with αβ-unsaturated acids. For example, even at −78° crotonyl chloride with diazomethane gives a pyrazoline diazoketone, which decomposes very readily with evolution of nitrogen.[18] However, a good yield of the diazoketone can be obtained from α-methylcinnamoyl chloride, although some of the pyrazoline diazoketone (VII; R = Me) is also formed; the diazoketone was converted by the Wolff rearrangement into the methyl ester of the homologous acid.[19] Cinnamoyl chloride yields corresponding products,[18–20] but a polymeride resulted from attempted Wolff rearrangement of the diazoketone. In the case of *cyclo*butene-1 : 2-dicarbonyl chloride the only isolable product was the pyrazoline diazoketone (VIII), the

---

[10] Wren, *J.*, 1956, 2208.

[11] Gerrard and Thrush, *J.*, 1952, 741.

[12] Vogel, *Angew. Chem.*, 1956, **68**, 189.

[13] Braude and Evans, *J.*, 1956, 3238.

[14] Boeseken, *Rec. Trav. chim.*, 1926, **45**, 838; English and Gregory, *J. Amer. Chem. Soc.*, 1947, **69**, 2120; Swern, *Chem. Rev.*, 1949, **45**, 50.

[15] Mugdan and Young, *J.*, 1949, 2988; Church and Blumberg, *Ind. Eng. Chem.*, 1951, **43**, 1780.

[16] Wille, *Annalen*, 1939, **538**, 237.

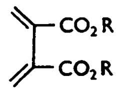
[17] Bachmann and Struve, " Organic Reactions," Vol. I (1942), p. 38.

[18] Wotiz and Buco, *J. Org. Chem.*, 1955, **20**, 210.

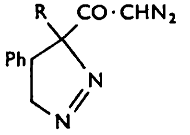
[19] Moore, *ibid.*, p. 1607.

[20] Cf. Bradley and Schwarzenbach, *J.*, 1928, 2904.

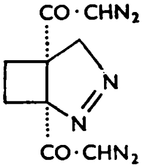
structure of which was proved by its infrared spectrum, and more particularly by its ultraviolet spectrum which is not that of an αβ-unsaturated diazoketone, as is shown in Table 1. Using varying dilutions of reactants, experiments were conducted at 0°, at −80°, and at −105° : the mother-liquors after crystallisation of the pyrazolone diazoketone showed weak absorption maxima at 330—345 mμ, which suggested the presence of small amounts only of the desired 1 : 2-bisdiazoacetyl*cyclo*butene.



(VI)



(VII)



(VIII)

TABLE 1. *Ultraviolet spectra of diazoketones.*

Compound	$\lambda_{max.}$ (mμ)	ε	Solvent	Source
$(CH_2 \cdot CH_2 \cdot CO \cdot CHN_2)_2$	248·5	18,200	EtOH	Present work
	270·5	17,370		
(−)-$CH_3 \cdot CH_2 \cdot CHMe \cdot CO \cdot CHN_2$	250	8,800	EtOH ?	Ref. 21
	267 •	7,600		
(+)-$Ph \cdot CH_2 \cdot CHMe \cdot CO \cdot CHN_2$	250	9,500	,,	,,
	270 •	7,700		
Long-chain aliphatic diazoketones	247	10,500	Pr^iOH	Ref. 22
$Ph \cdot CH{:}CMe \cdot CO \cdot CHN_2$	276 *	16,000	EtOH	Ref. 19
	304	18,500		
(VII ; R = H)	255 *	9,000	,,	,,
	276	10,400		
(VII ; R = Me)	273	10,500	,,	,,
*cyclo*Butane derivative (VIII)	257 •	14,050	,,	Present work
	281	19,630		

* Inflection.

