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Perchloro-compounds. IV. *anti*-Perchloro-(3,4,7,8-tetramethylenetricyclo-[4.2.0.0^{2,5}]octane), a Dimer of Perchloro-(3,4-dimethylenecyclobutene)

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The structure of the first of the four thermolytic dimers of perchloro-(3,4-dimethylenecyclobutene) was characterized as *anti*-perchloro-(3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane) (II). This structure elucidation was principally based on: (a) the permanganate oxidation of II to perchloro-(dimethylenesuccinic) acid; (b) the two-step reduction of II to 1,2,3',4',5,6,7',8'-octachloro-3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane and 1,2,5,6-tetrachloro-3,4,7,8-tetramethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene (VII), and (c) the hydrogenation of the ozonized product from VII to two tetraacetylcyclobutanes (XVII and XVIII). The physical and chemical properties of II and of those substances derived from II and VII were discussed in detail. The stereochemical configurations of II and XVII were estimated to be *anti* and all-*trans* respectively.

It has already been briefly reported that the temperature-controlled thermolysis of perchloro-(3,4-dimethylenecyclobutene) (I)[1,2] affords, besides perchlorofulvene, perchloro-(4-methylenecyclopentene), and perchlorobenzene, at least four dimeric products, the first isomer of which is formed in the vicinity of 160°C and may be characterized as a cycloadduct, *anti*-perchloro-3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane) (mp 266°C) (II).[3,4] The differential thermal analysis data suggest that the successive transformation of II takes place, step by step as the thermolysis temperature rises, to

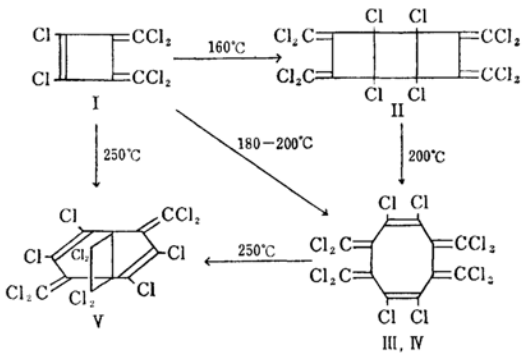


Chart 1

1) A. Roedig, F. Bischoff, B. Heinrich and G. Märkl, *Ann.*, **670**, 8 (1963).
2) A. Fujino, Y. Nagata and T. Sakan, This Bulletin, **38**, 295 (1965).
3) K. Mano, K. Kusuda, A. Fujino and T. Sakan, *Tetrahedron Letters*, **1966**, 489.
4) A. Furusaki, Y. Tomiie and I. Nitta, *ibid.*, **1966**, 493.

give the second isomer, labile perchloro-(3,4,7,8-tetramethylenecyclooctadiene) (mp 215°C) (III),[5] mixed with the third isomer (rigid form of III) (mp 262°C) (IV)[5] and the fourth isomer, perchloro-(4,8-dimethylenetricyclo[3.3.2.0^{1,5}]deca-2,6-diene) (mp 273°C) (V)[6] (Chart 1). The present paper will describe a detailed study of the structure elucidation of II as well as the physical and chemical properties of some related compounds obtained in the course of our investigation.

Results

The material necessary for the elucidation was best supplied by means of the ionic dimerization of I in dichloromethane with anhydrous aluminum chloride,[3] since the average yield of *ca.* 60% was much higher than that in thermolysis. It was observed that II is hardly soluble in ordinary nonpolar organic solvents (*e. g.*, approx. 2 g/*l* carbon tetrachloride), is inert to acid or alkaline hydrolysis, and is stable against the UV-light irradiation in solution, in contrast to its remarkable thermal instability. The attempted chlorination of II in liquid chlorine or with chlorine gas in a heated solution was unsuccessful, only the unreacted substrate being recovered. The permanganate oxidation of II in acetone proceeded rapidly to give perchloro-(dimethylenesuccinic) acid in a yield as low as that in the similar oxidation of I.[1] The reduction of II with zinc in ethanol or acetic acid smoothly furnished 1,2,3′,4′,5,6,7′,8′-octachloro-3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane (mp 223—225°C) (VI), which was then further hydrogenated over palladium charcoal at room temperature to give 1,2,5,6-tetrachloro-3,4,7,8-tetramethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene (mp 180°C, decomp.) (VII). The latter compound was also directly obtained in 77% yield from II by hydrogenation with the same catalyst. In this case there was isolated as a by-product a small amount of hydrocarbon (bp 80°C(bath)/20 mmHg) (VIII) to which the structure of 3,4,7,8-tetramethylbicyclo-

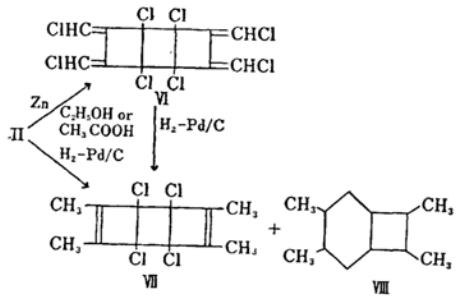


Chart 2

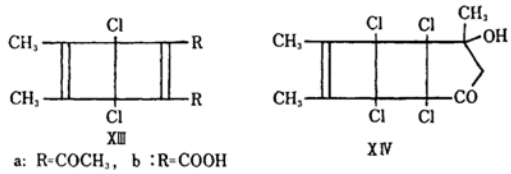
[4.2.0]octane was assigned. These reactions are illustrated in Chart 2.

