Thermal Decomposition of Substituted Norbornadienone Ketals

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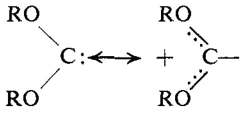
Abstract: The Diels–Alder reaction of tetrachlorocyclopentadienone ketals with acetylenic dienophiles yielded 1,2,3,4-tetrachloronorbornadienone ketals, some of which decomposed *in situ* and some were obtained in pure form. When pyrolyzed, these compounds gave two kinds of aromatic products: those which had lost the ketal bridge and those which had retained it in the form of an ester function. Both ionic and radical pathways for aromatization have been postulated; the influence of solvent polarity and of substituents on the choice between these mechanisms is discussed. Evidence is presented that the ketal bridge was lost in the form of a dioxycarbene, though ethylenedioxycarbene may have fragmented as it was generated. The products derived from dimethoxycarbene were highly dependent upon the reaction conditions. Whereas the dimer tetramethoxyethylene was formed in good yield in concentrated solution, trimethyl orthoformate was a major product in dilute solution and methyl acetate, carbon dioxide, and methyl radicals were generated in the vapor phase.

The present study[1] was undertaken with the goal of generating dioxycarbenes and elucidating their chemistry. These species were of considerable interest for the reason *inter alia* that their chemistry was difficult to predict. By virtue of the electron-donating capacity of oxygen, dioxycarbenes were expected to display properties intermediate between the electrophilic dihalo- and monoxycarbenes[3] on the one hand and the markedly nucleophilic aminocarbenes[4] on the other; the middle ground, however, obviously covers a broad range of reactivity. Indeed, there was no *a priori* basis for excluding the possibility that dioxycarbenes would rearrange or fragment in preference to undergoing familiar reactions of heteroatom-substituted carbenes.

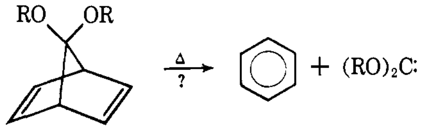


Early claims to the synthesis of dialkoxycarbenes were subsequently proven to be incorrect.[3,7] In 1960 Hine and his co-workers showed that such species were very likely intermediates in the complex transformations of haloforms into ortho esters by alkoxides,[8] but these systems would be particularly difficult ones from which to extract information about the properties of the divalent intermediates. During the present investigation, Corey's group reported that desulfurization of 1,2-thionocarbonates results in fragmentation into carbon dioxide and olefins[9]; this interesting reaction may involve a dioxycarbene intermediate, but there is as yet no clear proof.

The first experiments to provide direct evidence for the existence of dialkoxycarbenes involved thermal decomposition of a sulfonylhydrazone salt[10] and of a norbornadienone ketal.[2,11] This paper is a detailed account of the ketal work carried out in our laboratory.

Discussion

Norbornadienone ketals were attractive as potential carbene precursors on two grounds. First, the combination of aromatization with relief of strain in the bicyclic system was expected to provide a driving force of considerable magnitude, very likely sufficient to expel the methano bridge as a carbene at elevated temperatures. Loss of carbon monoxide, carbon dioxide, and a variety of olefins from appropriately bridged 1,4-dihydrobenzenes has long been known, and in fact Mc Bee[12] had reported loss of the elements of dimethoxycarbene from a hypothetical intermediate of this type prior to the present study (*vide infra*).[13] In addition, this approach promised the advantage



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[1] (a) This paper is based in large part on the Ph.D. Dissertation of E. P. Gosselink, University of Wisconsin, 1964. Portions of the work have appeared in the form of a communication.[2] (b) Inquiries should be sent to D. M. Lemal, whose present address is Department of Chemistry, Dartmouth College, Hanover, N. H.

[2] D. M. Lemal, E. P. Gosselink, and A. Ault, *Tetrahedron Letters*, 579 (1964).

[3] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

[4] Much of the evidence that aminocarbenes are nucleophilic has been based on the premise that tetraaminoethylenes dissociate into carbene fragments, an assumption which has recently been disproven.[5] Since the early work of Breslow,[6] however, there has been no doubt that these carbenes are good nucleophiles.

[5] H. E. Winberg, J. E. Carnahan, D. D. Coffman, and M. Brown, *J. Am. Chem. Soc.*, **87**, 2055 (1965); D. M. Lemal, R. A. Lovald, and K. I. Kawano, *ibid.*, **86**, 2518 (1964); N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3000 (1963).

[6] R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).

[7] On the other hand, diphenoxycarbene (or a carbenoid equivalent) may have been present as an intermediate in the reaction of diphenoxychloromethane with powerful bases to give tetraphenoxyethylene: H. Scheibler and M. Depner, *Ber.*, **68**, 2151 (1935); H. Scheibler, U. Faass, and Berty Hadji-Walassis, *J. prakt. Chem.*, **279**, 70 (1958); see also G. Wittig and W. Boll, *Ber.*, **95**, 2526 (1962).

[8] J. Hine, A. D. Ketley and K. Tanabe, *J. Am. Chem. Soc.*, **82**, 1398 (1960).

[9] E. J. Corey and R. A. E. Winter, *ibid.*, **85**, 2677 (1963); E. J. Corey, F. A. Carey, and R. A. E. Winter, *ibid.*, **87**, 934 (1965).

[10] R. J. Crawford and R. Raap, *Proc. Chem. Soc.*, 370 (1963).

[11] (a) R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 197 (1964); (b) *Tetrahedron* **21**, 891 (1965).

[12] E. T. Mc Bee, W. R. Diveley, and J. E. Burch, *J. Am. Chem. Soc.*, 77, 385 (1955); E. T. Mc Bee, J. D. Idol, and C. W. Roberts, *ibid.*, 77, 6674 (1955).

[13] Similar observations were later disclosed by Feichtinger and Linden[14] and it is noteworthy that the elements of difluorocarbene have been expelled from a bridged 1,4-dihydrobenzene.[15] Literature cited in ref. 11b covers all other known reactions of this type.

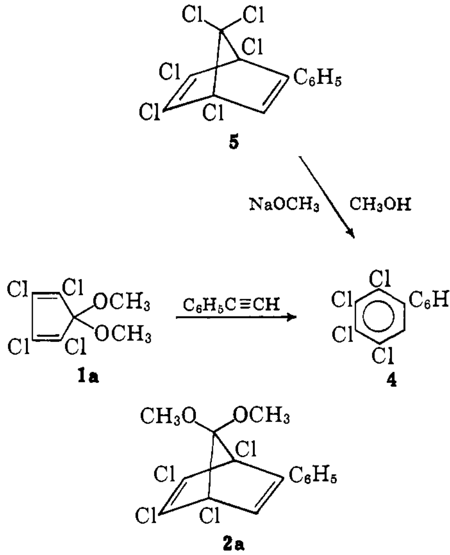
[14] H. Feichtinger and H. Linden, German Patent 1,105,862 (1961); *Chem. Abstr.*, 56, 12803 (1962).

[15] E. T. Mc Bee, D. K. Smith, and H. E. Ungnade, *J. Am. Chem. Soc.*, 77, 387 (1955).

that the carbene intermediate could be generated from a single substance in a medium of one's choice.

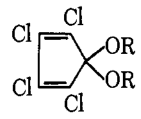
Direct ketalization as a route to the desired compounds was clearly precluded by the notorious instability of norbornadienones. Hence, the most obvious synthetic route required Diels-Alder addition of an acetylene to a cyclopentadienone ketal. Just as norbornadienones are unstable with respect to decarbonylation, however, most cyclopentadienones are unstable with respect to dimerization.[16] De Puy, Vogel, and their respective co-workers independently sought to circumvent this problem by ketalizing cyclopentenone and then introducing the second double bond. They were ultimately successful, but cyclopentadienone ethylene ketal was never isolated because it too dimerizes immediately.[17]

Earlier, Newcomber and Mc Bee[18] had demonstrated that tetrachlorocyclopentadienone dimethyl and diethyl ketals could be prepared by treating hexachlorocyclopentadiene with alcoholic solutions of the corresponding alkoxides. Since these substances were stable with respect to dimerization and were susceptible to Diels-Alder addition, they appeared to be eminently well suited for the present study. Moreover, in attempts to prepare adduct **2a** from phenylacetylene and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**1a**) and also from **5** and sodium methoxide, Mc Bee had isolated only **4**, albeit in poor yields.[12] The products of bridge loss had not been investigated, but these observations provided initial encouragement for the carbene-extrusion hypothesis.



Tetrachlorocyclopentadienone Ketals. The published procedures for preparing the dimethyl and diethyl ketals (**1a,f**) were found not to be very general: modifications were used in obtaining the several other ketals shown in Table I. Newcomber and Mc Bee had attempted preparation of the ethylene ketal with sodium ethylene glycolate in ethylene glycol, but had isolated only a dimer which they formulated with a ten-membered ring. When the experiment was repeated it was found that rapid vacuum distillation of the reaction mixture afforded the desired monomeric ketal,[2,19] which dimerized readily to the substance described earlier. Thus the latter is actually a Diels-Alder adduct as Scherer[20] and Chang[19] have also concluded.

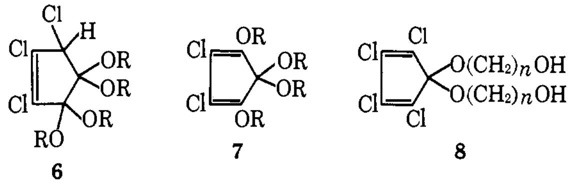
Table I. N.m.r. Spectra of the Tetrachlorocyclopentadienone Ketals[a]



Ketal	R	δ_{CCl_4}, p.p.m.	Multiplicity, J (c.p.s.)	Assignment
1a	CH_3	3.34	1	
b	CH_2CH_2	4.27	1	
c	$CH_2C_6H_5$	4.63	1	Methylene
		7.24	1	Aryl
d	$CH_2C(CH_3)_2CH_2$	1.06	1	Methyl
		3.98	1	Methylene
e	C_6H_5	7.17	1[b]	
f	CH_2CH_3	1.25	3 (7)	Methyl
		3.62	4 (7)	Methylene
g	$CH_2CH_2CH_2$	1.97	5 (6)	Central Methylene
		4.36	3 (6)	Terminal Methylene

[a] All spectra were measured at 60 Mc./sec. using tetramethylsilane or hexamethyldisiloxane (δ = 0.06 p.p.m. in CCl_4) as internal standard. Where more than one signal was present, relative areas were in agreement with the assignments. [b] Splitting was visible at the base of the signal.

It was discovered during the preparation of the dibenzyl ketal (**1c**) that presence of an excess of either alcohol or base led to products containing four benzyloxy groups instead of two. Both of these products were somewhat unstable at room temperature, but their n.m.r. and ultraviolet spectra (see the Experimental Section) allowed assignment of structures. Compound **6a** arose in the presence of excess alcohol and **7a** in the presence of excess base; Mc Bee had encountered analogous substances (**6b**, **7b**) in his study of the dimethyl ketal **1a**.[21] Optimum yields of the tetrachloroketal **1c** were obtained using stoichiometric quantities of sodium benzyloxide and diene in ether.



a, R = $CH_2C_6H_5$
b, R = CH_3

The six-membered ring ketals (**1d,g**) were by far the most difficult to prepare, and yields were the poorest. This was apparently attributable to dimerization

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(16) C. F. H. Allen, *Chem. Rev.*, 62, 653 (1962).

(17) C. H. De Puy, B. W. Ponder, and J. D. Fitzpatrick, *Angew. Chem.*, 74, 489 (1962); *J. Org. Chem.*, 29, 3508 (1964); E. Vogel and E.-G. Wyes, *Angew. Chem.*, 74, 489 (1962). Very recently the synthesis of several unsubstituted cyclopentadienone ketals and their interception by dienophiles has been reported by P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, 87, 2769 (1965).

(18) J. S. Newcomber and E. T. Mc Bee, *ibid.*, 71, 946 (1949).

(19) W.-H. Chang, *Chem. Ind.* (London), 709, 1491 (1964).

(20) K. V. Scherer, Jr., Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p. 23N.

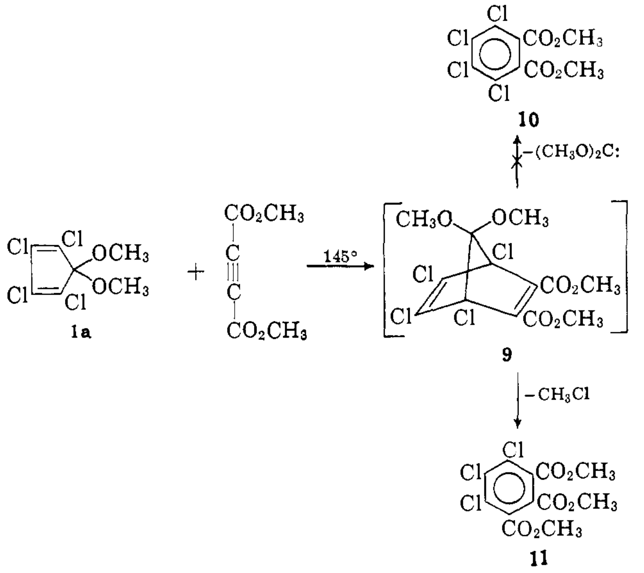
(21) E. T. Mc Bee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *J. Am. Chem. Soc.*, 84, 3557 (1962).

and/or polymerization reactions which were especially important in concentrated solution. Best results were obtained when a tetrahydrofuran solution of equimolar quantities of diol and diene was added very slowly to a dilute suspension of sodium hydride in the same solvent. In Chang's recent investigation[19] of the base-catalyzed reactions of 1,3- and 1,4-diols with hexachlorocyclopentadiene in the diols as solvent, he has isolated fair yields of the diolketals **8** but none of the corresponding cyclic ketals.

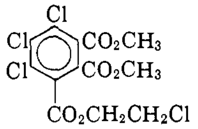
When hexachlorocyclopentadiene was employed in excess in the reaction with phenoxide, a monophenoxy derivative was isolated, a result which has no counterpart in the methoxy series.[21] The desired diphenyl ketal (**1e**) was also produced under these conditions, but the yield was better when the calculated amount of diene was used.

The structures of the new crystalline ketals (**1b–e**) were assigned of the basis of microanalyses and n.m.r. spectra (Table I); they were later confirmed in studies of the decomposition of their Diels–Alder adducts. Ketal **1g** was prepared only in very small amount and identified solely on the basis of its n.m.r. spectrum.

Norbornadiene Ketals. Because of its effectiveness as a dienophile, dimethyl acetylenedicarboxylate was initially chosen for the preparation of adducts with the cyclopentadienone ketals. The reaction of **1a** with an excess of the acetylenic ester at 145° yielded very little or none, as determined by vapor phase chromatography, of the desired dimethyl 2,3,4,5-tetrachlorophthalate (**10**), but instead gave trimethyl 4,5,6-trichlorohemimellitate (**11**, 59%).[22] N.m.r. in CCl_4 showed singlets at $\delta = 3.76$ (center methoxyl) and 3.80 p.p.m., relative areas 1:2. This result suggested that a corresponding quantity of methyl chloride had been generated, which was subsequently verified by vapor phase chromatographic and mass spectrometric analysis of the gas evolved in the reaction (methyl chloride yield, 64%). When the reaction was carried out in the 300° injection chamber of a vapor chromatograph, a peak corresponding in retention time to the phthalate ester (**10**) was observed in addition to the hemimellitate (**11**) peak (relative areas 1:4). Probably attributable just to the much higher reaction temperature, this change in product composition finds a counterpart in the behavior of ketal **2a**.