If the double bond of the *cyclo*butene acid could be protected by the formation of a Diels–Alder adduct with anthracene the carboxyl function could then be twice bishomologated to give the adduct of anthracene with *cyclo*butene-1 : 2-dipropionic acid, which might then be dissociated[23] to give the dipropionic acid. The *cyclo*butene ester (V) was found to be rather unreactive as a dienophil. No adduct was formed when solutions in benzene, toluene, xylene, or dioxan were refluxed with anthracene during several days. Crystalline ester could be recovered from the benzene solution, but not from the others (nor could crystalline acid be obtained after hydrolysis), and this is attributed to the thermal cleavage mentioned above. The ester also failed to react with 2 : 3-dimethylbutadiene at room temperature. The activity of maleic anhydride as a dienophil has been correlated with enhanced ultraviolet absorption which it shows when it is dissolved in benzene.[24] The *cyclo*butene ester showed no enhanced absorption in benzene solution above 273 mμ, and addition of 0·1% of benzene to its methanolic solution caused no spectral change, thus apparently confirming its weakness as a dienophil.

Diene synthesis was therefore attempted by using the more reactive pentacene instead of anthracene. The desired adduct has been obtained, but so far only in small yield based on the ester used. An isomeric adduct was also obtained when the ester was added

---

[21] Wiberg and Hutton, *J. Amer. Chem. Soc.*, 1956, **78**, 1640.

[22] Vandenheuvel and Yates, *Canad. J. Res.*, 1950, **25**, *B*, 556.

[23] Diels and Friedrichsen, *Annalen*, 1934, **513**, 145; Diels and Thiele, *Ber.*, 1938, **71**, 1173; Bartlett and Tate, *J. Amer. Chem. Soc.*, 1953, **75**, 91; Baumgartner and Hugel, *Bull. Soc. chim. France*, 1954, 1005; Applequist and Roberts, Abs. 128th Meeting, Amer. Chem. Soc., 1955, 62-O; *J. Amer. Chem. Soc.*, 1956, **78**, 4012.

[24] Barb, *Trans. Faraday Soc.*, 1953, **49**, 143; Andrews and Keefer, *J. Amer. Chem. Soc.*, 1953, **75**, 3776.

to a solution of pentacene in boiling nitrobenzene, and this appears to be derived from dimethyl fulgenate.

EXPERIMENTAL

M. p.s are corrected, b. p.s uncorrected. Infrared spectra were examined in Nujol mull, and ultraviolet spectra on Unicam S.P. 500 spectrophotometers.

Bromination of cis-cyclo*Butane*-1 : 2-*dicarboxylic Anhydride.*—Anhydride (40 g.) was converted into the mixture of dibromo-dicarbonyl bromides (I and II) (b. p. 104—117°/0·4 mm.).[6] The crude mixture was poured into anhydrous methanol (300 ml.) in a cooled 1-l. flask fitted with an efficient reflux condenser. Excess of methanol was evaporated, the residue shaken with water (2 l.) and ether, and the ethereal layer washed successively with aqueous sodium hydrogen sulphite, aqueous sodium carbonate, and water, dried ($CaCl_2$), and evaporated to give the crude mixture of dibromides (III and IV) (94·2 g., 90%), which partly solidified. Crystallisation from methanol (charcoal; 2 crops) yielded nearly colourless plates of the *trans*-dibromide (IV) (46 g., 44%); the pure material (40 g.), obtained after further crystallisation from methanol (charcoal) and light petroleum (b. p. 60—80°), had m. p. 87—87·5° (Perkin gave m. p. 88—89°) (Found: C, 29·1; H, 2·9. Calc. for $C_8H_{10}O_4Br_2$: C, 29·1; H, 3·1%). Its infrared spectrum showed bands at 1730 (s; C:O str.) and 924 cm.$^{-1}$ (m; *cyclo*butane ?[25]).