The residual chlorine substituents in VII strongly resisted the attack of other reducing or basic reagents, such as lithium alanate - lithium hydride in ether, nickel carbonyl in benzene, Raney nickel in methanol, zinc-acetic acid, liquid ammonia, and alcoholic potassium hydroxide. So far as we have examined, only *n*-butyllithium in ether reacted with VII, but even if did so without any conclusive result. On the other hand, a variety of the ring-cleaved products were obtained when VII was subjected to ozonization. There was observed a marked dependence of the product on the solvent employed. Thus, in dichloromethane or carbon tetrachloride - chloroform at −20°C, VII was transformed by ozone to an unstable viscous oil which then gradually decomposes, liberating a gas with a phosgene-like odor. When this oil was treated with mineral acid, a crystalline compound, $C_{12}Cl_4H_{12}O_3$ (mp 125—127°C) (IX) was obtained. In ozonization in petroleum ether at room temperature, an isomer (mp 122—124°C) (X), possibly isoozonide of VII, and 5,6-diacetyl-1,4,5,6-tetrachloro-2,3-dimethylbicyclo[2.2.0]hexene-2 (mp 113—115°C) (XI) were the products, along with a small amount of IX. The low reactivity toward ozone of the remaining ring-double-bond in XI had already been briefly described.[3] Further careful work has revealed that the ozonization of VII in carbon tetrachloride-methanol at −20°C resulted in the production of a new crystalline isoozonide, $C_{12}Cl_4H_{12}O_5$ (mp 182°C, decomp.) (XII) (16% yield), in addition to X (4%) and XI (66%). A trend to form this extremely stable isoozonide was demonstrated in the experiment; the result of the ozonization of XI in ethyl acetate in the presence of tetracyanoethylene, a very effective oxygen-acceptor of ozonide,[7] was essentially the same as that in an experiment without such a special reagent. In a much higher yield (70—80%), XII was obtained by the ozonization of VII either in carbon tetrachloride or in acetic acid at room temperature, and later, quantitatively from XI under the same conditions.

Several attempts to synthesize a compound like XIIIa or XIIIb bearing a "Dewar-benzene" structure were made, since it appeared that the substituents on the ring were bulky enough to stabilize it rather than the benzene derivative.[8] However, the high cyclizing tendency between the vicinal acetyl groups in XI was a decisive disadvantage for any dechlorinating agent used; with zinc metal in ethanol or nickel carbonyl in benzene, the only product isolated was a ketol (XIV) (mp

5) K. Mano, K. Kusuda and A. Fujino, *ibid.*, **1968**, 1375.
6) a) A. Furusaki and I. Nitta, *ibid.*, **1966**, 6027. b) A. Furusaki, This Bulletin, **49**, 2518 (1967).
7) R. Criegee and P. Günther, *Chem. Ber.*, **96**, 1564 (1963).
8) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962); **85**, 3297 (1963).

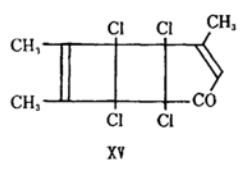
160°C, *ca.* a 50% yield in either case), while with a freshly-prepared nickel metal in benzene, the reaction again ended with the production of XIV (20% yield), along with the dehydrated dienone (mp 192—193°C) (XV). Contrary to our expectations, attempts at the degradation of XI by oxidation with sodium hypobromite or with nitric acid to dicarboxylic acid also resulted in cyclization to XIV or a lactol (mp 167—169°C) (XVI).



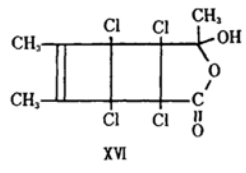
XIII

a: R=$COCH_3$, b: R=COOH

XIV



XV



XVI

The isoozonide ring in XII was opened by catalytic hydrogenation over palladium charcoal in ethanol, giving all-*trans*-tetraacetylcyclobutane (mp 145°C) (XVII), identical with that reported by Griffin,[9] and the tetraketal (mp 282°C, decomp.) (XVIII) of its all-*cis*-isomer in a ratio of approximately 4 : 1. When a similar hydrogenation was carried out in the presence of sodium acetate, XVIII dominated XVII in the product yield. Chart 3 summarizes the results of the ozonization and hydrogenation of the compounds concerned.

Discussion

The reactivities of I toward various chemical reagents have been discussed in previous papers.[2,10,11] It can easily be inferred that II is a cycloaddition product, since the dimerization takes place in the thermal reaction at a high temperature, where the process is known to be essentially homolytic. The structural evidence for II and its degradation will be briefly discussed below.

Evidently, there is a close relationship between both the ultraviolet and the infrared spectral data of II and those of perchloro-(1,2-dimethylenecyclobutane) (XIX). The former gives rise to UV absorptions with the $\lambda_{max}^{n\text{-hexene}}$ of 287, 299, and 314 mμ ($\log \varepsilon$ 4.44, 4.65 and 4.43), which are, respectively, 8, 11 and 9 mμ shorter in their positions and 2—3 times more intense in their ε values than those described for the latter[1] (Fig. 1). The IR absorptions for the dichloromethylene groups of II ($\nu_{C=C}^{Nujol}$ 1610s, 1580s; $-C(=CCl_2)-$ 910s[2] (cm^{-1})) consistently correspond to those (1605s, 1570s and 910s (cm^{-1}), Nujol mull) of XIX. The former compound resists chlorination under mild conditions, as, indeed, does the latter.

These data can reasonably be explained by assuming that II is composed of two units of the carbon skeleton of XIX. The permanganate oxidation of II to perchloro-(dimethylenesuccinic) acid has

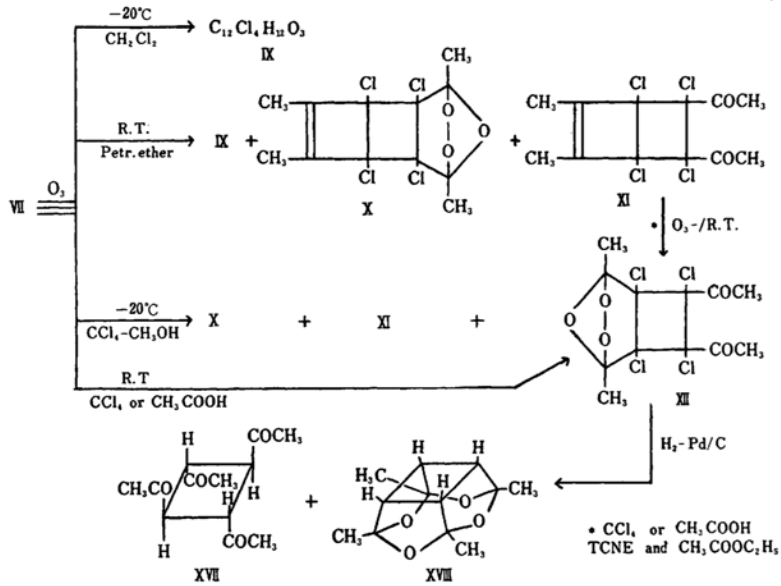


Chart 3

9) G. W. Griffin and R. B. Hager, *Rev. Chim. (Acad. Rep. Populaire Roumaine)*, **7**, 901 (1962).
10) A. Fujino, K. Kusuda and T. Sakan, This Bulletin, **39**, 160 (1966).
11) K. Mano, K. Kusuda, A. Fujino and T. Sakan, *ibid.*, **40**, 1188 (1967).

