

*Anal.* Calcd. for  $C_{12}H_{22}N_3O_4$ : C, 42.10; H, 6.48. Found: C, 42.03; H, 6.74.

**Tetraethyl Bicyclo[3.3.0]octane-2,4,6,8-tetracarbamate (XIV).**—To a solution of 500 mg. of the tetrahydrazide XIII in 20 ml. of 5% hydrochloric acid there was added 25 ml. of ether and the mixture was cooled in an ice-bath. A solution of 860 mg. of sodium nitrite in 10 ml. of water was added dropwise with stirring. After the mixture had been stirred with cooling an additional 20 min., the ether layer was separated and the aqueous layer was extracted twice with ether. The combined ether extracts were washed with a 5% aqueous bicarbonate solution and then dried. Absolute ethanol (25 ml.) was added and the solution was concentrated until a boiling point of 70° was reached. Then, the alcoholic solution was boiled under reflux for 5 hr. Removal of the ethanol gave a yellow solid which, on crystallization from acetone-water, gave 200 mg. (30%) of white leaflets, m.p. 250–252° dec.

*Anal.* Calcd. for  $C_{20}H_{34}N_4O_3$ : C, 52.39; H, 7.47; N, 12.22. Found: C, 52.22; H, 7.37; N, 12.19.

**2,4,6,8-Tetra-(dimethylamino)-bicyclo[3.3.0]octane, (XVI).**—A solution of 200 mg. of the tetracarbamate XIV in 16 ml. of concd. hydrochloric acid was boiled under reflux for 24 hr. Removal of the solvent under reduced pressure followed by drying in the presence of potassium hydroxide pellets in a desiccator gave 136 mg. (100%) of grainy white crystals, which darkened at 225° but did not melt below 350°. The tetraamine XV tetrahydrochloride was soluble in water and ethanol but not in organic solvents. Since attempts to purify it were not successful, it was converted directly to the corresponding dimethylamino derivative. To a solution of 136 mg. of the tetraamine XV tetrahydrochloride in 20 ml. of water there was added 2 ml. of 5% hydrochloric acid, 2 ml. of aqueous formaldehyde (35%) and 100 mg. of Adams catalyst. The mixture was subjected to hydrogenation at room temperature and 3 atm. pressure of hydrogen for 12 hr. After removal of the catalyst, the solution was made basic and extracted with ether. When the ether extracts had been dried over solid potassium hydroxide, concentration gave a gummy solid. This was taken up in petroleum ether and chromatographed over Woelm basic alumina. Elution with a 3:1 petroleum ether-ether mixture gave 135 mg. (45%) of white crystals, m.p. 92.5–93.5°. Attempts to convert XV to XVI using the conditions of the Eschweiler-Clarke procedure gave the same product but only in 10% yield.

*Anal.* Calcd. for  $C_{16}H_{24}N_4$ : C, 68.03; H, 12.13; N, 19.84. Found: C, 68.54; H, 12.15; N, 19.92.

**Thermal Decomposition of the Tetraoxide of XVI.**—The preparation of the tetraoxide of XVI and its thermal decomposition was carried out following the procedure described by Cope and Bumgardner for the preparation of 1,4-pentadiene.<sup>25</sup> Vigorous decomposition of the tetraoxide of XVI occurred in the range of 95–120° under 10 mm. pressure of nitrogen. No evidence for a volatile hydrocarbon fraction was obtained. The contents of the first trap cooled with Dry Ice-acetone were washed out with 5% hydrochloric acid and extracted with pentane. The pentane solution was transparent in the ultraviolet region and left no residue on concentration. Evaporation of the aqueous layer gave a solid which, after recrystallization from ethanol-ether, was obtained as white needles, m.p. 98–101° (the melting point reported<sup>26</sup> for N,N-dimethylhydroxylamine is 104.5–106°). The residue in the flask from the thermal decomposition was a black solid insoluble in water, acid or the common organic solvents, suggesting that it is polymeric in nature. When the experiment was repeated in the presence of tetracyanoethylene using bis(2-methoxyethyl) ether as solvent, the outcome was essentially the same. It was hoped that an adduct might be formed to indicate the transient existence of pentalene. No such simple adduct was isolated although the black solid residue in this instance showed an altered infrared spectrum having absorption at 4.56  $\mu$  (nitrile) indicating that the tetracyanoethylene had become involved in the reaction product.

**Attempted Degradation of XVI by the Hofmann Exhaustive Methylation Procedure.**—Treatment of the tetraamine XVI (77 mg.) with methyl iodide (1.6 g.) and 1.5 ml. of methanol under nitrogen at 50° for 40 hrs. gave the quaternary tetramethiodide as a gum. A similar result was obtained when the mixture was heated at 100° for 23 hr. The tetramethiodide was somewhat unstable and attempts to purify it by recrystallization from methanol apparently led to some displacement by iodide giving material of continually increasing carbon content. Thus, after two crystallizations from methanol a yellow solid, decomposing about 205°, was obtained whose composition (C, 30.40; H, 5.90; N, 7.56) indicated it to be a mixture of tetramethiodide and presumably some trimethiodide. Because of this instability the crude tetramethiodide was converted directly to the corresponding tetrahydroxide by passage over an ion exchange column (Dowex 2) and the resulting gum was decomposed by heating it in a short path still under reduced pressure. Although trimethylamine was evolved, there was no indication of a volatile hydrocarbon. The residue in the distilling flask was again an insoluble black solid.

(33) A. C. Cope, R. A. Pike and C. F. Spencer, *THIS JOURNAL*, **75**, 3212 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

## Schroeter and Vossen's "Red Salt" and Related Bicyclo[3.3.0]octane Derivatives<sup>1</sup>

BY PETER YATES,<sup>2</sup> ELLI SMAKULA HAND AND GARGI BHAT FRENCH

RECEIVED JULY 7, 1960

The "red salt,"  $C_{16}H_{15}O_{10}Na$ , obtained by the condensation of dimethyl (2,2,2-trichloroethylidene)-malonate (I) with dimethyl malonate in the presence of sodium methoxide has been shown to be tetramethyl sodio-3,7-dioxobicyclo[3.3.0]oct-1-ene-2,4,6,8-tetracarboxylate (II), as originally suggested by Schroeter and Vossen. Its transformation to a series of other bicyclo[3.3.0]octane derivatives has been effected and one of these, a bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic acid (XII), has been correlated with an acid of the same structure, but different stereochemistry, obtained by other workers from the oxidation of the Diels-Alder adduct (XIV) of bicyclo[2.2.1]heptadiene and cyclopentadiene. A study of dianhydride formation in this series has permitted the assignment of the stereochemistry of the acid XII. The bromination products of tetramethyl bicyclo[3.3.0]octadiene-2,4,6,8-tetracarboxylate (X) and of the "red salt" have been investigated.