The mother-liquor yielded no further crystals, and after evaporation was treated with ethanolic potassium iodide (see below); the product gave the cis-*dibromide* (III) (16·3 g., 15%) from ether at −40°; recrystallisation from ether afforded colourless rods, m. p. 41—42° (Found: C, 29·4; H, 3·1. $C_8H_{10}O_4Br_2$ requires C, 29·1; H, 3·1%). Its infrared spectrum showed bands at 1724 (s) and 918 cm.$^{-1}$ (m). Without the potassium iodide treatment, the *cis*-dibromide could be obtained from ether at −40°, but less pure.

The remaining mixture of *cyclo*butene ester (V) and *cis*-dibromide could not easily be separated by distillation, and was therefore treated with zinc dust in boiling ethanol (see below), and the product distilled. An almost colourless oil (b. p. 77—97°/1·0 mm.) was thus obtained, which solidified at −40° but melted again at room temperature; it consisted of dimethyl *cyclo*butene- and dimethyl *cyclo*butane-dicarboxylate, and its ultraviolet spectrum ($\lambda_{max.}$ 235 mμ, ε 6890, in MeOH) indicated that about 80% of the former was present. Hydrolysis (see below) yielded *cyclo*butene-1 : 2-dicarboxylic acid (4 g., 9%), and the mother-liquor from its crystallisation was shown by paper chromatography to contain *trans*-*cyclo*butane-1 : 2-dicarboxylic acid. It was calculated that the reaction had produced roughly 25% of *cis*- and 75% of *trans*-dibromide.

cis- *and* trans-1 : 2-*Dibromo*cyclo*butane*-1 : 2-*dicarboxylic Acid.*—A distilled mixture of the dibromo-dicarbonyl bromides was dissolved in warm aqueous acetone, and the solution evaporated. When the solid residue was heated at 170°/0·5 mm. *cis*-1 : 2-dibromo*cyclo*butane-1 : 2-dicarboxylic anhydride distilled. Crystallised from anhydrous benzene it formed colourless rods, m. p. 103—104° (Perkin gives m. p. 103—104°) (Found: C, 25·5; H, 1·25. Calc. for $C_6H_4O_3Br_2$: C, 25·4; H, 1·42%). Its infrared spectrum showed a strong doublet, 1822 and 1805 cm.$^{-1}$, characteristic of the anhydride grouping. It dissolved in boiling water and, on cooling, colourless hexagons of the pure *cis*-acid were deposited; they had m. p. 204—205° (sintered above 190°) [Perkin gives m. p. 202—205° (decomp.)] (Found: C, 24·0; H, 2·1. Calc. for $C_6H_6O_4Br_2$: C, 23·9; H, 2·0%). Its infrared spectrum showed strong bands at 2640, 2520, 1735, 1707, 1690, and 1672 cm.$^{-1}$. After the *cis*-anhydride has ceased to distil the temperature of the residue was raised to 210° and trans-1 : 2-*dibromo*cyclo*butane*-1 : 2-*dicarboxylic acid* sublimed from it. The acid formed colourless prisms, m. p. 247·5—248° (sintered above 190°) from xylene (Found: C, 24·1; H, 1·9. $C_6H_6O_4Br_2$ requires C, 23·9; H, 2·0%); its infrared spectrum showed strong bands at 2645, 2520, and 1705 cm.$^{-1}$.

Debromination of Dimethyl trans-1 : 2-*Dibromo*cyclo*butane*-1 : 2-*dicarboxylate* (IV).—The pure dibromide in ethanol was treated with powdered potassium iodide according to Perkin's directions; the colourless prisms of dimethyl *cyclo*butene-1 : 2-dicarboxylate (V), crystallised from light petroleum (b. p. 40—60°), had m. p. 45—46° (Perkin gives m. p. 44—46°), $\lambda_{max.}$ 232 mμ (ε 8700, in MeOH) (Found: C, 56·4; H, 5·9. Calc. for $C_8H_{10}O_4$: C, 56·5; H, 5·9%). Its infrared spectrum showed bands at 1735 (C:O str.) and 1635 cm.$^{-1}$ (C:C str.).