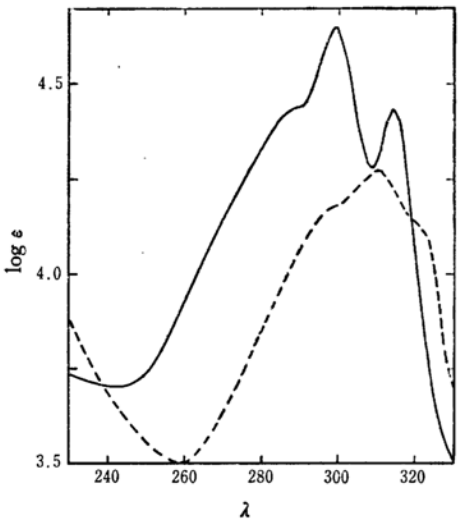
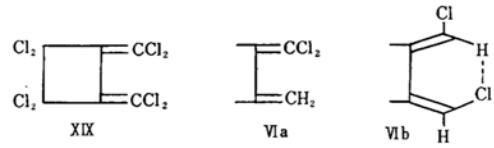


Fig. 1
—— Perchloro-(3,4,7,8-tetramethylenetricyclo-[4.2.0.0^{2,5}]octane) (II)
---- Perchloro-(1,2-dimethylenecyclobutane) (XIX)

proved the presence of at least one vicinal dichloromethylene pair in the molecule. As for the position where the new bonding results, no other possibility than C_1 and C_2 in I can be considered in view of the relative reactivity of the double bonds.[2] The $\Delta\lambda_{max}$ (*ca.* 10 mμ) between II and XIX may well be interpreted by evaluating the hyperconjugative effect[12] of allylic chlorine substituents on both and a double bond-central ring interaction for the former. If the λ_{max} of 246 mμ for 1,2-dimethylenecyclobutane[13] is taken as a reference value, the substitution of its four exomethylene hydrogens by chlorines should cause a bathochromic shift of 32—34 mμ.[14] This is a common factor in both. The further increment of *ca.* 30 mμ for XIX was discussed by assigning it to the hyperconjugative effect of four allylic chloro-substitutions on the ring (7.5 mμ/Cl).[2] However, a similar interaction does not seem so effective in II, where the increment of 20 mμ is to be ascribed only to the paired angular chloro-substitution. On the contrary, X-ray crystallographic analysis[15] suggests that in II the angle, for instance, between the C_1–Cl bond and the p_z orbital of C_2 is near 42°, which is significantly wider than is the corresponding one in XIX (*cf.* near 35° in perchlorocyclobutane[16]). This relationship holds also in solutions (less than 7.5 mμ/Cl in II). Therefore, it may be speculated that there exists some interaction between the double bonds and the central cyclobutane ring in II. White and Dunathan[17] observed similar spectral evidence in a tricyclo[4.2.0.0^{2,5}]octa-3,7-diene system. A few additional pieces of evidence supporting this interpretation have been obtained in the course of our study and will be published later.

The assignment of the VI structure to the tetrahydro-compound rests on the following observation: (a) VI is further smoothly reduced to VII suggesting that no hydrogen atom is attached to the angular carbons; (b) the appearance of some new characteristic IR-absorptions, $\nu_{=CH}^{Nujol}$ 3060 and 3050 and $\delta_{=CH}$ 810 vs (cm^{-1}); (c) the value calculated (282 mμ) for the λ_{max} of the UV-absorption based on the reference hydrocarbon[13] is in good accordance with the observed value (278 mμ) if the same bathochromic displacement factor (20 mμ) as above is again taken into account. Unfortunately, it was impossible to examine the stereochemical configuration of the four hydrogens by means of NMR spectrometry because of the extremely low solubility of the sample. However, an alternative structure, partly shown by VIa, may be ruled out since only one strong singlet absorption is observed in the frequency range 970—830 cm^{-1} in IR, where VIa should give rise to at least two strong, distinguishable bands, corresponding to dimethylene and dichloromethylene groups. The band at 810 cm^{-1}, the most intense band over the whole range, could be due to the deformations of the four –C(Cl)=CHCl groups. The observed doublet due to $\nu_{=CH}$ absorption appears to indicate the non-equivalence of the hydrogens like VIb in each paired chloromethylene group, although the data of measurement in solution are lacking.



It is of interest to speculate on a possible course of the reduction of II to VI, in which the attack of the nascent hydrogen would first cause the replacement of one of the *endo*-chlorine atoms in each half of the molecule, resulting in some effective release of the Cl–Cl interaction. The distances in crystals[15] of Cl_2–$Cl_{3'(exo)}$ and $Cl_{4'(exo)}$–Cl_5 (both 3.32 Å), and of $Cl_{3'(endo)}$–$Cl_{4'(endo)}$ (3.28 Å), closer than twice the van der Waals radius of the chlorine atom, may reflect an interaction sufficient to make this stereospecificity possible.

12) E. A. Braude and E. S. Waight, "Progress in Stereochemistry," Vol. 1, ed. by W. Klyne, Butterworth Scientific Publication, London (1954), p. 154.
13) A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **77**, 1806 (1955).
14) A. Roedig and E. Klappert, *Ann.*, **605**, 126 (1957).
15) A. Furusaki, This Bulletin, **40**, 758 (1967).
16) T. B. Owen and J. L. Hoard, *Acta Cryst.*, **4**, 172 (1951).
17) E. H. White and H. C. Dunathan, *J. Am. Chem. Soc.*, **86**, 453 (1964).