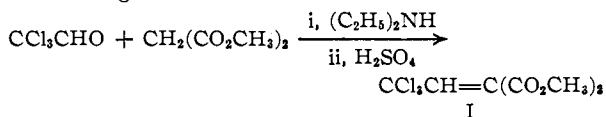
In 1910, Vossen,<sup>3</sup> working in Schroeter's laboratory, reported that dimethyl (2,2,2-trichloroethylidene)-malonate (I), gave with dimethyl malonate

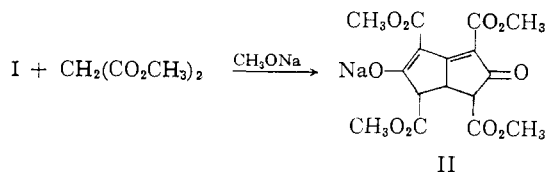
in the presence of sodium methoxide a red crystalline salt,  $C_{16}H_{15}O_{10}Na$ , to which he assigned the interesting structure II. Vossen made a careful

(1) A preliminary account of part of this work has appeared previously: P. Yates and G. Bhat, *Chemistry & Industry*, 1237 (1954).

(2) Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

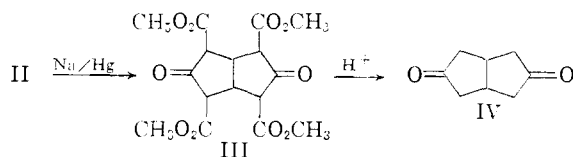
(3) G. Vossen, *Dissertation*, Bonn, 1910.





study of several reactions of the "red salt" but obtained no conclusive evidence for the presence of the bicyclo[3.3.0]octane ring system. Schroeter<sup>4</sup> later described its conversion to the parent hydrocarbon, but the physical constants given for this material did not correspond well with those of either *cis*- or *trans*-bicyclo[3.3.0]octane.<sup>5</sup> Strength was lent to the structural proposal II by the results of oxidation experiments carried out by Brüggemann,<sup>6</sup> also working in Schroeter's laboratory. He degraded the "red salt" to a compound considered to be a 2-carboxycyclopentaneacetic acid, but no direct comparison was made with either of the diastereoisomers of this compound.

We were led to investigate further the structure and reactions of the "red salt" because of its possible use as an *entrée* into the pentalene series. Reduction of the "red salt" with sodium amalgam gave a reduction product which on acid hydrolysis yielded a compound which was formulated by Vossen<sup>3</sup> as a bicyclo[3.3.0]octane-3,7-dione (IV) on the basis of his assignment of structure II to the "red salt"; he assigned structure III to the reduction product. We have found that the



infrared spectrum of the hydrolysis product shows a single sharp peak at 5.75  $\mu$ . This observation, demonstrating the presence of five-membered cyclic ketone groups only, taken together with the earlier observations that this compound forms a dioxime and a tetracinnamal derivative,<sup>3</sup> showing the presence of two ketone groups each flanked by two methylene groups, establishes the structure IV unambiguously, and thus confirms the structure II assigned to the "red salt" by Vossen and Schroeter. It may be anticipated that the sodium amalgam reduction of II would lead to the more stable<sup>5</sup> *cis*-ring fusion of the bicyclo[3.3.0]octane system, and thus the diketone IV can be assigned the *cis* structure.<sup>7,8</sup>

The infrared spectrum of the "red salt" itself is complex, showing bands at 5.78, 5.91, 6.01, 6.15 (weak), 6.35 (infl.) and 6.50 (v. strong)  $\mu$ . The complexity of the conjugated system (*cf.* IIa)

(4) G. Schroeter, *Ann.*, **426**, 1 (1922).

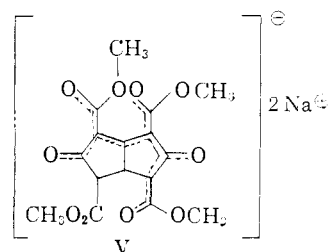
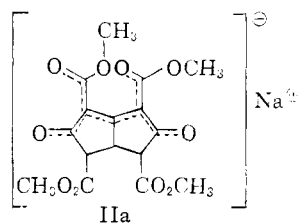
(5) *Cf.* R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934); J. W. Barrett and R. P. Linstead, *ibid.*, 436 (1935).

(6) J. Brüggemann, Dissertation, Berlin, 1940.

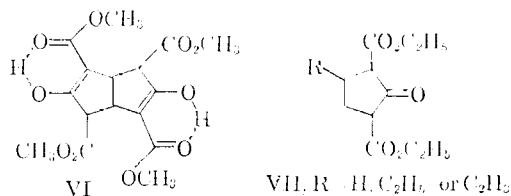
(7) H. W. Wanzlick, *Chem. Ber.*, **86**, 269 (1953), has independently confirmed the structure of the diketone IV and demonstrated its stereochemistry by converting it to the known *cis*-bicyclo[3.3.0]octan-3-one semicarbazone.

(8) Other contributions have been made recently to the study of the structure of the "red salt" and related compounds: (a) H. Paul and I. Wendel, *Chem. Tech.*, **8**, 189 (1956) [*C. A.*, **51**, 5713 (1957)]; (b) S. Tanaka, *THIS JOURNAL*, **80**, 5264 (1958).

makes vibrational assignments difficult; however, the presence of unconjugated ester groups is vouchsafed by the band at 5.78  $\mu$ .<sup>9</sup> The ultraviolet



spectrum<sup>10</sup> of the "red salt" in aqueous solution shows maxima at 257  $m\mu$  ( $\epsilon$  11,700), 340  $m\mu$  ( $\epsilon$  52,800) and 473  $m\mu$  ( $\epsilon$  47),<sup>11</sup> shifted in *ca.* 1 *N* methanolic sodium methoxide to 287  $m\mu$  ( $\epsilon$  22,000), 339  $m\mu$  ( $\epsilon$  23,050) and 385  $m\mu$  ( $\epsilon$  6000); the change in the spectrum can be attributed to the formation of the dianion corresponding to the "yellow salt,"  $\text{C}_{16}\text{H}_{14}\text{O}_{10}\text{Na}_2$  (V), prepared by Vossen.<sup>3</sup> The reduction product III shows bands in its infrared spectrum at 5.73, 5.95 and 6.10  $\mu$ , and in ethereal solution a maximum in its ultraviolet spectrum at 247  $m\mu$ , shifted to 279  $m\mu$  ( $\epsilon$  34,000) in aqueous 2% potassium hydroxide. The 5.95 and 6.10  $\mu$  bands can be assigned to the chelated enolized  $\beta$ -ketoester system in tautomers such as VI,<sup>12</sup> and the band at 5.73  $\mu$  to the isolated ester groups, perhaps superimposed on carbonyl absorption due to tautomers with unenolized ketonic groups.<sup>13</sup> The maximum at 247  $m\mu$  is similar in position to the maxima reported for the enolized tautomers of



(9) The very strong band at 6.50  $\mu$  is reminiscent of the strong bands observed in the spectra of other compounds containing similar highly conjugated systems; *cf.* (a) P. Yates, D. G. Farnum and G. H. Stout, *ibid.*, **80**, 196 (1958); (b) H. J. Dauben, Jr., and G. Feniak, quoted in *ref.* 8b.

