hexane gave 0.70 g., m.p. 90–91°), and 0.07 g. (9% of glycol isolated) of glycol IIIb, m.p. 45–57°. In a parallel experiment reduction of a sample of ketol Vb derived from glycol IIIb (m.p. 62°) gave 89% glycol IIIc, m.p. 85–90°, and 11% glycol IIIb, m.p. 54–60°.

The glycols (III) were shown to be stable to epimerization under the reaction conditions of formation. A 1.0-g. sample of glycol IIIc, m.p. 88–90°, 2.0 g. of sodium hydroxide, 4 ml. of water, and 2 ml. of ethanol were heated at reflux for 29 hr.; the product was crystallized from hexane to yield 0.84 g., m.p. 85–89°, of recovered IIIc; no other isomer could be crystallized from the solution. In separate experiments, glycol isomers IIIa (liquid) and IIIb (m.p. 62°) were also heated under the same conditions and recovered unchanged without formation of other isomers.

6-Hydroxymethyl-5-propyl-2,4,6-triethyl-1-cyclohexan-1-ols (VIIa and b).—A 1.0-g. sample of glycol isomer IIIb (m.p. 62°) in 25 ml. of absolute ethanol and 1.0 g. of 5% rhodium–charcoal catalyst were stirred in hydrogen (700 mm., 25°) until hydrogen uptake practically ceased (4 hr., 1.0 mole equiv. absorbed). The mixture was filtered and concentrated; the product and that from a second run of 2.0 g. were combined (total recovery, 2.5 g.). Distillation through a short column at 0.1 mm. gave (1) 0.7 g., b.p. 120–123°, $n^{25}\mathrm{D}$ 1.4845; (2) 1.3 g., b.p. 123–125°, $n^{25}\mathrm{D}$ 1.4870; and (3) 0.1 g., b.p. 125°, $n^{25}\mathrm{D}$ 1.4865. The infrared spectra of all fractions were examined (smear). All showed no C=C stretching band at 1640 cm.$^{-1}$, but some nonconjugated, hydrogen-bonded carbonyl absorption at 1685 cm.$^{-1}$ [absorbance values for fractions 1, 2, and 3 were 0.38, 0.06, and 0.03, respectively, at 1685 cm.$^{-1}$ and 0.53, 0.65, and 0.65 respectively, at 3300 cm.$^{-1}$ (hydroxyl); CH absorbance, 1.3 in each sample]. Fraction 2 (principally VIIb) was submitted for analysis. Adams catalyst was ineffective for the hydrogenation of IIIb at 3.5 atm., 60°, the reactant being recovered.

Anal. Calcd. for $C_{16}H_{32}O_2$: C, 74.94; H, 12.58; mol. wt., 256. Found: C, 75.08; H, 12.63; mol. wt., 254.

The hydrogenation procedure just described (rhodium–charcoal catalyst) was applied to the reduction of liquid glycol isomer IIIa (19 hr.). The undistilled product had carbonyl absorption at 1685 cm.$^{-1}$ (absorbance 0.63), hydroxyl absorption at 3300 cm.$^{-1}$ (absorbance 0.85), and CH absorbance 1.5 (smear). These absorbance values and those in 0.006 *M* solution (2.0-cm. cell) indicate the crude product to be a mixture of *ca.* 30% saturated ketol VIIIa and 70% saturated glycol VIIa; this product was used without purification for the measurement of infrared spectra reported in Table II.

Application of the rhodium–charcoal-catalyzed hydrogenation procedure to glycol IIIc (m.p. 90°) gave principally saturated ketol VIIIb (7-hr. reaction time); the undistilled product had carbonyl absorption at 1680 cm.$^{-1}$ (absorbance 1.5), hydroxyl absorption at 3400 cm.$^{-1}$ (absorbance 0.60), and CH absorbance 1.5 (smear). Adams catalyst was ineffective for hydrogenation of IIIc and gave principally unchanged reactant.

A 0.1-g. sample of the unsaturated glycol IIIb (m.p. 62°) was stirred with 5% rhodium–charcoal catalyst (0.2 g.) in 15 ml. of 95% ethanol for 24 hr. After removal of the catalyst the product was recovered unchanged (carbonyl absorption absent). A parallel experiment with the saturated glycol VIIb derived from glycol IIIb (6-hr. reaction time) provided a product with carbonyl absorption at 1690 cm.$^{-1}$ (absorbance 0.29), OH absorbance 1.8, and CH absorbance 1.9 (smear).

Platinum-Catalyzed Oxidation of 6-Hydroxymethyl-5-propyl-2,4,6-triethyl-2-cyclohexen-1-ol (IIIc).—In separate experiments samples of each of the four glycol isomers (IIIa–d) (0.1–0.2 g.) in 95% ethanol and equivalent weights of Adams catalyst, prereduced before use, were stirred in air for 2 hr. The products were recovered reactants (carbonyl absorption absent)—except with isomer IIIc (m.p. 90°) which produced ketol Vb [carbonyl absorption at 1650 cm.$^{-1}$ (absorbance 0.40), hydroxyl (absorbance 0.45), C=C absorption at 1680 cm.$^{-1}$ (absorbance 0.11), and CH absorbance 0.81 (smear)].

Acknowledgment.—The author is indebted to Dr. A. L. Olsen for assistance in securing the infrared spectra and for helpful discussions and to Professor A. T. Blomquist for providing some of the samples employed in this study. He wishes to thank Dr. Lester P. Kuhn for helpful comments and suggestions.

Reactions of Nitrogen Dioxide with Organic Halogen Compounds. III.[1] Oxidation of Some Cyclic Chloro Olefins to Cyclic Chloro Ketones

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Received March 12, 1965

Hexachlorocyclopentadiene undergoes a novel reaction with nitrogen dioxide at 60° to afford tetrachlorocyclopentene-1,2-dione (**1**) in about 90% yield. Another conjugated chloro olefin, decachlorobis(cyclopentadienyl) (**4**), reacts with nitrogen dioxide at 100° to give two isomeric diketones, $C_{10}Cl_8O_2$, in approximately equal amounts and in a total yield of about 85%. Spectral data show that these two diketones must have two of four possible structures: octachloro-*cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-dione (**5a**), octachloro-*cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]deca-3,9-diene-5,8-dione (**5b**), octachloro-*cis,cis,cis*-tricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-dione (**5c**), or octachloro-*cis,cis,cis*-tricyclo[5.3.0.0^{2,6}]deca-3,9-diene-5,8-dione (**5d**). Physical measurements, a partial resolution, and mechanistic considerations indicate that the preferred structures are the *cis,trans,cis* isomers, **5a** and **5b**. Trichloroethylene reacts with nitrogen dioxide at 80° to afford trichloronitroethylene in about 32% yield.