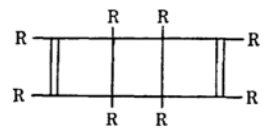
Nenitzescu *et al.*[18] reported obtaining *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (XXa and XXb) from 3,4-dichlorocyclobutene by dechlorination. A more analogous pair (XXc and XXd) was synthesized by, respectively, the dechlorination of the suitable cyclobutene derivative (XXIb)[19] and by the thermal decomposition of tetramethylcyclobutadienenickel chloride.[20] Mechanistically, the formations of *syn*-stereomer involving those with other substituents[17,21] have been classified as by way of true cyclobutadiene intermediates.[22] Table 1 lists some physical properties of VII and XXa—XXd, along with those for cyclobutene (XXIa) and its derivatives (XXIb—XXId). The difference (0.45) in τ values between VII and XXc and XXd seems too large even if some difference in the shielding effect of the β-positioned angular

TABLE 1. COMPARISON OF TETRAMETHYL-DERIVATIVE WITH RELATED COMPOUNDS

	IR $\nu_{C=C}$ (cm^{-1})	NMR =C-CH_3 (τ)	Dipole moment (D)
VII	1680[a]	8.12	0.46[b]
XXa	1545[c]		
XXb	1555[c]		
XXc	1684[a]	8.57[d]	0.64±0.19
XXd	1681[a]	8.57	
XXIa	1566[c,e]		
XXIb	1684[a,f]	8.35	2.38[g]
XXIc	1684[c,g]		
XXId		8.59[d]	

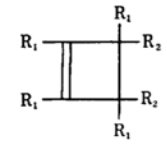
a) In carbon tetrachloride.
b) Measured with a dilute carbon tetrachloride solution.
c) Liquid film.
d) T. J. Katz and E. H. Gold, *J. Am. Chem. Soc.*, **86**, 1600 (1964).
e) R. C. Lord and K. W. Walker, *ibid.*, **76**, 2518 (1954).
f) Same value as with the *trans*-isomer.
g) R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959).

substituents is considered. The unusually low τ value of VII might be explained by assuming an especially sterically-enhanced shielding of the γ-positioned chlorine atoms which are, in the *anti*-form, on the same side of the paired methyl groups with respect to the central ring. Inasmuch as a value higher by far than 2.38 D (for XXIb) may be expected as the dipole moment for the *syn*-form, the ring configuration in VII may be ascribed to the *anti*-form.



XX

a: R=H(*syn*)
b: R=H(*anti*)
c: R=CH_3(*syn*)
d: R=CH_3(*anti*)

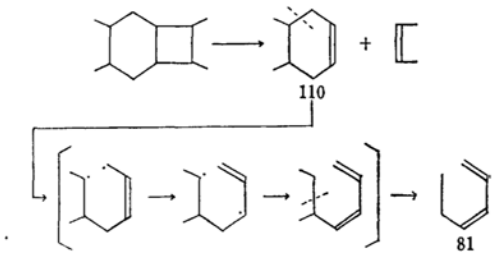


XXI

a: $R_1=R_2=H$
b: $R_1=CH_3$, $R_2=Cl$(*cis*)
c: $R_1=CH_3$, $R_2=H$
d: $R_1=R_2=CH_3$

The extreme low reactivity of bridge-head chlorine substituents in compounds having a fused ring has been reported in many cases.[23] The four angular chlorines in VII were also very inert to reducing or hydrolyzing agents, even when the most drastic conditions were used.

Supporting evidence for the VIII structure was obtained in the mass spectrometric analysis as well as in the UV (no chromophore above 210 mμ) and the IR (no C=C band) spectra. The observed spectrum contains main peaks of m/e=166 (molecular ion), M−15, M−29, M−42, 110, 95 (base peak), 81, 69, and 55, and one metastable ion peak of m* 59.65 (110→81). These data are in accord with the bicyclic structure and the following degradation pattern.



The NMR spectrum also indicates the presence of, ten and twelve protons in the ranges of, respectively, 7.70—9.00 τ and 9.00—9.45 τ; this is consistent with the formula shown above.

In co-operation with us, Furusaki *et al.*[15] have made a detailed X-ray analysis of II as well as a two-dimensional X-ray analysis of VII and have confirmed, in agreement with our estimation,[24] that the *anti*-form is referred to both the compounds.

Although the composition of IX corresponds to the ozonide of VII, its structure has remained uncertain. The isomeric product, X, may be presumed to be a stable isoozonide of VII on the

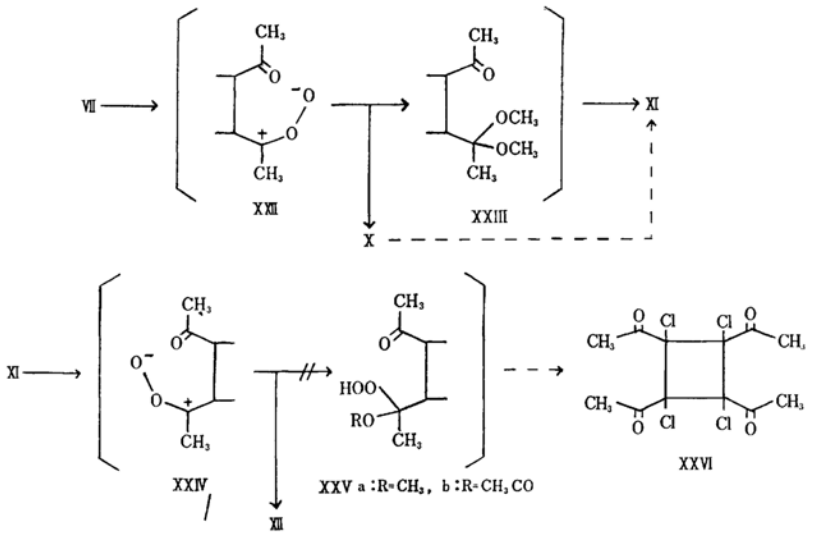
18) M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964).
19) R. Criegee and G. Louis, *ibid.*, **90**, 417 (1957).
20) R. Criegee, G. Schröder, G. Maier and H. G. Fischer, *ibid.*, **93**, 1553 (1960).
21) a) H. H. Freedman and D. R. Petersen, *J. Am. Chem. Soc.*, **84**, 2837 (1962). b) Y. Kitahara, M. C. Caserio, F. Scardiglia and J. D. Roberts, *ibid.*, **82**, 3106 (1960).
22) M. P. Cava and M. J. Mitschell, "Cyclobutadiene and Related Compounds," Academic Press, New York and London (1967), Chapter 1 and 2.
23) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Company, Inc., New York (1962), Chapter 13.

basis of its behavior toward a potassium iodide-starch solution being similar to that of XII (to be described below), as well as on the basis of the spectral data ($\nu_{C=C}$ 1680 m (cm^{-1}), 8.13 τ for $C{=}CCH_3$ and 8.13 τ for $\rangle CCH_3$). Compare these values with those of the related compounds, VII (Table 1), XI ($\nu_{C=C}$ 1680 w (cm^{-1}); 8.15 τ for $C{=}CCH_3$ and 7.63 τ for $COCH_3$), and XII (8.10 τ for $\rangle CCH_3$ and 7.70 τ for $COCH_3$). In X there is no λ_{max} in the UV spectrum observable above 215 mμ, but there are signals in NMR for the vinylic methyl groups coinciding with those for the saturated C-methyl groups. As expected from the least-satisfactory peroxide detection, X does not suffer any hydrolysis with mineral acid, reduction with zinc - acetic acid, or oxidation with permanganate.