(10) These ultraviolet spectral studies were made in collaboration with Mr. George F. Field.

(11) The major band may be compared with that of the sodium salt of 4-cholestene-3,7-dione at 392  $m\mu$  ( $\epsilon$  62,000): C. W. Greenhalgh, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 2375 (1952).

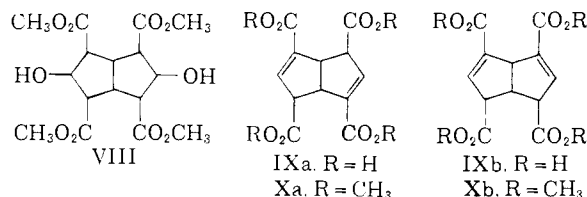
(12) *Cf.* N. J. Leonard, H. S. Gutowsky, W. J. Middleton and E. M. Petersen, *THIS JOURNAL*, **74**, 4070 (1952).

(13) The sharpness of the 5.73  $\mu$  band favors an interpretation of the spectrum in terms of a high preponderance of doubly enolized tautomers of type VI in chloroform solution. However, to accommodate this interpretation it is necessary to reverse the previous assignments<sup>12</sup> for isolated ester and unenolized ketonic groups in the spectra of related cyclopentanone derivatives. Such a reversal of assignment appears not to be unreasonable.

ethyl acetoacetate (244  $m\mu$ )<sup>14</sup> and ethyl 2-oxocyclopentanecarboxylate (254  $m\mu$ ).<sup>15,16</sup>

When the "red salt" was hydrogenated in aqueous acetic acid over platinum, approximately three molar equivalents of hydrogen was taken up slowly. Unusually large amounts of catalyst were required to ensure completion of this process at atmospheric pressure; the amount of catalyst could be reduced if the hydrogenation was carried out at an initial pressure of 3–4 atmospheres. The product thus obtained was a semi-solid material which is considered to be a mixture of stereoisomeric diols of structure VIII on the basis of its method of formation and infrared spectrum (bands at 2.85, 5.76 and 5.82  $\mu$ ). A sample was subjected to repeated recrystallization, yielding a crystalline product, m.p. 182–186° (softening at 170°), with an infrared spectrum similar to that of the crude product; elementary analysis of the crystalline product gave results concordant with the composition  $C_{16}H_{22}O_{10}$ , but the wide melting range of this material indicated that resolution of the stereoisomers was not complete.

The crude, semi-solid hydrogenation product was subjected directly to dehydration. This process was found to be effected best by reaction of the diol mixture with concentrated sulfuric acid on the steam-bath. When the reaction mixture was quenched in water there was obtained a crystalline acid,  $C_{12}H_{10}O_8$ , which is formulated as a bicyclo-[3.3.0]octadiene-2,4,6,8-tetracarboxylic acid (IXa or IXb). Its infrared spectrum (bands at 3.2–



3.8, 5.78, 5.84 and 6.13  $\mu$  in dioxane) shows the presence of both unconjugated and conjugated carboxylic acid groups.<sup>18</sup> Its ultraviolet spectrum ( $\lambda_{\max}^{E:OH}$  (app.) 210  $m\mu$  ( $\epsilon$  16,600)) is consistent with the presence of two  $\alpha,\beta$ -unsaturated acid chromophores.<sup>19</sup> The position of the apparent ultraviolet maximum excludes alternative formulations of the diene in which the ethylenic bonds are conjugated. The maximum falls at a shorter wave length than

(14) P. Grossmann, *Z. physik. Chem.*, **109**, 305 (1924).

(15) E. S. Levin, *Bull. acad. sci. U.R.S.S., Ser. phys.*, **11**, 413 (1947) [*C. A.*, **42**, 3261 (1948)].

(16) Closer models are available from work on the series of compounds VII; in aqueous 2% potassium hydroxide these all show ultraviolet maxima at 290–291  $m\mu$  with  $\epsilon = 14,000$ –17,500 (together with an inflection at 282–283  $m\mu$  in two cases).<sup>17</sup> This high intensity absorption is clearly due to the anions of the compounds VII, and the band at 279  $m\mu$  in the spectrum of III in basic medium may similarly be assigned to anions related to VI. The intensity of this band indicates that in the aqueous 2% potassium hydroxide III is converted almost completely to a dianion. The hypsochromic shift of the band relative to the bands of anions derived from the series of compounds VII may be attributed to dipole interactions between the two chromophoric systems.

(17) R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.*, 3616 (1952).

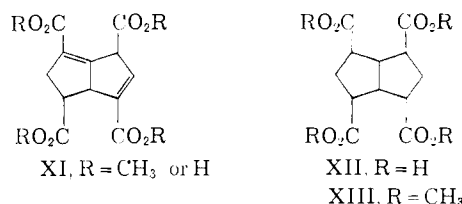
(18) Cf. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co., Ltd., London, 2nd ed., 1958, p. 166.

(19) A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

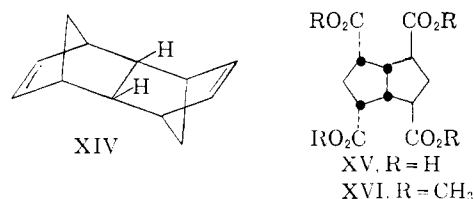
that observed for 1-cyclopentencarboxylic acid ( $\lambda_{\max}^{E:OH}$  222  $m\mu$  ( $\epsilon$  9,500)).<sup>20</sup> This hypsochromic shift may be attributed to dipole interaction between the two chromophoric systems.<sup>21</sup>

Since the dehydration of the diol VIII was effected under strongly acidic conditions, the possibility that skeletal rearrangement had occurred during the reaction could not immediately be excluded. This possibility could be eliminated, however, on the grounds that dehydration of the diol with phosphorus oxychloride and pyridine or with *p*-toluenesulfonyl chloride and pyridine gave an ester,  $C_{16}H_{18}O_8$ , identical to the product obtained by esterification of the acid IX with diazomethane. The ester, which shows infrared bands at 5.78 (infl.), 5.85 and 6.12  $\mu$  (in  $CHCl_3$ ) and an ultraviolet maximum similar to that of the acid, is therefore formulated as Xa or Xb.<sup>22</sup>

Hydrogenation of the unsaturated ester X over platinum proceeded with the uptake of two molar equivalents of hydrogen and gave a saturated ester, m.p. 94.5–95°, with a single band in the carbonyl region of its infrared spectrum; this is assigned



structure XIII. Hydrogenation of the unsaturated acid IX in similar fashion gave the corresponding saturated acid XII, which could be converted to the ester XIII by the action of diazomethane. Recently, an acid of the same gross structure has been obtained in two other laboratories<sup>23,24</sup> by an entirely different route, *viz.*, by the oxidation with potassium permanganate of the Diels–Alder adduct XIV of cyclopentadiene and bicyclo[2.2.1]heptadiene. The demonstration of the stereochemistry of the adduct permitted both groups of workers to assign the full structure XV to the tetra-acid obtained on oxidation.