In hopes of isolating the intermediate adduct, the more reactive diene **1b** was allowed to stand at room temperature with dimethyl acetylenedicarboxylate. The Diels–Alder reaction proceeded under these mild conditions, *but so did decomposition of the adduct.* Bridge-opened ester **12** was obtained in 88% yield. Saponification of **12** followed by re-esterification with diazomethane produced trimethyl trichlorohemimellitate, identical with the sample obtained from **1a**. An ionic decomposition pathway, depicted below for adduct **9**, provides an attractive explanation for the bridge-opening reaction.[23,24]



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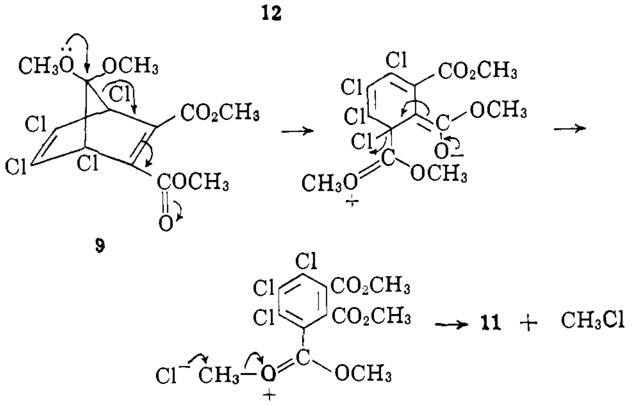

In light of this hypothesis and Mc Bee's observation of bridge loss in the reaction of ketal **1a** with phenylacetylene, this acetylene, a much weaker electron acceptor than the diester, was chosen as dienophile. Under carefully controlled conditions it was possible to isolate and purify the crystalline adducts **2a–2d** (Table II).[25] For a vapor phase pyrolysis study it was necessary to prepare ketals of lower molecular weight. Preliminary attempts to dechlorinate **2a** gave mixtures from which none of the desired ketal was obtained free of impurities. Similarly, efforts to bisdecarboxylate 1,4,5,6-tetrachloro-7,7-dimethoxy-5-norbornene-2,3-dicarboxylic acid with lead tetraacetate met with failure. An acceptable solution to the problem was found in the prolonged reaction of the poor dienophile propyne with **1a** and **b**, which gave the adducts **3a** and **b**, respectively, though in low yield (Table II).[26] The structures of all of the norbornadienone ketals in Table II were established on the basis of microanalytical and spectral data, particularly n.m.r. spectra.[28]

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(22) J. Diekmann, *J. Org. Chem.*, **28**, 2880 (1963), independently discovered this reaction.

(23) The Diels–Alder ring cleavage reaction was repeated in the presence of lithium carbonate to assure that ring opening was not attributable to acid catalysis. Again 12 was obtained.

(24) The ketal cleavage reactions observed by K. Mackenzie, *J. Chem. Soc.*, 457 (1962), and by P. Kniel, *Helv. Chim. Acta*, **46**, 492 (1963), are closely related to those yielding 11 and 12.

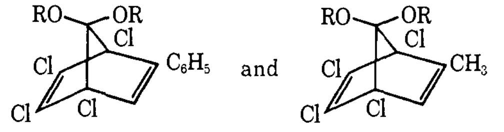
(25) Efforts to prepare pure adducts from 1e and 1f were frustrated. In both cases, though 2,3,4,5-tetrachlorobiphenyl (4) was identified in the reaction products, thus indicating that adduct formation had occurred followed by bridge loss.

(26) It is now possible to prepare the parent compounds, norbornadienone dimethyl ketal, and ethylene ketal *via* quadricyclanone.[27]

(27) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965).

(28) Fairly concentrated sulfuric acid transformed 2a into the tetra-

Table II. N.m.r. Spectra of the Norbornadienone Ketals[a]



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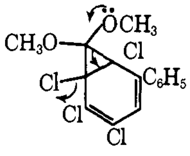
Ketal	R	δ_{CCl_4}, p.p.m.	Multiplicity, J (c.p.s.)	Assignment
2a	CH_3	3.47, 3.51	1	Methyl
		6.35	1	Vinyl
		7.23	1	Aryl
b	CH_2CH_2	4.18	1	Methylene
		6.43	1	Vinyl
		7.28	1	Aryl
c	$CH_2C_6H_5$	4.97, 4.88	1	Methylene
		6.43	1	Vinyl
		7.20	m	Aryl
d	$CH_2C(CH_3)_2CH_2$	1.01	1	Methyl
		3.88	1[b]	Methylene
		6.36	1	Vinyl
		7.27	1	Aryl
3a	CH_3	1.88	2 (2)	C-Methyl
		3.48, 3.49	1	O-Methyl
		6.04	4 (2)	Vinyl
b	CH_2CH_2	1.88	2 (2)	Methyl
		4.10	1	Methylene
		6.06	4 (2)	Vinyl

[a] Spectra were measured at 60 Mc./sec. using tetramethylsilane or hexamethyldisiloxane (δ = 0.06 p.p.m. in CCl_4) as internal standard. Relative peak areas were consistent with the structural assignments in every case. [b] Shows hints of splitting.

Confirmation of the assignment in every case was provided by the products obtained in the pyrolysis experiments to be described.

Results of the Pyrolyses. Ketal **2a**.[29] Decomposition of this substance occurred rapidly with little darkening at temperatures as low as 100–150°, depending upon the choice of solvent. Tetrachlorobiphenyl (**4**) (corresponding to loss of the elements of dimethoxycarbene) and a pair of isomeric esters (corresponding to loss of methyl chloride) were formed. Analysis by vapor phase chromatography of the products from decomposition in a variety of solvents revealed only one other nonvolatile component (an unidentified methyl ester, ~2% or less), and peak area comparisons with pure samples confirmed that these compounds accounted for essentially all of the starting material (when bridge and methyl chloride loss were taken into account).

Saponification followed by hydrogenolysis transformed the major ester into *m*-phenylbenzoic acid (Chart I). This acid had the reported ultraviolet spectrum and melting point,[30] it was shown by direct comparison to differ from *o*-phenylbenzoic acid,[31] and its n.m.r. spectrum confirmed the *meta* orientation (see the Experimental Section). Because of the possibility of rearrangement in the ketal decomposition, it was important to establish the pattern of chlorine substitution in the ester. Allylic rearrangement of the methano bridge of **2a** could give as many as four different norcaradienone ketals, **14–17** (or tropone ketals), the first three of which could decompose with loss of methyl chloride to *m*-phenylbenzoate esters by a well-recognized reaction of cyclopropanes.[32] The meta ester (**18**) from **15** and **16** would be the same as that obtained in the absence of allylic rearrangement, but **14** could yield the isomeric ester **19**. That **18** was the correct structure was demonstrated by saponification of the unknown ester followed by decarboxylation in boiling quinoline. The resulting trichlorobiphenyl (**20**) differed in melting point, vapor phase chromatographic retention time, and n.m.r. spectrum from an authentic sample of 2,4,5-trichlorobiphenyl prepared by the Gomberg reaction from 2,4,5-trichloroaniline; in fact the n.m.r. spectrum (CCl_4) indicated the presence of *adjacent* hydrogens on the substituted ring (singlet at δ = 7.34 p.p.m. for five protons, partially obscuring a two-proton AB quartet (J = 9 c.p.s.) with doublets centered at 7.13 and 7.37).



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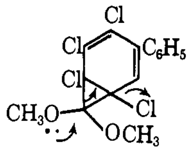

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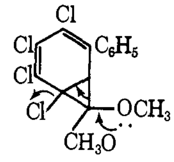

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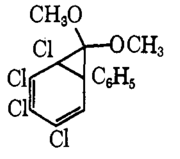

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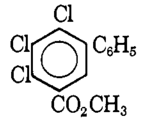

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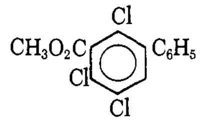

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The isomer of ester **18** formed in the decomposition of **2a** was invariably a minor product. Treatment with concentrated sulfuric acid transformed this compound into a high-melting, yellow trichlorofluorenone (**22**), thus indicating an *ortho* relationship between the phenyl and carbomethoxyl functions (Chart I). Structure **21** is the only reasonable possibility for the ester even if intermediates of the type **14–17** are taken into account.

The predominance of meta over ortho ester is contrary to arguments based on resonance stabilization of the ring cleavage transition state by the phenyl sub-

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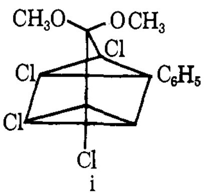
chlorobiphenyl 4 almost instantaneously. This hydrolysis–decarbonylation reaction provides a convenient check on the structure of a norbornadienone ketal.

(29) An attempt to photolyze 2a led only to rapid ring closure to the quadricyclic tautomer i, which reverted rather quickly even at room temperature to the original diene. The reversion was *not* a simple first-order process, and its rate was unaffected by the presence of triethylamine (*cf.* ref. 27).



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(30) E. T. Mc Bee, C. W. Roberts, and C. G. Hsu, *J. Am. Chem. Soc.*, **78**, 3394 (1956).

(31) C. Graebe and A. S. Rateanu, *Ann.*, **284**, 319 (1895).

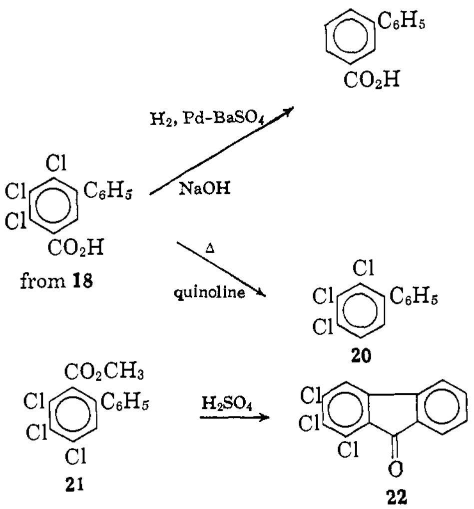
(32) See, for example, S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959).

Table III.[a] Aromatization of Ketal **2a**. Rates and Product Distributions

Solvent	Temp., °C.	10^5k, sec.$^{-1}$	Biphenyl, wt. %	Meta ester, wt. %	Ortho ester, wt. %	Biphenyl/ester, wt./wt.
Cyclohexane	115	3.5	91.8	6.5	0.8	12.6
Cyclohexane	145	91	92.9	7.1	Trace	13.1
Acetonitrile	115	121	12.5	67.4	20.1	0.143
Acetonitrile	80	4.6	6.9	73.2	19.2	0.075
Methanol	115	50	23.2	58.4	16.2	0.311
Methanol	80		17.4	63.8	17.2	0.215
Glyme	115		34.7	50.0	14.0	0.543

[a] The difference between the total percentage and 100 for a given run is accounted for by the area of the unidentified vapor phase chromatographic peak.

Chart I. Structure Proof for Esters from Ketal **2a**

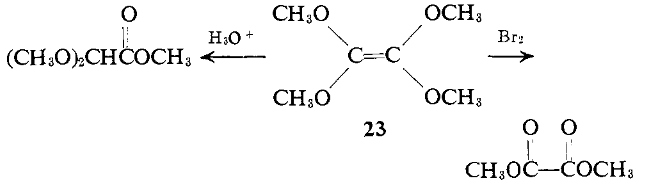


stituent. Models of **2a** and the low extinction coefficients of its ultraviolet maxima (see the Experimental Section) indicate, however, that the phenyl is twisted out of coplanarity with the conjugated double bond. As a result one of the orthohydrogens may interact sterically with the ketal bridge, thus favoring cleavage of the skeletal bond closer to the phenyl.

A kinetic study of the decomposition of **2a** was carried out using 2% solutions in cyclohexane, methanol, and acetonitrile. The disappearance of the vinyl hydrogen was followed by n.m.r. spectroscopy using aliquots which had been concentrated and then injected with mesitylene as an internal area standard. First-order kinetics were observed in all three solvents, and the reaction rates were found to vary considerably with the solvent, as indicated in Table III. The apparent activation parameters proved to be more sensitive to solvent than rate comparison at a single temperature would suggest, since the change in ΔH^* was in opposition to that in ΔS^*. In cyclohexane, $\Delta H^* = 34.2$ kcal. and $\Delta S^* = +8.7$ e.u.; in acetonitrile, $\Delta H^* = 24.7$ kcal. and $\Delta S^* = -8.8$ e.u. The uncertainties in these numbers are rather large, but the minimum values of $\Delta\Delta H^*$ and $\Delta\Delta S^*$ for the change cyclohexane → acetonitrile are estimated to be -7.4 kcal. and -11.8 e.u., respectively.

Table III reveals that the distribution of aromatic products, determined by vapor phase chromatography, varied dramatically with solvent. *The switch from cyclohexane to acetonitrile at 115°, for example, resulted in an 88-fold decrease in the biphenyl/ester ratio, and this factor was approximately doubled when the latter solvent was used at 80°.* The aromatic product ratios were determined in another series of solvents as well. When rather concentrated solutions were decomposed by immersion in a 150° bath, the biphenyl/ester ratio was found to diminish in the order decalin > di-*n*-butyl phthalate ~ triglyme > benzonitrile > dimethyl sulfoxide-formamide. All values lay between the extremes shown in Table III for cyclohexane and acetonitrile, but the (inverse) correlation with solvent polarity was unmistakable.

Turning attention to the question of greatest interest, namely the fate of the ketal bridge of **2a**, the product composition here also was a sensitive function of the reaction conditions. Pyrolyzed as a melt or in concentrated solution (*e.g.*, in di-*n*-butyl phthalate) at 150°, **2a** yielded in addition to the biphenyl **4**, the esters **18** and **21** and methyl chloride, a mobile liquid which distilled *in vacuo* at room temperature. Vapor phase chromatographic analysis revealed that the liquid consisted principally of a substance which displayed a single sharp signal in the n.m.r. spectrum at $\delta = 3.50$ p.p.m. (CCl_4). Gentle hydrolysis of this compound with dilute acid gave methyl dimethoxyacetate and its violent reaction with bromine yielded dimethyl oxalate. Combined with microanalytical data, these results identified the liquid as tetramethoxyethylene (**23**).[33,34]



When a solution of **2a** was pyrolyzed by dropwise addition to a large volume of rapidly stirred solvent (*e.g.*, decalin), no compounds in the volatility range of tetramethoxyethylene were obtained. Trimethyl orthoformate (~50% based on the yield of biphenyl **4**) was the major product traceable to the ketal bridge. No dimethyl ether was detectable, very little or no carbon monoxide was present, and methane was found in trace amounts only.