Relatively little has been reported about the reactions of nitrogen dioxide with chloro olefins. In 1869, Kolbe[2] described the synthesis of 1,2-dinitrotetrachloroethane by reaction of nitrogen dioxide with tetrachloroethylene. Burrows and Hunter[3] later reported that di- and trichloroethylene react with nitrogen dioxide to "undergo partial oxidation to oxalic acid, yielding also small amounts of lachrymatory substances of uncertain constitution." This appears to be the extent of published work on the reactions of nitrogen dioxide (or nitrogen tetroxide) with chloro olefins.

We now report (1) some interesting reactions of nitrogen dioxide with two cyclic chlorodienes and (2) a brief re-examination of the reaction of nitrogen dioxide with trichloroethylene.

Hexachlorocyclopentadiene reacts smoothly with nitrogen dioxide at 60°[4] to produce a yellow solid (m.p.

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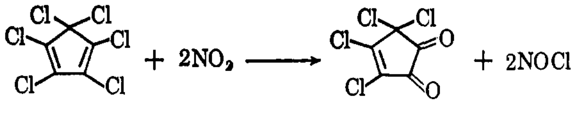
(1) Parts I and II: R. M. Scribner, *J. Org. Chem.*, **29**, 279, 284 (1964); *cf.* also *ibid.*, **29**, 3429 (1964).

(2) H. Kolbe, *Ber.*, **2**, 326 (1869); *cf.* also H. Blitz, *ibid.*, **35**, 1528 (1902), and W. L. Argo, E. M. James, and J. L. Donnelly, *J. Phys. Chem.*, **23**, 578 (1919).

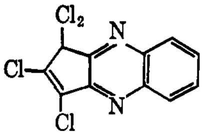
(3) R. B. Burrows and L. Hunter, *J. Chem. Soc.*, **134**, 1357 (1932).

(4) At 120° reaction of hexachlorocyclopentadiene with nitrogen dioxide gave dichloromaleic anhydride in small yield as the only identifiable product (*cf.* Experimental Section).

44.0–45.5°), having the composition $C_5Cl_4O_2$, in about 90% yield. Chemical and spectral evidence show that this new[5] compound is tetrachlorocyclopentene-1,2-dione (1). Its infrared spectrum exhibits a band at 1795 cm.$^{-1}$ due to the unconjugated carbonyl group, a band at 1748 cm.$^{-1}$ due to the conjugated carbonyl, and a band at 1558 cm.$^{-1}$ due to the conjugated chloro olefinic linkage.[6] In confirmation of the 1,2-diketo structure, this compound in aqueous ethanol rapidly reduces periodic acid.[7] With *o*-phenylenediamine in acetic acid, diketone **1** reacts to form the quinoxaline **2** in 90% yield.



1



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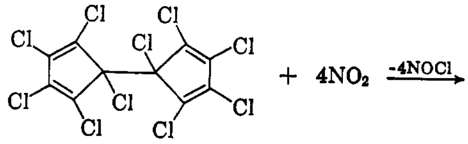
Aniline reacts with diketone **1** by substitution of a vinyl chlorine atom and formation of 4-anilino-3,5,5-trichlorocyclopentene-1,2-dione (**3**). The infrared absorption spectrum of this compound indicates that it exists primarily as the inner salt **3b**. Whereas the stretching frequency (1785 cm.$^{-1}$) of the nonconjugated carbonyl group of **3** is close to that of the parent diketone **1**, the other carbonyl group is shifted 53 cm.$^{-1}$ to lower frequency (1695 cm.$^{-1}$). Similar enhancement of single-bond character has been observed by Cromwell, *et al.*,[8] in the infrared spectra of a number of β-amino α,β-unsaturated ketones.

3a **3b**

Turning to a study of the reactions of other chloro olefins having some of the structural characteristics of hexachlorocyclopentadiene, we found, surprisingly, that hexachloro-1,3-butadiene, octachlorocyclopentene, and hexachloro-2-cyclopentenone were recovered unchanged after treatment with nitrogen dioxide for 6 hr. at 100°.

However, decachlorobis(cyclopentadienyl) (**4**) reacts with nitrogen dioxide at 100° to give, in addition to nitrosyl chloride, two ketones, A (m.p. 267–269°) and B (m.p. 190–192°), in approximately equal amounts and in about 85% conversion. Elemental analyses and molecular weight measurements show that these ketones are isomeric and correspond to $C_{10}Cl_8O_2$. Spectral analyses indicate that ketones A and B must have two of four possible structures: octachloro-*cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-dione (**5a**),[9,10] or octachloro-*cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]-deca-3,9-diene-5,8-dione (**5b**),[9] or the corresponding *cis,cis,cis* isomers **5c** and **5d**. Physical measurements, a partial resolution, and mechanistic considerations indicate that the preferred structures for A and B are **5a** and **5b**, respectively. These assignments must be considered provisional, however, pending further investigation.



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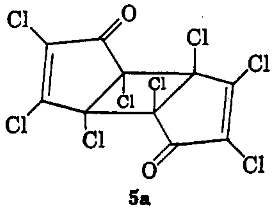
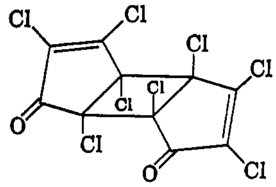
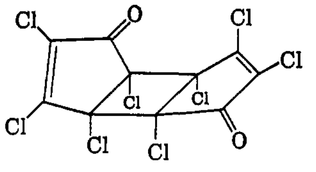


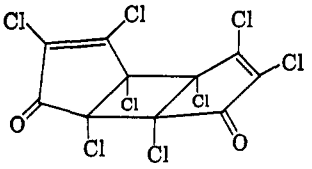
5a



5b



5c



5d

The ultraviolet absorption spectra (Table I) of A

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF A AND B

Isomer A	$\lambda_{max}^{EtOH\ a}$, mμ (ϵ):	258 (21,000), 315 (183), 328 (138), 342 (222), 357 (166), 373 (68)
	$\lambda_{max}^{dioxane\ b}$, m$\mu$ (ϵ):	255 (20,600), 323 (233), 337 (252), 352 (196), 370 (65)
Isomer B	$\lambda_{max}^{EtOH\ a}$, mμ (ϵ):	256 (19,400), 315 (125), 328 (157), 342 (171), 357 (136), 373 (53)
	$\lambda_{max}^{dioxane\ b}$, m$\mu$ (ϵ):	252 (19,700), 322 (170), 337 (177), 351 (137), 370 (48)

[a] See footnote 11. [b] See footnote 12.

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(5) The preparation of tetrachlorocyclopentene-1,2-dione (1) was claimed by H. J. Prins [*Rec. trav. chim.*, **65**, 455 (1946)]. Later A. Roedig and G. Märkel [*Ann.*, **636**, 1 (1960)] showed that the greenish yellow compound, m.p. 51°, of Prins was not **1** but probably impure tetrachloro-5-hydroxy-2,4-pentadienoic acid δ-lactone. Whereas the Prins compound was uneffected by steam distillation, our compound reacts with moist air, which behavior might be expected for structure **1** (see Experimental Section). In view of the work of E. T. McBee, *et al.* [*J. Am. Chem. Soc.*, **84**, 3557 (1962)], we suspect that, contrary to an additional claim of Roedig and Märkel, the precursor to the Prins compound was correctly identified as 1,2,5-trichloro-1-cyclopentene-3,4-dione. The latter was described by Prins as moisture sensitive.