Boekelheide and his co-workers<sup>24</sup> prepared the tetramethyl ester XVI of the acid XV and thus made possible a correlation between this series and the saturated ester XIII derived from Vossen's

(20) O. H. Wheeler, *THIS JOURNAL*, **78**, 3216 (1956).

(21) Cf. V. Georgian, *Chemistry & Industry*, 930 (1954), 1480 (1957); cf. also ref. 16.

(22) It may be noted that XI, the remaining double bond isomer without conjugated double bonds, can be rejected as the structure for the ester or acid, since its formation from the diol would require intermediate states of excessively high energy.

(23) J. K. Stille and D. A. Frey, *THIS JOURNAL*, **81**, 4273 (1959).

(24) E. R. Hanna, K. T. Finley, W. H. Saunders, Jr., and V. Boekelheide, *ibid.*, **82**, 6342 (1960).

salt. For, provided that XIII has a *cis*-fused ring system, both it and the ester XVI should give the same product on base-catalyzed equilibration.

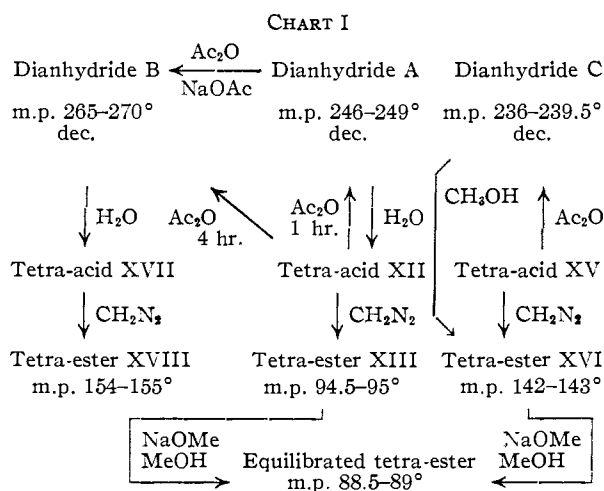
The ester XVI differed in both its m.p., 142–143°, and its infrared spectrum from the ester XIII, m.p. 94.5–95°.<sup>25</sup> When either ester was equilibrated with sodium methoxide in boiling methanol, an oil was obtained which upon chromatography and crystallization yielded as the major crystalline fraction a product, m.p. 88.5–89°, whose elementary analysis indicated it to be isomeric with the esters XIII and XVI.<sup>26</sup> The products from both sources were shown to be identical by a mixture m.p. and by infrared spectral comparison. Thus the structures assigned to the "red salt" and its derivatives stand confirmed and the *cis*-ring junction of the derived tetra-ester XIII is demonstrated.<sup>27</sup>

When the acid XII was heated with boiling acetic anhydride for one hour it was converted to a dianhydride, C<sub>12</sub>H<sub>10</sub>O<sub>6</sub>, m.p. 246–249° dec., infrared bands at 5.51, 5.66 and 9.42  $\mu$ . This compound ("dianhydride A") was reconverted to XII on hydrolysis in aqueous acetonitrile, demonstrating that no change of configuration occurs in its formation. When XII was heated with boiling acetic anhydride for four hours it was converted to a compound, m.p. 265–270° dec., with infrared bands at 5.55, 5.65 and 9.05  $\mu$ , isomeric with dianhydride A. This product ("dianhydride B") could also be obtained by treating dianhydride A with sodium acetate in boiling acetic anhydride. When dianhydride B was hydrolyzed in aqueous acetonitrile, it was converted to a new acid, XVII, isomeric with XII and XV, which gave with diazomethane an ester XVIII, m.p. 154–155°, isomeric with XIII and XVI. A third isomeric dianhydride, m.p. 236–239.5° dec. (here referred to as "dianhydride C"), has been obtained both by Stille and Frey<sup>23</sup> and by Boekelheide and co-workers<sup>24</sup> by the action of boiling acetic anhydride on their acid XV. The latter group of workers has shown that dianhydride C is formed from XV without change of configuration since it could be converted to the corresponding tetramethyl ester XVI. The relationship between the dianhydrides, acids and esters is summarized in Chart I.

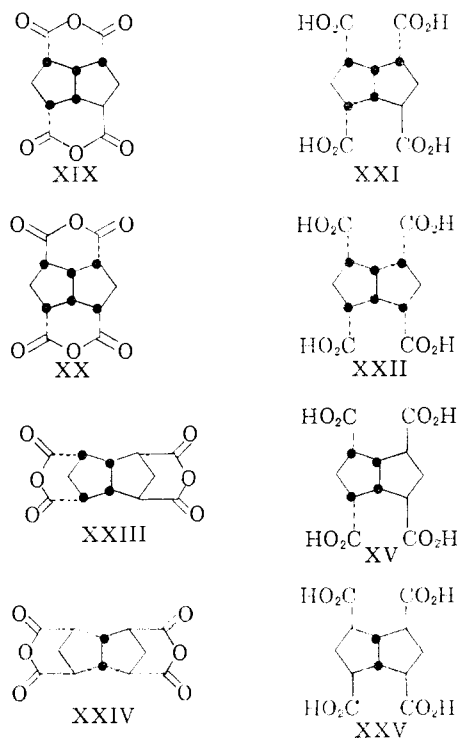
(25) We are grateful indeed to Professor Boekelheide for his courtesy in supplying us with a sample of his ester, XVI, and in informing us of his results prior to publication.

(26) In spite of the sharp melting point of this product and the constancy of this melting point over several recrystallizations, it is very likely that the product is not a single stereoisomer, but is a eutectic mixture of stereoisomers, since on rechromatography it yielded fractions with wide melting point ranges. It was of interest to find that one such fraction from the product derived by equilibration of XIII gave on repeated recrystallization a small quantity of a crystalline product, m.p. 142–143°, shown to be identical to the ester XVI. Thus, this compound must either be a component of the product, m.p. 88.5–89°, or be formed from it by equilibration on the alumina column during chromatography. This observation serves as an additional point of correlation between the esters XIII and XVI.

(27) Hanna, Finley, Saunders and Boekelheide<sup>24</sup> have also achieved the correlation of the esters XIII and XVI in a similar manner. Their fraction "A," m.p. 88–89°, from the base-catalyzed equilibration of XIV which they consider may be a eutectic mixture, clearly corresponds to our equilibration product. They succeeded in obtaining a second product from the equilibration reaction, fraction "B," m.p. 94–95°, which probably corresponds to our ester XIII.