The spectral data (UV: no λ_{max} with an ε value higher than 10^3 above 210 mμ; IR: $\nu_{C=O}^{CCl_4}$ 1720s, doublet; $\nu_{C=C}$ 1680 w, δ_{CH_3} 1380 m, 1360s (cm^{-1}); NMR: as above; two singlets equal in intensity) of XI support the diketone structure.

The observation that there is a complicated solvent- and temperature-dependency of the products in the ozonization of VII is noteworthy. Attention should also be paid to the fact that the exhaustive ozonization of VII, or the successive ozonization of XI, at room temperature affords a unique product, isoozonide XII, in good yields regardless of the type of solvent used. In our interpretation, it seems most possible that the ozone-adduct (XXII) first formed from VII is normally converted to the methoxy hydroperoxide (XXIII) according to the Criegee mechanism for the low-temperature reaction in a polar solvent (containing methanol),[25] and that hence XI is obtained as a preponderant product. Although the isolation of XXIII as substantial evidence has been unsuccessful, the alternate process through the X isoozonide does not seem to fit, particularly when the solvent contains methanol. Evidently, the ozonization of XI in such a solvent as carbon tetrachloride-methanol or acetic acid does not afford an analogous hydroperoxide (XXVa or XXVb) which, if produced, could eventually be converted to the isolable tetraacetyl-compound (XXVI). The difference in the ozonization modes shown above may be accounted for by the difference in the ease of isoozonide formation from the corresponding intermediate zwitter ions, XXII and XXIV, the former of which is bicyclic and the latter, monocyclic. The ring strain unfavorable for isoozonide formation would be significantly higher in the former than in the latter. The unexpected results of the ozonization of XI, even in the presence of tetracyanoethylene, indicate that the transfer of an oxygen atom from XXIV to the acceptor can not compete with the very smooth formation of the isoozonide ring.

Proofs for the structures of XIV and XV are as follows: (a) For XIV: IR: ν_{OH}^{Nujol} 3570s, 3490m, $\nu_{C=O}$ 1760s, $\nu_{C=C}$ 1680m, lack of a band at 1360 (cm^{-1}); NMR: 8.15 (6H, singlet, vinylic methyls), 8.72 (3H, singlet, saturated C-methyl), 6.80 (OH), and 6.50 and 7.27 (doublet, J=15.5 cps, methylene) (τ); (b) For XV: UV: λ_{max}^{EtOH} 225 mμ (log ε 3.97); IR: $\nu_{CH}^{CHCl_3}$ 3020w, $\nu_{C=O}$ 1740s, $\nu_{C=C}$ 1690w, 1625m (cm^{-1}); NMR: 3.90 (1H, quartet), 7.70 (3H, doublet, J=3 cps), 8.12 (6H, singlet) (τ).



24) Criegee *et al.*[20] describes an ozonization product of XXc, which can not be formulated as *syn*-5,6-diacetyl-1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexene-2 and probably be an unsaturated ketoether formed by a transannular reaction between the carbonyl groups and the sterically neighboring ring double bond in the expected bicyclohexene-2. If the *syn*-type is given to VII, the ozonolyzed product would be an analogous ketoether and not be diketone XI as is our case.

25) P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

The easy occurrence of the intramolecular aldol-type cyclization from XI to XIV, followed by the dehydration to dienone XV, has indeed been a high barrier to approaching the "Dewar benzene." It has also made unsuccessful the attempted oxidation of XI with hypobromite - methanol, which would lead to another potential compound for the especially interesting benzene isomer. Contrary to the reported case with a permethyl analog,[26] the undesired XIV was obtained almost quantitatively. Nitric acid (sp. gr. 1.38) oxidizes one of the acetyl groups of XI to the carboxyl, which is then lactonized with the residual keto-group to form XVI. The structural evidence for XVI is: IR: ν_{OH}^{Nujol} 3320s, $\nu_{C=O}$ 1780s, $\nu_{C=C}$ 1690m (cm^{-1}); NMR: 7.99 (1.4H, singlet, $COCH_3$ due to partial dissociation), 8.13 (6H, singlet), 8.34 (1.6H, singlet) (τ) (in $CDCl_3$).

Practically, the hydrogenation was the only way achieved to cleave the isoozonide ring of XII, which strongly resists conversion to XXVI. Thus, the products were two isomeric chlorine-free compounds, XVII and XVIII. The spectral data for XVII (UV: λ_{max}^{EtOH} 283 mμ log ε 2.08; IR: $\nu_{OH}^{CHCl_3}$ 3400w, ν_{CH_3} 3030m, 3005m, ν_{CH} 2910w, $\nu_{C=O}$ 1715vs, $\nu_{C=C}$ 1675w, δ_{CH_3} 1425m, 1360s (cm^{-1}); NMR: 6.39 and 7.79 (both singlets, intensity ratio 1 : 3) (τ)) do not contradict the structure of all-*trans*-1,2,3,4-tetraacetylcyclobutane. The identification has been established by an IR spectra comparison between XVII and an authentic sample kindly offered by Professor Griffin. With both samples, the spectra in the solid state indicate weak absorptions for hydroxyl group and the C=C double bond absorptions, which become much weaker still when measured in chloroform. No OH-signal can be noticed in the NMR spectrum taken in D-chloroform. These facts suggest that at least one of the four acetyl groups in XVII exists in an enol-form in the solid; the equilibrium in solution between keto- and enol-forms is by far in favor of the former (more than 90% in the saturated solution). The production of the all-*trans*-isomer further suggests the inversion of at least two of the carbon moieties attached to the cyclobutane ring of XII.

Product XVIII shows much lower solubilities in alcohol, acetone, chloroform, carbon tetrachloride, *etc.*, than those for XVII, which is easily isolated by the recrystallization of the mixture. The IR (no carbonyl) and the NMR (6.76 and 8.47 (τ)) spectral data accord with the suggested structure. An analogous compound with the intramolecular tetraketal type has been reported by Criegee *et al.*;[20] *i. e.*, XXc was converted to the tetraketal of all-*cis*-1,2,3,4-tetraacetyl-1,2,3,4-tetramethylcyclobutane. Although a certain similarity was observed between the mass spectral data of XVII and XVIII, a significant difference was found in their base peaks (*m/e* 43 for acetyl and 18 for H_2O respectively), a difference which can reasonably be explained in terms of the proposed structures.