(6) E. T. McBee, D. K. Smith, and H. E. Ungnade, *J. Am. Chem. Soc.*, **77**, 559 (1955).

(7) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 129.

(8) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank, and D. J. Wallace, *J. Am. Chem. Soc.*, **71**, 337 (1949).

(9) Alternative names for **5a** and **5b** are, respectively, octachloro-*cis,trans,-cis*-6a,6b-dihydrocyclobutadicyclopentene-1,6-(3aH,3bH)-dione and octachloro-*cis,trans,cis*-6a,6b-dihydrocyclobutadicyclopentene-1,4-(3aH,3bH)-dione. However, previous workers have named these ring systems by the method used in the text (*cf.* ref. 10).

(10) P. E. Eaton [*J. Am. Chem. Soc.*, **84**, 2344 (1962)] has prepared the unchlorinated analog of **5a**, *cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]-deca-4,9-diene-3,8-dione from the photodimer of cyclopentenone. The parent ring system is also found in the photodimer of cyclopentadiene: *cf.* G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

and B are very similar[11] and show that each isomer possesses *two* chlorocyclopentenone[15] systems. Thus, in ethanol their K bands fall close to those reported[16] for hexachloro-2-cyclopentenone (**6**), but the molar extinction coefficients associated with these peaks are 2.0–2.4 times as great as those of **6**.

Since conversion of **4** to A or B corresponds to the conversion of $C_{10}Cl_{10}$ to diketones $C_{10}Cl_8O_2$, it follows that the reaction must be accompanied by formation of a new carbon-to-carbon bond in each molecule of A and B. This bond must arise in one of three ways: formation of an acetylenic linkage from a double bond, formation of an olefinic linkage from a single bond, or formation of new carbon-to-carbon single bond. Only the last alternative leads to structures consistent with the ultraviolet spectra and with the infrared spectra (*vide infra*). We therefore conclude that addition of nitrogen dioxide to tetraene **4** results in the formation of a new interannular single bond.

Using a simple statistical approach, without regard to mechanistic or stereochemical restrictions, it can be seen that, if on *each* ring of **4** there are four possible positions which could eventually become carbonyl groups, and if ring bridging could occur either 1,2 or 1,4 with respect to carbonyl groups in two of these positions, but only 1,2 with respect to the carbonyl groups in the other two positions, then 6 × 6 combinations of bridge and carbonyl group positions are possible. Many of these combinations, of course, correspond to the same structures. The eight unique structures arising from all permutations are **5a** and its *cis,cis,cis* isomer **5c**; **5b** and its *cis,cis,cis* isomer **5d**; the *exo* and *endo* isomers of octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione, **8** and **9**; and the "*exo-exo*" and "*exo-endo*" isomers of octachlorotricyclo[4.2.1.1^{2,5}]octa-3,7-diene, **10** and **11**.

Unconjugated diketones **10** and **11** clearly can be excluded as possible structures for A and B on the basis of the ultraviolet absorption maxima. Diketones **8** and **9** with only one conjugated carbonyl group each can be excluded on the basis of the ultraviolet extinction coefficients of A and B.

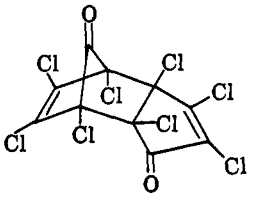
The infrared absorption bands of A and B are listed in Table II, together with the few bands that could be clearly detected in the Raman spectra of dioxane solutions of these sparingly soluble compounds. Both isomers exhibit a single, unresolved[17] infrared band in the region ascribed to olefinic unsaturation at 1583 cm.$^{-1}$. In the carbonyl region of their spectra, A and B exhibit single, unresolved[17] bands at 1751 and 1762 cm.$^{-1}$, respectively. In contrast, the dimer of tetrachlorocyclopentadienone (**8**) exhibits a strong carbonyl band at the unusually high frequency of 1808 cm.$^{-1}$, arising from its strained bridge carbonyl group, in addition to a band at 1720 cm.$^{-1}$ due to the chloro-

TABLE II

INFRARED AND RAMAN SPECTRA

Isomer A	Infrared,[a] ν_{max}^{Nujol} (cm.$^{-1}$): 1751 (vs), 1583 (vs), 1230–1240 (m), 1198 (s), 1070 (w), 1025 (m), 920 (m), 779 (m), 720 (m).
	Raman effect,[b] $\Delta\nu_{max}^{dioxane}$ (cm.$^{-1}$): 1760, 1585
Isomer B	Infrared,[a] ν_{max}^{Nujol} (cm.$^{-1}$): 1762 (vs), 1583 (vs), 1233 (m), 1200 (s), 1147 (vw), 1094 (w), 1064 (m), 1025 (w), 980 (m), 962 (m), 895 (m), 788 (m), 773 (m), 768 (w), 738 (m), 725 (s), 673 (w)
	Raman effect,[b] $\Delta\nu_{max}^{dioxane}$ (cm.$^{-1}$): 1760, 1585

[a] Measured on a Perkin-Elmer 237 grating spectrophotometer calibrated against a film of polystyrene. Estimated accuracy in the region of 1700 cm.$^{-1}$ is ±2 cm.$^{-1}$. [b] The Raman spectra were taken using blue-line excitation (4358 Å.) with an instrument similar to that described by D. H. Rank and E. V. Wiegand [*J. Opt. Sci. Am.*, **36**, 325 (1946)]. The instrument was equipped with a helical Toronto mercury arc source. Calibration was checked against acetone, at Δν = 1710 and 1750 cm.$^{-1}$ [F. F. Cleveland, M. T. Murray, J. R. Coley, and V. I. Komarewsky, *J. Chem. Phys.*, **10**, 18 (1942)], and against benzene, at 1584.8 and 1606.4 cm.$^{-1}$ (G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, p. 364). The estimated accuracy in the region of 1700 cm.$^{-1}$ is ±3 cm.$^{-1}$.



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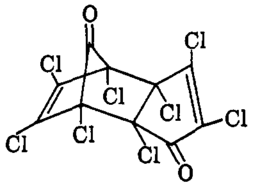

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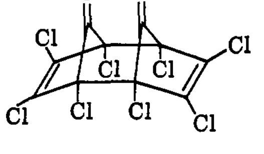

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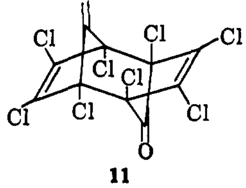

11

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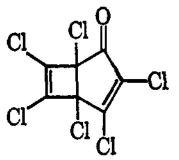
(11) A striking feature of the ultraviolet spectra of both A and B is the clearly defined fine structure of the R bands.[12] This is in contrast to the spectrum of hexachloro-2-cyclopentenone (**6**), which shows no detectable R-band fine structure. However, remarkably similar R-band fine structure does appear in hexachlorobicyclo[3.2.0]hepta-3,6-diene-2-one **7**[13,14] [λ_{max}^{EtOH} 255 mμ (ε 6000), 280 (2000), 336 (122), 350 (128), 367 (92), 385 (35)].