If an open vessel containing pure **2a** is immersed in a 150° oil bath, the decomposition is invariably violent, and frequently a flame is visible. Not surprisingly, the product composition is much more complex in the

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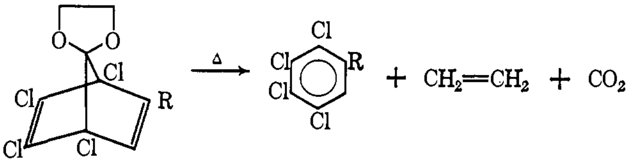
(33) Yield was 70% based on yield of biphenyl 4 when the decomposition was run in di-*n*-butyl phthalate.

(34) In the neat pyrolyses lesser amounts of a compound with longer vapor chromatographic retention time than tetramethoxyethylene were detected. Though not identified, this substance is presumably the pentamethoxyethane found by Hoffmann and Hauser.[11]

presence of air than under an inert atmosphere. Dimethyl oxalate (>80% based on **4**) and methyl dimethoxyacetate are the major compounds derived from the methano bridge. Methane, ethane, both oxides of carbon, and small amounts of methyl formate, methanol, dimethyl carbonate, and trimethyl orthoformate are invariably present along with several other unidentified (mostly trace) components.

Attempts to intercept dimethoxycarbene with a variety of olefins ranging from nucleophilic to electrophilic in character were uniformly unpromising. When air was bubbled through a hot di-*n*-butyl phthalate solution of **2a**, dimethyl carbonate was formed in ~17% yield (based on diphenyl **4**); whether or not the carbonate is derived from dimethoxycarbene, however, is uncertain.

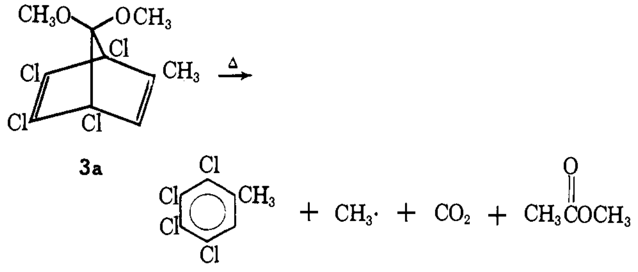
Other Ketals. Studied in the melt and in nonpolar solvents, pyrolysis of the cyclic ketal **2b** was a remarkably clean process. The yield of tetrachlorobiphenyl (**4**) was almost quantitative, and 95% of the ketal bridge was accounted for by the equimolar quantities of ethylene and carbon dioxide released. The kinetics of the reaction were studied in a preliminary fashion by gasometry in chlorobenzene solution and more carefully by the n.m.r. technique previously described in cyclohexane. Both methods revealed first-order kinetics, and it is noteworthy that the decomposition of **2b** was nearly eight times slower ($k = 4.5 \times 10^{-6}$ sec.$^{-1}$) than that of **2a** in cyclohexane at 115°. A qualitatively similar rate relationship has been observed by Mackenzie[35] for the pair of ketals corresponding to **2a** and **2b** but lacking the phenyl substituent. Though the cyclic compound yielded a small amount of ester, the chlorohydrocarbon/ester ratio was again much higher for this ketal than for its acyclic counterpart in neat decompositions.



2b, R = C_6H_5
3b, R = CH_3

4, R = C_6H_5
24, R = CH_3

Heated in decalin solution, **3a** gave high yields and **3b** gave essentially quantitative yields of 2,3,4,5-tetrachlorotoluene (**24**). As noted earlier, the main reason for preparing the lower molecular weight ketals was in order to study their decomposition in the gas phase. Dr. F. P. Lossing kindly examined the products obtained by pyrolysis of **3a** and **3b** at very low pressures in a capillary furnace mounted at the inlet of a mass spectrometer. Temperatures of ~350° were required since the residence times were on the order of 1 msec. In addition to tetrachlorotoluene, methyl radicals, methyl acetate,[36] and carbon dioxide were formed from **3a**, carbon dioxide, and ethylene from **3b**. It was not possible to detect either dimethoxycarbene or ethylenedioxycarbene in these experiments.[37]



3a

24

The dibenzyl ketal **2c** was investigated only in preliminary fashion. High-temperature vapor phase chromatographic analysis of nonvolatile products from pyrolysis of **2c** *in vacuo* revealed the biphenyl **4** and a pair of compounds of longer retention time, presumably the benzyl esters analogous to **18** and **21**. Peak area comparisons indicated that bridge loss was favored over retention by roughly 3:1, in good agreement with the 25% yield of benzyl chloride obtained from the vacuum-distillable fraction of the product.[38] Small amounts of toluene, benzyl formate, and two unidentified compounds with boiling points estimated at about 250° were present, but no benzyl alcohol was detected. Tetrabenzyloxyethylene would probably not have survived the vapor phase chromatographic analysis, so it may well have been present though not found.

A single pyrolysis experiment on ketal **2d** revealed that biphenyl **4** is generated, but the fate of the cylic bridge is not yet known.

Interpretation of the Pyrolyses. Ketal **2a**. Consider first pathways for formation of the aromatic decomposition products. Fission of one of the skeletal bonds to C-7 might occur either homolytically (path A) or heterolytically, as suggested earlier for the (unisolated) acetylenedicarboxylic ester adducts (path B). Either intermediate could, in principle, lead both to loss (or migration) of chloride, *i.e.*, to ester, and to loss of the bridge as a carbene. Another possibility for bridge loss must be considered: concerted cleavage of both skeletal bond to the ketal carbon (path C). These three choices are illustrated in Chart II.

It is possible to envisage a bimolecular process for loss of the ketal bridge which is consistent with the observed first-order kinetics, *viz.* head-to-head coupling of **25** followed by loss of tetramethoxyethylene. On the other hand, there can be little doubt that the ester formation which competes with bridge loss is unimolecular. Migration of chlorine in **25** (or loss of chloride to give an ion pair directly) would be a very facile process since chlorine migration occurs even in simple free radicals[39] which lack the migrational driving force of a biradical, not to mention the driving force of aroma-

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(35) K. Mackenzie, *J. Chem. Soc.*, 5710 (1964).

(36) The *m/e* 74 peak corresponded to methyl acetate and not to the isomeric dimethoxycarbene because its intensity was independent of decomposition temperature in the range 450–800° even when measurements were made using low-energy electrons. The carbene would surely have fragmented or rearranged to methyl acetate at the higher temperatures, and even the latter process would have altered the parent peak intensity due to the difference in ionization potential of the two species.

(37) Feichtinger and Linden[14] have stated that the reaction of **1a** with $CH_3O_2CCH_2C{\equiv}CCHROCOCH_3$ (R = H, CH_3) yields the appropriate benzene derivatives, dimethyl ether and carbon monoxide. Dimethyl ether has not been detected in any of our pyrolysis studies of ketals very closely related to their (intermediate) adducts, and carbon monoxide is ordinarily a very minor product if present at all (except in the open-air pyrolysis of **2a**, which results in combustion!).

(38) A direct comparison of **2c** and **2a** was made by pyrolyzing di-*n*-butyl phthalate solutions of each in a ~160° bath. Vapor chromatographic analysis indicated that the bridge loss/retention ratio was the same for both or slightly higher for **2c**.

(39) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2849 (1963).

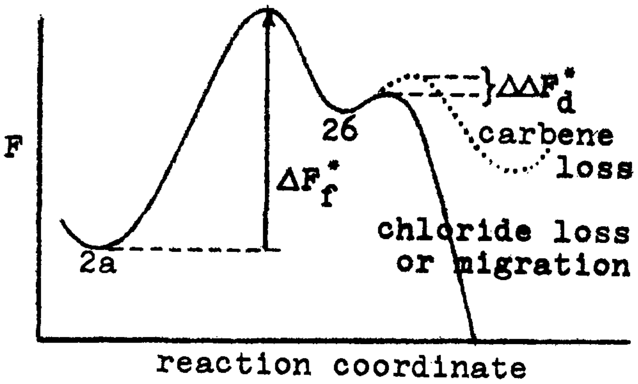
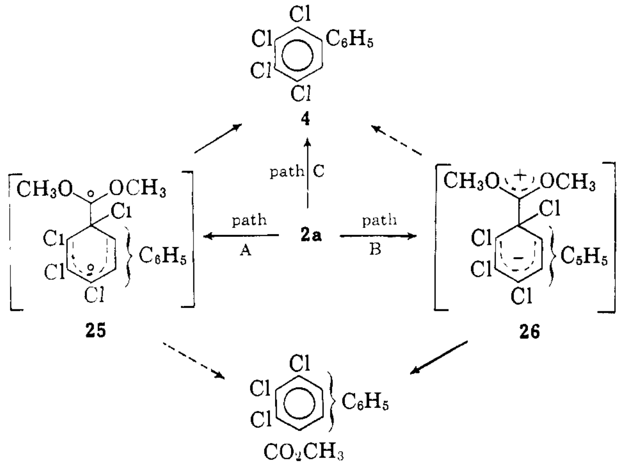


Figure 1. Schematic representation of path B for the decomposition of **2a** in acetonitrile. Subscripts f and d refer to formation and decomposition, respectively, of zwitterion **26**.

tization. Similar considerations apply if **26** is the ester progenitor. Hence the competition between biphenyl and ester formation as a function of concentration ought to provide information about the molecularity of bridge loss. When such experiments were carried out in cyclohexane the bridge loss/retention ratio was actually found to be higher in very dilute than in concentrated solution, so *bimolecular processes for bridge loss can be disregarded.*

Chart II. Possible Aromatization Mechanisms for Ketal **2a**



With regard to the feasibility of path A, Hoffmann and Häuser[11] have observed that styrene is polymerized by decomposing **2a** to a somewhat greater extent than anticipated on a purely thermal basis, but that cumene is not dimerized appreciably. Since biradical **25** need enjoy no more than fleeting existence *en route* to nonradical products, the failure of cumene to react does not provide a basis for eliminating **25** from consideration. Nevertheless, the rate data obtained on the decomposition of **2a** as a function of solvent show rather clearly that path A cannot be the *only* reaction mechanism. The rate ratios at 115° ($k_{\text{acetonitrile}}/k_{\text{cyclohexane}} = 35$ and $k_{\text{methanol}}/k_{\text{cyclohexane}} = 14$ are too high for a homopolar process, and the activation parameters for the former pair of solvents are even more divergent than the ratio 35 would suggest, as noted earlier. Leffler and Cook and their respective co-workers have shown that the activation parameters characterizing even homolytic cleavage reactions may be quite sensitive to solvent polarity, but for their systems *the changes in* ΔH^* *and* ΔS^* *with solvent were in the direction opposite to those observed in the present work.*[40]

The interpretation of solvent effects on ionic processes in nonhydroxylic media is a hazardous undertaking, as Wiberg has graphically emphasized.[41] Thus the question whether path B is the *sole* mechanism cannot be answered with complete confidence on the basis of presently available data. If it were the only pathway, the observed rate accelerations accompanying the dramatic polarity changes cyclohexane → methanol and cyclohexane → acetonitrile would apparently be among the smallest ever measured for reactions in which neutral starting material(s) gives charged product(s) in the rate-determining step. Nonetheless, a variety of processes fitting this description is known to show quite unimpressive rate enhancements with increasing solvent polarity.[42]

It will be useful to construct a crude representation of the probable energy profile for path B. As mentioned above, the barrier for chloride migration in (or loss from) **26** should be quite low, and that for bridge loss cannot differ from it greatly if it is assumed (for the moment) that path B is responsible for both biphenyl and ester formation. In fact the transition states for decomposition of **26** are probably lower in energy than that for its formation, because very substantial strain relief and enhanced charge delocalization stabilize the zwitterion relative to the initial transition state. Were this not the case, the original cleavage would of course be reversible and products derived from norcaradienes (allylic rearrangement) should have been found.[43] These energy relationships are depicted schematically in Figure 1. Recalling that the biphenyl/ester ratio is a more sensitive function of solvent (× 0.025 for cyclohexane → methanol, × 0.011 for cyclohexane → acetonitrile at 115°) than is the over-all reaction rate, one who places his faith solely in path B must conclude that the switch from cyclohexane to methanol or acetonitrile changes $\Delta\Delta F_d^*$ more than ΔF_f^*. Other things being equal, the influence of solvent should be much greater on the slow than on the rapid step (a manifestation of the Hammond postulate); special factors which would reverse this relationship in the present instance are not obvious.

The above dilemma can be circumvented by postulating that paths A and B both occur, the former leading predominantly or exclusively to biphenyl and the latter primarily to ester. According to this view path A is the major process in cyclohexane and path B in acetonitrile.[44] A substantial positive value for ΔS^* is to be

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(40) M. G. Alder and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 1425 (1954); C. D. Cook and B. E. Norcross, *ibid.*, **81**, 1176 (1959).

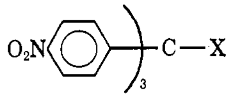
(41) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp. 379-388.

(42) R. E. Pincock, *J. Am. Chem. Soc.*, **87**, 1274 (1965), and references contained therein.

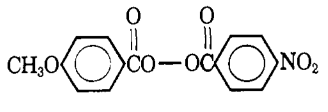
(43) Even if the norcaradienes (**14-17**) or cycloheptatrienes decomposed to the types of products observed, which is by no means obvious, esters isomeric with **18** and **21** would be expected. Though very small amounts of an unidentified methyl ester, noted earlier, accompanied the biphenyl and the known esters in the pyrolysate from **2a**, no other substances were detected or were required to account for all of the "nonvolatile portion" of the starting material. The importance of allylic bridge rearrangement is thus very doubtful, and n.m.r. spectra of partially decomposed solutions of **2a** failed to reveal the presence of norcaradienes or cycloheptatrienes. The reservation is necessary that if they decomposed rapidly and almost exclusively by loss of the original bridge, they could be major intermediates without our knowledge.

(44) It is interesting to note that the faster rate in acetonitrile than in methanol, though in line with their dielectric constants, is in opposition

expected for the former pathway, in which a rigid molecule is transformed into a biradical with additional degrees of freedom. Should the same bond be broken heterolytically, however, there should be a large additional contribution *of opposite sign* to ΔS^* attributable to orientation of solvent in the transition state. These considerations fit well the observed change in sign of ΔS^* from cyclohexane to acetonitrile.[46] When the over-all reaction rates are dissected into rates for the individual products, it is seen that the switch from cyclohexane to acetonitrile accelerates biphenyl formation only about fourfold at 115°, but ester formation about 400-fold. This fact also is nicely accommodated by the dual-mechanism hypothesis. Unimolecular cleavage of the same carbon–carbon bond both homolytically and heterolytically is not a familiar phenomenon, though several examples involving heteroatoms are known. The change with increasing solvent polarity from radical to ionic scission of the C–Br bond of tris(*p*-nitrophenyl)methyl bromide (**27a**),[47] the C–O bond of the corresponding nitrate (**27b**),[48] and the O–O bond of *p*-methoxybenzoyl *p*-nitrobenzoyl peroxide (**28**)[49] are cases in point.



