1094. *7-Norbornadienone Ketals.*

By K. MACKENZIE.

Ethylene, butylene, and methyl ketals of 1,2,3,4-tetrachloronorbornadien-7-one have been prepared and their properties compared with those of similar compounds.

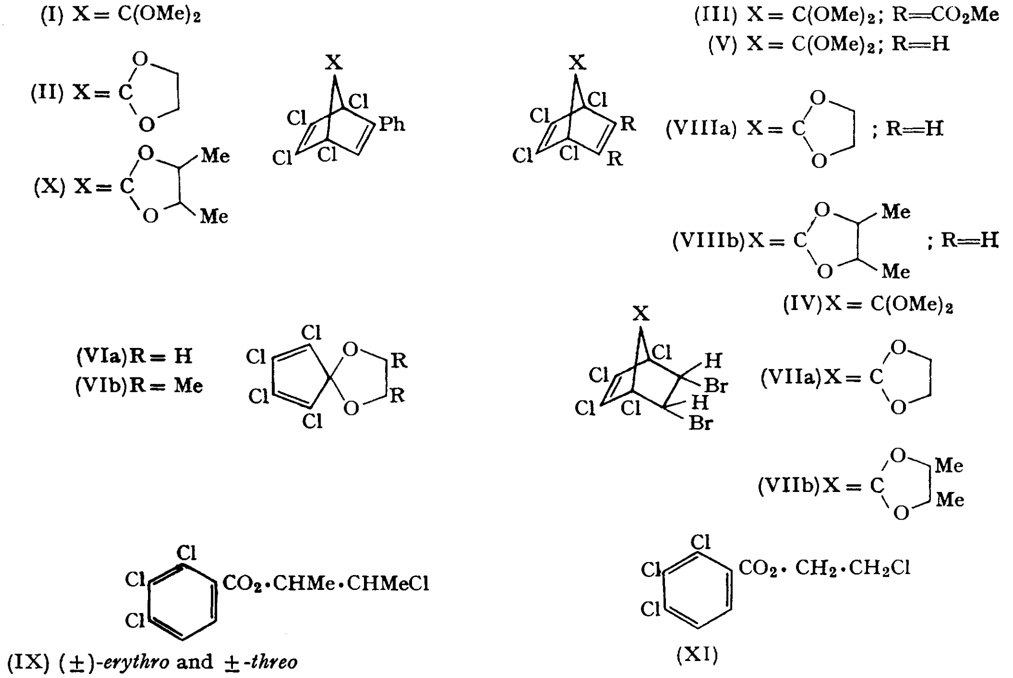
NORBORNADIENE derivatives substituted in the 7-position are of considerable practical and theoretical interest but few such compounds are known. Very recently, tetrachlorophenylnorbornadien-7-one ketals have been reported in connexion with attempted isolation of dialkoxy-carbenes by thermal cleavage of the bridge in analogy with the well-known decarbonylation reaction.[1,2] For example, compound (I) decomposes giving 2,3,4,5-tetrachlorobiphenyl, 3,4,5-trichloro-2-methoxycarbonylbiphenyl, and tetramethoxyethylene, the last-named presumably being formed by dimerization of the dimethoxycarbene produced; in contrast, the ethylene ketal (II) gives only tetrachlorobiphenyl, ethylene, and carbon dioxide. The ring-opening of compound (III) to give trichlorohemimellitic ester has also been described.[3]

The decomposition of the dibromide (IV) on mild heating with zinc to give mainly methyl 2,3,4-trichlorobenzoate had earlier been observed,[4] together with the high-temperature (> 150°) dechlorination of the *endo-cis*-dichloro-analogue to give mainly 1,2,3,4-tetrachlorobenzene (unpublished work). In later studies, similar conclusions had been reached to those advanced[1] in rationalizing the formation of trichloromethoxycarbonylbiphenyl from compound (I) as well as the tetrachlorobiphenyl earlier reported,[5] although no evidence for carbene formation had been found.

The main interest lay in the preparation and utility of tetrachloronorbornadienone ketals for the synthesis of fused-ring systems, and the earlier failure to isolate any of the dimethoxy-compound (V) from compound (IV) prompted an examination of the feasibility of preparing the corresponding ethylene ketal (VIIIa), which might be expected to be more stable than compound (V) on account of the compact and rigid nature of the bridge.