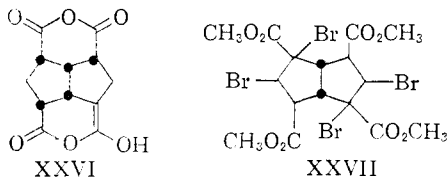


Examination of Stuart–Briegleb models suggests that only four dianhydrides can be formed in this series: the interannular anhydrides XIX and XX corresponding to the acids XXI and XXII, and the intraannular anhydrides XXIII and XXIV corresponding to the acids XV and XXV. Structure XXIII must be assigned to dianhydride C.<sup>23,24</sup> The pair of structures XIX and XX may be assigned to dianhydrides A and B since the isomerization of the former to the latter under mild conditions precludes the assignment of structure XXIV to either.<sup>28</sup> Further, since XIX possesses a

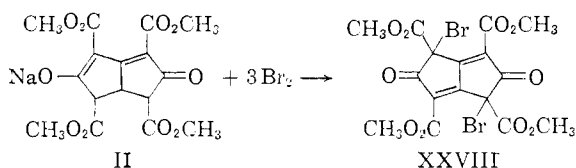


(28) The assignment of structure XXIV to dianhydride A may also be ruled out on the ground that this would require the assignment of structure XXV, in which the hydrogen atoms at C.2, 4, 6 and 8 are all *trans* to those at C.1 and 5, to the acid XII formed by hydrogenation of IX. This hydrogenation would not be expected to proceed *via* addition of hydrogen to the sides of the rings *trans* to the hydrogen atoms at C.1 and 5, for the geometry of the *cis*-bicyclo[3.3.0]octane system should make absorption on the catalyst in this sense very difficult.

strained *trans*-bridged anhydride ring, isomerization (*via* the enol XXVI) would be anticipated to favor XX, in which both anhydride rings are *cis*-bridged. Thus, structure XIX may be assigned provisionally to dianhydride A and XX to dianhydride B.<sup>29</sup> This view leads to the assignment of structure XXI to the acid earlier designated as XII and of XXII to the isomeric acid (XVII) obtained on hydrolysis of dianhydride B.



Attempts were made to introduce additional unsaturation into the unsaturated ester X. When this was treated with liquid bromine it was converted to a tetrabromo derivative, formulated as XXVII (or the similar structure corresponding to Xb). This compound on treatment with zinc and ethanol reverted to its progenitor X; this observation demonstrates that no rearrangement occurred during the bromination. When debromination of XXVII was attempted with boiling dimethylaniline, debromination occurred instead and the unsaturated ester X was again regenerated.<sup>30</sup> Attempts to debrominate XXVII with anhydrous sodium carbonate or acetate were also fruitless. In connection with these experiments involving the bromination of X, attention may be called to the bromination of the "red salt" itself. Vossen described the formation of a bright yellow product on treatment of the "red salt" with bromine water. He assigned to this the formula  $C_{16}H_{16}O_{10}Br_2$ ; this formulation, however, fails to account for the reported consumption of 2.5–3 molar equivalents of bromine during the reaction. We have repeated this preparation and have also obtained the same product more conveniently by bromination of the "red salt" in aqueous dioxane.<sup>31</sup> Although the instability of this product made it difficult to obtain satisfactory analytical data, the revised formulation  $C_{16}H_{12}O_{10}Br_2$  is proposed for this product. It shows in its infrared spectrum bands at 5.66, 5.69, 5.80 and 6.08  $\mu$ , and is tentatively assigned the structure XXVIII.<sup>32</sup> Its ultraviolet spectrum shows maxima at 257 and 302  $m\mu$ , compatible with this formulation.<sup>33</sup>



(29) Very recently the preparation of the *endo-endo* analog of XIV has been announced: P. Bruck, D. Thompson and S. Winsteln, *Chemistry & Industry*, 590 (1960). This paves the way for a direct test of the stereochemical assignment here suggested for dianhydride B.

(30) This debromination may occur by a purely thermal process, but is probably base-catalyzed; cf. A. Roedig and K. Klepert, *Ann.*, **593**, 55 (1955).

(31) These experiments were carried out in collaboration with Mr. Roy H. Karlson and Mr. George F. Field.

(32) An alternative formulation with a cyclopentadienone ring is also possible, but is considered to be less likely.

Attempted bromination of the unsaturated acid IX or ester X with N-bromosuccinimide failed to give crystalline products. Similar failures attended the attempted dehydrogenation and oxidation of these compounds or their congeners.

#### Experimental<sup>34</sup>

**Dimethyl (2,2,2-Trichloro-1-hydroxyethyl)-malonate.**<sup>35</sup>—Diethylamine (*ca.* 1 g.) was added drop by drop to a mixture of dimethyl malonate (freshly distilled, 33 g.) and chloral (freshly distilled, 36.9 g.). The first few drops produced a mist above the mixture (due, presumably, to formation of amine hydrochloride with small amounts of hydrogen chloride in the chloral); subsequent drops produced a rise in the temperature of the mixture, which was maintained below 40° by vigorous swirling in an ice-salt-bath when necessary. When further addition of diethylamine resulted in no further temperature rise, the mixture was left to stand for 2 hours. The solid product was dissolved in hot ligroin (500 g.); on standing overnight the solution deposited white prisms (56.3 g.), m.p. 87.5–89° (lit.<sup>3</sup> m.p. 86°);  $\lambda_{max}^{CHCl_3}$  2.93, 5.71, 5.78  $\mu$ . Concentration of the mother liquor gave a further 2.0 g. of product (combined yield 83%).

**Dimethyl (2,2,2-Trichloroethylidene)-malonate (I).**—Dimethyl (2,2,2-trichloro-1-hydroxyethyl)-malonate (35 g.) was finely powdered and added to concentrated sulfuric acid (152 ml.). The mixture was swirled until solution was complete. The solution was allowed to stand overnight and then poured onto crushed ice (1 kg.) with vigorous stirring. The solid which separated was filtered, washed with cold water and dried in a vacuum desiccator over concentrated sulfuric acid; the yield was quantitative. Recrystallization from ligroin gave the product as large prisms, m.p. 62.5–64° (lit.<sup>3</sup> m.p. 66°);  $\lambda_{max}^{CHCl_3}$  5.75, 6.04(w)  $\mu$ .

**Tetramethyl Sodio-3,7-dioxobicyclo[3.3.0]-oct-1-ene-2,4,6,8-tetracarboxylate ("Red Salt," II).**—Dimethyl malonate (79 g.) was added to a solution prepared by dissolving sodium (13.8 g.) in anhydrous methanol (300 ml.). The mixture was cooled in an ice-salt-bath at –10° and finely powdered dimethyl (2,2,2-trichloroethylidene)-malonate (26.1 g.) was added all at once. The mixture was removed from the cooling bath and swirled vigorously while the temperature rose to 30–40°. When the temperature rose above 40°, the mixture was cooled by vigorous swirling in the ice-salt-bath. When its temperature showed no further tendency to rise, the orange mixture was left to stand at room temperature overnight. It was then made just acid with methanolic hydrogen chloride and filtered immediately and rapidly through a hardened, fluted filter paper to remove sodium chloride. The dark red filtrate on standing overnight at 0° deposited the product (21.8 g., 51%) as bright red crystals. This was recrystallized from methanol to give the methanol solvate of II<sup>3</sup>;  $\lambda_{max}^{MeOH}$  5.78, 5.91, 6.01, 6.15(w), 6.35 (infl.), 6.50(vs)  $\mu$ ;  $\lambda_{max}^{H_2O}$  257  $m\mu$  ( $\epsilon$  11,700), 340  $m\mu$  ( $\epsilon$  52,800), 473  $m\mu$  ( $\epsilon$  47);  $\lambda_{max}$  (*ca.* 1 N  $CH_3ONa$  in  $CH_3OH$ ) 287  $m\mu$  ( $\epsilon$  22,000), 339  $m\mu$  ( $\epsilon$  23,050), 385  $m\mu$  ( $\epsilon$  6000).