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(12) As expected, the components of the R bands of A and B undergo bathochromic shifts in transition from the polar solvent ethanol to the less polar solvent dioxane. [Ultraviolet spectra run in dioxane generally resemble closely those run in the nonpolar solvents hexane or cyclohexane, in which A and B are quite insoluble. *Cf.*, for example, M. T. Davies and V. Petrow, *Tetrahedron*, **19**, 1771 (1963), and C. Djerassi, "Optical Rotary Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 30].

(13) Compound **7** was prepared by the method of Roedig and Höning [*Ann.*, **598**, 208 (1956)].

(14) Compound **7** was kindly supplied by Dr. H. E. Knipmeyer of the Film Department, E. I. du Pont de Nemours and Co., Inc.

(15) Excellent agreement between λ_{max}^{EtOH} observed for A (258 mμ) and B (256 mμ) is also found with λ_{max}^{EtOH} 257 mμ calculated for **5a** using the rules of McBee, *et al.*,[6] and the value λ_{max}^{EtOH} 225 mμ reported by Eaton[10] for the unchlorinated analog of **5a**.

(16) E. T. McBee, D. K. Smith, and H. E. Ungnade [*J. Am. Chem. Soc.*, **77**, 559 (1955)] reported for **6** λ_{max}^{EtOH} 259 mμ (log ε about 4.0). A low-intensity R band becomes clearly defined only when the spectrum is run in hexane and appears at 330 mμ. E. D. Weil and J. Linder [*J. Org. Chem.*, **28**, 2218 (1963)] reported for **6** $\lambda_{max}^{CH_3CN}$ 260 mμ (ε 8870) and 294 mμ (ε about 3100).

(17) No resolution of these bands into multiplets could be achieved by using a Perkin-Elmer 237 grating spectrophotometer operating at slowest scan speed. From this, for both A and B, we conclude (1) that the two carbonyl groups in each molecule are in similar or identical chemical environments and (2) that they are only weakly coupled, that is they are relatively far removed from each other. The same arguments apply to the double bonds in A and B.

cyclopentenone carbonyl group.[6] Thus, the carbonyl positions in the infrared spectra of A and B are also incompatible with the bridge carbonyl structures **8** and **9**.

In view of the chemical similarity of isomers A and B, the relative simplicity of the infrared spectrum of A (nine bands) compared with that of B (17 bands) is regarded as arising from a significant difference in molecular symmetry. Of the four structures remaining to be considered for A and B (*i.e.*, **5a**, **5b**, **5c**, and **5d**), **5a** is the only one which has a symmetry element which reduces the number of fundamental infrared-active bands. Twenty-seven fundamental bands are calculated for centrosymmetric **5a**, whereas isomers **5b** and **5c**, possessing twofold axes of symmetry, and isomer **5d**, possessing a plane of symmetry, are each calculated to have 54 fundamental infrared-active bands.[18] These considerations thus favor structure **5a** for isomer A.

This evidence for the higher molecular symmetry of A compared with "B" is augmented by the much higher melting point (269°) of A compared with that (187°) of B.

Further evidence[19] for the centrosymmetric structure of A and a noncentrosymmetric structure of B is based on dipole moment measurements made on solutions of A and B in dioxane. Using the approximation[21] that total induced polarization is equal to observed molar refraction at the sodium D line, values of either 0.6 or 0.7 D. were found for the dipole moment of A depending on the method of treating the data.[22] Since the refractivity method is unreliable[21] for measurements below 1.0 D., and since our measurements were necessarily made on very dilute solutions,[23] the accuracy of these values can be questioned. Nevertheless, these results are in striking agreement with the small, apparent moments that have been observed for solution measurements on other centrosymmetric diketones.[24,25]

Although data from no source conclusively establish that A has structure **5a**, we feel that the total weight of evidence strongly favors this structural assignment over the three alternatives, **5b**, **5c**, or **5d**.

For B a dipole moment of 3.9 D. was found. Though this value is probably more accurate than that found for A, we would hesitate to use it to distinguish between the structural alternatives remaining for B, especially since their exact geometry is uncertain. Clearly, though, B is not centrosymmetric.

Useful information regarding the structure of B has been deduced, however, by consideration of the fact that of the alternative structures remaining to be considered for B, **5b** and **5c** alone should exist as racemic mixtures. Structure **5d** (as well as **5a**) has a superimposable mirror image and should not be resolvable. Treatment of B with 0.5 equiv. of brucine[26] in boiling ethyl acetate gave recovered B having a very slight[27a,b] but real optical activity. The optical rotatory dispersion curve of partially resolved B is shown in Figure 1 together with a portion of its absorption spectrum. That optical activity arises from resolved B rather than from traces of brucine was shown by comparison of this spectrum with the plain negative dispersion curve of authentic brucine. Furthermore, there is the expected correspondence of o.r.d. extrema with the "optically active" absorption peaks of B (Figure 1 and Table I).

Preferential destruction of one enantiomer of B thus shows that B is racemic and must therefore have structure **5b** or **5c**. Since selection of a preferred structure

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(18) These calculations, kindly done by Dr. J. R. Downing, refer to the entire spectrum of infrared-active bands, many of which should fall below the range of our spectrometer (4000–750 cm.$^{-1}$).

(19) Efforts to verify the centrosymmetric structure of A by Raman spectroscopy have given inconclusive results. As predicted by the "rule of mutual exclusion"[20] for centrosymmetric molecules, the observed carbonyl frequencies in the infrared and Raman effect spectra of A are different. Yet the double-bond frequencies in these spectra coincide closely, and the Raman spectrum of a saturated solution of A in dioxane is too weak to permit comparison of additional, weaker bands. Coincidence of band positions is not considered incompatible with our argument for a centrosymmetric structure. Rather, it is interpreted as a consequence of a fairly large separation and low coupling between the identical double bonds of A. Though different double-bond frequencies are expected when the double bonds vibrate in phase (Raman active) and out of phase (infrared active), extremely weak coupling should make these two frequencies nearly the same and, in our case, experimentally indistinguishable. R. C. Lord and R. W. Walker [*J. Am. Chem. Soc.*, **76**, 2518 (1954)] have used this kind of argument to explain the coincidences observed in the infrared and Raman spectra of a dimer of cyclooctatetraene. [*Cf.* S. C. Nyburg and J. Hilton, *Chem. Ind.* (London), 1072 (1957).] Close agreement between the infrared and Raman effect frequencies observed for the carbonyl groups as well as double bonds of B (Table II) is consistent with our assignment to B of a noncentrosymmetric structure.