27a, X=Br
b, X=ONO_2



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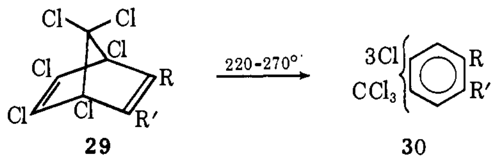
One might argue that a route to biphenyl other than path A, *viz.* the concerted fragmentation labeled path C, exists in competition with the ionic process path B. The extreme lability of norbornadienones is certainly suggestive of concerted carbon monoxide loss because biradical or zwitterionic intermediates generated during a hypothetical stepwise cleavage ought to be accessible only *via* a substantial activation energy barrier. The unique stability of carbon monoxide among divalent carbon derivatives makes this example misleading, however, and examination of molecular models indicates that stepwise decomposition is to be expected when the bridge is not a particularly stable fragment. This is a consequence of the large deviations from planarity in the hydroaromatic ring which greatly restrict overlap of the orbitals at C-1 and C-4 with the diene system in the transition state for concerted decomposition.

In summary, the presently available evidence regarding the decomposition of **2a** points to path B, the ionic mechanism,[50] but suggests that a homopolar process may override it in nonpolar media. Though the homopolar process could be synchronous fragmentation (path C), the biradical scheme (path A) is the more likely alternative. The concept of a duality of mechanism in the pyrolysis of **2a** seems to afford a clearer understanding of the rates and products of decomposition of other norbornadiene derivatives. The presence of carbomethoxyl functions in **11** and its dioxolane analog, for example, should considerably lower the ionic-cleavage transition state relative to that for **2a**, thus explaining both the failure to isolate these adducts and the formation of esters in preference to bridge loss.

Molotsky has shown that pyrolysis of a series of 1,2,3,4,7,7-hexachloronorbornadienes (**29**) yields trichloromethylbenzenes (**30**).[51] The greatly diminished electron-donating ability of chlorine relative to oxygen leaves little doubt that the rearrangement proceeds *via* a diradical analogous to **25**. Consistent with this interpretation, we have noted that **29** ($R = R' = CO_2CH_3$) is somewhat stabler thermally than **29** ($R = H$, $R' = C_6H_5$) in sharp contrast to the corresponding ketals.



29 **30**

R	R′
$ClCH_2$	$ClCH_2$
H	$ClCH_2$
H	CH_2OAc
H	CO_2Et
H	C_6H_5

The absence of bridge loss from the 7,7-dichloro compounds[52] helps confirm the prediction that dialkoxycarbenes should be stabler, and thus better leaving groups than dichlorocarbene.[53]

Attention may now be focused on the products derived from the methano bridge of **2a**. *Since bridge loss has been shown to be unimolecular, the isolation of tetramethoxyethylene constitutes excellent evidence for the intermediacy of dimethoxycarbene.* The absence of the carbene dimer when the pyrolysis is run at high dilution is to be expected, but the origin of the trimethyl orthoformate formed has not yet been accounted for entirely satisfactorily. It has been suggested that this product arises by addition of methanol to the carbene, and indeed the yield is good (~70% based on biphenyl **4**) when the ketal decomposition is run in methanol.[11] Nevertheless, very little or no methanol is detectable by vapor chromatography when **2a** is decomposed in dilute decalin, and yields of ortho ester (again based on total bridge loss), are ≥50%).[54]

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to expectations based on any one of the commonly cited empirical parameters measuring solvent polarity.[45] Hydrogen-bonding ability, the key to methanol's effectively higher "polarity," may not be very influential in the present case both because the anionic charge developing along path B is delocalized over several centers and because hydrogen bonding to the ketal oxygens should be important only in the *ground state*, where it opposes ionization.

(45) C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, 4, 29 (1965).

(46) (a) When a polar transition state is generated from nonpolar reactants, the decrease in entropy due to solvation is ordinarily *larger* in nonpolar than in polar media.[45] This fact is another reason for favoring the biradical mechanism in cyclohexane. (b) In all solvents investigated the biphenyl/ester ratio increased with temperature, another observation in accord with path A–path B competition.

(47) J. E. Leffler, *J. Am. Chem. Soc.*, **75**, 3598 (1953).

(48) M. F. Hawthorne, *ibid.*, **77**, 5523 (1955).

(49) J. E. Leffler, *ibid.*, **72**, 67 (1950).

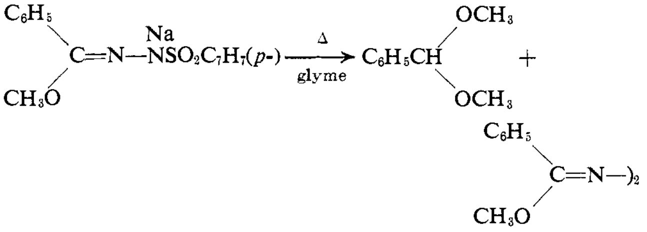
(50) This is the pathway favored by Hoffmann and Häuser for **2a** decomposition.[11]

(51) H. M. Molotsky, U. S. Patent 2,946,817 (1960); *Chem. Abstr.*, **55**, 5856 (1961).

(52) Vapor chromatography of the pyrolysate from **29** ($R = H$, $R' = C_6H_5$) in our laboratory revealed that little or no 2,3,4,5-tetrachlorobiphenyl (4) was present. It is noteworthy that hydrolysis of the pyrolysate with methanolic potassium hydroxide followed by diazomethane treatment gave ester **18**, indicating that the phenyl and trichloromethyl groups were *meta* to one another in what was probablv the major product isomer (see the Experimental Section).

(53) Mc Bee's observation[15] that pyrolysis of 2,3-dicarbomethoxy-1,4,5,6-tetrachloro-7,7-difluoronorbornadiene at 480° results in loss of the bridge is in harmony with the relative stability of difluoro- and dichlorocarbene.

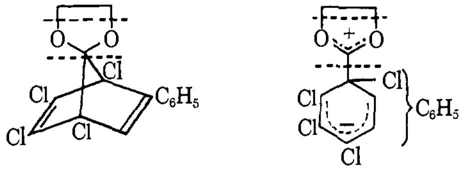
This result is analogous to the formation of acetals when ester p-toluenesulfonylhydrazone salts are decomposed in aprotic media, for example.[56]



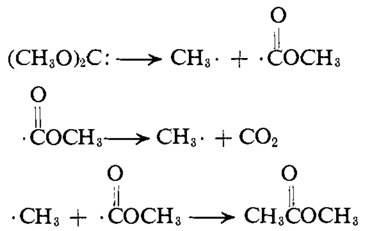
The tendency for the reaction mixture to catch fire when pure **2a** is heated in air to about 150° deserves comment. Since the decomposition of **2a** is quite exothermic, the temperature in the melt may rise so rapidly that the reaction becomes nearly adiabatic and radical concentrations reach high levels. Combination of these radicals with oxygen would furnish additional heat and provide chain carriers for combustion. The origin of the dimethyl oxalate formed in high yield (based on **4**) in the "open-air" pyrolyses is still in question. Air oxidation of initially formed tetramethoxyethylene (**23**) has been offered as an explanation,[11] but norbornadienone dimethyl ketal itself yields dimethyl oxalate when pyrolyzed neat in the absence of air.[27] Hydrolysis of **23** is presumed to be the source of the methyl dimethoxyacetate generated in "open-air" decomposition of 2a. It is not too surprising that little or none of the highly reactive **23** survives these reaction conditions.

The failure of trapping experiments with olefins is probably attributable to greater internal stabilization of oxygen-substituted carbenes relative to carbon-, hydrogen-, halogen-, or sulfur-substituted carbenes. Actually, cyclopropane formation from bis(alkylthio)-carbenes has been successful to date only with powerfully nucleophilic olefins, and even with these the yields have been low.[55a] Monoxycarbenes (or carbenoids) are intercepted by simple olefins,[57] but the combined electron-donating ability of two oxygens is apparently sufficient to deprive the divalent carbon of conventional reactivity. Isolation of dimethyl carbonate, incidentally, when 2a was decomposed in the presence of oxygen, does not provide any definite information about the reactivity of the carbene; the ester might be formed by a pathway not involving the carbene at all (*e.g.*, *via* the interception of the biradical **25** by oxygen).

Other Ketals. Because the dioxolane **2b** fragments cleanly into biphenyl **4**, carbon dioxide, and ethylene accompanied by essentially no ester, one is tempted to postulate a totally concerted pathway for the reaction. This would entail simultaneous rupture of four σ bonds and creation of the same number of π bonds. It could be argued that incipient formation of two stable molecules from the ketal bridge would lower the energy of the transition state for concerted cleavage of both C–C bridge bonds below that of the transition state for scission of one bond after the manner of **2a**. The concerted pathway is rendered unlikely, however, by the fact recorded above that **2b** *decomposes much more slowly than* **2a**. Again a biradical or zwitterionic intermediate is probably formed in the slow step, but the subsequent rapid collapse into three stable molecules may well be a synchronous event. This two-step sequence (designated "semi-concerted" and illustrated for the ionic case in the accompanying diagram) nicely explains the absence of esters in the product, but there is no compelling evidence against a three-step pathway which attributes a finite lifetime to ethylenedioxycarbene.



In light of the above discussion, the failure to detect ethylenedioxycarbene mass spectroscopically among the pyrolysis products from **3b** requires no comment, but the failure to observe dimethoxycarbene from **3a** merits consideration. The identification of methyl radicals, carbon dioxide, and methyl acetate in the latter experiment suggests a rapid radical fragmentation process for the carbene.



$$(CH_3O)_2C\colon \longrightarrow CH_3\cdot + \cdot\overset{\overset{O}{\|}}{C}OCH_3$$

$$\cdot\overset{\overset{O}{\|}}{C}OCH_3 \longrightarrow CH_3\cdot + CO_2$$

$$\cdot CH_3 + \cdot\overset{\overset{O}{\|}}{C}OCH_3 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}OCH_3$$

Whether the methyl acetate arises primarily by radical recombination, by rearrangement of the carbene, or by attack of methyl radicals on the carbene is not yet certain, though. The striking contrast between the vapor phase decomposition products from **3a** and the dilute solution decomposition products from **2a** finds a parallel in the pyrolysis of norbornadienone dimethyl ketal itself. Trimethyl orthoformate *inter alia* is generated in dilute solutions of the latter at 150°, but ethane, carbon dioxide, and methyl acetate are the major products from the bridge in the vapor phase at 200°.[27] As the temperature difference between the two experiments seems too small to explain the product contrast, it is likely that dimethoxycarbene is formed with excess energy (consistent with Figure 1) and that the above radical fragmentation pathway is precluded in solution by rapid dissipation of this excess.

Crawford and Raap[10] have reported that thermal decomposition of sodium N′-diethoxymethylene p-toluenesulfonhydrazide (**31**) yields (in addition to the expected nitrogen and sodium p-toluenesulfinate) N′-diethoxymethylene N-ethyl-p-toluenesulfonhydrazide, ethanol, carbon monoxide, ethylene, ethane, diethyl ether (trace), and butane (trace). Formation of these products was interpreted, quite reasonably, in terms of

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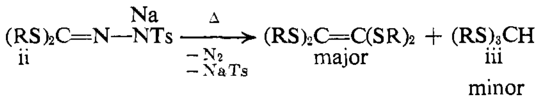
(54) Possibly related is the generation of ortho thioesters (iii) as minor products in the thermal decomposition of dithiolcarbonate p-toluenesulfonylhydrazone salts (*ii*) in aprotic solvents.[55]



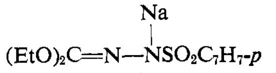
$$\underset{ii}{(RS)_2C{=}N{-}\overset{Na}{N}Ts} \xrightarrow[\substack{-N_2\\ -NaTs}]{\Delta} \underset{major}{(RS)_2C{=}C(SR)_2} + \underset{\substack{iii\\ minor}}{(RS)_3CH}$$

(55) (a) U. Schöllkopf and E. Wiskott, *Angew. Chem.*, **75**, 725 (1963); (b) D. M. Lemal and E. Banitt, *Tetrahedron Letters*, 245 (1964).

(56) (a) R. J. Crawford and R. Raap, *Can. J. Chem.*, 43, 356 (1965); (b) R. N. McDonald and R. A. Krueger, *Tetrahedron Letters*, 857 (1965).

(57) U. Schöllkopf and W. Pitteroff, *Ber.*, **97**, 636 (1964), and earlier papers; see also ref. 56a.

diethoxycarbene as an intermediate. An understanding of the contrast between this pattern of products and the pattern observed in the ketal pyrolyses must await the results of future research.



$(EtO)_2C{=}N{-}N(Na)SO_2C_7H_7\text{-}p$

31

Experimental Section[58]

Preparation of Tetrachlorocyclopentadienone Ketals[59] and Their Diels-Alder Reactions.

5,5-Dibenzyloxy-1,2,3,4-tetrachlorocyclopentadiene (**1c**). In 400 ml. of dry ether under N_2 was dissolved 27.3 g. (0.10 mole) of hexachlorocyclopentadiene. To this solution was added a slight excess of sodium hydride (0.21 mole) obtained by washing with petroleum ether (b.p. 40–60°) 10 g. of a 51% sodium hydride dispersion in mineral oil. A solution of 21.6 g. (0.20 mole) of benzyl alcohol in 100 ml. of ether was then added dropwise over a 6-hr. period with stirring. After 2 additional hr. of stirring, the solution was filtered and then evaporated on a rotary evaporator. The resulting oil was placed in the refrigerator overnight where it crystallized. After one recrystallization from 60–68° petroleum ether the crystals weighed 12 g. (28.8%) and melted at 58.8–62.8°. Recrystallization to analytical purity gave the ketal, m.p. 64.4–65.6°. *Anal.* Calcd. for $C_{19}H_{14}Cl_4O_2$: C, 54.84; H, 3.39; Cl, 34.09. Found: C, 54.66; H, 3.36; Cl, 34.15.

An alternative procedure for the preparation of **1c** met with failure but yielded interesting results. Fifteen grams (0.055 mole) of hexachlorocyclopentadiene was added slowly under nitrogen to a solution prepared by the portionwise addition of 2.66 g. (0.056 mole) of a 51% sodium hydride dispersion in mineral oil to a solution of 39 g. (0.362 mole) of benzyl alcohol in 200 ml. of glyme. After the addition the stirring was continued for 2 days. The glyme was removed on the rotary evaporator and a portion of the resulting oil was chromatographed on alumina. A crystalline material was eluted by carbon tetrachloride and benzene. This material was used to seed the remaining oil, whereupon a total of 6.0 g. of crystals formed. Repeated recrystallization from petroleum ether gave a crop with m.p. 59.5–60.8°. Spectra and analogy with McBee's work indicated that the compound was 3,3,4,4-tetrabenzyloxy-1,2,5-trichlorocyclopentene (**6a**): n.m.r. (CCl_4) sharp absorptions at $\delta = 4.60$ p.p.m. (allylic proton), $\delta = 4.78$ and 4.81 p.p.m. (methylene protons), and $\delta = 7.22$ p.p.m. (aromatic protons) in nearly the expected 1:8:20 ratio; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 258 mμ (ϵ 868) and 209 mμ (ϵ 4.26 × 10^4) with end absorption but no absorption in the region of 300 mμ.[60] The 6 g. of material then represented an 18% yield. The elemental analysis of this somewhat unstable compound was nearly within acceptable limits. *Anal.* Calcd. for $C_{33}H_{29}Cl_3O_4$: C, 66.51; H, 4.90; Cl, 17.85. Found: C, 66.12; H, 4.85; Cl, 17.45.

