154-155° (lit.[8] m.p. 152-154°). Filtrate from this operation was concentrated to a solid residue. Recrystallization from methanol gave 1.7 g. (4%) of isonicotinamide 1-oxide, m.p. 298-300° dec. (lit.[7] m.p. 303° dec.).

Anal. Calcd. for $C_6H_6N_2O_2$: C, 52.2; H, 4.4; N, 20.3. Found: C, 52.6; H, 4.7; N, 19.7.

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Chromic Acid Oxidation of Tetraarylethylenes[1]

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The oxidation of tetraphenylethylene (I) with diacetyl chromate (chromium trioxide in acetic anhydride) gives high yields of benzpinacol carbonate (III) in addition to tetraphenylethylene oxide (II) and benzophenone. A variety of other tetraarylethylenes have been oxidized to cyclic carbonates by this reagent, thus making available compounds which cannot be prepared from the glycols by normal methods. The reaction is not stereospecific when *cis* and *trans* forms of an olefin are oxidized. A mechanism for these oxidations is proposed, wherein the carbonate arises from the reaction of the intial olefin-chromic acid complex with a source of acetate ion, followed by the formation of an intermediate ketene acetal, which undergoes further oxidation. Tetraphenylethylene oxide was isolated from permanganate oxidation of I, this being the first example of the formation of an epoxide by olefin oxidation with this reagent. Infrared spectral data on a number of new cyclic carbonates are presented.

Much attention has recently been given to the mechanisms of chromic acid oxidation of organic compounds.[3] Of the various types of substrates studies, the isolated double bond has been somewhat overlooked and considerable disagreement seems to exist on the manner in which chromic acid attacks the olefinic linkage. Hickinbottom and his co-workers[4] have studied the nature of products obtained from aliphatic olefins by oxidation with chromium trioxide in aqueous sulfuric acid and in acetic anhydride; they propose electrophilc attack of chromium trioxide at the negative end of the double bond, followed by reaction with water (in the aqueous oxidations only) to give the conjugate acid of an epoxide, from which subsequent product-forming paths can be formulated. In acetic anhydride medium the epoxides were isolatable.[4] Zeiss and Zwanzig[5] have alternatively suggested a cyclic chromate ester to explain the absence of rearrangement products in the oxidation of 1-methyl-α-fenchene to camphor. Hickinbottoms's objections[4] to the Zeiss mechanism were its alleged inability to explain the formation of 1,4-enediones upon oxidation of terpenoid β,γ-unsaturated alcohols,[6] and the difference between chromic acid oxidation of olefins and the attack on alkenes by osmium tetroxide[7] or potassium permanganate,[8] both of which have been shown to proceed *via* cyclic ester intermediates. With regard to the first contention, regarding oxidation of unsaturated carbinols, Nichols and Schipper[9] showed that the chromic acid oxidation of ricinoleic acid to *trans*-9,12-dioxo-10-octadecenoic acid does not proceed *via* the β,γ-epoxide, which might have arisen from a cyclic chromate ester. However, the claim that chromic acid and permanganate oxidize to different products is not entirely valid. In the present work we report the first case of the isolation of an epoxide as product from a permanganate oxidation (*vide infra*). Moreover, Wiberg[10] has demonstrated the mechanistic similarity of these two reagents in the oxidation of benzaldehyde. Wiberg has also pointed out that the actual form of chromium trioxide in solution may change with the solvent and that this factor can lead to different types of products.[11]

The present study was undertaken in order to consider more closely the initial mode of attack by chromic acid upon an isolated double bond. Tetraphenylethylene (I) was chosen as a model compound for this investigation because the absence of vinylic and allylic hydrogens reduces potential complexities which might arise from allylic attack or further oxidation of rearranged primary products. Behr[12] reported the oxidation of I in boiling, glacial acetic acid and claimed that tetraphenylethylene oxide (II) was the major product,

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[1] Presented in part at the 135th meeting of the American Chemical Society, Boston, Mass., April, 1959.

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[3] W. A. Waters, *Quart. Revs.*, **12**, 277 (1958), and references cited therein.

[4] M. A. Davis and W. J. Hickinbottom, *J. Chem. Soc.*, 2205 (1958), and earlier papers in the series.

[5] H. H. Zeiss and F. R. Zwanzig, *J. Am. Chem. Soc.*, **79**, 1733 (1957).

[6] D. H. R. Barton, N. J. Holness, K. H. Overton, and W. J. Rosenfelder, *J. Chem. Soc.*, 3751 (1952).

[7] R. Criegee, *Annalen*, **522**, 75 (1936).

[8] K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 2822 (1957).

[9] J. Nichols and E. Schipper, *J. Am. Chem. Soc.*, **80**, 5705 (1958).

[10] K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958).

[11] K. B. Wiberg, Abstracts of the 16th National Organic Symposium, Seattle, Wash., July, 1959, pp. 105-106.

[12] A. Behr, *Ann.*, **5**, 277 (1872).