[1] R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 1964, **4**, 197.
[2] D. M. Lemal, E. P. Gosselink, and A. Ault, *Tetrahedron Letters*, 1964, **11**, 579.
[3] J. Dieckmann, *J. Org. Chem.*, 1963, **28**, 2880.
[4] K. Mackenzie, *J.*, 1962, 457.
[5] E. T. McBee, W. R. Diveley, and J. E. Burch, *J. Amer. Chem. Soc.*, 1955, **77**, 385.

The expedient Diels–Alder synthesis of compound (VIIIa) required the preparation of 5,5-ethylenedioxytetrachlorocyclopentadiene (VIa) and this was achieved by the usual method,[6] the ketal being obtained crystalline and readily dimerizing on being heated.[7] The butylene analogue was prepared from 60—70% (±)-butane-2,3-diol and had comparable properties. Both these dienes reacted readily with *cis*-dibromoethylene to give high yields of the adducts (VIIa) and (VIIb), no stereomutation of bromine having occurred. The dibromo-compounds were smoothly dehalogenated with zinc at 10° giving tetrachloronorbornadienone ethylene and butylene ketals (VIIIa) and (VIIIb), from which the *trans*-dibromo-isomers of (VIIa) and (VIIb) were isolated by bromination in the usual manner.



The ketals (VIIIa) and (VIIIb) decomposed rapidly, but behaved differently on being heated; (VIIIa) appeared to be much more stable than (VIIIb) for the latter ketal decomposed completely at 100—105° to give 1,2,3,4-tetrachlorobenzene and the chlorobutyl ester (IX) (mole ratio ~ 2·6), whilst ketal (VIIIa) required a somewhat higher temperature (120—130°) to decompose it and the product contained only 3—5% of the chloroethyl ester (XI) (mole ratio 40). The other products of decomposition were carbon dioxide in each case, ethylene from (VIIIa) and *trans*-but-2-ene from (VIIIb). The ketal (VIIIa) therefore closely resembles compound (II), whilst (VIIIb) is more like compound (I) in its behaviour and, in a similar manner, decomposed extremely vigorously above 120°. The 5-phenyl derivative of compound (VIIIb), prepared from phenylacetylene and compound (VIb), also decomposed to a mixture of tetrachlorobiphenyl and an ester, tentatively identified as a mixture of the 5- and 6-phenyl derivatives of compound (IX), together with carbon dioxide and *trans*-but-2-ene, establishing the generality of behaviour.

The successful isolation of the cyclic ketals prompted a re-investigation of the dehalogenation of compound (IV), and pure compound (V) was isolated from it by debromination at 0—5°. The ketal (V) proved to be somewhat less stable than the cyclic analogues (VIIIa) and (VIIIb), for it was smoothly and rapidly decomposed at 85°, whilst at higher temperatures

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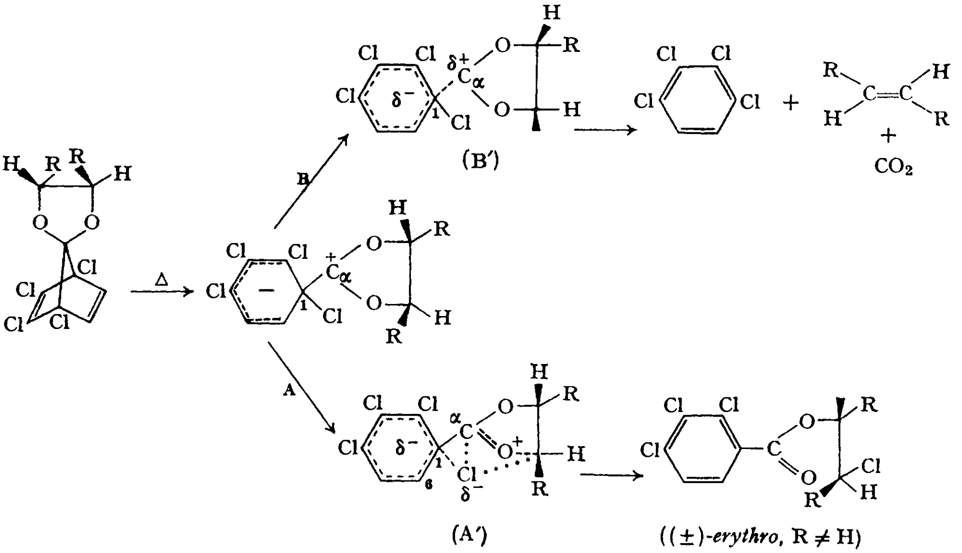
[6] J. S. Newcomber and E. T. McBee, *J. Amer. Chem. Soc.*, 1949, **71**, 949.