(20) The rule of mutual exclusion states that, for a molecule with a center of symmetry, transitions that are allowed in the infrared are forbidden in the Raman spectrum and, conversely, transitions that are allowed in the Raman spectrum are forbidden in the infrared. (G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, p. 256.)

(21) C. P. Smyth, "Techniques of Organic Chemistry," 3rd Ed., Vol. I, part III, J. Weissberger, Ed., Interscience Publishers, Inc., N. Y., 1960, p. 2599, *ff.* This approximation leads to serious errors for dipole moments below 1.0 D.

(22) The value of 0.6 D. was calculated from a polarization derived by direct extrapolations to zero concentration of polarizations at three concentrations. The value of 0.7 D. was calculated by extrapolation of dielectric constants and densities. "(The latter) method and the polarization method lead to similar results and both may be employed with profit, particularly when the experimental errors are large or the solutions very dilute."[23]

(23) Ideally, four or five concentrations ranging from 0.001 to 0.01 or 0.02 to 0.10 mole fraction of solute in nonpolar solvents are employed for measurements of dipole moments. Our measurements were made at three concentrations with maximum concentrations of 0.0029 mole fraction for A and 0.1 mole fraction for B, these concentrations corresponding to nearly saturated solutions in dioxane.

(24) For example, 0.87 D. for tetrachloro-*p*-benzoquinone in dioxane, 0.50–0.75 D. for *p*-benzoquinone in benzene, dioxane, carbon tetrachloride, or hexane, and 0.72 D. for tetramethylcyclobutan-1,4-dione in benzene [A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963]. At least in the case of *p*-benzoquinone it has been shown that the apparent net orientation polarization is not real and results from an extraordinarily high atom polarization [I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938); E. D. Becker, *ibid.*, 4468].

(25) Professor P. E. Eaton has pointed out that puckering of the cyclobutane ring might impart a small but real dipole moment to **5a**.

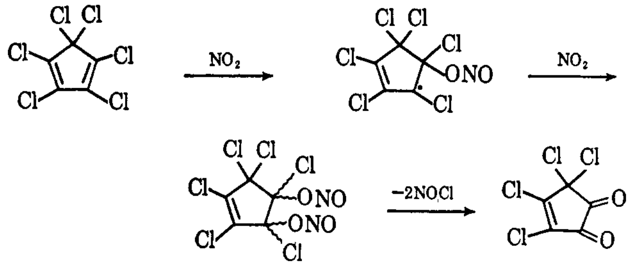
(26) We are indebted to Professor John D. Roberts for suggesting this convenient method for showing that B is racemic: *cf.* E. F. Jenney and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 2005 (1956).

(27) (a) Measured in a polarimeter at the sodium D line the specific rotation of partially resolved B was so small as to be barely significant: $[\alpha]^{24}\mathrm{D}$ $-0.5°$ (*c* 20.0, chloroform). (b) Treatment of A with 0.5 equiv. of brucine gave recovered A having, as expected, no detectable optical rotation in the range 300–450 mμ. (c) A referee has pointed out that this mechanism, involving the initial formation of a nitrite ester, is at variance with the generally accepted concept of the reaction of dinitrogen tetroxide with olefins in which initial attack takes place exclusively by C–N bond formation to give a nitro group [see, for example, H. Schechter, *Record Chem. Progr.*, **25**, 64 (1964)]. We do not, however, consider the experiments on which this generality is based pertinent to our experiments, for unlike ours they were carried out at -10 to 25° and in the presence of electron-donor solvents. In fact, it was not until Levy and Scaife [*J. Chem. Soc.*, 2627 (1949)] used the latter conditions that the oxidizing action of dinitrogen tetroxide on olefins could be *minimized* and nitro compounds isolated in good yields. In the absence of evidence to the contrary, we provisionally invoke the nitrite mechanism above in preference to the "accepted" nitro mechanism because of (1) the instability of α-chloro nitrites in contrast to the relative thermal stability of α-chloro nitro compounds, and (2) the necessity of accounting for the generation of nitrosyl chloride and ketones in high yields at moderate temperatures (60–100°).

for B from among these two alternatives cannot be made on the basis of the experimental data, we have considered the mechanism of the formation of A and B together with its steric consequences. These considerations lead us to choose **5b** as a tentative structure for B.

Failure of octachlorocyclopentene and hexachloro-2-cyclopentenone to react with nitrogen dioxide under the conditions we have tried (*vide supra*) suggests that facile reaction of nitrogen dioxide with chloro olefins to afford chloro ketones requires the presence of a *conjugated* chlorodiene system. Addition of the free-radical nitrogen dioxide to such a system can thus afford a resonance-stabilized (allyl) radical intermediate. Hexachlorocyclopentadiene ($\lambda_{\max}^{\mathrm{EtOH}}$ 323 mμ) and **4** ($\lambda_{\max}^{\mathrm{EtOH}}$ 330 mμ) with their double bonds constrained into coplanarity thus possess the conjugation required for reaction. Hexachloro-1,3-butadiene ($\lambda_{\max}^{\mathrm{EtOH}}$ 222 mμ) does not react with nitrogen dioxide at 100° presumably because its 1,3 double bonds are twisted out of conjugation.

Addition of nitrogen dioxide to a conjugated chloro ketone is thus expected to occur in such a direction as to afford a delocalized allyl radical. In the case of the radical intermediate derived from hexachlorocyclopentadiene, reaction of a second molecule of nitrogen dioxide at the vicinal carbon atom affords an unstable 1,2-bis(α-chloro nitrite), which by homolysis of the O–N bonds of the nitrite groups followed by β scission of chlorine atoms affords nitrosyl chloride and the 1,2 diketone **1**.[27c]



1

The allyl-radical intermediate derived by addition of nitrogen dioxide to the tetraene **4** is analogously represented[28] as **12** or its rotational isomer **13**. In this case, however, the unpaired electron evidently interacts with the nearby diene system to form a second interannular bond and a new allyl radical. Reaction of a second molecule of nitrogen dioxide with this new radical or its resonance isomer, followed by loss of the elements of two molecules of nitrosyl chloride, would thus afford the *cis,cis,cis* diketones **5c** and **5d** from rotomer **12** or the *cis,trans,cis* diketones **5a** or **5b** from rotomer **13**.

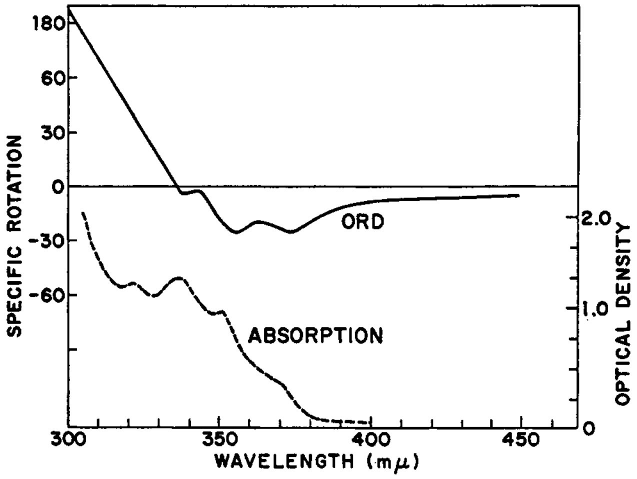
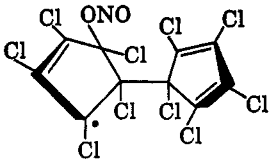
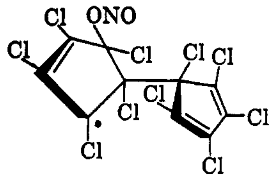


Figure 1.—Optical rotatory dispersion and absorption curves of partially resolved B, 0.3% by weight in dioxane.