TABLE I

OXIDATION OF TETRAPHENYLETHYLENE UNDER VARIED CONDITIONS

3 mmoles of alkene oxidized by 5–6 mmoles CrO_3 at 90–95°

Solvent	Added Salt	Products,[a] % Yield				
		T	E	P	C	K
H_2O, HOAc	—	—	36–56	5–16	—	26–44
HOAc	—	—	70	—	—	16
Ac_2O	—	—	57	—	19	11
HOAc, Ac_2O	—	—	51–69	—	13–27	10–20
HOPr, Pr_2O	—	23	43	—	8	10
HOAc, Ac_2O	NaOAc (30 mmoles)	—	59	—	30	Not isolated
HOAc, Ac_2O	NaOAc (100 mmoles)	—	52	—	29	Not isolated
HOAc, H_2O	NaOAc (100 mmoles)	—	77	Trace	—	Not isolated
HOAc, Ac_2O	KOAc (100 mmoles)	32	12	—	42	Not isolated
		32	14	—	41	3

[a] T = tetraphenylethylene; E = tetraphenylethylene oxide; P = benzpinacolone; C = benzpinacol carbonate; K = benzophenone.

in unstated yield and without mention of by-products. We have confirmed these results, noting that II can be consistently obtained in 50–70% yield (Table I) when the reaction mixture contains no water; in aqueous acetic acid medium some benzpinacolone is formed by rearrangement of the epoxide. An immediate objective, therefore, was to to determine what by-products are formed in the oxidation of I in acetic acid containing excess acetic anhydride to maintain anhydrous conditions.

Careful work-up of the mother liquors, after filtration of II, afforded benzophenone in 10–20% yield and also a second crystalline by-product, m.p. 170–171°, whose composition was $C_{27}H_{20}O_3$. This material was inert toward hot acetic acid which contained hydrochloric acid, but readily cleaved by alcoholic potash into benzophenone, benzhydrol and potassium carbonate. In accord with these data and the infrared spectrum, which displayed a strong broad carbonyl band at 5.60 μ,[13] the 171° product was formulated as benzpinacol carbonate (III). It is also significant that III was formed in an oxidation conducted in propionic acid-propionic anhydride medium, thus excluding the possibility that III possessed any acetate groups. All attempts to prepare III from benzpinacol by means of phosgene and pyridine, or with diethyl carbonate and sodium ethoxide (as well as other transesterification catalysts), failed.

Before proceeding to a discussion of scope and mechanism for this novel, one-step oxidation of olefins to carbonates, it is necessary to demonstrate that each product is a *primary* product, arising directly from some transition state or intermediate consisting of I and the oxidant[14] and not as a result of further reaction of an initially formed product. It was possible to recover II, III, and benzophenone, each in greater than 90% yield, when these materials were subjected to oxidizing conditions identical with those employed with I itself. When II was oxidized in aqueous acetic acid, rather than in the presence of acetic anhydride, some rearrangement to benzpinacolone was observed, as is the case when I is similarly treated. The epoxide was also recovered unchanged from prolonged treatment with lithium aluminum hydride, illustrating the remarkable stability of II toward nucleophiles.

Table I summarizes the results of some representative oxidations of I, using various solvents and additives. *No benzpinacol carbonate is formed unless the reaction mixtures contain acetic anhydride* (*or propionic anhydride*). Carbonate formation predominates when potassium acetate is added to the reaction mixture (62% yield, based on compound I used), there being a simultaneous drop in the rate of oxidation, as indicated by the slower color change from orange to green, and also incomplete consumption of I, whereas no olefin was recovered in runs without added acetate. Sodium acetate had a lesser effect on the rate of oxidation and the yield of III.

Table II summarizes the properties of other carbonates, all new compounds, obtained from other arylethylenes.

1,2-Diphenylacenaphthylene (IV) gave 1,8-dibenzoylnaphthalene (V) in approximately 90% yield, both in aqueous acetic acid and in the pre-

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[13] J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 618 (1957).

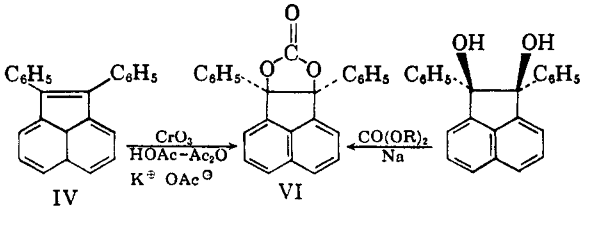
[14] Graham and Westheimer (*J. Am. Chem. Soc.*, **80**, 3030 (1958)) observed that isopropyl alcohol was oxidized much faster by chromic acid in acetic acid than in water, their explanation being that monoacetyl chromic acid was the oxidant in the former case and that this species would be more acidic than chromic acid. In acetic anhydride medium, however, the actual species is probably diacetyl chromate (Reference 11).

TABLE II

PHYSICAL PROPERTIES OF CYCLIC CARBONATES

						Infrared Bands	
		Calcd.		Found		Stretching Vibrations	
Name	M.P.	C, %	H, %	C, %	H, %	>C=O	—C—O—
Tetraphenylethylene carbonate (III)	170–171°	82.63	5.14	82.65	5.06	5.60 μ	7.97 μ
Tetrakis(*p*-bromophenyl)ethylene carbonate	210–211°	45.80	2.28	45.44	2.46	5.54	8.02 8.20 9.90
1,2-Diphenylacenaphthylene carbonate (VI)	196.5–197.5°	82.40	4.43	82.39	4.33	5.54	8.05 8.25 9.46
Diphenylenediphenylethylene carbonate	228–228.5°	83.06	4.65	82.65	4.79	5.55	8.05 8.22 9.77
dl-α,α′-Dimethylhydrobenzoin carbonate	120.5–121°	76.10	6.01	76.14	5.96	5.59	7.92 8.12, 9.50 9.86
meso-α,α′-Dimethylhydrobenzoin carbonate	129.5–130°	76.10	6.01	76.20	5.90	5.59	7.97 9.32, 9.75
dl-1,2-Bis(*p*-chlorophenyl)-1,2-diphenylethylene carbonate	164–166°	70.29	3.93	70.22	3.86	5.51	8.40, 9.45 9.95
meso-1,2-Bis(*p*-chlorophenyl)-1,2-diphenylethylene carbonate	142–144°	70.29	3.93	70.10	3.90	5.52	8.05, 9.05 9.65, 10.04