[7] Cf. C. H. De Puy, B. W. Ponder, and J. D. Fitzpatrick, *Angew. Chem.*, 1962, **74**, 489; B. W. Ponder, *Diss. Abs.*, 1961, **22**, 431; cf. Wen-Hsuan Chang, *Chem. and Ind.*, 1964, 709.

the decomposition was uncontrollable. Both 1,2,3,4-tetrachlorobenzene and methyl 2,3,4-trichlorobenzoate were formed, together with carbon dioxide and tetramethoxyethylene, the lability of this olefin even in the presence of only traces of acids being noted.[2] The mole ratio of chlorohydrocarbon to ester in this case was reduced to ~ 0·8.

No detailed investigation of the mode of decomposition of these ketals has been attempted, but there is an important difference between the behaviour of the cyclic ketal (VIIIb) and that of the open type as typified by compound (V) when decomposed in alcohols, for while the ketal (VIIIb) gave exclusively the chloro-compound (IX) as the ester component when decomposed in n-butanol, in contrast, compound (V), when heated in ethanol, gave a mixture of ethyl and methyl 2,3,4-trichlorobenzoate, tetrachlorobenzene being the other product in each case. Even under acidic conditions the rate of ester interchange of methyl trichlorobenzoate in ethanol appears to be slow and no exchange was detected in a control experiment under the conditions used for decomposition of compound (V) ($BaCO_3$). These results imply some difference in the detailed nature of the pathways leading to the formation of ester from the cyclic and open ketals, and may provide indications for future work.



[*Lines of dots* (. . .) *are electrostatic interactions:* Cl^- *is largely formed after* C–O *bond fission commences.*]

However, it seems likely that decomposition of the cyclic ketals proceeds through an intermediate similar to that suggested for compound (I),[1] which can react further to give chloro-alkyl ester by an *intramolecular* sequence (which could involve an ion-pair) (Path A) or tetrachlorobenzene by the alternative (path B) as shown in the scheme.*

The ester produced from compound (VIIIb) is similar to the authentic compound formed by half-esterification of (±)-butane-2,3-diol with 2,3,4-trichlorobenzoyl chloride to give the hydroxy-ester (IXa) followed by chlorination under conditions precluding retention of configuration at substituted hydroxyl ($SOCl_2$–pyridine), which must have given largely the more stable (±)-*erythro*-diastereoisomer. However, although compound (VIIIb) appeared homogeneous it may be a eutectic mixture of (±)-*cis*- and (±)-*trans*-stereoisomers. The position is complicated by the possibility of stereomutations; for this and other reasons, the ester composition may depend on the solvent (cf. first footnote p. 5715).

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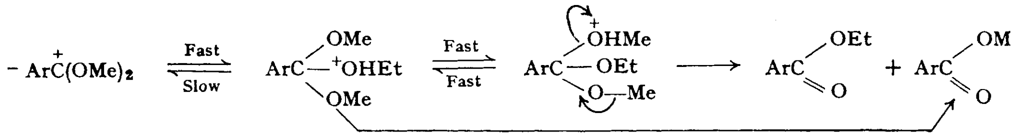
* Transition state A′ is one of four contributing forms, there being two possible modes of C–O bond fission for each of two optical isomers; the two modes of bond fission lead, however, to equivalent products, (±)-*threo*-(IX) if configuration is retained, and (±)-*erythro*-(IX) if inversion occurs; or *vice versa* for the (±)-*cis*-butylenedioxy-compound.