**Tetramethyl 3,7-Dioxobicyclo[3.3.0]octane-2,4,6,8-tetracarboxylate (III).**—A solution of II (5.0 g.) in water (50 ml.) was poured into a sturdy 1-l. separatory funnel half-filled with crushed ice. Sodium amalgam (2.5%, 21.6 g.) was added and the mixture was shaken thoroughly. The initial red color changed immediately to green and this had changed to yellow after 30 minutes. The solution was then emulsified with ether (100 ml.), and 10% sulfuric acid (30 ml.) was added. The ethereal layer was removed and combined with the ethereal layers obtained by extraction of the aqueous layer with two further 100-ml. portions of ether. The combined ethereal extracts were dried over sodium sulfate and stripped of solvent *in vacuo*. The residual yellow-brown oil was triturated with a little ether to give a white solid which was recrystallized from methanol giving the reduction product (1.2 g., 36%), m.p. 104–107.5° (lit.<sup>3</sup> m.p. 88°),<sup>33</sup>

(33) Cf. P. Karrer, C. H. Eugster and S. Perl, *Helv. Chim. Acta*, **32**, 1013 (1949).

(34) Melting points were recorded on a Kofler hot-stage and are corrected unless otherwise indicated.

(35) This procedure and those immediately following are adapted from those of Vossen<sup>3</sup> and are given here in full since his description is not generally available.

(36) The m.p.'s of different samples of this product, which apparently had similar degrees of purity, varied widely, presumably due to differences in tautomer ratios; cf. ref. 9a.

$\lambda_{\text{max}}^{\text{CHCl}_3}$  5.73, 5.95, 6.10  $\mu$ ;  $\lambda_{\text{max}}$  (aq. 2% KOH) 279  $m\mu$  ( $\epsilon$  34,000);  $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$  247  $m\mu$ .

**Bicyclo[3.3.0]octane-3,7-dione (IV).**—A mixture of the reduction product III (0.30 g.) and hydrochloric acid (25%, 5 ml.) was boiled under reflux for 30 minutes. Most of the hydrochloric acid was distilled under reduced pressure and the residue was cooled, made slightly basic with aqueous sodium hydroxide and extracted several times with chloroform. The extract was dried over sodium sulfate and stripped of solvent under reduced pressure. The residue was crystallized from ethanol to give a crystalline product (0.10 g., 90%), m.p. 84–86° (lit.<sup>3</sup> 79–80°);  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.75  $\mu$ .

**Tetramethyl 3,7-Dihydroxybicyclo[3.3.0]octane-2,4,6,8-tetracarboxylate (VIII).**—The "red salt" (5 g.) in aqueous 90% acetic acid (50 ml.) was hydrogenated at atmospheric pressure over prereduced platinum oxide (1 g.). Absorption ceased after 6–7 hours after the uptake of ca. 3 molar equivalents of hydrogen. The catalyst was filtered and the filtrate was freed of solvent under reduced pressure. The residue was taken up in ethyl acetate and the solution was washed with aqueous 5% sodium bicarbonate and with water. The ethyl acetate solution was dried and freed of solvent under reduced pressure. The diol VIII remained as a semi-crystalline material (4.7 g., 95%);  $\lambda_{\text{max}}^{\text{CHCl}_3}$  2.85, 5.76, 5.82  $\mu$ . This was used without further purification for the preparation of IX.

For the preparation of VIII on a larger scale, the following alternative procedure was found to be more convenient and economical. The crude "red salt" (32 g.) in aqueous 90% acetic acid (150 ml.) was hydrogenated in a Parr apparatus over prereduced platinum oxide (1.8 g.) at an initial hydrogen pressure of 40–50 p.s.i. After 8 hours the catalyst was filtered and rinsed with water; the combined filtrate and washings were concentrated under reduced pressure. The residue was taken up in ethyl acetate (150 ml.) and cold aqueous 5% sodium hydroxide (50 ml.); the layers were separated and the organic layer was washed with aqueous 5% sodium hydroxide until the washings were basic, and then was washed twice with water. These washings were combined and extracted with ethyl acetate (3  $\times$  50 ml.); the extract was washed twice with base and with water, and added to the original ethyl acetate layer. This solution after being dried and freed of solvent under reduced pressure gave the product as an oil (22.2 g., 79%) which solidified to a sticky, white solid on standing or on being seeded: the infrared spectrum of this product was identical to that of the product obtained by the procedure above.

A sample of this material was crystallized several times from chloroform–ether with charcoal treatment, giving a crystalline product, m.p. 182–186° (softening at 170°);  $\lambda_{\text{max}}^{\text{CHCl}_3}$  2.85, 5.76, 5.82  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{22}\text{O}_{10}$ : C, 51.33; H, 5.92. Found: C, 51.06; H, 5.88.

**The Bicyclo[3.3.0]octadiene-2,4,6,8-tetracarboxylic Acid (IX).**—The diol VIII (1.0 g.) was dissolved in concentrated sulfuric acid (20 ml.) and the solution was heated on the steam-bath for 3 hours with occasional swirling; it was then allowed to stand at room temperature overnight. The pale brown solution was poured onto ice and neutralized with cold aqueous 30% sodium hydroxide. The solution was reacidified to pH 2 with 6 *N* hydrochloric acid and extracted with ethyl acetate (5  $\times$  100 ml.). The extract was washed with saturated aqueous sodium chloride, dried, and concentrated under reduced pressure to ca. 5 ml. On standing for several hours in the cold, the concentrate afforded a powdery precipitate which was filtered and washed with ethyl acetate and ether. A small second crop could be obtained by evaporation of the mother liquor and crystallization of the residue from acetic acid–petroleum ether. The yield of the dehydration product was very variable, ranging from 0.22 g. to 0.37 g. (30–50%); this was probably due in part to variation in the purity of the diol. Large scale preparations were unfeasible since they usually gave considerably lower yields. An analytical sample of IX, prepared by crystallization from acetic acid–petroleum ether, had m.p. (uncor.) 235–241° dec. (block pre-heated to 190°)<sup>37</sup>;  $\lambda_{\text{max}}^{\text{diioxane}}$  3.2–3.8, 5.78, 5.84, 6.13  $\mu$ ;  $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$  (app.) 210  $m\mu$  ( $\epsilon$  16,600).