sence of acetic anhydride. Bartlett and Brown[15] have pointed out that the corresponding epoxide would not be stable because of strain already associated with the five-membered ring in IV, and all of their attempts to epoxidize IV were unsuccessful. Indeed the possibility of fusing another five-membered ring, such as a cyclic carbonate function, onto the acenaphthene bridge (*cis* fusion) seemed quite unlikely from an examination of molecular models. It is, therefore, not surprising that V is the major product. However, when IV was oxidized in the presence of potassium acetate, *cis*-1,2-diphenylacenaphthenediol carbonate (VI) was obtained in 25–30% yield, in addition to V. Compound VI was also synthesized by a base-catalyzed ester interchange of diethyl carbonate and *cis* - 1,2 - diphenylacenaphthenediol, which failed when applied to benzpinacol, thus providing unambiguous proof of the structure and sterochemistry of the carbonate.



The isolation of VI, in a case where the corresponding epoxide would be too strained to exist, provides further evidence that epoxide formation must neither precede nor occur concomitantly with carbonate formation.

The oxidation of a tetraarylethylene containing electron-attracting groups substituted on the rings seemed worthwhile in seeking more information pertainable to possible mechanisms. Gorvin[16] has expressed preference for a cyclic chromate[5] rather than a carbonium ion intermediate,[4] to rationalize the formation of tetrakis(*p*-nitrophenyl)ethylene oxide and 4,4′-dinitrobenzophenone from chromic acid oxidation of tetrakis(*p*-nitrophenyl)ethylene. Certainly, *p*-nitro substituents would lessen the stabilization of positive charge at a benzylic carbon atom. We oxidized tetrakis(*p*-bromophenyl)ethylene and found that the yields of carbonate ester were higher without (33%) or with added potassium acetate (66%) than in the analogous oxidation of I.

The oxidation of diphenylenediphenylethylene in the presence of potassium acetate gave a good yield of carbonate (48%) but no epoxide was isolated. 9,10-Diphenylphenanthrene, upon oxidation, gave some carbonate (identified by strong infrared absorption at 5.52 μ) although the product could not be isolated in pure form. In this hydrocarbon the tetraarylated double bond is actually part of the phenanthrene system. Hence, one might predict oxidative attack at a less substituted position on the nucleus. This appears to be the case, as an unidentified red product, probably an *ortho*-quinone, was isolated from this oxidation. The oxidation of

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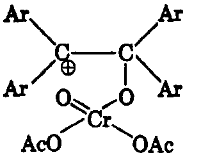
(15) P. D. Bartlett and R. F. Brown, *J. Am. Chem. Soc.*, 62, 2927 (1940).

(16) J. H. Gorvin, *J. Chem. Soc.*, 678 (1959).

trans-α,α′-dimethylstilbene gave a complex mixture of carbonyl compounds from which only about 1% yield of *dl*-α,α′-dimethylhydrobenzoin carbonate was obtained (*vide infra*). No carbonate ester was isolable when tetramethylethylene was oxidized, pointing up the need for using highly arylated ethylenes in this connection. Only tetraarylethylenes appear to give high yields of the corresponding pinacol carbonates. However, tetraaryl pinacols are susceptible to rearrangement by acids and cleavage by bases and hence this method of carbonate formation constitutes a useful synthesis of these heretofore unavailable compounds. From a preparative standpoint, carbonates not accessible by this oxidative method, such as pinacol carbonate, can be easily made by standard methods.