Route A will clearly be favoured by the presence of electron-donating substituents in the dioxy-system which will not only stabilize transition state A′ but will also reduce the tendency for C_1–C_α bond fission (transition state B′). Reduced ester formation from compound (VIIIa) is in accord with this and indicates the sensitivity of the system to quite small changes in electronic make-up, as expected if they have a dual co-operative effect. Steric effects of substituents on C_6 may be discerned in the difference between compounds (VIIIa) and (II).

In the case of the open ketals, the initial intermediate can either follow a pathway similar to B, giving tetrachlorobenzene from compound (V), but the alternative route leading to ester clearly cannot involve any large degree of intramolecular alkyl chloride elimination. Instead, an aryldialkoxymethyl cation develops and becomes sufficiently free from chloride anion to suffer attack of solvent (EtOH):



Although the required intermediate is at least as subject to steric effects as those involved in ester interchange, attack of hydroxylic solvent at a carbonium ion is, of course, much faster than at protonated oxygen.

The present results allow no firm conclusions regarding the detailed structure of B′, in particular whether or not fragmentation occurs by way of a carbene, or by a cyclic intramolecular sequence, but the failure to isolate other products apart from olefin and carbon dioxide suggests that the latter process is more likely.

EXPERIMENTAL

Infrared light absorptions were determined by using a Unicam SP 200 instrument for thin liquid films, Nujol mulls, or in the gas phase at 25—30 mm. pressure, in appropriate cases. M. p.s are not corrected. Ultraviolet light absorption measurements were made on a Unicam SP 800 recording instrument.

1,2,3,4-*Tetrachloro*-5,5-*ethylenedioxycyclopentadiene* (VIa).—Attempted preparation under the usual conditions[6] resulted in some discoloration, and the crude product dimerized on attempted distillation; the following procedure proved satisfactory.

Hexachlorocyclopentadiene (34·12 g., 0·125 mole) was suspended in freshly distilled ethylene glycol (50 ml.) with vigorous stirring, and a solution of potassium hydroxide (40 g., 0·715 mole) in ethylene glycol (100 ml.) was added dropwise whilst still warm (viscosity) to the mixture maintained at 15°; addition was complete in *ca.* 1 hr. and stirring was continued overnight. The pale yellow product was poured into water, and the precipitate filtered off and sucked dry to give crude ethylene ketal (28 g., 85%) which, recrystallized from petroleum (b. p. 60—80°), afforded 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene (20 g., 60%), m. p. 65—66° (lit.,[2] 65—67°) (Found: C, 31·8; H, 1·6. Calc. for $C_7H_4Cl_4O_2$: C, 32·1; H, 1·55%). The *dimer*, obtained by heating the ketal and recrystallized from ether, had m. p. 286—291° (decomp.) (Found: C, 32·1; H, 1·4; Cl, 54·3. $C_{14}H_8Cl_8O_4$ requires C, 32·1; H, 1·55; Cl, 54·2%); $\nu_{max.}$ 1606vs and 1641vs cm.$^{-1}$ (ClC=CCl, two types); the monomer showed only a single strong band in this region, 1600vs cm.$^{-1}$.

5,5-*Butylenedioxy*-1,2,3,4-*tetrachlorocyclopentadiene* (VIb).—The butylenedioxy-analogue of the ketal (VIa), prepared in a similar manner, was contaminated with side products including its dimer; preliminary experiments indicated that it could be purified by chromatography on silica gel, but the following variation was more satisfactory.