(37) The m.p. of this compound is exceedingly sensitive to the rate of heating; the value given previously<sup>1</sup> is unreliable in that thermal equilibrium between the compound and the pre-heated block was probably not approached.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{10}\text{O}_8$ : C, 51.07; H, 3.57. Found: C, 50.81; H, 3.84.

**Tetramethyl Bicyclo[3.3.0]octadiene-2,4,6,8-tetracarboxylate (X).**—The tetracarboxylic acid IX (1.0 g.) was suspended in ether (20 ml.) and ethereal diazomethane was added slowly with swirling until a pale yellow coloration persisted. The solution was allowed to stand at room temperature for 20 minutes and then a little of the ether was distilled to remove the slight excess of diazomethane. The remaining solution was filtered (from small amounts of polymethylene) and concentrated. The concentrate on standing deposited crystals of the tetramethyl ester X (0.61 g., 50%). An analytical sample, prepared by three recrystallizations from ether–petroleum ether, had m.p. 109–109.5°;  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.78 (infl.), 5.85, 6.12  $\mu$ ;  $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$  (app.) 210  $m\mu$  ( $\epsilon$  16,600).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{18}\text{O}_8$ : C, 56.80; H, 5.36. Found: C, 56.77; H, 5.53.

The same product could be obtained in poorer yields directly from the diol VIII by dehydration with either phosphorus oxychloride and pyridine or *p*-toluenesulfonyl chloride and pyridine; the identity of the products was established by mixture m.p.'s and comparison of infrared spectra.

**Bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic Acid (XII = XXI).**—The unsaturated acid IX (0.5 g.) dissolved in aqueous 80% acetic acid (8 ml.) was hydrogenated at atmospheric pressure over prereduced platinum oxide (0.05 g.). Uptake of hydrogen ceased after the absorption of ca. two molar equivalents. The catalyst was filtered and the filtrate was stripped of solvent under reduced pressure. The residue was crystallized from acetic acid–petroleum ether, affording the saturated acid XII (0.37 g., 73%), m.p. (uncor.) 252–253° dec. (rapid heating from room temperature to 240°, followed by a rise of 1°/min.)<sup>37</sup>;  $\lambda_{\text{max}}^{\text{diioxane}}$  3.2–3.7, 5.77  $\mu$ ; no high intensity ultraviolet absorption >210  $m\mu$ .

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}_8$ : C, 50.35; H, 4.93. Found: C, 50.08; H, 5.19.

**Tetramethyl Bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylate (XIII).** (i) From Hydrogenation of X.—The unsaturated ester X (0.90 g.) in aqueous 90% acetic acid (20 ml.) was hydrogenated at atmospheric pressure over prereduced platinum oxide (0.2 g.). Hydrogen uptake ceased after the absorption of 2 molar equivalents. The catalyst was filtered and the filtrate was evaporated to dryness under reduced pressure. The crystalline residue was recrystallized from ether, affording the saturated ester XIII (0.74 g., 81%) as long, fine needles, m.p. 94.5–95°,  $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$  5.77  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{22}\text{O}_8$ : C, 56.13; H, 6.48. Found: C, 55.86; H, 6.60.

(ii) From Esterification of XII.—The saturated acid (0.36 g.) was covered with ether and the mixture was cooled in ice-water. Ethereal diazomethane was added dropwise with swirling until the solution retained a permanent pale yellow tinge. Part of the ether was distilled on the steam-bath to remove the slight excess of diazomethane. The concentrate was filtered and freed of solvent; the solid residue was recrystallized three times from ether–petroleum ether, giving the saturated ester XIII (0.21 g., 50%), identical to that obtained by hydrogenation of X.

**Equilibration of XIII.**—Sodium (0.15 g.) was added to methanol (80 ml.) which had been boiled under reflux with calcium hydride for 2.5 hours and distilled. When reaction was complete the ester XIII (1.18 g.) was added and the solution was boiled under reflux for 6.5 hours and then allowed to stand at room temperature for 1 day. The solution was concentrated to small volume (ca. 15 ml.) under reduced pressure, brought to pH 3 with methanolic hydrogen chloride, and freed of solvent under reduced pressure. The crude product was extracted with ether; evaporation of the ethereal extract gave a semi-solid residue (1.05 g.). This was chromatographed on Merck alumina (75 g.). Elution with 20% ether–80% benzene gave seven 50-ml. fractions which yielded oils on removal of the solvent; the subsequent nine 50-ml. fractions gave solid material (0.33 g.) on evaporation. A further small amount of solid product (0.05 g.) was obtained by elution with 50% ether–50% benzene. All the solid fractions were combined and crystallized from ether–petroleum ether, giving the equilibration product, m.p. 88.5–89°  $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$  5.77  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{22}\text{O}_8$ : C, 56.13; H, 6.48. Found: C, 56.21; H, 6.66.

Repeated recrystallization did not change this m.p., but on rechromatography of the product on Merck alumina solid fractions with wide m.p. ranges were obtained. One of these fractions on repeated recrystallization yielded a small quantity of crystalline material, m.p. 142–143°; a mixture m.p. showed it to be identical to the ester XVI, m.p. 142–143°. <sup>24</sup>

**Equilibration of Tetramethyl Bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylate, M.p. 142–143° (XVI).**—A sample of this ester<sup>24</sup> supplied by Professor Boekelheide<sup>25</sup> was subjected to equilibration under the conditions described above. The mixture was worked up as before, giving a crystalline product, m.p. 88.5–89°, unaffected by further recrystallization. There was no depression of m.p. when this product was mixed with the equilibration product from XIII. The infrared spectra of the two products were identical.

**Dianhydride A from Bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic Acid (XIX).**—The acid XII (0.41 g.) was heated with boiling acetic anhydride (20 ml.) under reflux for 1 hour. The resulting pale brown solution was evaporated to dryness under reduced pressure; dry ethyl acetate was added to the residue and then evaporated in like manner. The crude product was warmed with ethyl acetate on the steam-bath; the undissolved solid material (0.11 g., 31%) was filtered and recrystallized three times from dry acetonitrile-chloroform with charcoal treatment. The pure anhydride A had m.p. (uncor.) 246–249° dec.;  $\lambda_{\text{max}}^{\text{Nujol}}$  5.51, 5.66, 9.42  $\mu$ .

*Anal.* Calcd. for C<sub>12</sub>H<sub>10</sub>O<sub>6</sub>: C, 57.60; H, 4.03. Found: C, 57.74; H, 4.14.

**Dianhydride B from Bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic Acid (XX).**—The acid XII (0.35 g.) was heated with boiling acetic anhydride (15 ml.) under reflux for 4 hours. The dark brown solution was filtered through charcoal, concentrated to ca. half-volume under reduced pressure, and allowed to stand at 0°. A crystalline product (0.09 g., 30%) deposited which after three recrystallizations from acetonitrile-chloroform had m.p. (uncor.) 265–270° dec.;  $\lambda_{\text{max}}^{\text{Nujol}}$  5.55, 5.65, 9.05  $\mu$ .