In order to check for the intermediacy of a carbonium ion intermediate (A), as opposed to a nonionic cyclic chromate (B), a pair of geometrically isomeric tetraarylethylenes, *cis*, and *trans*-1,2-bis-(*p*-chlorophenyl)-1,2-diphenylethylene, was prepared and oxidized in the usual manner, excluding potassium acetate.[17] It was felt that even though structure A might be involved, pinacolone formation in anhydrous oxidations would not be inevitable, as the —O—Cr— bonding electrons are pulled toward chromium; hence, the driving force associated with forming the carbonyl group, as in the pinacol rearrangement, is absent and the lack of rearrangement is explained. From either of the 1,2-bis(*p*-chlorophenyl)-1,2-diphenylethylenes was obtained a mixture of diastereomeric epoxides (22–24%) and carbonates (51–53%). By a series of fractional crystallizations from aqueous ethanol, the epoxide fraction afforded the less soluble *dl*-epoxide,[18] m.p. 218–220°, and the *meso*-epoxide, m.p. 165.5–167.5°, in approximately equal amounts. Likewise, the carbonate fractions from the oxidation of either isomer (the infrared spectra of both were superimposable) were separated into racemic carbonate, m.p. 164–166°, and the *meso* isomer, m.p. 142–144.°[19] A 50:50 mixture of these gave an infrared spectrum very similar to the crude reaction mixtures. This information indicates that the oxidation of tetraaryl-ethylenes is not stereospecific and must involve a carbonium ion intermediate. The fact that *trans*-α,α′-dimethylstilbene gave pure *dl*-α,α′-dimethylhydrobenzoin carbonate,[20] rather than a mixture of diastereomeric carbonates, is due, in this case, to the formation of the more stable isomer, in which the phenyl groups have acquired the favorable *trans* relationship. Thus,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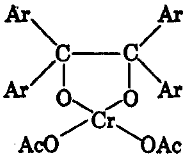
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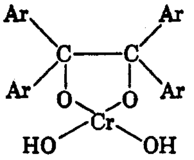
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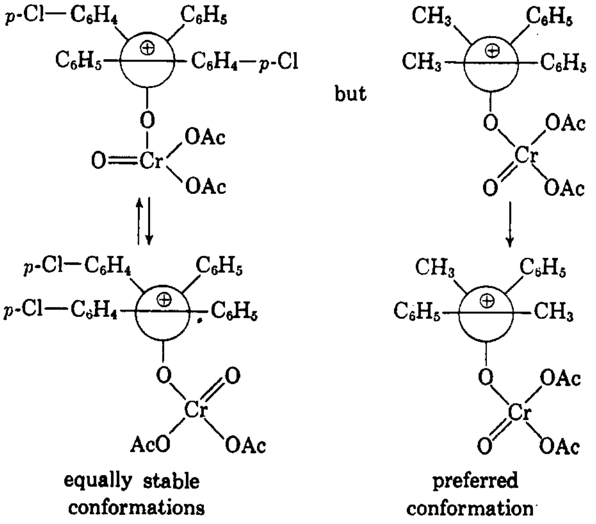

A mechanistic scheme consistent with the experimental data is presented below. Diacetyl chromate is pictured as the oxidant although monoacetyl chromate or free chromic acid can be equally adapted to this scheme. It is assumed that a cyclic chomate ester, which is in equilibrium with the open-chain chromate, may be involved. Several simultaneous modes of reaction are open to the intermediate. Decomposition, preferably of the cyclic ester, can readily account for the formation of epoxide and diaryl ketone by simple electronic shifts,[5] whereas the carbonate may arise from either structure.

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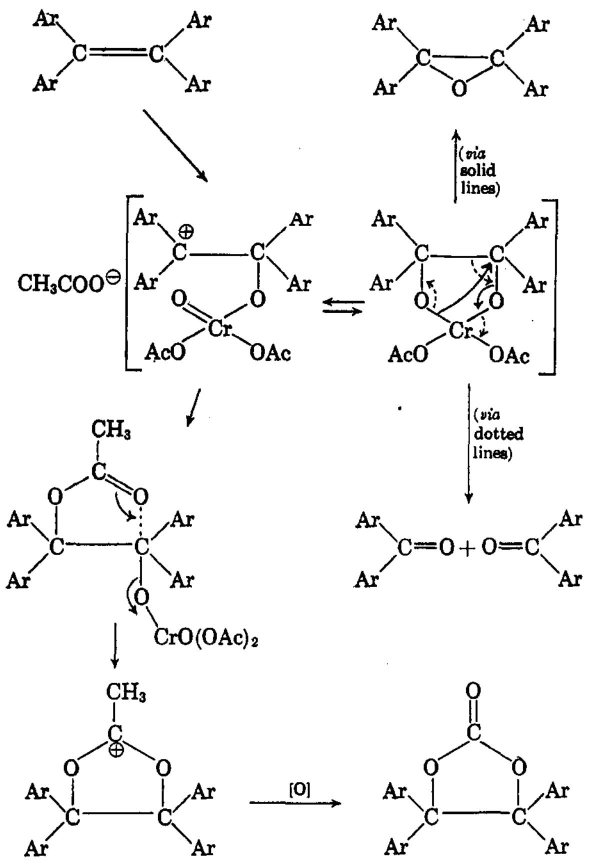
[17] This pair was chosen because both isomers should have nearly equal thermodynamic stability. It was established that strong acid of the type at hand in these oxidations does not isomerize the pure olefins, in accord with Gold's data (*J. Chem. Soc.*, 2167, 2181 (1952)) on the basicity of conjugated hydrocarbons. Another factor in selecting these olefins was the expectation that favorable yields of carbonate would result with electron-withdrawing *para*-substituents present, as was the case with tetrakis(*p*-bromophenyl)ethylene.

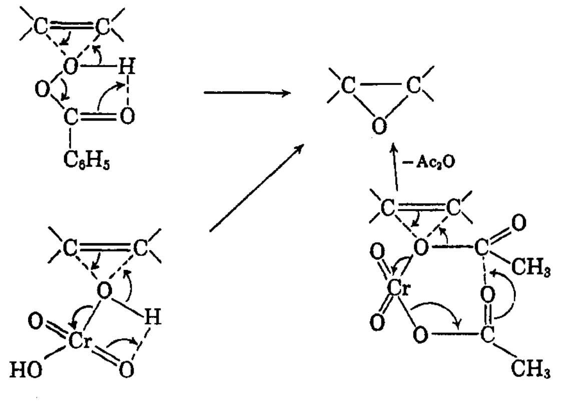
[18] Assignments of configuration are only arbitrary and are based on the solubilities of both the epoxides and carbonates. In each case the low-melting *meso*-isomer is much more soluble than the higher-melting one as expected.

[19] The *meso* form was slightly contaminated by the *dl*-form, as indicated by weak shoulders at 9.45 and 9.95 μ in the infrared.