Hexachlorocyclopentadiene (150 g., 0·55 mole) was suspended in 60—70% (±)-butane-2,3-diol (200 ml.) and potassium hydroxide (80 g., 1·43 mole) in butanediol (400 ml.) was added dropwise during *ca.* 2 hr. to the vigorously stirred suspension kept at 0°. Stirring was continued at 0° for 6 hr. and the mixture stirred overnight whilst the temperature rose to 20°. The mixture was poured into water (3 l.), the aqueous layer discarded, and the organic product several times suspended in water to remove excess of diol. Finally the product was taken up in petroleum (b. p. 40—60°), the solution washed with saturated brine, dried (Na_2SO_4), filtered, and carefully evaporated at 40—45° *in vacuo* to give the required ketal (VIb), (137 g., 85%), which on storage at 0° crystallized; a portion washed with petroleum (b. p. 40—60°) gave pure 5,5-*butylenedioxy*-1,2,3,4-*tetrachlorocyclopentadiene*, m. p. 40—41·5° (Found: C, 37·7; H, 2·85. $C_9H_8Cl_4O_2$ requires C, 37·3; H, 2·75%), $\nu_{max.}$ 1600vs cm.$^{-1}$ (conjugated C=C). Thin-layer chromatography of the crude product showed it to be virtually pure and it was used for the experiments described below. The ketal gave a *dimer* on attempted distillation or heating (120°), or even on storing at 0° (slowly), and this when crystallized from petroleum (b. p. 60—80°) had m. p. 202° (Found: C, 36·9; H, 2·75. $C_{18}H_{16}Cl_8O_4$ requires C, 37·3; H, 2·8%); $\nu_{max.}$ 1606vs and 1643vs cm.$^{-1}$.

Reaction of the Ketals (VIa, VIb) *with Dibromoethylene*.—In a typical experiment the ketal (VIa) (8 g., 0·031 mole) was heated with a large excess of *cis*-dibromoethylene (30 ml.) (in order to preclude the formation of dimer), in sealed glass tubes at 100—105° for 14 hr. The product was cautiously distilled *in vacuo* and excess of dibromoethylene recovered; the crude dark product was crystallized from petroleum (b. p. 60—80°) (charcoal) to give cis-endo-2,3-*dibromo*-1,4,5,6-*tetrachloro*-7,7-*ethylenedioxynorborn*-5-*ene* (VIIa) (8·3 g., 61%), m. p. 169—170° (Found: C, 24·1; H, 1·45. $C_9H_6Br_2Cl_4O_2$ requires C, 24·1; H, 1·4%). Concentration of the mother liquors gave only the dimer of (VIa) (*ca.* 1·5 g.).

In an identical experiment the ketal (VIb) (4 g.) was heated with *cis*-dibromoethylene (15 ml.), and the product isolated as before to give cis-endo-2,3-*dibromo*-7,7-*butylenedioxy*-1,4,5,6-*tetrachloronorborn*-5-*ene* (VIIb) (5·2 g., 80%), m. p. 152—153° (Found: C, 27·7; H, 2·1. $C_{11}H_{10}Br_2Cl_4O_2$ requires C, 27·7; H, 2·1%). In this case, no dimer of the cyclopentadienone ketal appeared to have formed.

Debromination of the Adducts (VIIa, VIIb).—The adduct (VIIa) (6·71 g., 0·015 mole) was dissolved in hot acetic acid (100 ml.) and the solution cooled to 10°; zinc dust (2 g., 0·030 g.-atom) was added and the suspension magnetically stirred for 1 hr. and then poured into ice–water (500 ml.), and precooled ether (250 ml.) added. The aqueous layer was discarded and the ether layer washed several times with ice-water, and finally with ice-cold saturated sodium carbonate solution; after being dried (Na_2SO_4) the ethereal solution was evaporated *in vacuo* to give 1,2,3,4-*tetrachloro*-7,7-*ethylenedioxynorborna*-2,5-*diene* (VIIIa) (3·8 g., 88%), which had m. p. 43—45° after trituration with petroleum (b. p. 40—60°) (Found: C, 37·7; H, 2·2. $C_9H_6Cl_4O_2$ requires C, 37·5; H, 2·1%). The product (1·44 g., 0·005 mole) was treated with bromine (880 mg., 0·0055 mole) in carbon tetrachloride (15 ml.); the solution rapidly decolorized in daylight and evaporation of the solution and crystallization (from methanol) gave trans-2,3-*dibromo*-1,4,5,6-*tetrachloro*-7,7-*ethylenedioxynorborn*-5-*ene* (1·4 g.), m. p. 143—144° (Found: C, 24·3; H, 1·45. $C_9H_6Br_2Cl_4O_2$ requires C, 24·1; H, 1·4%).