cyclo*Butene*-1 : 2-*dicarboxylic Acid.*—The pure ester (V) was digested for 20 min. with

---

[25] Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, pp. 28—29.

excess of alcoholic potassium hydroxide. After evaporation the residue was shaken with water and ether, and the aqueous layer acidified with hydrochloric acid and continuously extracted overnight. Evaporation of the ethereal extract left colourless crystals, m. p. 174·5 – 177·5° after crystallisation from water (yield 75%). Further crystallisation from water or dioxan gave plates of the pure acid, m. p. 178—178·5° (decomp.) [Perkin gives m. p. 178° decomp.)] (Found : C, 51·0; H, 4·3. Calc. for $C_6H_6O_4$: C, 50·7; H, 4·3%). Its infrared spectrum showed bands at 2600(m), 2470(m), 1695(s), 1650(mw), and 1590 cm.$^{-1}$ (s). Its ultraviolet spectrum ($\lambda_{max.}$ 235 mμ, ε 10,600, in H_2O) shows an auxochromic effect due to the *cyclo*butene ring.[10] Dehydronorcaryophyllenic acid (3 : 3-dimethyl*cyclo*butene-1 : 2-dicarboxylic acid) has $\lambda_{max.}$ 238·5 mμ (ε 11,300, in H_2O), and so shows a similar auxochromic effect, enhanced by a second-order contribution of the *gem*-dimethyl groups. We are grateful to Professor H. N. Rydon for supplying a specimen of this acid (m. p. 194—195° after sintering).

Debromination of Dimethyl cis-1 : 2-*Dibromo*cyclo*butane*-1 : 2-*dicarboxylate* (III) *by Zinc Dust in Boiling Solvents.*—In none of the solvents used did a spontaneous reaction occur at room temperature (contrast Berson and Swidler,[26] etc.). No debromination occurred in anhydrous benzene or xylene (2 hr.), but it was effected, together with extensive reduction, in glacial acetic acid and in propan-1-ol. Less reduction occurred in commercial methanol (impure *cyclo*butene ester could be crystallised at −40°), but in anhydrous methanol reduction was exclusive : paper chromatography of the product after hydrolysis revealed none of the *cyclo*butene ester, but only *trans-cyclo*butane-1 : 2-dicarboxylic acid. The latter was isolated from the product of the acetic acid experiment in the following way : the product (3·0 g.) was heated at 210° for 7 hr. in a sealed tube with concentrated hydrochloric acid (10 ml.); the resulting brownish solution was boiled with charcoal, filtered, and evaporated, and the residue crystallised from benzene–dioxan (twice) and benzene (twice), giving colourless *trans*-acid (0·5 g., 25%), m. p. (and mixed m. p.) 130—131°.

Ethanol proved to be the most satisfactory solvent, as the following experiment (after Kon and Nandi) shows : Zinc dust (0·4 g.) was added in five roughly equal portions during 1 hr. to a stirred and refluxing solution of the *cis*-dibromide (1·0 g.) in ethanol (8 ml.). After a further hour the mixture was cooled, filtered, and evaporated. Addition of water then gave a little precipitate which was dissolved on the addition of a few drops of acetic acid. After two extractions of the product with ether the extracts were combined, dried ($CaCl_2$), and evaporated, yielding a colourless oil which gave crystals of the *cyclo*butene ester (V), m. p. *ca.* 30°, from ether–light petroleum (b. p. 60—80°) at −40°. Distillation of the oil failed to separate its components; hydrolysis afforded crystalline *cyclo*butene acid and some *trans-cyclo*butane-1 : 2-dicarboxylic acid (paper chromatogram).

Application of this method of debromination to the *trans*-dibromide (IV) gave interesting results : when acetic acid or anhydrous methanol was used the products were the same as from the *cis*-dibromide, but with ethanol the starting material was recovered unchanged.