Another attempt at producing **1c** using excess base led to yet a third product. One-tenth of a mole (27.3 g.) of hexachlorocyclopentadiene was dissolved in 400 ml. of glyme. To this solution under nitrogen was added 12.7 g. (0.53 mole) of sodium hydride obtained by washing a mineral oil dispersion with petroleum ether. Then 65 g. (0.60 mole) of benzyl alcohol was added slowly with stirring over about 2 hr., while the temperature was maintained at 40–45° by controlling the rate of addition. After standing for 24 hr., the solution was filtered and the glyme was removed on the rotary evaporator. The remaining dark oil was taken up in 300 ml. of 60–68° petroleum ether, 250 g. of alumina was added, and the mixture was swirled for 1 min. The mixture was filtered through a Büchner funnel containing a 1-in. layer of fresh alumina; the alumina was washed on the filter with 200 ml. of benzene. When evaporated, the filtrate gave a light brown oil which crystallized on standing at room temperature. The crystals weighed 15.3 g. after recrystallization from 60–68° petroleum ether. A portion of the remaining oil was chromatographed, revealing that the oil contained a total of 6 g. (10%) of **6a**. The absorption spectra of the main product indicated that it was 1,4,5,5-tetrabenzyloxy-2,3-dichlorocyclopentadiene (**7a**): n.m.r. (CCl_4) four sharp peaks at $\delta = 4.17$ and 5.32 p.p.m. (methylene protons) and $\delta = 7.19$ and 7.28 p.p.m. (aromatic protons); $\lambda_{\max}^{95\%\ \mathrm{ethanol}}$ 308 mμ (ϵ 1670) and end absorption.[60]

1,2,3,4-Tetrachloro-5,5-[2′,2′-dimethyl]propylenedioxycyclopentadiene (**1d**). A solution of 23.7 g. (0.10 mole) of 2,2-dimethyl-1,3-propanediol in tetrahydrofuran (THF, 100 ml.) was added under nitrogen with stirring to 800 ml. of THF containing 5.60 g. (0.234 mole) of sodium hydride obtained from a 51% mineral oil dispersion by washing with petroleum ether. The addition was carried out very slowly over a 3-day period and stirring was continued for an additional 6 hr. The solvent was then removed by rotary evaporation, leaving 28 g. of a dark oil which was chromatographed on alumina. The ketal **1d** was eluted with a mixture of 60–68° petroleum ether and carbon tetrachloride. Recrystallization from methanol yielded 2.0 g. (6.6%) of **1d**. Several additional recrystallizations were required to reach analytical purity, m.p. 42.6–43.8°. *Anal.* Calcd. for $C_{10}H_{10}Cl_4O_2$: C, 39.50; H, 3.32; Cl, 46.65. Found: C, 39.47; H, 3.39; Cl, 46.65.

1,2,3,4-Tetrachloro-5,5-diphenoxycyclopentadiene (**1e**). Phenol (23.5 g., 0.25 mole) was dissolved in 500 ml. of THF, 6.5 g. (0.28 mole) of finely chopped sodium wire was added, and the mixture was stirred under nitrogen until reaction was complete (4 hr.). The sodium phenoxide solution then was transferred to a

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(58) Spectra were measured using the following instruments: Varian HR-60 and A-60 for n.m.r. spectra, Applied Physics Corp. Cary Model 11 and 15 for ultraviolet spectra, and Perkin-Elmer Infracord Model 137b for infrared spectra. Gas chromatography was carried out using a Perkin-Elmer vapor fractometer 154D with either a 6 m. × 0.25 in. Ucon Polar on acid washed Chromosorb P (20% w/w) column or a 6″ × 0.25 in. 28/200 activated silica gel column and an Aerograph A-90-P2 with a 5 ft. × 0.25 in. silicone SF-96 on 60/80 firebrick (20% w./w.) column. Glyme solvents, olefinic solvents, decalin, cyclohexane, and tetrahydrofuran were distilled from lithium aluminum hydride before use. Other purifications are indicated in the body of the Experimental Section.

(59) Ketals 1a and 1f were prepared by the methods of Mc Bee, *et al.*[18,21] Our procedure for 1b is not presented here since Mackenzie's gives superior yields.[35] 1,2,3,4-Tetrachloro-5,5-propylenedioxycyclopentadiene (1g) was prepared in low yield *via* the procedure given in this paper for 1d. After recrystallization from methanol, it melted at 63–64.8°.

(60) Whereas 1a shows a maximum at 307 mμ (ϵ 2583) and 2,3-dichloro-1,4,5,5-tetramethoxycyclopentadiene (7b) at 304 mμ (ϵ 1746), 1,2,5-trichloro-3,3,4,4-tetramethoxycyclopentene (6b) absorbs at 212 mμ (ϵ 8241) but not in the 300-mμ region.[21]

dropping funnel and added over a 3-hr. period to a solution of 36 g. (0.13 mole) of hexachlorocyclopentadiene in 500 ml. of THF at room temperature. This mixture was stirred at room temperature for 14 hr. and at reflux for 2 hr. When the THF had been stripped on a rotary evaporator, the residue was partitioned between a mixture of pentane and water. The pentane layer was separated, washed three times with water, dried over anhydrous magnesium sulfate, and evaporated. The residual oil was freed of most of the hexachlorocyclopentadiene by vacuum distillation and chromatographed on 800 g. of alumina eluting first with pentane and gradually changing to carbon tetrachloride. Ketal **1e** followed the remaining hexachlorocyclopentadiene off the column and was obtained as a buff-colored solid. Three recrystallizations from methanol gave 11.3 g. (22%) of white needles, m.p. 44–45°, and the analytical sample melted at 44.9–45.5°; infrared $\lambda_{\max}^{\mathrm{CHCl_3}}$ 3.30, 6.20, 6.28, 6.72, ~8.45, 8.60, 10.0 μ. *Anal.* Calcd. for $C_{17}H_{10}Cl_4O_2$: C, 52.61; H, 2.60; Cl, 36.55. Found: C, 52.68; H, 2.67; Cl, 36.70.

A small quantity of a pentachlorophenoxycyclopentadiene was eluted from the above column shortly after the **1e**. Three recrystallizations from methanol gave yellow crystals, m.p. 55–56°. This compound was obtained in much higher yield and **1e** in lower yield when the original reaction was run at room temperature. *Anal.* Calcd. for $C_{11}H_5Cl_5O$: C, 39.98; H, 1.53; Cl, 53.66. Found: C, 39.73; H, 1.58; Cl, 53.50.

Reaction of 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene (**1a**) *with Dimethyl Acetylenedicarboxylate.* Ketal **1a** (3.064 g., 11.6 mmoles) was mixed with 3.29 g. (23.2 mmoles) of the acetylenic ester and heated at 145° in a nitrogen-filled system. Volatile products were collected in a trap cooled in liquid nitrogen. After 4.5 hr., a stopcock between the reaction flask and the trap was closed and the volatile material was allowed to expand into a eudiometer. The gas volume increase, corrected for the decrease in volume of the nitrogen gas in the system when the U-tube was cooled, was 40.0 ± 0.8 ml. at 25.5° (740.2 mm.). A gas phase chromatographic check on the purity of the gas indicated that it was 95% methyl chloride (64% corrected yield). Column chromatography of the pot residue after removal of the remaining reactants by vacuum distillation yielded 0.487 g. of trimethyl trichlorohemimellitate (**11**, 59%). In another experiment the identity of the methyl chloride was confirmed by mass spectrometry and the ester was purified for analysis (m.p. 93–94°). *Anal.* Calcd. for $C_{12}H_9Cl_3O_6$: C, 40.53; H, 2.55; Cl, 29.91. Found: C, 40.58; H, 2.53; Cl, 30.10.

An Aerograph Model A-90-P2 was set at temperatures of 300° for the injector, 250° for the column, and 270° for the detector. Samples (10-μl.) of an equimolar mixture of **1a** and dimethyl acetylenedicarboxylate were injected. Small peaks having the retention times of hemimellitate **11** and phthalate **10** were observed with a peak area ratio of about 4:1. Heating the mixture of **1a** and acetylenic ester at 160° for 10 min. before injecting a portion of it into the gas chromatograph gave a peak for hemimellitate **11** but none for phthalate **10**. Equal weights of the two esters gave, within 5%, equal detector response.

Reaction of Ethylene Ketal **1b** *with Dimethyl Acetylenedicarboxylate.* One gram (3.82 mmoles) of **1b** was dissolved in 5 g. (35.2 mmoles) of dimethyl acetylenedicarboxylate and allowed to stand at room temperature for 2 weeks. The infrared spectrum was measured. Excess starting ester was removed on the rotary evaporator without heating the liquid above 80°; the resulting clear sirup crystallized on scratching. Recrystallization from methanol gave a first crop of 1.10 g. (86.5%), m.p. 67.8–69.5° and a second crop of 0.024 g. (1.9%), m.p. 66.6–68.3°. Comparison of the infrared spectrum of the pure triester **12** with the spectrum taken before removal of the excess acetylenic ester showed that little if any decomposition had occurred during the evaporation. The infrared spectrum of **12** $CHCl_3$ showed strong bands at 5.75, 6.98, 7.92, 8.43, 8.58, and 9.01 μ; n.m.r. (CCl_4) triplet at $\delta = 3.74$ (methylene protons adjacent to chlorine), intense singlets at $\delta = 3.87$ and 3.90 p.p.m. (methoxyl protons), and a triplet at $\delta = 4.52$ p.p.m. (methylene protons adjacent to oxygen, $J_{\mathrm{methylenes}} = 6$ c.p.s.). A small additional splitting of the methylene protons could be detected. *Anal.* Calcd. for $C_{13}H_{10}Cl_3O_6$: C, 38.64; H, 2.50; Cl, 35.11. Found: C, 38.81; H, 2.59; Cl, 35.21.

In order to be certain that acid catalysis was not responsible for decomposition of the intermediate in the above experiment, the reactants were stirred with lithium carbonate in a second run. The reaction time was only 5 days and the temperature was never raised above room temperature even in the work-up, but again the ring-opened triester was formed in good yield.

A small portion of **12** was saponified in methanolic potassium hydroxide. After evaporation of the methanol, the residue was acidified and the free acid was dissolved in ether. The ethereal solution was treated with excess diazomethane and then boiled dry in the hood. Recrystallization of the product from methanol gave material showing no depression in melting point when mixed with trimethyl trichlorohemimellitate (**11**).

1,2,3,4-Tetrachloro-7,7-dimethoxy-5-phenylbicyclo[2.2.1]hepta-2,5-diene (**2a**). A solution of 15 g. (0.0569 mole) of ketal **1a** in 15 ml. (0.147 mole) of phenylacetylene was allowed to stand for 5 days at 70°. The excess phenylacetylene was then removed on the rotary evaporator; crystallization was induced by scratching and allowed to continue in the refrigerator for 12 hr. The slighly yellow crystals were then collected by filtration. They were washed on the filter with a small amount of 60–68° petroleum ether and recrystallized twice from the same solvent to yield 9.58 g. (46.2%) of the white bridge ketal **2a**, m.p. 96–98°. The infrared spectrum showed strong multiple bands in the 8.4–9.1-μ region presumably due to the ketal function: ultraviolet $\lambda_{\max}^{\mathrm{isooctane}}$ 275 mμ (ϵ 2.94 × 10^3), 247 mμ (ϵ 9.1 × 10^3), and 218 mμ (ϵ 1.03 × 10^4). *Anal.* Calcd. for $C_{15}H_{12}Cl_4O_2$: C, 49.22; H, 3.31; Cl, 38.73. Found: C, 49.20; H, 3.47; Cl, 38.52.

A chloroform solution of **2a** was evaporated, leaving a thin, noncrystalline film on the bottom of an erlenmeyer flask. One milliliter of concentrated sulfuric acid and 3 drops of water were poured into the flask. An immediate effervescence was observed followed shortly by crystallization of 2,3,4,5-tetrachlorobiphenyl (**4**), identified by comparison of the infrared spectrum with that of authentic material obtained in later experiments.

Reversible Transformation of Ketal **2a** *to its Quadricyclic Valence Tautomer.* Dimethyl ketal **2a** (19.2 mg.) was dissolved in 192 ml. of spectral-quality isooctane and the solution was poured into the annular space between a water-cooled quartz immersion well and a cylindrical Pyrex vessel immersed in a cold (4°) water bath. The immersion well contained a Hanovia 450-w. type L mercury lamp fitted with a Pyrex filter sleeve. An irradiation time of 2.25 hr. was found sufficient for ring closing all of the diene, as judged by the total disappearance of absorption at 280 mμ. The solution then was transferred to a flask and placed in a 33° constant temperature bath. Aliquots were withdrawn at 15-min. intervals for 4 hr. and the absorbance at 280 mμ immediately was measured. The ring opening was half complete after 1.75 hr., but the data did not conform to a simple rate law. A second run, like the first except that 1 ml. of triethylamine had been added to neutralize any hydrogen chloride formed, gave an essentially identical set of rate data. The n.m.r. spectrum of the quadricyclic tautomer (measured as a ~2:3 mixture with **2a** in CCl_4) displayed singlets at δ = 2.87 (cyclopropyl proton), δ = 3.51 and 3.67 p.p.m. (methoxyl protons), and δ = 7.28 p.p.m. (aryl protons).

1,2,3,4-Tetrachloro-7,7-ethylenedioxy-5-phenylbicyclo[2.2.1]hepta-2,5-diene (**2b**). Ethylene ketal **1b** (2.5 g., 9.6 mmoles) was dissolved in 10 g. (98 mmoles) of phenylacetylene. The solution was heated at 65–70° for only 24 hr. and worked up in the same manner as that yielding **2a**. Recrystallization of the product from methanol gave 2.3 g. (66%) of the ethylene ketal **2b**, m.p. 120–121°. The melting point of analytically pure material was 127.5–128.3°. *Anal.* Calcd. for $C_{15}H_{10}Cl_4O_2$: C, 49.50; H, 2.77; Cl, 38.95. Found: C, 49.24; H, 2.82; Cl, 39.00.

7,7-Dibenzyloxy-1,2,3,4-tetrachloro-5-phenylbicyclo[2.2.1]hepta-2,5-diene (**2c**). The same conditions applied to preparation of the dimethyl ketal **2a** transformed **1c** into the adduct **2c**, 32% yield after one recrystallization from methanol. Analytically pure material melted at 96.2–97.2°. *Anal.* Calcd. for $C_{27}H_{20}Cl_4O_2$: C, 62.56; H, 3.89; Cl, 27.36. Found: C, 62.65; H, 3.67; Cl, 27.20.