From the adduct (VIIb) (2·38 g., 0·005 mole), on debromination 1,2,3,4-*tetrachloro*-7,7-*butylenedioxynorborna*-2,5-*diene* (VIIIb) (1·35 g., 85%) was obtained, m. p. 68—69° from petroleum (b. p. 60—80°) (Found: C, 41·9; H, 3·55. $C_{11}H_{10}Cl_4O_2$ requires C, 41·8; H, 3·2%).

Debromination of the Adduct (IV).—The adduct (IV), prepared as previously described[4] (18·0 g., 0·04 mole), was dissolved in warm acetic acid (100 ml.), the solution cooled to 0—5°, and zinc dust (5·2 g., 0·08 g. atom) added; the mixture was magnetically stirred for 30 min. only, with occasional warming to maintain fluidity. Finally, the mixture was worked up, essentially as described above, to give 1,2,3,4-*tetrachloro*-7,7-*dimethoxynorborna*-2,5-*diene* (V) (11 g., 95%), the liquid product eventually crystallizing; the crystals were washed with petroleum (b. p. 40—60°) and had m. p. 54—55° (Found: C, 37·3; H, 3·55. $C_9H_8Cl_4O_2$ requires C, 37·3; H, 2·8%). A part of the product (1 g.) was treated with bromine (600 mg., 10% excess), the solution decolorising only slowly in the dark, but evaporation and working-up as before gave 2,3-trans-*dibromo*-1,4,5,6-*tetrachloro*-7,7-*dimethoxynorborn*-5-*ene* (*ca.* 1 g.), m. p. 115—116·5° (Found: C, 23·8; H, 1·9. $C_9H_8Br_2Cl_4O_2$ requires C, 24·0; H, 1·8%).

Decomposition of Norbornadienone Ketals: Ethylene Ketal (VIIIa).—Pure ketal (VIIIa) (1·44 g., 0·005 mole) was heated at 115—120° in a slow current of nitrogen for 3 hr. and then finally at 130° for a brief period; carbon dioxide in the visibly evolved gases was absorbed in a "Carbsorb" tube (colour change brown to grey) and ethylene (infrared spectrum[8]) was collected in a liquid-nitrogen trap. Chromatography of the liquid residue on silica gel in petroleum cleanly separated the mixture into tetrachlorobenzene (720 mg., 0·0033 mole), m. p. and mixed m. p. 47—48° (infrared spectrum), and impure unchanged ketal (VIIIa) (450 mg.) which was eluted with chloroform and was contaminated with 2-*chloroethyl* 2,3,4-*trichlorobenzoate* (characteristic infrared bands at 1733, 1578, 1448, 1370, 1310, 1250, and 776 cm.$^{-1}$ absent in the pure ketal

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[8] R. H. Pierson, A. N. Fletcher, and E. St. Clair Ganz, *Analyt. Chem.*, 1956, **28**, 1228.

but all very strong in the authentic ester, prepared in the usual manner from 2,3,4-trichlorobenzoyl chloride and ethylene chlorohydrin in benzene–pyridine solution), b. p. ~ 140°/0·1 mm. (Found: C, 37·75; H, 2·3. $C_9H_6Cl_4O_2$ requires C, 37·5; H, 2·1%). Thin-layer-chromatographic comparison of the mixed product from compound (VIIIa) and the chloroethyl ester confirmed its presence. Spectrophotometric determination of the ester in the mixed fraction, using absorption at 245 mμ, showed that the total yield of ester was 23 mg. (8×10^{-5} mole).

Decomposition of the Ketal (VIIIb).—In a similar experiment the pure ketal (VIIIb) (1·58 g., 0·005 mole) was heated in a slow current of nitrogen at 103—105° for 3 hr. and finally at 110° for 30 min. The gaseous products were trapped as before and the olefin identified as *trans*-but-2-ene (infrared spectrum[9]). Chromatography of the liquid residue as before gave tetrachlorobenzene (805 mg., 0·0037 mole) and 2-*chloro*-1-*methylpropyl* 2,3,4-*trichlorobenzoate* (IX) (440 mg., 0·0014 mole). The ester fractions from a number of decompositions were combined and distilled; the product had b. p. 138°/0·05—0·1 mm., n_D^{25} 1·5476 (Found: C, 42·0; H, 3·65. $C_{11}H_{10}Cl_4O_2$ requires C, 41·8; H, 3·2%); $\nu_{max.}$ 1730vs cm.$^{-1}$ (CO_2R). In a similar experiment the liquid residue formed from ketal (1 g.) was hydrolysed in aqueous-ethanolic potassium hydroxide (10%; 15 ml.) under reflux overnight, the ethanol removed *in vacuo*, the cooled residue diluted with water, and tetrachlorobenzene filtered off. Acidification of the aqueous layer gave an acid (120 mg.) which when twice recrystallized from benzene–petroleum (b. p. 60—80°) gave 2,3,4-trichlorobenzoic acid, identified by m. p., mixed m. p., and infrared spectrum.[4]