26) R. Criegee, W. D. Wirth, W. Engel and H. A. Brune, *Chem. Ber.*, **96**, 2230 (1963).

Experimental[27]

***anti*-Perchloro - (3,4,7,8 - tetramethylenetricyclo-[4.2.0.0^{2,5}]octane (II) from Perchloro-(3,4-dimethylenecylobutene) (I).** *a) By Pyrolysis.* In a sublimation apparatus, I (10 g, 35 mmol) was carefully heated at 155—165°C (oil bath temperature) for 3 hr without water in the cold finger. When the pyrolysis was over, water running was allowed to enter and there was collected a small amount of unreacted I by vacuum sublimation at 130—140°C/3 mmHg. The residue was refluxed with ligroin (300 m*l*) to remove the tarry by-product, and the insoluble fraction was, after filtration, recrystallized from carbon tetrachloride to give II (2.8 g, 5 mmol). Yield: 28%. Mp 266°C.

Found: C, 25.77; H, 0.90; Cl, 75.04%. Calcd for $C_{12}Cl_{12}$: C, 25.30; H, 0.00; Cl, 74.70%.

b) With Anhydrous Aluminum Chloride. To crystals of I (2.5 g, 8.8 mmol) well-mixed with anhydrous aluminum chloride (2.5 g, 19 mmol), dichloromethane (3 m*l*) was added while the moisture was shut off. The mixture immediately turned green, evolving hydrogen chloride. It was then allowed to stand at room temperature overnight. The reaction mixture was poured onto ice water, shaken with carbon tetrachloride (10 m*l*), and an insoluble fraction was separated by the decantation of the aqueous layer. Crude crystals (1.6 g, 2.8 mmol) of II were thus obtained. Yield: 64%.

Oxidation of II with Potassium Permanganate. A suspension of II (570 mg, 1.0 mmol) in acetone (100 m*l*) was vigorously stirred under refluxing, and then powdered potassium permanganate (1.4 g, 7.8 mmol) was added, portion by portion. After the complete consumption of the oxidizing agent, manganese dioxide was filtered off and washed with hot water. The filtrate was evaporated under reduced pressure to give the residue, which was, after being dissolved in ether, separated into acidic and neutral parts by the ordinary procedure. From the acidic fraction there was obtained a crystalline product (50 mg) which was recrystallized from water to furnish a pure sample (mp 215°C, decomp.) identical in all respects with authentic perchloro-(dimethylenesuccinic) acid.[2] The neutral fraction gave recovered II (26 mg).

Reduction of II with Zinc in Ethanol, *anti*-1,2,3',4',5,6,7',8'-Octachloro-3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane (VI). Zinc powder freshly treated with dilute hydrochloric acid was added to a suspension of II (2.60 g, 4.5 mmol) in ethanol (280 m*l*), and the mixture was then heated under refluxing for 1.3 hr. The reaction mixture was centrifuged to separate

27) The differential thermal analysis data will be described in the succeeding paper. All melting points are measured under microscope and not corrected. Ultraviolet spectra are taken with Hitachi Ultraviolet Spectrophotometer EPS-2U, infrared spectra with Perkin-Elmer Infrared Spectrophotometer Model 337, and NMR spectra with Nuclear Magnetic Resonance Spectrometer JNM-C-60.

the insoluble material. The mud thus obtained was extracted with a large amount of boiling benzene to give the crude VI (1.20 g, 2.8 mmol) in a 62% yield. Recrystallization from carbon tetrachloride afforded a pure sample, mp 223—225°C.

Found: C, 32.96; H, 1.25; Cl, 66.03%. Calcd for $C_{12}Cl_8H_4$: C, 33.38; H, 0.93; Cl, 65.74%. λ_{max}^{EtOH} 278 (4.26), λ_{sh} 290 (4.04) mμ (log ε). ν_{CH}^{Nujol} 3060m, 3050m, $\nu_{C=C}$ 1650w, 1620s; $\delta_{=CH}$ 810vs (cm^{-1}).

Similarly, the reduction of II (570 mg) with zinc powder (5.0 g) in acetic acid (35 ml) at room temperature for 1 hr resulted in the isolation of VI (99 mg). Yield: 23%.

***anti*-1,2,5,6-Tetrachloro-3,4,7,8-tetramethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene (VII).** *a) Catalytic Hydrogenation of II.* In an autoclave (500 cc), a suspension of II (5.70 g, 10 mmol) in ethanol (300 ml) was, after the addition of 5% palladium-charcoal (5.0 g) and sodium acetate (12.0 g), stirred at room temperature under a compressed hydrogen atmosphere for 50 hr, during this period the initial pressure (60 atm) dropped to 32 atm. The product solution was filtered, concentrated, and extracted with petroleum ether, from which solution crude crystals (2.3 g, 7.7 mmol) of VII were isolated with a slight contamination of an oily material. Recrystallization from ethanol and subsequent sublimation at 100°C/3 mmHg afforded a pure sample. Mp 180°C, decomp.

Found: C, 48.35; H, 4.06; Cl, 47.43%. Calcd for $C_{12}Cl_4H_{12}$: C, 48.32; H, 4.02; Cl, 47.65%. No absorption maximum above 210 mμ (ethanol solution).

b) Catalytic Hydrogenation of VI. In an autoclave (50 cc), VI (650 mg, 1.5 mmol), 5% palladium-charcoal (800 mg), and sodium acetate (1.50 g) were suspended in methanol (300 ml), after which the whole mixture was shaken with an initial hydrogen pressure of 60 atm at room temperature for 77 hr. The final pressure was 30 atm. The same subsequent treatment as above gave VII (100 mg, 34% yield).

3,4,7,8-Tetramethylbicyclo[4.2.0]octane (VIII). The oily fraction separated in the recrystallization of VII in a) was vacuum-distilled; bp 80—100°C (bath)/20 mmHg. The gas chromatographic analysis of the colorless distillate showed a purity of approx. 98%.[28] No chlorine appeared in a Beilstein test.

Found: C, 86.80; H, 13.20%. Calcd for $C_{12}H_{22}$: C, 86.74; H, 13.25%. No absorption maximum above 210 mμ (ethanol solution). IR: 2950s, 2920s, 2860s, 1470s, 1460s, 1380s, 1010w (cm^{-1}) (liquid film). NMR: 7.70—9.00 (10H), 9.00—9.45 (multiplet, 12H) (τ) (CCl_4).