The energy required for formation of a transition state from **12** should be significantly greater than from rotational isomer **13**. In the former case, the four chlorine atoms at the corners of the potential cyclobutane ring would have to move into two essentially *eclipsed* conformations.[29] Formation of products from **13** would, on the other hand, require only that each pair of chlorine atoms move into a *gauche* relationship.



12



13

Rather than assume that **5c** is formed from the energetically less-favored[30] rotamer **12** to the *complete exclusion*[31] of **5b** which would arise from the energetically favored rotamer **13**, we provisionally assign structure **5b** to chloro ketone B.

Trichloroethylene.—Turning to the study of some other chloro olefins, we have re-examined[2,3] briefly the reactions of nitrogen dioxide with some simple chloroethylenes. The reaction of tetrachloroethylene with nitrogen dioxide is fairly straightforward and affords

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[28] Formulation of rotomers **12** and **13** as discrete radicals is, of course, arbitrary. Thus, addition of nitrogen dioxide to the tetraene **4** could be accompanied by concerted interannular bond formation, or elimination of NOCl from radicals **12** and **13** could occur *before* ring closure, so that the intermediates existing just before ring closure would be monoketones rather than α-chloro nitrites. In either case, the arguments pertaining to the steric effects of the four cyclobutyl chlorine atoms on formation of **5b** or **5c** still pertain.

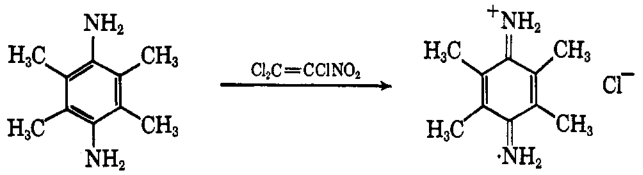
[29] Because the skeletons of the *cis,cis,cis*- and *cis,trans,cis*-tricyclo$[5.3.0^{2,6}]$decanes are quite rigid, their precursors **12** or **13** at the instant before ring closure must have conformations very similar to those of the final products. Conformations were studied with the aid of Dreiding models.

[30] This reasoning assumes that intermediates **12** or **13**, if they are discrete radicals, are sufficiently long lived to be able to assume the energetically favored rotational configuration before ring closure occurs. Precedence for this kind of stability of similar free-radical intermediates is found in the recent work of P. D. Bartlett (Abstracts of the 18th National Organic Chemistry Symposium of the American Chemical Society, Columbus, Ohio, June 1963, p. 45) who has shown that in the 1,2 cycloaddition of fluorinated olefins to 2,4-hexadienes a number of isomeric adducts are formed which can be considered to result from intermolecular reaction of the radical intermediate in each of several rotameric forms.

[31] Thin layer chromatography on fluorescent, activity grade III alumina using ethanol–ethyl acetate–dioxane (2:48:48 v./v.) as the solvent showed on examination of the developed plate under ultraviolet light that the total crude product from reaction of nitrogen dioxide with decachlorobis(cyclopentadienyl) (**4**) contained, in addition to a very small amount of unchanged **4**, only the two α,β-unsaturated ketones A and B. This conclusion was verified by the infrared spectrum of the total crude reaction product (*cf.* Experimental Section).

dinitrotetrachloroethane[32] in good yield. However, reaction of trichloroethylene with nitrogen dioxide affords a complex mixture of products. Confirming the observation of Burrows and Hunter,[3] one of the components of this mixture was found to be oxalic acid. We have also found that, by careful distillation of the yellow lachrymatory liquid obtained from this reaction, trichloronitroethylene[33] can be isolated in 32% yield.

Treatment of this nitro olefin with an equimolar amount of 1,4-diaminodurene in benzene did not afford the expected charge-transfer complex.[34] Instead, there was formed a dark green Würster salt,[35] the monomeric form of which can be represented as the radical **14**. This salt precipitates from the reaction mixture in a state of analytical purity and in 89% yield.



14

Experimental Section[36]

Tetrachlorocyclopentane-1,2-dione (1).—Hexachlorocyclopentadiene[37] (20 g., 0.073 mole) and nitrogen dioxide[38] (27 g., 0.59 mole) were heated in an autoclave at 80° for 4 hr. The vessel was cooled to room temperature and vented slowly, leaving a residue of a viscous brown oil weighing 13.5 g. Preliminary distillation of this oil through a short-pass column followed by fractional distillation through a spinning-band column[39] gave about 10 g. of a yellow oil, b.p. 80–82° (2 mm.), that on standing gradually crystallized. After being pressed on filter paper the yellow crystals melted at 41–42°. An analytical sample, prepared by sublimation at 40° (2 mm.), existed as yellow cubes: m.p. 44.0–45.5°; $\nu_{\max}^{\mathrm{CCl_4}}$ 1795 (s), 1748 (vs), 1558 (vs), 1232 (s), 1166 (m), 926 (w), 877 (w), 833 (s) cm.$^{-1}$; $\lambda_{\max}^{\mathrm{hexane}}$ 226 mμ (ϵ 12,300), 283 (7840), sh 330 (75), 463 (28), 475 (19); n.m.r. (CCl_4, 1000-c.p.s. scan) showed the absence of hydrogen.

Anal. Calcd. for $C_5Cl_4O_2$: C, 25.67; H, 0.00; Cl, 60.64; neut. equiv. for a dibasic acid, 117. Found: C, 25.78; H, 0.41; Cl, 60.68; neut. equiv. (in ethanol-water to phenolphthalein end point), 111.

The diketone dissolved readily in hexane or petroleum ether (b.p. 60–90°) and could be recrystallized from these solvents. With water it reacted to give a colorless solution which rapidly reduced potassium permanganate or periodic acid.

A subsequent preparation of diketone **1** was carried out by placing 100 g. (0.367 mole) of hexachlorocyclopentadiene[37] in a 1-l., Hastelloy-lined autoclave, cooling the autoclave to −78°, evacuating it to about 1 mm. pressure, and adding 100 g. (2.24 moles) of nitrogen dioxide.[38] The autoclave was heated slowly (3 hr.) to 60° and maintained at that temperature for 6 hr. It was then cooled to room temperature, vented, emptied, and rinsed with 25 ml. of methylene chloride, taking care to keep the reaction product and the rinsings under an atmosphere of nitrogen. The combined liquid contents of the vessel and the rinsings were concentrated in a rotating evaporator at 40° (30 mm.). Distillation of the residual amber liquid through an 18-in. spinning-band column[39] gave 78 g. (90% yield) of tetrachlorocyclopentene-1,2-dione, b.p. 73° (0.85 mm.), m.p. 31–43°. The diketone **1** was stable on storage but reacted slowly with moist air.