1,2,3,4-Tetrachloro-5-phenyl-7,7-[2′,2′-dimethyl]propylenedioxybicyclo[2.2.1]hepta-2,5-diene (**2d**). When ketal **1d** was used as the dienophile and the conditions were those for making **2b**, **2d** was obtained in 36.8% yield after a recrystallization from methanol. *Anal.* Calcd. for $C_{18}H_{16}Cl_4O_2$: C, 53.24; H, 3.97; Cl, 34.93. Found: C, 53.25; H, 4.01; Cl, 34.80.

Attempt to Prepare 1,2,3,4-Tetrachloro-7,7-diethoxy-5-phenylbicyclo[2.2.1]hepta-2,5-diene. Conditions similar to those used in preparation of the dimethyl ketal **2a** did not lead to isolation of its diethyl analog in a pure state. Another attempt using a 50-fold excess of phenylacetylene with a 24-hr. reaction time also produced material which refused to crystallize even following chromatography on alumina. The chromatogram did yield material with the infrared spectrum of the tetrachlorobiphenyl **4**, indicating that the adduct had formed and in part decomposed with the loss of the bridge atoms. The lower rate of formation and smaller crystallization tendency to be expected with the diethyl ketal probably account for the failure to isolate it in crystalline form.

1,2,3,4-Tetrachloro-7,7-ethylenedioxy-5-phenylbicyclo[2.2.1]hept-2-ene.[61] One gram (3.68 mmoles) of ketal **1a**, 0.400 g. (3.85 mmoles) of styrene, and a trace of hydroquinone were heated at 66° in benzene solution for 24 hr. After removal of the benzene, crystallization was induced by prolonged scratching to give 1.27 g. (91%) of the adduct melting at 85–90°. After ten recrystallizations the melting point was 85–94°, but the substance gave a correct analysis for the desired adduct. Though these facts suggest that *endo–exo* isomerism is involved, the n.m.r. spectrum is interpretable in terms of a single isomer. It displayed an ABX pattern corresponding to the C-5 and C-6 protons, with the eight AB lines centered at δ = 2.48 p.p.m. and the 4X lines at δ = 3.74 (δ_{AB} = 0.47 p.p.m., J_{AB} = 12.3 c.p.s., J_{AX} = 10.2 c.p.s., J_{BX} = 3.6 c.p.s.), a symmetrical multiplet whose major feature was a sharp line at δ = 4.23 p.p.m. attributable to the dioxolane protons, and a multiplet in the δ = 6.89–7.37 p.p.m. region for the aryl protons. Relative areas of these features were 3.0:4.0:5.0. Infrared showed $\lambda_{max}^{CHCl_3}$ 6.27, 7.87, 9.05, 9.59, and 10.48 μ. *Anal.* Calcd. for $C_{15}H_{12}Cl_4O_2$: C, 49.52; H, 3.27. Found: C, 49.20; H, 3.31.

1,2,3,4-Tetrachloro-7,7-dimethoxy-5-methylbicyclo[2.2.1]heptadiene (**3a**). Dimethyl ketal **1a** (30 g., 0.114 mole) was dissolved in ~150 ml. of propyne in a Pyrex tube; the tube was sealed *in vacuo* and heated at 70° in a hydrogenation bomb for 2 weeks. The tube was then cooled in a Dry Ice bath and broken open, and the propyne was allowed to evaporate. A major portion of the unreacted ketal **1a** was removed by distillation through a short-path vacuum distillation apparatus. Attempts to distill **3a** resulted in partial decomposition, so the pot residue was chromatographed on silica gel (150 g.) using pentane as the initial eluent and gradually changing to benzene. 2,3,4,5-Tetrachlorotoluene (~0.5 g., identified in a later experiment), **3a** (1.342 g., 3.8%), mixtures of **3a** and **1a**, and **1a** were eluted in succession; the fractions were analyzed by n.m.r. spectroscopy. A liquid at room temperature, **3a** was purified for analysis by several low-temperature crystallizations from ethanol. *Anal.* Calcd. for $C_{10}H_{10}Cl_4O_2$: C, 39.50; H, 3.32. Found: C, 39.57; H, 3.31.

A small amount of methyl 2,3,4-trichloro-5-methylbenzoate (m.p. ≈110°) was eluted with chloroform from the above column: n.m.r. (CCl_4) singlets at δ = 2.42 p.p.m. (C-methyl), δ = 4.10 p.p.m. (O-methyl), and δ = 7.48 p.p.m. (aryl protons).

1,2,3,4-Tetrachloro-7,7-ethylenedioxy-5-methylbicyclo[2.2.1]heptadiene (**3b**). Ethylene ketal **1b** (18 g., 0.069 mole) was dissolved in ~200 ml. of propyne in a Pyrex tube; the liquid was frozen and the tube was sealed under vacuum. The tube then was heated in a hydrogenation bomb, using pentane as a pressure equalizer,

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(61) This compound was prepared in order to compare its thermal stability with that of its diene counterpart **2b**. The difference is really great, for a portion of the monoolefin was heated at 310° for 45 min. without decomposition (as indicated by the lack of any change in the infrared spectrum).

at 70–75° for 30 hr. Cooled to −80°, the tube was broken open and the propyne was allowed to evaporate as it warmed up. When petroleum ether was added to the oily residue, 9.25 g. of a solid melting above 200° was precipitated. The solid was removed by filtration, the petroleum ether was evaporated, and two volumes of ethanol was added to the residue. Left in the refrigerator overnight, the solution deposited about 8 g. of **1b**, which was also removed by filtration. The ethanol was then evaporated, and the oil was vacuum distilled. The last fraction (b.p. 90–91° (0.1 mm.)) was shown by n.m.r. to be a 3:7 mixture of **1b** and **3b**. This was chromatographed on silica gel starting with pure pentane and gradually changing to pure benzene as the eluent. Ketal **3b** (0.94 g., (4.5%) came off the column first with **1b** immediately following it. After distillation at 0.1 mm., the **3b** melted at 51–52°. *Anal.* Calcd. for $C_{10}H_8Cl_4O_2$: C, 39.77; H, 2.67. Found: C, 39.84; H, 2.63.

Pyrolyses of Dimethyl Ketal 2a

Neat Pyrolysis of **2a** *in an Inert Atmosphere.* A 0.222-g. (0.607 mmole) portion of ketal **2a** was placed in a small flask attached to a eudiometer system. The system was alternately evacuated and filled with helium several times and was then left under helium at atmospheric pressure. The pyrolysis flask was heated in a 180° oil bath until the volume became constant. When the system had cooled to room temperature, the volume increase was found to be 6 ml. (5.3 ml. at STP) (39%). The gas produced was identified as methyl chloride by gas chromatographic comparison with authentic material.

Another neat pyrolysis of 0.994 g. (2.72 mmoles) of **2a** was carried out in a 1-l. flask which had been evacuated and filled with helium four times. The flask was then quickly evacuated to about 100 mm. and lowered about 1 in. into an oil bath at 160°. A vigorous pyrolysis occurred soon after melting was complete. The flask was adjusted to atmospheric pressure with helium and a 1-ml. sample of the gas inside was chromatographed on a silica gel column. No ethane could be detected although a trace of methane appeared to be present. The vacuum-volatile materials were transferred to a trap cooled in liquid nitrogen. Gas chromatography of the nonvolatile residue showed the ratio of bridge loss to bridge opening to be 3:1 by comparison of the peak areas for the tetrachlorobiphenyl **4** and the two carbomethoxybiphenyls **18** and **21**. The vacuum-volatile material (0.091 g.), after warming to room temperature, was found to be 70–80% tetramethoxyethylene (**23**) by relative peak areas in gas chromatography. After correction for the fraction of bridge opening this represented a 40–50% yield from bridge loss.

Pyrolysis of **2a** *in Concentrated Solution.* All glassware for this experiment was rinsed with ammonium hydroxide and dried before use. A 1.706-g. (4.66 mmoles) portion of ketal **2a** was placed in a 100-ml. flask with 4 g. of distilled di-*n*-butyl phthalate and warmed until solution was complete. The flask was attached to a U-tube cooled in liquid nitrogen which in turn was attached to a three-way stopcock leading to either a nitrogen line or a vacuum pump. The system was cleared of oxygen by alternately evacuating and filling with nitrogen. The flask was then left open to the nitrogen line at atmospheric pressure; the reaction flask was lowered into an oil bath at 145° and the temperature gradually was raised. After 3 min., the temperature was 150° and bubbling had started. Bubbling persisted for about 2 min. and then tapered off quite rapidly. The oil-bath temperature reached 160° in 7 min. and was held there for an additional 3 min. before heating was discontinued. When the bath had cooled to 110°, the vacuum-volatile materials were transferred to the U-tube at 0.12 mm. Clear liquid (0.138 g.) remained after the U-tube had been warmed to room temperature to allow methyl chloride to escape. Gas chromatography showed this material to be almost pure tetramethoxyethylene (**23**), representing a 40% over-all yield and a 77% yield corrected for the amount of bridge opening as determined by gas phase chromatography of the nonvolatile materials.

Identification of Tetramethoxyethylene (**23**). Vacuum-volatile material from the pyrolysis of **2a** in concentrated di-*n*-butyl phthalate solution was vapor chromatographed using a silicone column at 140°. Tetramethoxyethylene was trapped in a U-tube at −78° as it came off the column. The ultraviolet absorption spectrum in 95% ethanol showed end absorption at λ 212 mμ (ϵ 3.9 × 10^3); infrared $\lambda_{\max}^{\text{neat}}$ 3.40, 3.53, 6.94, 8.15, 8.95, 9.94, and 10.30 μ; n.m.r. (CCl_4) δ = 3.50 p.p.m. *Anal.* Calcd. for $C_6H_{12}O_4$: C, 48.63; H, 8.16. Found: C, 48.41; H, 8.08.

Tetramethoxyethylene (**23**) could be converted to methyl dimethoxyacetate either by brief treatment of its benzene solution with dilute hydrochloric acid or by passing it through a Ucon polar-on-acid-washed Chromosorb P gas chromatography column. Identification was made by comparison of the retention time with that of authentic material (*vide infra*). Addition of a tiny droplet of bromine to 10 μl. of **23** in a centrifuge tube produced a small report. Insertion of a syringe needle into the liquid product induced the liquid to crystallize. A small amount of benzene was added to the tube and the resulting solution was gas chromatographed. The major product was found to have a retention time identical with that of authentic dimethyl oxalate.

Identification of Nonvolatile Products of **2a** *Pyrolysis.* Gas chromatography of the nonvolatile products of the pyrolysis of **2a** either neat or in polar solvents always showed a group of four peaks with estimated boiling points in the 350° range. The first and last of these were by far the largest with two small peaks between them. A typical ratio of these peak areas for a neat pyrolysis in the presence of air was 141:7:3:95 in the order in which the peaks appeared. Column chromatography on alumina yielded pure 2,3,4,5-tetrachlorobiphenyl (**4**, which had been isolated by McBee in 17–21% yield[12]); m.p. 91.8–92.6°; $\lambda_{\max}^{CHCl_3}$ 7.12, 7.47, and 12.15 μ. This was shown to account for the first and largest of the four peaks. Also obtained in pure form from the adsorption chromatogram was methyl 2,3,4-trichloro-5-phenylbenzoate (**18**), which was responsible for the other large peak (the fourth) in the gas chromatographic separation: m.p. 105–106°; $\lambda_{\max}^{CHCl_3}$ 5.75, 7.12, 7.77, 7.95, 8.60, 9.27, and 11.27 μ. *Anal.* Calcd. for $C_{14}H_9Cl_3O_2$: C, 53.29; H, 2.88; Cl, 33.71. Found: C, 53.46; H, 2.95; Cl, 33.46.

The *meta* orientation of the phenyl and carbomethoxyl groups in **18** was confirmed by conversion to *m*-phenylbenzoic acid. A 0.1005-g. (0.508 mmole) portion of the free acid, 2,3,4-trichloro-5-phenylbenzoic acid, obtained by saponification of **18**, was hydrogenated in sufficient aqueous sodium hydroxide to neutralize all the hydrogen chloride formed. The catalyst used was 0.359 g. of 5% palladium on barium sulfate. Hydrogenation at atmospheric pressure was nearly complete in 15 hr., but was allowed to continue for a total of 3 days at which time 24.95 ml. (STP, 111%) had been taken up. The catalyst was removed by filtration and the solution was acidified to pH 1 with dilute sulfuric acid; the resulting cloudy solution was extracted twice with ether. The dried ether solution was evaporated to give after recrystallization 0.0477 g. (72%) of *m*-phenylbenzoic acid whose melting point 166.3–166.7°) and ultraviolet spectrum ($\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 229 mμ (log ϵ 4.36) and 250 mμ shoulder (log ϵ 4.08)) agreed satisfactorily with the literature values[30] (m.p. 166°, $\lambda_{\max}^{95\%\ \mathrm{ethanol}}$ 231 mμ (log ϵ 4.32) and 250 mμ-shoulder (log ϵ 4.10)). The n.m.r. spectrum ($CDCl_3$) of the hydrogenolysis product was also in agreement with the *meta* orientation: a six-proton multiplet centered at δ = 7.52 p.p.m., two 0.5-proton triplets at δ = 7.83 and 7.96 p.p.m. (C-6 proton), two 0.5-proton triplets at δ = 8.10 and 8.22 p.p.m. (C-4 proton), a one proton triplet at δ = 8.42 p.p.m. (C-2 proton), and a one proton singlet at δ = 12.46 p.p.m. (carboxyl proton) ($J_{2,4} = J_{2,6} = J_{4,6}$ = 1.8 c.p.s., $J_{4,5}$ = 7.9 c.p.s., $J_{5,6}$ = 7.4 c.p.s.). *Anal.* Calcd. for $C_{13}H_{10}O_2$: C, 78.78; H, 5.09. Found: C, 79.07; H, 5.31.

A sample of 2-phenylbenzoic acid was prepared by the method of Graebe and Rateanu,[31] *viz.* heating fluorenone with potassium hydroxide at 180°, m.p. 112–113°, $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 240 mμ (log ϵ 3.91), and end absorption. These differences from the above compound constituted additional proof that the principal product of bridge opening was not an *o*-phenylbenzoate ester.