[20] Both *meso*- and *dl*-α,α′-dimethylhydrobenzoin carbonates were prepared from the isomeric pinacols and were shown to be recovered unchanged from hot chromic acid treatment. Thus the initial formation of some *meso* isomer, with subsequent isomerization to the *dl* form, was ruled out.



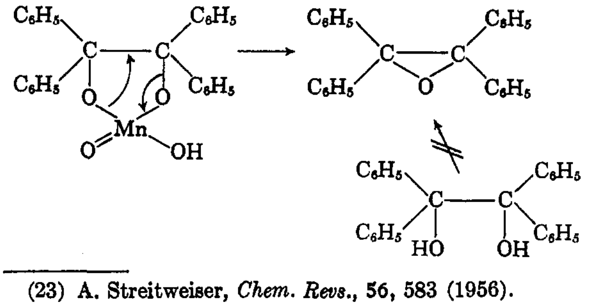
Another possible mechanism for epoxidation of I is a "three-center" type addition of the oxidant, similar to that pictured in the epoxidation of I with perbenzoic acid.[21]



Nucleophilic attack by acetate ion, or some source of acetate, on the initial complex yields an acetoxy chromate. With the groups oriented *trans* and coplanar, the acetoxy group may participate[22] in ionization of the Cr^{IV} moeity and the resultant acetoxy ion could then lose a proton to yield a ketene acetal. Immediate further oxidation of the ketene acetal would give the carbonate ester.

In accord with the proposed mechanism, the addition of acetate ion and the use of negatively substituted tetraarylethyenes result in higher yields of carbonate. The high nucleophilicity of acetate ion, compared with acetic acid or acetic anhydride, allows for more effective competition of the carbonate-forming reaction with the epoxide- and ketone-forming paths. The addition of chloride ion to the acetic acid–anhydride reaction mixture, rather than acetate, resulted in a large decrease in carbonate formation, as expected from the high nucleophilicity of chloride, relative to other species present.[23] In this latter case the reaction products were comparable to those found when chromyl chloride was the oxidant (*vide infra*). Another factor favoring carbonate formation appears to be low electron density on the benzylic carbon atoms, thus facilitating nucleophilic attack of acetate. This hypothesis is supported by the high yields of carbonate obtained from 1,2-bis-(*p*-chlorophenyl)-1,2-diphenylethylene and tetrakis-(*p*-bromophenyl)ethylene in comparison with tetraphenylethylene. The nature of the chromic acid–olefin complex may also affect the electron density at the α-carbon atoms. Hence, one reason for the requirement of acetic anhydride for carbonate formation may be that intermediate B (above) with two acetoxy groups on chromium has a greater −I effect with respect to C_α than does intermediate C (which might apply in aqueous media), in which no acetoxy groups are bonded to chromium.

One objection[4] to invoking cyclic chromates as intermediates in olefin oxidation has been the different products (*cis*-glycols initially) formed with oxidants which have definitely been shown to proceed by similar cyclic ester formation[7,8] such as permanganate. In addition to the recently reported similarity in benzaldehyde oxidation by chromium trioxide and potassium permanganate,[10] it has now been demonstrated that the analogy can be extended to tetraarylethylene oxidations, since we have isolated II in 26% yield by oxidation of I with potassium permanganate in acetic acid–acetic anhydride medium, with or without added potassium acetate. The possibility of initial glycol formation, followed by dehydration, was removed by a control experiment with benzpinacol, from which no II was obtained. This appears to be the



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[21] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

[22] E. S. Gould, ***Mechanism and Structure in Organic Chemistry***, Henry Holt and Company, New York, N. Y., 1959, Chapter 14, and references cited therein.

[23] A. Streitweiser, *Chem. Revs.*, **56**, 583 (1956).

first case of epoxide formation in permanganate oxidation and its occurrence lends further support to the similarity between this reagent and chromic oxide, in certain situations at least.

Cristol has suggested a cyclic intermediate for the Etard reaction of olefins.[24] This complex might also be expected to give rise to epoxides (since chromium oxychloride should behave somewhat like $CrO_2(OAc)_2$[11]), although *trans*-chlorohydrins were isolated from aliphatic and alicyclic olefins,[24] and therefore I was treated with chromyl chloride in acetic acid-anhydride. As anticipated, II was again obtained in 25% yield although the possibility of its formation *via* dehydrohalogenation of the chlorohydrin, rather than by direct decomposition of the Etard complex, cannot be discarded. In both this reaction and a diacetyl chromate reaction which contained added chloride ion, the epoxide could not be obtained in the usually pure form, the chief contaminant apparently being the chlorohydrin (suggested by infrared spectra and positive Beilstein test).

Finally, some discussion pertaining to the infrared spectra of the new carbonates seems worthwhile, as data of this class of compounds is comparatively scarce [13,25] and nonuniform with regard to techniques used. The position of bands in the spectra of cyclic carbonates, in particular, is extremely susceptible to the state of the sample.[13] In the present work, all spectra were recorded with samples dispersed in potassium bromide (1% concentration) and the pertinent bands recorded in Table II. Only the chief bands in the 1300–950 cm.$^{-1}$ region are listed, these being not necessarily attributed to C—O stretching vibrations.[13] The effects of negative substituents on C_α[13] and ring size[25] on the position of the C=O stretching vibrations of cyclic carbonates have been noted. It can be seen in the present series of compounds that electron-withdrawing substituents shift the carbonyl band toward higher frequencies, the greatest effect being noted in the 1,2-bis(*p*-chlorophenyl) - 1,2 - diphenylethylene carbonates, which were obtained in highest yields upon oxidation of the ethylenes (over 50%, without added acetate). One can, therefore, obtain a qualitative relationship between the tendency to form carbonates (assisted by low electron density at C_α in the olefin–chromic acid complexes, as discussed above) and the position of carbonyl absorption, which is also susceptible to inductive effects,[13] in the final product.