Paper Chromatography of Hydrolysates containing cyclo*Butene*-1 : 2-*dicarboxylic Acid.*—Whatman No. 54 paper was used, with cineole (25 ml.), *tert.*-butyl alcohol (25 ml.), formic acid (*d* 1·2; 5 ml.), and water (5 ml.) as the mobile phase. After development (ascending; 2 days) the paper was dried at 100° for 1 day and examined under ultraviolet light : the *cyclo*butene acid then showed as a dark spot. Bromocresol-green spray was then used to reveal all acid spots. In model experiments on the pure acids the following R_F values were found : *cyclo*butene acid, 0·67—0·72; *cis-cyclo*butane-1 : 2-dicarboxylic acid, 0·73—0·79; *trans-cyclo*butane-1 : 2-dicarboxylic acid, 0·81—0·86. All hydrolysates from reactions of the *cis*-dibromide (III) with zinc contained the *trans*-acid, but in none was the *cis*-acid detected with certainty.

Addition of Bromine to Dimethyl cyclo*Butene*-1 : 2-*dicarboxylate.*—Excess of the ester was dissolved in an anhydrous solution of bromine in carbon tetrachloride (Perkin used bromine vapour). The colour of the bromine had not disappeared overnight, but was slowly discharged when the solution was boiled; more bromine was added until the reaction was complete. The product after evaporation was crystallised from methanol; it had m. p. and mixed m. p. with *trans*-dibromide (IV), 86—87°.

Catalytic Hydrogenation of cyclo*Butene*-1 : 2-*dicarboxylic Acid.*—The acid (0·2 g.) in " AnalaR " acetic acid (7 ml.) was shaken for 10 hr. with a little platinic oxide in hydrogen at atmospheric pressure and temperature. The product was filtered and evaporated, and the

---

[26] Berson and Swidler, *J. Amer. Chem. Soc.*, 1954, **76**, 4057.

residue crystallised from ether–benzene, giving *cis-cyclo*butane-1 : 2-dicarboxylic acid, m. p. and mixed m. p. 138—140°.

Attempted trans-*Hydroxylation of* cyclo*Butene*-1 : 2-*dicarboxylic Acid*.—A filtered solution of tungstic oxide (10 mg.) in aqueous sodium hydroxide was acidified with concentrated hydrochloric acid, and the precipitate separated and washed four times with water by centrifugation. It was then dissolved in 100-vol. hydrogen peroxide (1 ml.) and added to the *cyclo*butene acid (1·0 g.) in water (20 ml.) at 85—90°. Drops of the solution were tested periodically with potassium iodide, further portions of peroxide being added when necessary. After 5 hr. (total, 8 ml. of peroxide added) all the *cyclo*butene acid had reacted since the solution no longer showed any absorption maximum at 235 mμ. Excess of peroxide was then destroyed at 100° and the solution evaporated to small bulk; succinic acid (0·46 g.) crystallised (m. p. 188°). Its identity was confirmed by its infrared spectrum and by the diphenacyl ester, m. p. 151—151·5° (lit.,[27] 147·5°, uncorr.).

cyclo*Butene*-1 : 2-*dicarbonyl Chloride*.—Prepared from the acid by refluxing it for 3 hr. with thionyl chloride, the chloride had b. p. 65°/1·0 mm. (70% yield). Atmospheric moisture rapidly hydrolysed it to the acid; with methanol it yielded the ester (V), m. p. and mixed m. p. 43·5—45°.