Decomposition of Ketal (VIIIb) *in n-Butanol*.—The pure ketal (3·16 g., 0·01 mole) was decomposed in dry n-butanol (100 ml.) at 118° for 3 hr., the solvent removed *in vacuo*, and a portion of the residue (1 g.) chromatographed as before to give tetrachlorobenzene (428 mg.), m. p. 47°, and the ester (IX) (555 mg.), b. p. 138°/0·05—0·1 mm., n_D^{25} 1·5488—1·5509, infrared spectrum identical with that of the previous specimen, and different from that of n-butyl 2,3,4-trichlorobenzoate (Found: C, 42·0; H, 3·5. Calc. for $C_{11}H_{10}Cl_4O_2$: C, 41·8; H, 3·2%). In a similar experiment on a larger scale the final fractions of the distillate contained a small quantity of the hydroxy-ester (IXa) which must have been formed from compound (IX) during the working-up.

Preparation of Authentic Ester (IX).—2,3,4-Trichlorobenzoyl chloride, prepared in the usual manner from trichlorobenzoic acid (2·25 g., 0·01 mole), was dissolved in benzene (5 ml.), and the solution added to a mixture of 85% (±)-butanediol (900 mg., 0·01 mole) and pyridine (1·6 ml., *ca.* 0·02 mole); the reactants became warm and pyridine hydrochloride was immediately precipitated. The mixture was kept for 30 min. and then pure thionyl chloride (0·8 ml., 0·01 mole) was added, the mixture again becoming warm. Finally, further pyridine (3 ml.) was added and the solution was heated on a water-bath overnight, then cooled and diluted with benzene (25 ml.), and the dark mixture washed with water, dilute hydrochloric acid (2N), dilute sodium hydroxide, and then water, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residual oil distilled to give the (±)-*erythro*-ester (IX) (1·4 g., 44%), n_D^{25} 1·5510—1·5516, which was further purified by chromatography on silica gel and treatment with activated charcoal to remove sulphurous impurity, and again distilled, b. p. 136—137°/0·05—0·1 mm., n_D^{25} 1·5513; the infrared spectrum was exactly like that of the ester derived from ketal (VIIIb).*

Preparation and Decomposition of 7,7-*Butylenedioxy*-1,2,3,4-*tetrachloro*-5-*phenylnorborna*-2,5-*diene*.†—5,5-Butylenedioxy-1,2,3,4-tetrachlorocyclopentadiene (4·5 g.) was heated with a large excess of phenylacetylene (10 g.) in a sealed tube at 70° for 20 hr. Excess of phenylacetylene was stripped off *in vacuo* and the residual oil diluted with petroleum (b. p. 40—60°) and kept at 0—5° until crystals appeared; these were filtered off and recrystallized from petroleum (b. p. 40—60°) to give 7,7-*butylenedioxy*-1,2,3,4-*tetrachloro*-5-*phenylnorborna*-2,5-*diene* (X) (2·55 g., 42%), m. p. 138° (decomp.) (Found: C, 52·5; H, 3·85. $C_{17}H_{14}Cl_4O_2$ requires C, 52·1; H, 3·6%).