When hexachlorocyclopentadiene (30.0 g., 0.11 mole) and nitrogen dioxide (35 g., 0.76 mole) were heated in a Hastelloy-lined autoclave for 6 hr. at 120° and the autoclave was cooled to room temperature and evacuated to about 2 mm. to remove gaseous products, there was obtained 4.5 g. of a brown solid. Three crystallizations from hexane gave dichloromaleic anhydride as white plates: m.p. 121–123° (lit.[40] m.p. 118–119°); $\nu_{\max}^{\mathrm{KBr}}$ 1870, 1770, 1260, 1210, 725 cm.$^{-1}$. The anhydride dissolved readily in aqueous sodium bicarbonate.

Anal. Calcd. for $C_4Cl_2O_3$: C, 28.80; H, 0.00; Cl, 42.47. Found: C, 29.19; H, 0.71; Cl, 42.39.

1,1,2,3-Tetrachloro-1H-cyclopenta[*b*]quinoxaline (**2**).—A solution of 8.50 g. (0.036 mole) of distilled diketone **1** in 10 ml. of glacial acetic acid was added with stirring to a solution of 4.30 g. (0.040 mole) of *o*-phenylenediamine in 15 ml. of glacial acetic acid. When the vigorous exothermic reaction subsided, the mixture was heated at 80° for 1 hr. with stirring and then cooled to room temperature and poured into about 300 ml. of ice–water. Filtration gave an amber yellow solid which after thorough washing with water and drying weighed 10.4 g. (90% yield) and melted at 186–188°. An analytical sample, prepared by crystallization from cyclohexane, existed as light yellow needles: m.p. 187–188°; $\nu_{\max}^{\mathrm{CHCl_3}}$ (no N–H bands) 3012 (m), 1618 (m), 7582 (s), 1577 (s), and 1513 (s) cm.$^{-1}$, and strong bands at 1323, 1149, 1021, 1002, 917, and 826 cm.$^{-1}$; n.m.r. (in $CDCl_3$ *vs.* internal tetramethylsilane), two complex multiplets centered at $\delta = 4.0$ p.p.m., superficially resembling the spectrum of *o*-dichlorobenzene.

Anal. Calcd. for $C_{11}H_4Cl_4N_2$: C, 43.18; H, 1.31; N, 9.15; Cl, 46.36; mol. wt., 306. Found: C, 43.19; H, 1.48; N, 9.07; Cl, 46.48; mol. wt. (ebullioscopic in benzene), 333.

4-Anilino-3,5,5-trichlorocyclopentene-1,2-dione (**3**).—A solution of diketone **1** (4.68 g., 0.02 mole) and aniline (3.72 g., 0.04 mole) in 50 ml. of ether was allowed to stand at room temperature for 24 hr. The insoluble solids were separated by filtration and triturated with water to give 2.5 g. of brown-orange crystals. Recrystallization of this solid from ethyl acetate–hexane (1:1) gave yellow cubes: m.p. 214° with decomposition from 170°; $\nu_{\max}^{\mathrm{KBr}}$ 3125, 1785, 1695, 1563 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_6Cl_3NO_2$: N, 4.83; Cl, 36.62. Found: N, 5.15; Cl, 36.50.

Octachloro-*cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-dione (A) and Octachloro-*cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]deca-3,9-diene-5,8-dione (**B**).—Bis(pentachlorocyclopentadienyl) (25.0 g., 0.053 mole, m.p. 123.5–125.5° after one crystallization of the commercial[37] product from ethyl acetate) and nitrogen dioxide[38] (30 g., 0.65 mole) were heated in a 240-ml. autoclave lined with Hastelloy C at 100° for 10 hr. The vessel was cooled to room temperature, and the gases were vented. The infrared spectrum of a sample of this gaseous product showed the presence of a mixture of the oxides of nitrogen and 5–10 mole % of nitrosyl chloride, the latter characterized by bands at 2140, 2120, 1810, 1790, 9350, and 9090 cm.$^{-1}$. The light yellow solid remaining in the bomb weighed 19.5 g. (85%). Its infrared spectrum was identical with respect to band position and magnitude with the spectrum of a mixture prepared from equal weights

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[32] In his review of the chemistry of nitrogen dioxide, J. L. Riebsomer [*Chem. Rev.*, **36**, 157 (1945)] has with justification pointed out that, since nitrogen dioxide adds to olefins to give nitro nitrites, it may be questioned whether early workers actually had prepared 1,2-dinitrotetrachloroethane, especially since only elemental analyses were quoted to support their assignment of structure. We have prepared the tetrachloroethylene–nitrogen dioxide adduct, m.p. 156–157°, and find that infrared and chemical evidence as well as elemental analyses fully support the dinitro structure. The infrared spectrum (potassium bromide) exhibits only three bands in the 1000–4000-cm.$^{-1}$ region. A very weak band appears at 3425 cm.$^{-1}$ and is probably a harmonic from the nitro group, since hydrogen n.m.r. spectroscopy proves the absence of hydrogen. Two strong bands appear at 1603 and 1309 cm.$^{-1}$ and are in very good agreement with the nitro group stretching frequencies, 1610 and 1312 cm.$^{-1}$, observed for chloropicrin and, in general, with the stretching frequencies observed for other negatively substituted nitro compounds [J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955)]. Chemical evidence supports the dinitro structure since the compound is recovered unchanged after prolonged treatment with aqueous sodium bicarbonate or concentrated sulfuric acid.

[33] (a) G. B. Bachman, T. J. Logan, K. R. Hill, and N. W. Standish [*J. Org. Chem.*, **25**, 1312 (1960)] prepared trichloronitroethylene (4.2% conversion) by the action of a mixture of chlorine and nitrogen tetroxide on trichloroethylene. (b) H. Johnston [U. S. Patent 3,054,828 (1962)] claims the preparation of trichloronitroethylene by boiling trichloroethylene with 70% aqueous nitric acid.

[34] *Cf.*, for example, D. J. Cram and G. S. Hammond, "Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, pp. 219–220; R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

[35] L. Michaelis and S. Granik, *ibid.*, **65**, 1747 (1943).

[36] Melting points and boiling points are uncorrected.

[37] Hooker Chemical Corp., Niagara Falls, N. Y.

[38] Used as supplied by the Matheson Co., East Rutherford, N. J.

[39] R. G. Nester, U. S. Patent, 2,712,520 (1955).

[40] P. Karrer and E. Testa, *Helv. Chim. Acta*, **32**, 1025 (1949).

of pure A and B (*vide infra*). Thin layer chromatography[31] verified that the total, crude, solid product of reaction was composed primarily of equal parts of the diketones A and B.