EXPERIMENTAL[26]

Preparation of starting materials. Tetraphenylethylene (I) was most conveniently prepared from benzpinacolone by reduction with excess lithium aluminum hydride (the ketone was introduced by Soxhlet extraction) followed by treatment of the unisolated, crude benzpinacolyl alcohol with hot acetic acid containing a few drops of sulfuric acid, (overall yield, 88%), m.p. 222–223° (from ethanol-benzene).

Tetrakis(*p*-bromophenyl)ethylene was obtained from I by bromination in the absence of solvent, using the procedure of Norris and Tibbetts[27]; yield 77%, m.p. 251–252°.

1,2-Diphenylacenaphthylene (IV) was prepared from 2,2-diphenylacenaphthenone[28] using the method of Letsinger and Lansbury.[29] The lithium aluminum hydride reduction product was not isolated but dehydrated directly with formic acid containing *p*-toluenesulfonic acid; yield, 90%, m.p. 162–162.5°.

trans-α,α'-Dimethylstilbene was kindly furnished by Dr. C. R. Hauser, Duke University.

Racemic α,α'-dimethylhydrobenzoin was prepared by the method of Ramart-Lucus and Salmon-Legagneur.[30] The *meso* isomer was obtained by reduction of acetophenone with aluminum and ethanol, according to Sisido and Nozaki.[31]

Diphenylenediphenylethylene was prepared from fluorene by metalation with phenyllithium, followed by reaction with benzophenone. The crude carbinol was dehydrated with acetic acid–anhydride, containing sulfuric acid, to yield the ethylene, m.p. 229° (yellow melt) (reported,[32] m.p. 229.5°).

9,10-Diphenylphenanthrene was prepared by the same method[29] as IV, starting from 10,10-diphenylphenanthrone; yield 48%, m.p. 239–239.5°. Reported,[33] m.p. 235°.

cis and *trans*-1,2-Bis(*p*-chlorophenyl)-1,2-diphenylethylene were prepared according to the method of Buckles and Meinhardt.[34] By fractional crystallization from ethanol-chloroform, the *trans* isomer was obtained with m.p. 203–205° (reported,[34] m.p. 205°) and the *cis* isomer had m.p. 156–158° (reported,[34] m.p. 157–158°).

General procedure for oxidations with chromium trioxide. All reactions were performed in three neck, standard taper flasks, equipped with a mercury-sealed stirrer, an addition funnel and a condenser, the latter bearing a calcium chloride drying tube in runs when water was to be exluded. Heating was provided by a steam bath (90–95°). In general, about 3 mmoles of the tetraarylethylene was dissolved in *ca.* 100 ml. of solvent (*vide infra*) and, while being stirred on the steam bath, the solution was treated dropwise (usually 15–30 min.) with 5–6 mmoles of chromium trioxide dissolved in 100 ml. of aqueous acetic acid, glacial acetic acid, or in a mixture of acetic anhydride and acetic acid. The chromium trioxide was usually initially dissolved in an equal weight of water before addition of the major solvent. For reactions in acetic anhydride, the amount of anhydride added was in great excess of the water used for dissolving the oxidant. About 5–10 min. after the oxidizing solution had been added,

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[24] S. J. Cristol and K. R. Eilar, *J. Am. Chem. Soc.*, **72**, 4355 (1950).

[25] H. K. Hall, Jr., and R. Zbinden, *J. Am. Chem. Soc.*, 6428 (1958).

[26] Melting points were taken on a Fisher-Johns block, and are uncorrected. Elemental analyses were performed by Dr. Alfred Bernhardt, Max Planck Institute, Mulheim, Germany. All infrared spectra were taken in a Baird double beam spectrometer, equipped with sodium chloride optics, using samples dispersed in potassium bromide pellets.

[27] J. F. Norris and D. M. Tibbetts, *J. Am. Chem. Soc.*, **42**, 2085 (1920).

[28] W. E. Bachman and E. Chu, *J. Am. Chem. Soc.*, **58**, 1118 (1936).

[29] R. L. Letsinger and P. T. Lansbury, *J. Am. Chem. Soc.*, **81**, 938 (1959).

[30] (a) M. Ramart-Lucus and M. E. Salmon-Legagneur, *Bull. Soc. Chim. France*, (4), **45**, 727 (1929). (b) D. J. Cram and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 2748 (1959).

[31] K. Sisido and H. Nozaki, *J. Am. Chem. Soc.*, **70**, 776 (1948).

[32] H. Klinger and C. Lonnes, *Ber.*, **29**, 2152 (1896).

[33] A. Werner and A. Grob, *Ber.*, **37**, 2887 (1904).