The adduct (1·96 g., 0·005 mole) was heated in a slow current of nitrogen at 140—150° for 1 hr. and the gaseous products trapped as before and identified as carbon dioxide and *trans*-but-2-ene. The residual oil was hydrolysed in ethanolic potassium hydroxide overnight, the ethanol removed *in vacuo*, and the residue diluted with water. The flocculent yellow solid was extracted with ether, the combined extracts were washed, dried, and evaporated in the usual

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* Decomposition of compound (VIIIb) in acetic acid gave a specimen of ester (IX), infrared spectrum identical, but consistently having a lower n_D^{25} on redistillation; it may have contained a considerable amount of the racemic *threo*-diastereoisomer.

† Experiment performed by B. Wood.

[9] R. B. Barnes, U. Liddel, and V. Z. Williams, *Analyt. Chem.*, 1943, **15**, 678.

way, and the residue was crystallized from methanol to give 2,3,4,5-tetrachlorobiphenyl, m. p. 88—89·5° (1·19 g., 0·004 mole before purification). The alkaline aqueous layer was warmed to expel ether and then acidified to give an acid (150 mg., 0·0005 mole), m. p. 200—207°, from methanol, tentatively identified as a mixture of 1-carboxy- and 5-carboxy-2,3,4-trichlorobiphenyl, by comparison of the infrared spectrum with that of a similar acidic product obtained from a similar reaction of the 5,5-dimethoxy-analogue of (VIb) with phenylacetylene, which gave a methyl ester, m. p. 104·5—105° (cf. ref. 2) (Found: C, 53·1; H, 2·9. Calc. for $C_{14}H_9Cl_3O_2$: C, 53·3; H, 2·85%). This methyl ester was hydrolysed to an acid, m. p. 218—219·5° (Found: C, 51·7; H, 2·2. Calc. for $C_{13}H_7Cl_3O_2$: C, 51·8; H, 2·3%). This same acid was also obtained by hydrolysis of the adduct formed from compound (VIb) with phenylacetylene, in hydrobromic acid–acetic acid.

Decomposition of the Methyl Ketal (V).—The pure ketal, freed from traces of acid immediately before use by washing an ethereal solution with aqueous ammonia, drying, and evaporation (1 g., 0·00345 mole), was decomposed at 85° in the usual manner and the gaseous products trapped as before. The olefin produced had prominent infrared bands at 718, 733, and 750vs cm.$^{-1}$ (C–H def.) and at 1143, 1170m (doublet) cm.$^{-1}$ (C–OR), besides absorption in the 3000 cm.$^{-1}$ region. Treatment of the condensed olefin with excess of bromine (300—500 mg.) in carbon tetrachloride (5 ml.) and warming to room temperature, followed by evaporation of the solvent *in vacuo*, gave a residual semisolid product (10 mg.), the infrared spectrum of which was almost identical with that of methyl oxalate.[2]

The liquid residue from the decomposition was chromatographed in the usual manner giving tetrachlorobenzene (286 mg., 0·0013 mole) and methyl 2,3,4-trichlorobenzoate (416 mg., 0·0017 mole), m. p. and mixed m. p. 66—67°.[4]

The ketal (V) was also decomposed in ethanol as follows. The ketal (2·0 g., 0·0069 mole) was heated under reflux in ethanol (20 ml.) over barium carbonate (500 mg.) for 18—20 hr., the hot solution filtered and evaporated *in vacuo*, and the residue chromatographed in the usual manner; the ester component (900 mg.) was twice distilled (b. p. 110°/0·05 mm.) (Found: C, 41·7; H, 2·5. Calc. for $C_8H_5Cl_3O_2$: C, 40·15; H, 2·1%. Calc. for $C_9H_7Cl_3O_2$: C, 42·6; H, 2·8%). Infrared-spectral comparison of the product with ethyl and methyl 2,3,4-trichlorobenzoate showed that it was a mixture, the ethyl ester predominating; this was confirmed by thin-layer chromatography using an alkaline permanganate spray. Under similar conditions, methyl 2,3,4-trichlorobenzoate (1 g.) was recovered quantitatively from ethanol (20 ml.) in the presence of barium carbonate (500 mg.), and even in the presence of 2% sulphuric acid, ester interchange was incomplete, the mixed product obtained fortuitously resembling the mixed product obtained above. Authentic ethyl ester was however obtained in the usual manner from 2,3,4-trichlorobenzoyl chloride and ethanol, in benzene–pyridine solution.

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