*Anal.* Calcd. for C<sub>12</sub>H<sub>10</sub>O<sub>6</sub>: C, 57.60; H, 4.03. Found: C, 57.30; H, 4.07.

**Conversion of Dianhydride A to Dianhydride B.**—When pure dianhydride A (0.10 g.) was heated with boiling acetic anhydride (6 ml.) under reflux for 3 hours, it remained unchanged. Sodium acetate (10% by wt.) was added, and the mixture was boiled under reflux for 1 hour. It was then evaporated to dryness under reduced pressure. Extraction of the residue with acetonitrile and concentration of the extract gave dianhydride B (0.03 g., 30%).

**Hydrolysis of Dianhydride A.**—A solution of dianhydride A (0.08 g.) in purified acetonitrile (20 ml.) and distilled water (20 ml.) was allowed to stand at room temperature for 28 hours. The solution was then evaporated to dryness under reduced pressure. The residue was shown by infrared spectral comparison to be identical to the bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic acid (XII) from which the dianhydride had been prepared originally. This identity was confirmed by the conversion of the hydrolysis product with ethereal diazomethane in the usual manner to an ester, m.p. 94–95°, identical to XIII.

**Hydrolysis of Dianhydride B; Tetramethyl Bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylate, M.p. 154–155° (XVIII).**—Hydrolysis of dianhydride B (0.08 g.) by the method used for A gave a new acid (0.07 g., 75%) whose infrared spectrum differed from that of the acid from which the two dianhydrides were derived. It was not further characterized, but converted directly to its methyl ester with ethereal diazomethane in the usual manner; the time required for completion of the reaction was appreciably greater than that required for the other acids in this series. The crude product, m.p. 145–149°, was crystallized from chloroform-hexane and then three times from chloroform-ether. The ester had m.p. 154–155°,  $\lambda_{\text{max}}^{\text{KBr}}$  5.78  $\mu$ .

*Anal.* Calcd. for C<sub>16</sub>H<sub>22</sub>O<sub>8</sub>: C, 56.13; H, 6.48. Found: C, 55.94; H, 6.69.

**Tetramethyl Tetrabromobicyclo[3.3.0]octane-2,4,6,8-tetracarboxylate (XXVII).**—Bromine (6 ml.) was added to the unsaturated ester X (0.50 g.). The solution thus obtained was allowed to stand in the hood overnight, during which time most of the excess of bromine evaporated. The residual bromine was removed by evaporation under reduced

pressure and several treatments with ether followed by evaporation under reduced pressure. The resulting pale yellow solid was slurried three times with small amounts of ether and taken up in chloroform. The solution was filtered through charcoal and freed of chloroform under reduced pressure, giving a white solid (0.34 g., 35%) which was crystallized three times from chloroform-petroleum ether. The product had m.p. (uncor.) 202–202.5° dec. (block preheated to 175°);  $\lambda_{\text{max}}^{\text{Nujol}}$  5.68 (infl.), 5.71  $\mu$ .

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>8</sub>Br<sub>4</sub>: C, 29.21; H, 2.76; Br, 48.58. Found: C, 29.15; H, 3.00; Br, 48.24.

Attempts to brominate this product further in solution in acetic acid returned starting material only. Attempts to brominate IX or X with N-bromosuccinimide failed to give crystalline products.

**Debromination of Tetramethyl Tetrabromobicyclo[3.3.0]octane-2,4,6,8-tetracarboxylate. (i) With Zinc.**—The tetrabromoester XXVII (0.05 g.) was covered with 95% ethanol (4 ml.) and zinc dust (washed with dilute hydrochloric acid, water to pH 7, methanol, and ether; 0.04 g.) was added. The mixture was boiled under reflux for 6.5 hours, and then evaporated to dryness. The solid residue was extracted with chloroform and the extract was filtered through a plug of glass wool. It was extracted with 5% aqueous ammonia, washed with water, and dried. Evaporation of the chloroform gave a residue (0.03 g.) whose infrared spectrum was identical to that of the unsaturated ester X.

**(ii) With N,N-Dimethylaniline.**—The tetrabromoester (0.05 g.) was treated with boiling N,N-dimethylaniline (1.5 ml.) under reflux for 2 minutes. The solution assumed a violet color almost immediately. The solution was cooled rapidly and treated with chloroform. The mixture was poured onto ice and acidified with dilute hydrochloric acid. The organic layer was washed with 10 N hydrochloric acid until the purple color had been largely destroyed, then four times with water. It was filtered through a plug of silica gel and freed of solvent, giving a semi-solid residue (0.02 g.) which after two crystallizations from ether-petroleum ether yielded fine needles, m.p. 104.5–106.5°; the m.p. was undepressed when this product was mixed with the unsaturated ester X, and its infrared spectrum was identical to that of X.

Attempted dehydrobromination of the tetrabromoester with anhydrous sodium carbonate or acetate in chloroform-ethanol returned starting material as the only isolable product.

**Bromination of the "Red Salt."**—The "red salt" (15.4 g.) was dissolved in warm water (200 ml.) and the solution was diluted with dioxane (200 ml.). A solution of bromine (20 g.) in the minimum volume of ice-cold water was added with stirring to the solution of the "red salt," cooled in an ice-bath. After the reaction mixture had stood at 0° for 3 hours, the precipitate was filtered, washed thoroughly with water and partially dried by aspirator suction. The crude product was crystallized from chloroform-hexane, with treatment of the solution with anhydrous magnesium sulfate to remove residual water, giving golden yellow crystals (13.5 g., 70%). Recrystallization of this material from the same solvent pair gave an analytical sample, m.p. (cap., uncor.) 188–191° with prior dec.;  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.66, 5.69, 5.80, 6.08  $\mu$ ;  $\lambda_{\text{max}}^{\text{CH}_2\text{CN}}$  257, 302  $\mu\text{m}$ .

*Anal.* Calcd. for C<sub>16</sub>H<sub>12</sub>O<sub>10</sub>Br<sub>2</sub>: C, 36.67; H, 2.29; Br, 30.53. Found: C, 36.4; H, 2.2; Br, 31.3.

This product was shown by infrared spectral comparison to be identical to the product obtained by bromination of the "red salt" using the method of Vossen.<sup>3,38</sup>

**Oxidation and Dehydrogenation Experiments.**—The following reactions were attempted but gave no crystalline products: oxidation of X with selenium dioxide in acetic acid, oxidation of the "red salt" with selenium dioxide in acetic acid, dehydrogenation of IX with selenium, dehydrogenation of tetramethyl bicyclo[3.3.0]oct-1-ene-3,7-dione<sup>3</sup> with sulfur.

**Acknowledgments.**—We thank Messrs. George F. Field and Roy H. Karlson for their collaboration in certain phases of this work. Fellowship support from Radcliffe College to E. S. H. and G. B. F. is gratefully acknowledged.

(38) The earlier analytical results<sup>3</sup> were: C, 36.60, 30.74; H, 3.06, 2.75; Br, 30.49, 30.07.