[34] R. E. Buckles and N. A. Meinhardt, *J. Am. Chem. Soc.*, **74**, 1175 (1952).

the solution was diluted with hot water in stages, with intermittent cooling, whereby any unchanged olefin, the tetraarylethylene oxide, the corresponding carbonate, and ketonic cleavage products could be obtained fairly pure, in the above order. In aqueous oxidations of tetraphenylethylene (I), the epoxide (II) and benzpinacolone crystallized together. After isolation of crystalline products from the dilute reaction mixtures was complete, the mother liquors were taken nearly to dryness, using a capillary bubbler and water aspirator, diluted with water, and extracted with ether and/or benzene. Work-up of the ether-benzene extracts afforded part of the carbonate and all of the benzophenone. Reactions in which chromyl chloride and potassium permanganate were the oxidant were performed in the same manner.

When sodium acetate or potassium acetate was used as an additive, it was dissolved in the initial reaction medium, together with the olefin to be oxidized.

No effort was made to exclude air from the reactions. In several cases carbon dioxide was bubbled through the mixtures during reaction but no significant changes in product distribution occurred. More specific experimental details are presented below, under individual runs.

Oxidation of tetraphenylethylene (I). (A). *In aqueous acetic acid.* One gram of I (3.01 mmoles) in 100 ml. of acetic acid was oxidized (30 min.) with 0.50 g. (5 mmoles) of chromium trioxide in 10 ml. of water and 90 ml. of acetic acid. Addition of 140 ml. of water to the dark green reaction mixture, together with cooling, gave 0.56 g. of crystalline material, m.p. 158–180°, in two crops. This was shown to consist of benzpinacolone and tetraphenylethylene oxide (II) in the following manner: A weighed portion of this mixture gave benzpinacolone quantitatively when refluxed with acetic acid which contained a trace of sulfuric acid; also, treatment of a portion of the mixture with ethanolic potassium hydroxide cleaved the ketone and left pure II,[13] m.p. 206–207°. The filtrate from the original reaction was distilled under reduced pressure, diluted with water, and extracted several times with ether. Work-up of the ether afforded 0.48 g. of benzophenone.

The products of this reaction (material balance, 96%) were: II, 36%; benzpinacolone, 16%; and, benzophenone, 44%. Several duplicate runs gave comparable yields (see Table I). When 100 mmoles of sodium acetate was used in the above oxidation, II was obtained in 77% yield, and only a trace of the pinacolone was found.

(B). *Oxidation in approximately 100% acetic acid.* One gram of I in 100 ml. of 100.2% acetic acid (prepared by addition of acetic anhydride to the acid) was oxidized by 0.50 g. of chromium trioxide, dissolved first in 1 ml. of water[35] and then diluted with 75 ml. of "100%" acetic acid and 5 ml. of acetic anhydride (giving a solution equivalent to 99.9% acetic acid). The time of addition was 40 min. and when the reaction mixture was diluted with 50 ml. of water and cooled, pure II, m.p. 206–207° was obtained (0.68 g.). Further work-up gave a small amount of II (total yield, 70%) and benzophenone (16%).

(C). *Oxidation in acetic anhydride and acetic acid.* The olefin (1 g.) was dissolved in 85 ml. of acetic acid and 15 ml. of acetic anhydride and the oxidant (0.50 g.) dissolved in 0.5 ml. of water, which was then diluted with 75 ml. of acetic acid and 25 ml. of acetic anhydride. During 30 min., the solution of diacetyl chromate was gradually added and the reaction mixture, after 5 min. more stirring, worked up as above. A sample of II (0.53 g., 50%) crystallized from the diluted solution, whereas 0.32 g. of III (27%) and 0.07 g. of benzophenone (7%) were obtained by concentration of the mother liquors, using the ether extraction procedure.

In Table I are tabulated data pertaining to the effect of added sodium or potassium acetate in these reactions. In all oxidations of tetraarylethylene which utilized acetate, the orange color of Cr^{VI} usually persisted until almost half of the oxidant had been added (10–20 min.), whereas in the absence of the added salt, the characteristic emerald green color of Cr^{III} appeared as soon as the oxidizing solution was added to the olefin. When potassium acetate was the additive, unchanged I was recovered in *ca.* 30% yield and the yields of II (14%) and benzophenone (3%) were sharply reduced in favor of carbonate formation (42%).

Addition of 30 mmoles of lithium chloride to the reaction mixture gave 0.46 g. of solid, m.p. 180–190°, whose infrared spectrum resembled that of II, except for additional low intensity bands at 7.05, 9.10, 9.82, and 12.13 μ. Further work-up gave 0.01 g. of solid, m.p. 110–135°, which showed carbonate absorption at 5.60 μ. No other products were isolated.

(D). *Oxidation in acetic anhydride.* One gram of I and 0.50 g. of chromium trioxide were allowed to react in the usual manner, in 200 ml. of acetic anhydride. Initial dilution of the reaction mixture was quite exothermic in this case. 87% of the starting material was accounted for, as follows: II, 57%; III, 19%; and, benzophenone, 11%.

(E). *Oxidation in propionic acid and propionic anhydride.* A mixture of 85 ml. of propionic acid and 15 ml. of propionic anhydride containing 1.0 g. of I was slowly treated with 0.50 g. of chromium trioxide in 75 ml. of the acid and 25 ml. of the anhydride. The reaction mixture was worked up in the usual manner, giving rise to 23% recovery of I, 43% of II, 8% of III, and 10% of benzophenone.