Ozonization of VII under Various Conditions. *a) In Carbon Tetrachloride-Methanol at a Low Temperature.* A stream of oxygen-ozone was passed into a suspension of VII (3.00 g, 10 mmol) in a mixture of carbon tetrachloride (220 ml)) and methanol (300 ml) which had been cooled at −20°C until the suspension disappeared and the solution VII became completely clear. On the evaporation of the solvent under diminished pressure at 0°C, white crystals (3.11 g) were obtained. The crude product was dissolved in carbon tetrachloride and chromatographed on silica gel (Mallinckrodt Chem. Works, 100 mesh,[29] 40 g) with the same developing solvent. From the No. 1 fraction (20 ml) unreacted VII (230 mg) was obtained. The No. 4, 5, and 6 fractions furnished, on the evaporation of the solvent, colorless crystals (130 mg in total, 4.0% yield), which were then recrystallized from ethanol to give a pure sample (mp 122—124°C) of X.

Found: C, 42.03; H, 3.56; Cl, 40.64%. Calcd for $C_{12}Cl_4H_{12}O_3$: C, 41.62; H, 3.47; Cl, 41.04%. No absorption maximum above 215 mμ (ethanol solution). $\nu_{C=C}^{Nujol}$ 1680 cm^{-1}. 8.13 τ (singlet, CCl_4).

The adsorbed product was further developed with carbon tetrachloride - chloroform (1 : 1 by vol.). The eluted crystals (2.04 g, 66% yield) were recrystallized from ethanol. The pure XI melted at 113—115°C.

Found: C, 43.75; H, 3.68; Cl, 42.78%. Calcd for $C_{12}Cl_4H_{12}O_2$: C, 43.64; H, 3.64; Cl, 43.03%. $\nu_{C=C}^{CCl_4}$ 1720s, 1710s, $\nu_{C=C}$ 1680w, δ_{CH_3} 1380m, 1360s (cm^{-1}); 7.63 (singlet, 6H), 8.15 (singlet, 6H) (τ) (CCl_4).

Finally, an ether - chloroform mixture (1 : 1) eluted the third fraction (549 mg) of crystals, which were purified to XII by recrystallization from ethanol. Mp 182°C (decomp.). Yield: 16%. Positive to a potassium iodide-starch test.

Found: C, 38.41; H, 3.24; Cl, 38.17%. Calcd for $C_{12}Cl_4H_{12}O_5$: C, 38.10; H, 3.17; Cl, 37.57%. $\nu_{C=C}^{CCl_4}$ 1750s, 1730s, δ_{CH_3} 1380s, 1360s (cm^{-1}); 7.70 (singlet, 6H), 8.10 (6H) (τ) ($CDCl_3$).

b) In Dichloromethane or Carbon Tetrachloride - Chloroform at a Low Temperature. By essentially the same procedure as above, a viscous oil (800 mg) was obtained from a solution of VII (600 mg, 2 mmol) in dichloromethane (100 ml) by ozonization, followed by solvent evaporation. Nitric acid (sp. gr. 1.38, 2 g) was then added to the oil, and the mixture was heated at 100°C on a water bath for 1 hr, during this time some crystals were sublimated on the wall of the cooler. Ether extraction from the aqueous solution and the subsequent fractionation of the neutral part furnished a crystal sludge (300 mg). The chromatography of the benzene solution on aluminum oxide (Woelm, neutral, activation grade 1, 6 g) gave a fraction of IX (180 mg, 26% yield), which was then eluted with acetone and further purified by recrystallization from benzene or by vacuum sublimation (100°C (bath)/3 mmHg). Mp 125—127°C. 25 mg.

Found: C, 41.75; H, 3.56; Cl, 40.51%. Calcd for $C_{12}Cl_4H_{12}O_3$: C, 41.62; H, 3.47; Cl, 41.04%. No absorption maximum above 215 mμ (ethanol solution). Starting with the same amount of VII, ozonization in carbon tetrachloride - chloroform at −20°C afforded the identical oily product (720 mg), from which IX (155 mg, crude) was isolated.

c) In Petroleum Ether at Room Temperature. After the ozonization of VII (600 mg, 2 mmol) in petroleum ether (boiling below 45°C, 70 ml) at room temperature, a crystal sludge (600 mg) was obtained. It was dissolved again in petroleum ether and chromatographed on silica gel much as in a). 1) Petroleum ether - carbon tetrachloride eluted first a crystalline material (mp 122—124°C, 59 mg) identical with X. Yield:

28) Hitachi Perkin-Elmer Gas Chromatography Model F6D; Carrier gas: nitrogen; Column: 3 mmOD × 1 m packed with SE-30 Silicon Oil on Chromosorb W. Programmed from 50°C to 150°C.

29) The same silica gel will be used hereinafter.

8%. 2) The next crop, eluted with carbon tetrachloride alone, was the crude XI (107 mg, 16% yield), melting at 113—115°C after recrystallization from methanol. 3) Finally, crystals (40 mg) identical with IX were eluted with chloroform. Yield: 6%. Mp 125—127°C.

d) In Carbon Tetrachloride or Acetic Acid at Room Temperature. From VII (300 mg, 1 mmol) dissolved in carbon tetrachloride (10 ml) and water (1 ml), a crystalline product (220 mg) identical with XII was obtained; it was then recrystallized from carbon tetrachloride. Mp 182°C (decomp.). The runs with acetic acid as a solvent resulted in a comparable yield of XII.

Ozonization of 5,6-Diacetyl-1,4,5,6-tetrachloro-2,3-dimethylbicyclo[2.2.0]hexene-2 (XI). *a) In Acetic Acid or Carbon Tetrachloride at Room Temperature.* At room temperature, XI (900 mg, 2.7 mmol) dissolved in acetic acid (40 ml) and water (10 ml) was ozonized for 3 hr after which period some solid material crystallized out. The ozone-passing was stopped after an additional hour, and the solvent was evaporated. The residue consisted of colorless prisms of XII melting at 182°C (1.00 g). When carbon tetrachloride (15 ml) was used as the ozonization solvent, the yield of XII was 72% from XI (750 mg, 2.1 mmol).

b) In Ethyl Acetate at Room Temperature in the Presence of Tetracyanoethylene (TCNE). From XI (330 mg, 1 mmol) dissolved in ethyl acetate (20 ml), after working up ozonization in the presence of TCNE (160 mg, 1.25 mmol) afforded XII (230 mg, 61% yield).