Reaction of cyclo*Butene*-1 : 2-*dicarbonyl Chloride with Diazomethane*.—The chloride (467 mg.) in dry ether (20 ml.) was added rapidly to a vigorously stirred solution (100 ml.) of diazomethane (439 mg., 4 mol.) which had been distilled and dried over sodium.[28] Stored overnight at −40° the mixture deposited pale yellow crystals (201 mg.), which were separated and washed with ether by decantation. Crystallisation from ether gave pale yellow prisms of cis-3 : 4-*bisdiazoacetyl*-3 : 4-cyclo*butano*-Δ^1-*pyrazoline* (VIII), m. p. 137—138° (decomp.) (Found: C, 46·6; H, 3·3. $C_9H_8O_2N_6$ requires C, 46·5; H, 3·5%). Its infrared spectrum showed bands at 2116 (s; N_2 in diazoketone), 1623 (s; C:O str.), 1550 (m; N:N str.), and 920 cm.$^{-1}$ (w; *cyclo*butane ? [25]); in related compounds [18,19,21,29] corresponding bands have been reported at 2270—2070 (N_2), 1645—1610 (C:O), and 1555—1550 cm.$^{-1}$ (N:N) : see also 1 : 4-bisdiazoacetylbutane (below).

1 : 4-*Bisdiazoacetylbutane*.—Obtained [30] from pure benzene as slim pale yellow plates, m. p. 69—70°, this gave an infrared spectrum with characteristic bands at 2100 and 1622 cm.$^{-1}$.

Pentacene (cf. refs. 31—35).—4 : 6-Dibenzoyl-*m*-xylene, colourless prisms, m. p. 105·5—106° (lit.,[33] 104°), was prepared in 28% yield from *m*-xylene. Pyrolysis of this diketone induces an Elbs reaction followed by disproportionation, to give 6 : 13-(symmetrical)dihydropentacene and not pentacene itself. A number of experiments were made to discover the best pyrolysis temperature, the dihydropentacene from each being isolated by chromatography. A Pyrex boiling tube containing the diketone (5 g.) was immersed in a metal-bath at 450—460° during ½ hr. After cooling, four such tubes were broken together and the hard black product extracted for 24 hr. with pure benzene (1·2 l.) in a universal extractor. The cooled extract was run on to an alumina column (750 g.; diam., 52 mm.) which was then developed with benzene. 6 : 13-Dihydropentacene formed a colourless zone (pale blue fluorescence in ultraviolet light) which was rapidly eluted, and obtained fairly pure from the pale yellow eluate (which fluoresced intensely pale blue). The yield was 7·9 g. (44%); once a yield of 62% was obtained. A specimen recrystallised twice from xylene and once from chloroform gave colourless jagged plates, m. p. 278—279° (lit.,[31] 273°), which fluoresced intensely pale blue in ultraviolet light (Found: C, 93·9; H, 5·7. Calc. for $C_{22}H_{16}$: C, 94·2; H, 5·8%). This fluorescence is rather surprising, being more characteristic of an anthracene than of a naphthalene structure. However, the ultraviolet spectrum is characteristic of a naphthalene structure, as Table 2 shows.

Dehydrogenation of 6 : 13-dihydropentacene, by phenanthrene-9 : 10-quinone in boiling nitrobenzene,[32] gave violet crystals of pentacene (25%) which were washed successively with nitrobenzene, ethyl acetate, and ether.

---

[27] Rather and Reid, *ibid.*, 1919, **41**, 75.
[28] *Org. Synth.*, Coll. Vol. II, p. 165.
[29] Bose and Yates, *J. Amer. Chem. Soc.*, 1952, **74**, 4703; ref. 25, p. 229.
[30] Walker, *J.*, 1940, 1304.
[31] Clar and John, *Ber.*, 1929, **62**, 3021.
[32] *Idem, ibid.*, 1930, **63**, 2967.
[33] *Idem, ibid.*, 1931, **64**, 981.
[34] Clar, John, and Hawran, *ibid.*, 1929, **62**, 940.
[35] Clar, *Chem. Ber.*, 1949, **82**, 495.