Although the relationship of carbomethoxy and phenyl substituents had been clearly established at this point, the orientation of the chlorines in the ester was not yet certain. Accordingly, the corresponding acid was dissolved in 40 times its weight of quinoline (distilled from barium oxide and zinc dust) and the solution was refluxed under nitrogen overnight. The dark product was partitioned between dilute hydrochloric acid and methylene chloride; the organic layer was washed twice with additional acid to remove remaining quinoline, then twice with aqueous sodium hydroxide to remove any unchanged starting acid. When the methylene chloride solution had been dried, treated with Norit, and filtered, it was stripped and the residue (as a benzene solution) subjected to gas chromatography on the 5-ft. silicone oil (SF-96) column at 250°. The trichlorobiphenyl was trapped from the column as white crystals, hot stage m.p. 100.5–102.5° (with prior sublimation to give droplets on the cover glass). Its n.m.r. spectrum (see Discussion) indicated the presence of orthohydrogens, thus establishing the correctness of structure **18** for the original ester. For further evidence, an authentic sample of 2,4,5-trichlorobiphenyl, the other reasonable possibility for the decarboxylation product, was synthesized by the Gomberg reaction from benzene and 2,4,5-trichloroaniline (Eastman technical, once recrystallized from ligroin). The general procedure of Weingarten[62] was employed. For partial purification, the dark brown oily product was placed on a column of ~50 times its weight of Fisher alumina and eluted with 1:5 benzene–petroleum ether. A benzene solution of the residue from evaporation of the eluate was gas chromatographed under the conditions described above, and the 2,4,5-trichlorobiphenyl was trapped as a colorless oil which soon crystallized (m.p. 76–78°, with prior sublimation reminiscent of the other isomer; lit.[63] m.p. 78–79°). This compound differed greatly from the 2,3,4-isomer in its n.m.r. spectrum, and its gas chromatographic retention time was ~1.5 min. shorter.

Adsorption chromatography of the nonvolatile **2a** pyrolysis products on an alumina column yielded some fractions rich in the two minor components originally detected by gas chromatography. From these fractions a small amount of the more abundant compound of this pair was isolated by gas chromatography. The melting point was 58–60° and the infrared spectrum was similar to that of **18**, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.76, 8.00, 8.50, 8.97, and 11.37 μ. Treatment of the remainder of the selected fractions from column chromatography with concentrated sulfuric acid resulted in a dark red-brown coloration. Dilution with water yielded bright yellow, crystalline material. The aqueous mixture was made basic with potassium hydroxide and then extracted with benzene to separate the yellow compound from acids. The aqueous solution was saved; the benzene solution was dried and concentrated, whereupon yellow needles formed, m.p. 233–234.5°. The infrared spectrum and the elemental analysis confirmed the structural assignment as 1,2,3-trichloro-9-fluorenone (**22**), $\lambda_{\max}^{\mathrm{Nujol}}$ 5.83, 6.30, and 8.81 μ. Thus the ester was the *o*-phenylbenzoate **21**. *Anal.* Calcd. for $C_{13}H_5Cl_3O$: C, 55.06; H, 1.78; Cl, 37.52. Found: C, 55.13; H, 2.03; Cl, 37.38.

The aqueous solution from the benzene extraction above was acidified and extracted with ether, and the ether solution was treated with diazomethane. The product of the esterification was obtained by evaporation of the ether solution. A gas chromatographic check of this material showed that it consisted almost entirely of the meta ester **18** and the unknown compound which is produced in very small amount. This indicates that the unknown compound is a methyl ester and probably not an *o*-phenylbenzoic acid derivative since it was not converted to a fluorenone by the sulfuric acid treatment.

Pyrolysis of **2a** *in Dilute Solution.* All glassware was treated with ammonium hydroxide and dried before use in this experiment. A 0.766-g. (2.09 mmoles) portion of ketal **2a** was dissolved in 20 ml. of decalin,[58] and 4 ml. of decalin in a 100-ml. flask was heated under nitrogen in a 190° oil bath. The ketal solution was added dropwise with rapid stirring to the hot solvent over a 1-hr. period. An expansion chamber attached to the reaction flask collected all gases produced. After the addition, the gases were sampled for chromatography while the reaction flask was still in the oil bath. Gas chromatography on a silica gel column

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[62] H. Weingarten, *J. Org. Chem.*, **26**, 730 (1961).

[63] W. Zerweck and K. Schütz, U. S. Patent, 2,280,504 (April 1942); *Chem. Abstr.*, **36**, 5658^6 (1942).

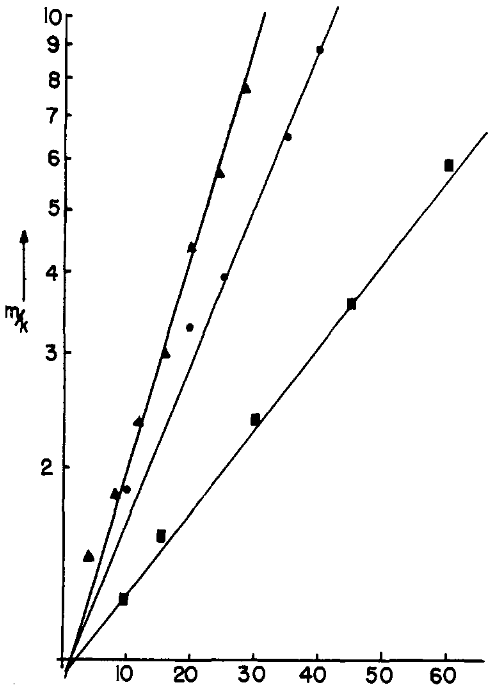

Figure 2. Effect of solvent on the rate of **2a** decomposition: ▲, acetonitrile at 115°; ■, methanol at 115°; ●, cyclohexane at 145°. The lines intersect the abscissa to the right of the origin because of the finite time required for the ampules to come to temperature.

showed a trace of material with the retention time of methane, but no carbon monoxide or ethane could be detected. The vacuum-volatile products were transferred to a U-tube cooled in liquid nitrogen. The material was warmed to room temperature, weighed, and analyzed on the gas chromatograph using a silicone column. Trimethyl orthoformate was the major component other than the decalin, which accounted for about 90% of the total. The ortho ester was assayed by comparing peak heights with those of standard samples of trimethyl orthoformate in decalin (0.060 g., 0.56 mmole, 53% yield if it is assumed that 2 moles of starting material produced 1 of the ortho ester. Preceding the ortho ester off the column were a number of poorly resolved peaks. There appeared to be about six components in this group, all in small amount. The total peak area of this group was 56% of the area of the ortho ester peak and therefore represented ~0.043 g. of material. The total recovery of bridge fragments then amounted to 0.094 g. or 61% of the theoretical amount. High-temperature gas chromatography showed that bridge loss had accounted for better than 95% of the reaction course so no correction was made for the amount of bridge-opened product. The fate of the bridge fragments not appearing as vacuum-volatile material was not determined, but gas chromatography of the reaction solvent showed at least three poorly resolved peaks with retention times slightly longer than either decalin peak.

In a separate experiment pure trimethyl orthoformate was trapped from the gas chromatograph, and the n.m.r. spectrum, as well as the retention time, was shown to be identical with those of authentic material; n.m.r. (CCl_4) two sharp singlets at δ = 3.21 and 4.77 p.p.m., area ratio 9:1.

Solvent Effects on the Pyrolysis of **2a**. To check detector response a standard solution was prepared by dissolving 0.124 g. of the tetrachlorobiphenyl **4** and 0.076 g. of the meta ester **18** in 1 ml. of decalin. Several 10-μl. samples of this standard were gas chromatographed on a silicone column at a column temperature of 250°. The integrated peak areas were in the ratio 1.77:1; the molar ratio was 1.76:1, indicating that detector response was essentially identical for equimolar quantities. Several 0.201-g. samples of ketal **2a** were dissolved in 1-ml. portions of different solvents in 10-ml. flasks. The flasks were evacuated and filled with nitrogen several times and then left open to the nitrogen line. They were heated without any agitation in a 160° oil bath for 20 min. Ten 2-μl. samples from these flasks were checked on the gas chromatograph under the same conditions as the standard solution. Average relative values of the area of the tetrachlorobiphenyl **4** peak, the combined areas of the two small center peaks **21** and U, and the area of the meta ester **18** peak were as shown in Table IV.

Table IV

Solvent	Relative peak areas		
	(4)	(21) + (U)	(18)
Decalin	76.8	5.7	17.6
Triglyme	37.6	15.6	46.8
Di-*n*-butyl phthalate	38.6	12.2	49.3
Benzonitrile	27.4	16.8	55.8
Triglyme (heated in 200° bath)	44.4	13.3	42.4
Di-*n*-butyl phthalate (pyrolyzed in the injection chamber at 310°)	61.2	9.7	29.1
Decalin[a]	1	0.10–0.18	
Dimethylsulfoxide/formamide (1:2 by vol.)[a]	1	5.2–5.7	

[a] Relative peak areas cannot be compared directly with the previous sections of the table. Because of solubility problems in the polar solvent mixture, these two 1-ml. portions of solvent each contained only 0.078 g. of **2a**. For the same reason they were swirled during the first 2 min. in the oil bath which resulted in a higher pyrolysis temperature.

Except for the last two entries in the table (which were less reproducible than the others), the total peak areas were all within ±10% of the theoretical value calculated from the standard solutions. Thus essentially all of the nonvolatile products of the pyrolysis are accounted for.

Kinetics of **2a** *Pyrolysis. Materials.* Dimethyl ketal **2a** was recrystallized several times from ethanol for these experiments. Cyclohexane was purified by extracting eight times with concentrated sulfuric acid and distilling from lithium aluminum hydride under nitrogen. Reagent grade methanol was dried by refluxing with magnesium methoxide and distilling under nitrogen. Refluxed over phosphorus pentoxide, reagent grade acetonitrile was distilled under nitrogen. All solvents were stored in the dark under nitrogen.

Procedure. Solutions of **2a** were prepared by dissolving 3.200 g. of the ketal in 80.00 ml. of cyclohexane or acetonitrile or, because of solubility limitations, in 110 ml. of methanol. Aliquots (5.00-ml. for the first two solvents, 7.10-ml. for methanol) were transferred to thick-wall tubes; they were frozen and the tubes were sealed under vacuum. These were placed in a wire basket and immersed in a constant temperature bath. Two of the tubes then were withdrawn simultaneously from the bath at appropriate time intervals and immediately cooled in an ice bath. The samples were prepared for analysis by breaking the tubes open, quantitatively transferring the contents to a 25-ml., pear-shaped flask, and removing the solvent on a rotary evaporator. Standard n.m.r. solvent (0.5 ml., a 3% by weight solution of mesitylene in chloroform-*d* or carbon tetrachloride) was added to the flask which was stoppered and swirled. The solution was then transferred to an n.m.r. sample tube for analysis. Zero-time samples were prepared by transferring an aliquot of the ketal solution to the pear-shaped flask and proceeding as with the other samples. Complete n.m.r. spectra were taken at each kinetic point and then at least ten integrals of the aromatic mesitylene (δ = 6.64 p.p.m.) and the ketal vinyl (δ = 6.36 p.p.m.) protons region were taken using the 50-c.p.s. sweep width of the Varian A-60 spectrometer. The average value for aromatic mesitylene protons/ketal vinyl proton area ratio (*M*/*K*) was calculated for each point and all values adjusted so that *M*/*K* at time zero was 1.00. Rate constants (Table III) were determined from plots of log *M*/*K* *vs.* time. Data from several runs are recorded and plotted below (Figures 2 and 3); a run with **2b** using the above procedure is also recorded. Though linear plots were obtained up to about 4 half-lives most runs were interrupted after 2–3 half-lives. As the graphs indicate, it was not possible to obtain very precise data by this method, and the precision was variable from run to run (see Table V).

Table V

Time, min.	*M*/*K*
2a in Cyclohexane at 145°	
0.00	1.00
10.0	1.84
20.0	3.24
25.0	3.90
35.0	6.41
40.0	8.88
2a in Acetonitrile at 115°	
0.00	1.00
4.0	1.46
8.0	1.81
12.0	2.31
16.0	2.96
20.0	4.31, 3.51
24.0	5.61, 5.83
28.0	7.60
29.0	8.13
2a in Methanol at 115°	
0.0	1.00
8.0	1.42
15.0	1.55
30.0	2.36
45.0	3.54
60.0	5.92
Time, hr.	***M*/*K***
2a in Cyclohexane at 115°	
0.0	1.00
0.45	1.15
0.87	1.06
1.25	1.28
1.92	1.23
3.78	1.44
5.52	1.96
7.77	2.70
10.30	3.77
2a in Acetonitrile at 80°	
0.0	1.00
0.50	1.09
2.00	1.37
3.58	1.87
4.58	2.18
5.50	2.53
7.50	3.29
9.83	4.99
2b in Cyclohexane at 115°	
0.00	1.00
6.48	1.07
13.40	1.25
25.67	1.50

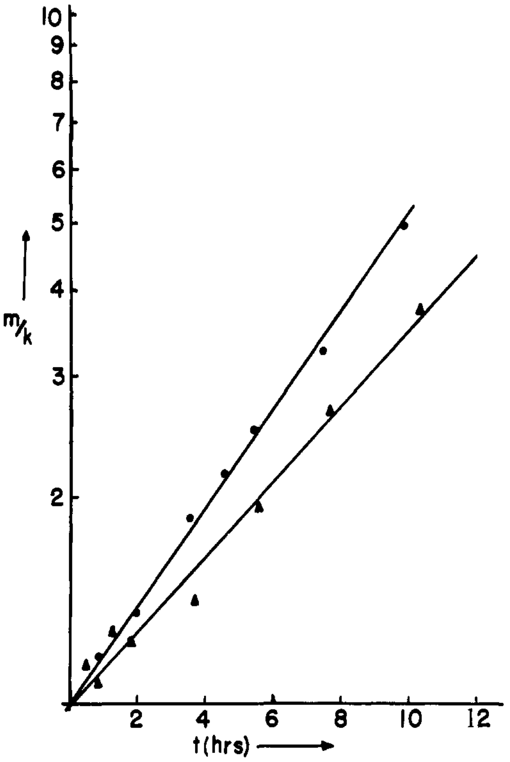

Figure 3. Effect of solvent on the rate of **2a** decomposition: ●, acetonitrile at 80°; ▲, cyclohexane at 115°.

The nonvolatile product distributions for the pyrolyses of **2a** (Table III) were determined by comparison of peak areas of vapor phase chromatography traces. The silicone oil (SF-96) column was used at 253°. A standard solution of **4** and **18** was used to determine relative detector response. Errors in product percentages are estimated to be within ±2%.

Effect of Dilution on the Biphenyl/Ester Ratio in Cyclohexane. Ketal **2a** (0.100 g.) was dissolved in 0.300 ml. of cyclohexane in a tube containing a glass rod whose diameter was only slightly smaller than the inside diameter of the tube. The tube was cooled in liquid nitrogen and sealed under vacuum. The reason for the narrow annulus was to ensure efficient heat exchange between the pyrolysis solution and its surroundings so that the heat of reaction would not raise the temperature of the concentrated solution. A second tube was prepared in a similar manner, but this one contained only 0.0033 g. of **2a** in 0.300 ml. of cyclohexane. Both tubes were immersed in an oil bath at 145–160° for 0.5 hr. and then the nonvolatile products were analyzed by vapor phase chromatography. In the dilute solution 96.4% of biphenyl **4** and 3.6% of ester **18** were found; in the concentrated solution the corresponding values were 92.2 and 7.8%. None of the *o*-phenylbenzoate ester **21** was present in the former solution, and only a trace in the latter.