Attempted Dechlorinations of XII to a Dewar Benzene (XIII). *a) With Zinc Powder-Ethanol or Nickel Carbonyl in Benzene; 1,2,5,6-Tetrachloro-7-hydroxy-3,4,9-trimethyl-7-oxotricyclo[4.3.0.0^{2,5}]nonene-3 (XIV).* After XI (400 mg, 1.2 mmol) had been refluxed with zinc powder (250 mg) in ethanol (10 ml) for 3 hr the soluble material was filtered off. The evaporation of the solvent of the filtrate furnished a crystalline product, which was then purified by chromatography on silica gel (5 g). The fraction eluted with chloroform afforded, on solvent evaporation, white crystals (206 mg) of XIV. Mp 150—156°C. Recrystallization from carbon tetrachloride gave a pure sample melting at 160°C. Yield: 52%.

Found: C, 43.91; H, 3.95; Cl, 42.86%. Calcd for $C_{12}Cl_4H_{12}O_2$: C, 43.64; H, 3.64; Cl, 43.03%.

The run with XI (300 mg, 1 mmol) and nickel carbonyl (27% benzene solution, 2 ml) also resulted in the production of XIV (150 mg, 0.5 mmol).

b) With Freshly-Prepared Nickel Metal; 1,2,5,6-Tetrachloro-3,4,9-trimethyl-7-oxotricyclo[4.3.0.0^{2,5}]nona-3,7-diene (XV). Nickel formate (10.6 g, 71 mmol) was pyrolyzed under reduced pressure at 245°C. After complete decarboxylation and spontaneous cooling, a solution of XI (580 mg, 1.75 mmol) in anhydrous benzene (20 ml) was added under a nitrogen atmosphere and the suspension was refluxed for 2 hr. The reaction mixture was then cooled and filtered, and the solid residue was washed with benzene. On the evaporation of the solvent of the filtrate, a crystalline product (crude XV, 470 mg) was obtained. Chromatographical purification on silica gel (10 g) afforded a fraction (200 mg, 0.64 mmol) eluted with carbon tetrachloride. Further recrystallization from the same solvent gave colorless prisms melting at 192—193°C.

Found: C, 46.24; H, 3.37; Cl, 45.68%. Calcd for $C_{12}Cl_4H_{10}O$: C, 46.15; H, 3.21; Cl, 45.51%.

A second crop (116 mg), isolated by subsequent elution with chloroform, was identical with the XIV obtained in a). Mp 160°C. Yield 21%.

Oxidation of XI with Sodium Hypobromite; Conversion to XIV. A methanol solution (20 ml) of XI (100 mg) was added to a 10% aqueous solution (30 ml) of sodium hydroxide and bromine (0.2 ml), whereupon an exothermal reaction occurred, turning the solution dark yellow. After the solution had been allowed to stand overnight, the product was isolated according to the ordinary procedure. From the neutral fraction XIV was obtained in an almost quantitative yield. Mp 160°C. No detectable amount of the acidic fraction was found.

Nitric Acid Oxidation of XI; Lactol (XVI). A mixture of the crude XI (900 mg, 2.7 mmol) and nitric acid (sp. gr. 1.38, 50 ml) was kept at 80°C for 2.5 hr. From the bicarbonate-soluble fraction, the product (200 mg) was precipitated on acidification. It was purified by chromatography on silica gel. The fraction eluted with chloroform consisted of colorless crystals, which were then further recrystallized from the same solvent to give a pure sample. Mp 167—169°C.

Found: C, 39.74; H, 3.12; Cl, 42.29%. Calcd for $C_{11}Cl_4H_{10}O_3$: C, 39.76; H, 3.01; Cl, 42.77%. No 1360 cm^{-1} band originally observed in XI was found.

Catalytic Hydrogenation of XII; all-*trans*-Tetraacetylcyclobutane (XVII) and Tetraketal of all-*cis*-Tetraacetylcyclobutane (XVIII). *a) Without Sodium Acetate.* The solution of XII (1.00 g, 2.65 mmol) in ethanol (100 ml) was subjected to hydrogenation at an ordinary pressure over 5% palladium-charcoal (1.0 g). The absorption of hydrogen ceased when a 5.42 equimolar amount had been consumed. The catalyst was then filtered and washed. The filterate was concentrated by evaporation at reduced pressure to approx. one-third the original volume. During this process, the solution gradually turned dark brown. Complete evaporation resulted in a mixture of white crystals and a brown oil, the latter of which was removed by being dissolved in water. White crystals (250 mg), when showed no chlorine contamination when submitted to a Beilstein test, were recrystallized from methanol to give pure needle crystals of XVIII (50 mg) melting at 282°C under decomposition. No carbonyl band was observed in the IR spectrum. Yield: *ca.* 8%.

Found: C, 64.20; H, 7.37%. Calcd for $C_{12}H_{16}O_4$: C, 64.28; H, 7.14%. IR: 3020m, 2980s, 2940m, 1460m, 1380s (hexachlorobutadiene mull); 1330s, 1300s, 1260s, 1200—1130 (broad), 1000—880 (5 bands), 805—800 (doublet), 650—635 (doublet), 530s (Nujol mull) (cm^{-1}) NMR: 6.76 (singlet, 4H), and 8.47 (singlet, 12H) (τ) ($CDCl_3$).

The filtrate of the recrystallization of XVIII furnished on the evaporation of the methanol, crystals (mp 133—134°C) slightly contaminated by XVIII. Recrystallization from acetone gave pure needle crystals of XVII (mp 145°C), identical with an authentic sample of all-*trans*-tetraacetylcyclobutane[9] (reported melting point: 139—140°C) in a comparison of the IR spectra.

Found: C, 64.05; H, 7.20%. Calcd for $C_{12}H_{16}O_4$: C, 64.28; H, 7.14%.

b) With Sodium Acetate. In ethanol (80 ml), XII

917 mg, 2.42 mmol) was hydrogenated at ordinary pressure over 5% palladium-charcoal with sodium acetate (1.62 g). In all 5.04 equimolar hydrogen was absorbed. Treatment similar to that in a) gave a mixture of colorless oil and crystals. The mixture was washed with dilute hydrochloric acid to remove the sodium acetate recovered and the sodium chloride formed. The crystals thus obtained were almost XVII-free. Vacuum sublimation at 100°C (bath)/3 mmHg afforded pure needle crystals (mp 282°C, decomp.). Yield: *ca.* 20%.

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