Fractional crystallization of a 5-g. portion of this product from ethyl acetate by the "pyramid scheme" of combining filtrates, gave 1.1 g. (22%) of A as plates, m.p. 267–269°, as the least soluble component of the mixture, and 1.9 g. (38%) of B as star clusters, m.p. 190–192°. The n.m.r. spectra of A and B in deuteriochloroform verified the absence of hydrogen.

Anal. Calcd. for $C_{10}Cl_8O_2$: C, 27.56; H, 0.00; Cl, 65.09; mol. wt. 436. Found for isomer A: C, 27.44; H, 0.26; Cl, 64.76; mol. wt. (ebullioscopic in dioxane), 481. Found for isomer B: C, 27.13; H, 0.24; Cl, 64.88; mol. wt. (freezing point in dioxane), 422, 446.

In a subsequent preparation of A and B it was found convenient, though less efficient, to separate these isomers by crystallizing the total, crude, reaction product (49 g.) from the minimum amount of boiling ethyl acetate (300 ml.), giving A as crystals, m.p. 260–265°, which after recrystallization from fresh ethyl acetate melted at 270–271° (6.83 g.). Evaporation of the filtrate from the first crystallization and three recrystallizations of the residue from boiling amyl acetate gave moderately pure B (17 g.), m.p. 185–186°.

Partial Resolution of Diketone B.—To a solution of diketone B (1.74 g., 0.002 mole) in ethyl acetate (100 ml.) was added brucine (0.79 g., 0.002 mole), and the mixture was heated at reflux temperature for 12 hr. After being kept 1 day at room temperature, the black reaction mixture was filtered, and the filtrate was evaporated to dryness *in vacuo*. The black residue obtained was sublimed at 130° (0.05 mm.) giving 0.8 g. (46%) of a light yellow sublimate which was recrystallized from ethyl acetate and resublimed, giving white needles of B, m.p. 192.0–193.0°, $\nu_{max}^{CHCl_3}$ 1760 and 1587 cm.$^{-1}$ (*cf.* Table II). A solution of 0.403 g. of B in 2.0 ml. of chloroform had $[\alpha]^{24}D$ −0.5°. Rotatory dispersion in dioxane (*c* 0.30), *ca.* 25° showed $[\alpha]_{374}$ −25°, $[\alpha]_{363}$ −20°, $[\alpha]_{356}$ −25°, $[\alpha]_{343}$ −2°, $[\alpha]_{338}$ −3°.

Anal. Calcd. for $C_{10}Cl_8O_2$: C, 27.56; H, 0.00; Cl, 65.09. Found: C, 27.76; H, 0.30; Cl, 64.73.

Trichloronitroethylene.—Trichloroethylene (26 g., 0.2 mole) and nitrogen dioxide[38] (27 g., 0.6 mole) in an 80-ml. Hastelloy-lined autoclave were heated slowly (3–4 hr.) to 80° and held at that temperature for 6 hr. The vessel was cooled to room temperature and vented slowly, giving 19 g. of a light brown, mobile liquid. Flash distillation of one-half of this liquid through a short Vigreux column gave 6 ml. of a light yellow liquid, b.p. 48–65° (20 mm.), which was refractionated through an 8-in. spinning-band column[39] and gave 5.6 g. (32%) of trichloronitroethylene, b.p. 64° (33 mm.) [lit. b.p. 55° (4 mm.),[33a] 59° (18 mm.)[33b]]. The infrared spectrum of this yellow liquid exhibited nitro bands at 1550 and 1325 cm.$^{-1}$ and a band at 1639 cm.$^{-1}$ assignable to the olefinic linkage. The presence of unsaturation was verified by the rapid oxidation of its solution in acetone by aqueous potassium permanganate.

Anal. Calcd. for $C_2Cl_3NO_2$: N, 7.95; Cl, 60.2. Found: N, 8.09; Cl, 60.2.

Reaction of Trichloronitroethylene with Diaminodurene.—To 0.1769 g. (1.0 mmole) of trichloronitroethylene in 10 ml. of benzene was added dropwise and with stirring 0.1572 g. (0.86 mole) of pure diaminodurene in 15 ml. of benzene. The green solid that formed was centrifuged, washed with 20 ml. of benzene, centrifuged, and dried *in vacuo*, giving 0.17 g. (89%) of a dark green salt, soluble in alcohol or water. The infrared spectrum (KBr) of this salt was similar to that of an authentic sample[41] of the Würster salt,[35] diaminodurene chloride, having in common bands at 3333, 3175, 1739, 1650, 1600, 1471, and 1379 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}ClN_2$: N, 14.0; Cl, 17.80. Found: N, 14.23; Cl, 17.86.

Acknowledgment.—It is a pleasure to acknowledge helpful discussions during the preparation of this paper with Professor Richard C. Lord, Professor John D. Roberts, and Dr. Howard E. Simmons. Dr. Victor E. Shashoua kindly provided the optical rotatory dispersion data. Thanks are due Miss Naomi E. Schlichter, Miss Ellen Wallace, Dr. Carl E. Willoughby, and Mr. John Myers for their expert and generous assistance in making physical measurements.

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[41] Supplied by Dr. L. R. Melby of these laboratories, who prepared it by the action of chlorine on diaminodurene in chloroform.

Compounds of Phosphorus and Fluorine. II. Reaction of Phosphite, Phosphonite, and Phosphinite Esters with 1,2-Dichloroperfluorocycloalkenes[1]

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Received June 24, 1965

Trialkyl phosphites, unlike other nucleophilic reagents, react with 1,2-dichloroperfluorocycloalkenes with the displacement of both chlorine atoms, regardless of the order of addition or the ratio of reactants. The products are tetraalkyl perfluoro-1-cycloalken-1,2-ylenediphosphonates. Similar reactions take place with phosphonous and phosphinous esters giving the corresponding diphosphinates and bis(phosphine oxides). The reason for the difference in mechanism is discussed.

In part I of this series we showed that trialkyl phosphites abstract vicinal halogen atoms from saturated chlorofluorocarbons without forming C–P bonds, the products being fluoro olefins, dialkyl phosphorochloridates (or -fluoridates), and alkyl chlorides.[1] The fluoro olefins thus formed are capable of reacting further with trialkyl phosphites giving products which do contain C–P bonds. Knunyants,[2] *et al.*, described the preparation of numerous dialkyl perfluoroalkenylphosphonates from perfluoro olefins by the displacement of vinylic fluorine, but fluoro olefins containing chlorine substituents have not hitherto been examined, with the sole exception of chlorotrifluoroethylene.[2c] The present paper deals with the reactions of trialkyl phosphites with 1,2-dichloroperfluorocycloalkenes (I), which proceed with the displacement of both chlorine atoms giving tetraalkyl perfluoro-1-cycloalken-1,2-ylenediphosphonates (II).

The stoichiometry was established in a reaction between 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene

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[1] Part I: A. W. Frank and C. F. Baranauckas, *J. Org. Chem.*, **30**, 3970 (1965).

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