Adduct of Pentacene with Dimethyl cyclo*Butane*-1 : 2-*dicarboxylate*.—A suspension of pentacene (0·22 g.) in pure benzene (20 ml.) containing the ester (2·0 g., 15 mol.) was heated in a sealed tube at 95° during 8 days. The product was filtered to remove traces of pentacene and brownish solid, and the filtrate evaporated, giving a viscous, orange-brown oil. None of the ester could be recovered from this oil by vacuum-sublimation. It slowly deposited rods (*ca.* 25 mg.) of the *adduct*, which was recrystallised from chloroform–light petroleum (b. p. 40—60°) and from methyl propionate, then having m. p. 278—278·5°; it showed a pale blue fluorescence in ultraviolet light, weaker than that of 6 : 13-dihydropentacene [Found: C, 80·2; H, 5·4%; *M* (Rast), 350. $C_{30}H_{24}O_4$ requires C, 80·3; H, 5·4%; *M*, 448]. Its ultraviolet spectrum (in $CHCl_3$) was similar to that of 6 : 13-dihydropentacene (see Table 2): $\lambda_{max.}$ 272 (ε 17,750), 281·5 (ε 15,300), 309·5 (ε 1400), and 324·5 mμ (ε 1810); at 254 mμ, ε = 69,920. Its infrared spectrum showed one characteristic band at 1725 cm.$^{-1}$ (s; C:O str.). Both this and the adduct described below liberated pentacene when heated in capillary tubes with a naked flame.

Adduct of Pentacene with Dimethyl Fulgenate (*Buta*-1 : 3-*diene*-2 : 3-*dicarboxylate*).—Pentacene (440 mg.) was dissolved in boiling nitrobenzene (440 ml.), and the ester (total *ca.* 3 mol.) added portionwise until the colour of the solution changed from maroon to reddish-brown (20 min.). The solution was left to cool and then evaporated at 0·3 mm. on the water-bath, leaving a brown, partly solid residue which was dissolved in pure benzene (90 ml.); the filtered solution was run on to a column of neutral activated alumina (90 g., diam. 19 mm.). The column was developed with benzene and eluted in fractions. The first 525 ml. of eluate afforded minor quantities of oil; a colourless zone (3·5 cm.), which fluoresced intensely pale blue in ultraviolet light, then occupied the lower part of the column, and came off in the next 1300 ml. of eluate, evaporation of which left 360 mg. (53%) of the *adduct*. Recrystallised from methyl propionate it had m. p. 233·5—234·5° (decomp.), and fluoresced intensely pale blue in ultraviolet light [Found: C, 80·1; H, 5·3%; *M* (Rast), 343. $C_{30}H_{24}O_4$ requires C, 80·3; H, 5·4%; *M*, 448]. Its ultraviolet spectrum in $CHCl_3$ (cf. above and Table 2) had max. at 271·5 (ε 18,200), 280·5 (ε 15,600), 309 (ε 1500), 324 mμ (ε 1870); at 254 mμ, ε = 50,970. Its infrared spectrum showed bands at 1750 (s; C:O str. in ester), 1726 (s; C:O str. in αβ-unsaturated ester), and 1631 cm.$^{-1}$ (m.; C:C str., adjacent to carbonyl).

TABLE 2.

2 : 3-Dimethylnaphthalene (in 2-methylheptane) [36]		6 : 13-Dihydropentacene (in 2-methylheptane)		6 : 13-Dihydropentacene (in ethanol) [35]	
$\lambda_{max.}$ (mμ)	ε × 2	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
—	—	214	50,600	—	—
226·5	287,800	235	186,000	234·5	144,500
—	—	261	10,400	261	11,500
268·5	9,820	270	12,200	271	12,900
278·5	10,440	279·5	12,000	281	11,800
288	7,020	290·5	7,640	292	7,240
302	790	—	—	—	—
306	930	305·5	1,760	305·5	1,580
315	556	315	786	315	794
320	706	320	1,690	319·5	1,450

A Maintenance Grant provided by the Department of Scientific and Industrial Research is gratefully acknowledged (J. J. W.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

Received, December 5th, 1956.]

---

[36] A.P.I. Ultraviolet Spectrum, No. 222.