Neat Pyrolysis of **2a** *in Air.* Dimethyl ketal **2a** (0.389 g., 1.05 mmoles) was placed in a 10-ml. flask fitted with an expansion chamber and a serum cap for sampling of the gases. The flask was lowered about 1 cm. into an oil bath at 190°. Vigorous pyrolysis began soon after melting was complete.[64] A small flash was visible in the gas phase, leaving a smoke-filled flask. The pyrolysis appeared to be complete at this point, and the gas in the system was sampled while the flask was still being heated. Chromatography of the sample on the silica gel column at room temperature and comparison of peak areas with those from standard samples showed that the gas contained 6% methane, 13% ethane, and 5% carbon dioxide. Carbon monoxide was not completely resolved from the air peak but was shown to be present in about the same amount as methane (6%). The total volume of the system after pyrolysis was estimated at 27 ml. After correction to STP this represented 0.057 mmole of methane, 0.12 mmole of ethane, and 0.047 mmole of carbon dioxide. The vacuum-volatile material was collected in a cold trap and found to weigh 0.040 g. after warming to room temperature to allow methyl chloride to escape. The mostly solid material was dissolved in a small amount of benzene and subjected to gas chromatography. Dimethyl oxalate (*vide infra*) was found to be the major component, accounting for 75% of the vacuum-volatile material on the basis of relative peak areas (0.030 g., 0.25 mmole). Gas chromatography of the nonvolatile materials on a silicone column at 250° showed the ratio of the tetrachlorobiphenyl **4** to the esters **18** and **21** to be 1.38:1. This made the theoretical yield of oxalate 0.30 mmole and the observed yield ~83% of theoretical.

In a second experiment the vacuum-volatile fraction of the reaction product was investigated more closely. Pyrolysis of **2a** in an open flask followed by vacuum transfer of the volatile materials to a U-tube cooled in liquid nitrogen yielded crystalline material identified as dimethyl oxalate by comparison of melting point, absorption spectra, and gas chromatographic retention time with those of authentic material. In addition, a liquid portion was trapped and investigated by gas chromatography. Methyl formate, methanol, dimethyl carbonate, and trimethyl orthoformate were identified as minor products by their retention times. A large dimethyl oxalate peak was followed by a smaller peak which was trapped and shown to be methyl dimethoxyacetate by comparison with authentic material prepared by the method of Wohl and Lange[65] from dichloroacetic acid: $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.40, 5.68, 6.97, 8.94, and 10.19 μ; n.m.r. (CCl_4) three sharp singlets at δ = 3.35 p.p.m. (ketal methoxyl protons), δ = 3.72 p.p.m. (ester methoxyl protons), and δ = 4.66 p.p.m. in the ratio 6:3:1.

Pyrolysis of **2a** *in Aerated Solution.* This experiment was treated with the respect due one that may form peroxides. To 5 g. of di-*n*-butyl phthalate in a 100-ml., three-neck flask was added 1.982 g. (5.43 mmoles) of **2a**. The flask was warmed to effect solution. An air train was set up to flow through a calcium chloride tube, a U-tube in Dry Ice, and then a fritted disk below the level of the solution in the reaction flask. The air flow proceeded out of the reaction flask through two U-tubes in liquid nitrogen and then to an aspirator. The aspirator was turned on to draw a stream of air bubbles through the solution as the reaction flask was lowered into a 140° oil bath. The temperature was raised until it reached 160° in 7 min. and was held there for an additional 3 min. Vacuum volatiles remaining in the reaction flask were transferred to the first U-tube after closing off the air supply and replacing the aspirator with an oil pump. The liquid obtained was weighed at room temperature and then investigated by gas chromatography. Dimethyl carbonate was shown to be present by retention time and a sample was trapped for mass spectral analysis. The mass spectrum was found to be identical with that of authentic material. The dimethyl carbonate peak accounted for 21% of the total peak area for the vacuum-volatile material. Proceeding on the crude assumption that the weight percentage was the same, the yield was estimated at 0.043 g., 0.48 mmole, 17% after correcting for the fraction of bridge opening (or 9% over-all). The observed ratio of the tetrachlorobiphenyl **4** and the two carbomethoxybiphenyls **18** and **21** was 52:9:39, identical with that observed in the previously discussed pyrolysis in concentrated solution under nitrogen at the same temperature.

Pyrolysis of **2a** *in Olefin Solutions.* Ten milliliters of cyclohexene was used to dissolve 0.625 g. (1.71 mmoles) of dimethyl ketal **2a**. The solution was sealed in a glass tube, heated slowly in a hydrogenation bomb to 160°, and held there for 5 min. The cooled tube was opened and the contents were distilled at atmospheric pressure in a microstill. The various fractions and pot residue were checked by gas chromatography. The pot residue showed traces of substances different from those obtained by pyrolysis in the absence of cyclohexene, but the amounts were too small to permit isolation. Pyrolyses of a preliminary nature were carried out in ketene diethyl acetal and in ethyl acrylate; again no trapping products of dimethoxycarbene were isolated.

Other Pyrolyses

Neat Pyrolysis of Ethylene Ketal **2b**. Ketal **2b** (0.3466 g., 0.953 mmole) was placed in a 25-ml., round-bottom flask attached to a 6-in. water-jacketed, vertical condenser which led to a stopcock, U-tube, and finally a eudiometer. An open manometer allowed adjustment to atmospheric pressure. The system was freed of oxygen by alternately evacuating and filling with nitrogen. The system was adjusted to atmospheric pressure and the flask was heated in an oil bath whose temperature was gradually raised from 130 to 170°. After 18 hr., the system was allowed to cool and the change in volume was determined and corrected to STP (43.9 ml., 94.5%).

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[64] The minimum temperature at which vigorous pyrolysis occurs is ~140°.

[65] A. Wohl and M. Lange, *Ber.*, 41, 3612 (1908).

A sample of the gas in the system analyzed by chromatography on a silica gel column showed two peaks with relative areas 1:1.02.

A separate experiment was carried out to obtain a mass spectral sample of the gases. A 0.84-g. (2.3 mmoles) portion of **2b** was placed in a 100-ml. flask attached to a liquid nitrogen cooled U-tube which led in turn to a three-way stopcock. The system was placed under nitrogen by alternately evacuating and filling with nitrogen and was left at 10 mm. The flask then was heated slowly to 180° and held there until bubbling nearly was finished. An evacuated mass spectral sample tube was attached to the three-way stopcock and the gas was allowed to expand into this sample tube as the U-tube was warmed to room temperature. The mass spectrum showed very large peaks at masses 25, 26, 28, and 44 and additional smaller peaks all in excellent agreement with the reported mass spectra of ethylene and carbon dioxide.[66]

Pyrolysis of **2b** *in Solution.* Pyrolyses of 1-mmole samples of the ethylene ketal were carried out in 12-ml. portions of chlorobenzene[67] and 4-vinylcyclohexene using the same equipment and general procedure as in the neat pyrolysis. The oil bath, however, was kept at 135–140° and the pyrolyses were thus carried out at or near the boiling points of chlorobenzene (132°) and 4-vinylcyclohexene (128°). The reactions were complete in less than 24 hr. as indicated by constant volumes, and the volume change with time was recorded for the pyrolysis in chlorobenzene. A plot of log $(V_\infty - V)$ *vs.* time gave a good straight line in agreement with first-order kinetics ($k = 1.2 \times 10^{-4}$ sec.$^{-1}$). After the pyrolyses, with the reaction flask still in the oil bath, the U-tube was placed in liquid nitrogen and the mercury in the eudiometer was raised slowly to the top. Alternately applying and releasing pressure at the open end of the manometer assisted diffusion of the carbon dioxide and ethylene into the U-tube from the reaction flask. The stopcock between the U-tube and the reaction flask was closed, and the mercury in the eudiometer was lowered slowly until atmospheric pressure was reached. The U-tube then was removed from the liquid nitrogen, and the volume change was noted. A correction was made for the change in volume due to expansion of the nitrogen gas in the U-tube; this correction was obtained in a blank run with only nitrogen in the system. The volume of gas produced was 94.5% of theoretical in chlorobenzene and 92.6% in 4-vinylcyclohexene, values which differ by no more than the estimated experimental error.

Nonvolatile Products of **2b** *Pyrolysis.* Ketal **2b** (1.035 g., 2.85 mmoles) was pyrolyzed neat by heating slowly to 170° and maintaining that temperature for 2 hr. The resulting material was recrystallized from methanol to give a first crop of 0.705 g. (m.p. 93.7–94.6°) and a second crop of 0.064 g. (m.p. 89.2–90.4°), representing 85 and 7.7% yields. A third crop melted at 75–85°. The first crop was observed to melt higher than previously obtained **4**, but recrystallization from petroleum ether (the previously used solvent) gave crystals which melted at 90.5–91.2°, in agreement with previous samples. The infrared spectrum of the first crop was identical with that of previously obtained **4**. A weak carbonyl absorption was present in the infrared spectrum of the mother liquors of the third crop. High-temperature gas chromatography of the total nonvolatile material, however, failed to show any peak other than that for **4**, indicating a very clean reaction.

Neat Pyrolysis of Dibenzyl Ketal **2c**. A 0.50-g. (0.97-mmole) portion of **2c** was placed in a 25-ml., round-bottom flask which was then evacuated to 0.1 mm. through a U-tube. Then with the system still open to the vacuum pump, the U-tube was immersed in liquid nitrogen and the flask was lowered into a 195° bath. Melting and quite gentle boiling occurred followed by a calm and then bumping. The vacuum transfer was stopped after 5 min. and the trapped material (0.040 g.) was subjected to gas chromatography. Retention times and relative peak areas showed this material to be mostly benzyl chloride (~0.03 g., 25%) and toluene (~0.005 g., 6%). A small amount of benzyl formate also appeared to be present, but no benzyl alcohol could be detected. High-temperature gas chromatography of the nonvolatile materials revealed the presence of **4**, and this was followed off the column by two compounds with long retention times thought to be the two esters analogous to **18** and **21**. The relative peak areas of **4** and the two following compounds led to an estimate of 3:1 for the ratio of bridge loss to bridge opening, in good agreement with the benzyl chloride yield. Two other major products with boiling points estimated in the 250° range were also detected by gas chromatography of the nonvolatiles but were not identified.

Relative Amounts of 2,3,4,5-Tetrachlorobiphenyl Produced on Pyrolysis of **2a** *and* **2c**. Equimolar amounts (0.273 mmole) of the dimethyl ketal **2a** (0.100 g.) and the dibenzyl ketal **2c** (0.143 g.) were added to separate, 1-ml. portions of di-*n*-butyl phthalate. The mixtures were warmed to effect solution and then were placed under a nitrogen atmosphere by evacuating and filling with nitrogen several times. The flasks were heated in a 160° oil bath for 20 min. Resulting solutions were gas chromatographed to determine the ratio of the peak areas of the solvent di-*n*-butyl phthalate and the tetrachlorobiphenyl **4**. The ratio was found to be 17.6:1 for the solution originally containing the dimethyl ketal and 16.3:1 for the other solution. This indicates that a slightly higher percentage of **2c** fragments to give bridge loss than does **2a** under the same conditions.

Pyrolysis of Ketal **2d** *in the Injection Chamber of the Gas Chromatograph.* A small amount of **2d** was dissolved in benzene and injected into the Aerograph gas chromatograph with the injector at 310° and the silicone column at 150°. A small peak was observed between the air peak and the large benzene peak. Raising the temperature of the column to 250° was followed shortly by the appearance of a peak for **4** and eventually by two more peaks possibly attributable to esters analogous to **18** and **21**.

Pyrolysis of Ketals **3a** *and* **3b** *in Decalin.* Ketal **3a** (0.262 g.) was dissolved in 2.62 ml., and **3b** (0.300 g.) was dissolved in 3.00 ml. of decalin. Both solutions were heated at 155–165° under nitrogen for 1 hr. A very approximate analysis of the pyrolysis products by

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[66] "Mass Spectral Data," American Petroleum Institute Research Project 44, 1947–1961, No. 23 and 157.

[67] Purified by Dr. Kyung Shim according to the procedure of P. D. Bartlett and R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

vapor chromatography showed a 102% yield of 2,3,4,5-tetrachlorotoluene from **3b** and an 84% yield of the same from **3a**; none of the trichlorotoluate ester was detected in either case. The two pyrolysis solutions were combined and the decalin distilled to give 413 mg. (96.5% total yield, m.p. 95–97°) of the toluene after one recrystallization from ethanol. Further recrystallization gave analytically pure material: m.p. 97–98° (lit.[68] m.p. 97–98°); infrared $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.93, 7.12, 7.45, 8.50, 9.20, 9.89, 11.55, and 12.03 μ; n.m.r. (CCl_4) singlets at $\delta = 2.40$ p.p.m. (methyl) and $\delta = 7.23$ p.p.m. (aryl).

Pyrolysis of 2,3-Dicarbomethoxy-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene. The Diels–Alder adduct of hexachlorocyclopentadiene and dimethyl acetylenedicarboxylate was prepared by heating 8.0 g. (0.03 mole) of the diene with 4.25 g. (0.03 mole) of the acetylene at 150° for 2 days. Cooling the resulting solution and adding methanol gave 8.6 g. (65%) of nearly white crystals. After one recrystallization from methanol the material melted at 82–84°. A portion of the product was placed in a test tube which was then heated in a Wood's metal bath. One-half hour at 250° was sufficient to give a dark coloration, but the infrared spectrum showed little change from that of starting material. A temperature of 270° for the same amount of time did cause the decomposition reflected in the infrared spectrum.

Pyrolysis of 1,2,3,4,7,7-Hexachloro-5-phenylbicyclo-[2.2.1]hepta-2,5-diene.[69] The hexachlorodiene (1.0 g.) was pyrolyzed at 270–280° for 30 min. and the resulting dark oil was chromatographed on alumina. Ninety per cent of the material was eluted by 60–68° petroleum ether in the first four fractions as a colorless oil which refused to crystallize. A 0.1585-g. (0.422-mmole) portion of this oil was dissolved in excess methanolic potassium hydroxide and the solution was heated at reflux for 3 days. The methanol was evaporated and the residue was dissolved in water. An ether extraction removed the water-insoluble materials. Acidification of the aqueous solution followed by ether extraction and evaporation of the ether yielded 0.084 g. (66%) of crystalline, acidic material. This was treated with diazomethane in ether solution and the product was recrystallized from methanol to give a first crop of 0.032 g. (36%), m.p. 104.5–105.8°, and a second crop of 0.024 g. (27%), m.p. 101–103.2°, of **18**. The melting point of the first crop was undepressed when mixed with authentic **18**. The two crops represent only a 37% yield from the original diene, but since the yields in each step were well over 50% it appears that the pyrolysis yielded more 2,3,4-trichloro-5-(trichloromethyl)-biphenyl than the isomer bearing *ortho* phenyl and trichloromethyl substituents.

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(68) J. B. Cohen and H. D. Dakin, *J. Chem. Soc.*, **89**, 1453 (1906).

(69) This compound was kindly furnished by Dr. Albert J. Fry who prepared it according to McBee's procedure,[12] but obtained it as crystals, m.p. 96–98°, after one recrystallization from heptane, instead of as an oil.