Characterization of benzpinacol carbonate (III). This ester, m.p. 170–171° (from dilute ethanol or benzene-ligroin), was characterized by a strong carbonyl band at 5.60 μ in the infrared spectrum. III was cleaved[36] quantitatively with ethanolic potassium hydroxide into benzophenone, benzhydrol, and carbon dioxide (isolated as potassium carbonate)

Anal. Calcd. for $C_{27}H_{20}O_3$: C, 82.63; H, 5.14; M.W. 392. Found: C, 82.65; H, 5.06; M.W. (Rast), 389.

III was recovered unchanged from refluxing acetic acid which contained hydrochloric acid.

Oxidation of the tetraphenylethylene oxidation products. A solution of II (0.42 g.) and chromium trioxide (0.13 g.) in 65 ml. of acetic acid and 50 ml. of acetic anhydride was warmed on the steam bath for 30 min., then diluted with water and allowed to cool. 93% of the epoxide was recovered. No other products were isolated. In aqueous acetic acid, this treatment partially converted II into benzpinacolone.

Compound III was recovered in 96% yield from similar treatment. Likewise, benzophenone was obtained in 89% recovery from the action of hot diacetyl chromate.

Oxidation of tetrakis(p-bromophenyl)ethylene. (A) Following the same procedure as with I, the olefin (1 g.) was oxidized in acetic acid and water (200 ml. volume), to which 15 ml. of benzene had been added to insure solution of the olefin, with 0.20 g. of chromium trioxide. After the usual heating and dilution, tetrakis(*p*-bromophenyl)oxirane was obtained as a white, granular solid, m.p. 285–286°, in 64% yield. The infrared spectrum showed no carbonyl absorption.

Anal. Calcd. for $C_{26}H_{16}OBr_4$: C, 47.02; H, 2.43. Found: C, 47.12; H, 2.60.

Tetrakis(*p*-bromophenyl)oxirane was slowly rearranged to the pinacolone,[37] m.p. 238–239.5°, by hot acetic acid-sulfuric acid. The ketone was subsequently cleaved by alkali, into *p*-bromobenzoic acid and tris(*p*-bromophenyl)-methane.

Concentration of the filtrates from the oxidation gave bis-(*p*-bromophenyl)ketone,[38] m.p. 171–173°, in 30% yield.

(B) Using procedure C (above) the oxidation in acetic acid–acetic anhydride afforded 40% yield of the epoxide, 21% yield of the ketone, and 33% yield of the cyclic car-

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[35] Chromium trioxide does not dissolve in "100%" acetic acid.

[36] W. Thörner and T. Zincke, *Ber.*, **10**, 1473 (1877).

[37] A. Schonberg, *Ann.*, **436**, 205 (1924).

[38] H. Biltz, *Ann.*, **296**, 235 (1903).

bonate ester of tetrakis(*p*-bromophenyl)ethylene glycol, m.p. 210–211° (from ethanol).

Anal. Calcd. for $C_{27}H_{16}O_3Br_4$: C, 45.80; H, 2.28; Br, 45.15; M.W. 708. Found: C, 45.44; H, 2.46; Br, 45.68; M.W. (Rast) 680.

The infrared spectrum had a strong carbonyl band at 5.55 μ. Ethanolic potassium hydroxide converted the carbonate into potassium carbonate (86% yield), bis(*p*-bromophenyl)ketone, and bis(*p*-bromophenyl)carbinol, m.p. 115–116° (from dilute ethanol), the latter being oxidizable to the ketone.

Another oxidation of tetrakis(*p*-bromophenyl)ethylene (2.7 mmoles) by chromium trioxide (6 mmoles) in acetic acid–acetic anhydride, to which 30 mmoles of potassium acetate had been added, resulted in a 39% recovery of starting material and a 39% yield of carbonate (66%, based on olefin used).

Oxidation of 1,2-diphenylacenaphthylene (IV). (A) *In acetic acid–acetic anhydride.* Using the same conditions and techniques employed for the oxidation of I, 0.92 g. (3 mmoles) of 1,2-diphenylacenaphthylene was oxidized by 5 mmoles of chromium trioxide. Extensive dilution and cooling of the reaction mixture afforded 0.90 g. (89%) of 1,8-dibenzoylnaphthalene (V), m.p. 183–186°, which had m.p. 190–191.5° after recrystallization from ethanol-acetone. No mixed melting point depression was observed with an authentic sample of the diketone and the two infrared spectra were identical. No other products were isolated.

(B) *In aqueous acetic acid.* The procedure was essentially that used for I. A sample of, IV, 0.92 g., gave 0.96 g. (95%) of pure V, m.p. 189–190°. Again, no epoxide or 2,2-diphenylacenaphthenone, both of which should be less soluble than V, were found.

(C) *In acetic acid–acetic anhydride with added potassium acetate.* Following the usual procedure and using a total of 95 ml. of acetic acid and 75 ml. of acetic anhydride, 1.84 g. (6 mmoles) of IV was treated with 1.2 g. (12 mmoles) of chromium trioxide, in the presence of 5.86 g. (60 mmoles) of potassium acetate. Dilution of the reaction mixture with 150 ml. of hot water and subsequent cooling afforded 1.04 g. of crystalline product, m.p. 164–183°, whose infrared spectrum showed strong bands at 6.07 μ (V) and 5.55 μ (VI), the former being of higher intensity. Further dilution and cooling furnished an additional gram of mixed V and VI, m.p. 144–158°, whose infrared spectrum indicated that VI was the major component. Fractional sublimation (185°/3 mm.) of this mixture did not provide any separation of the compounds (the intensity ratios of the two carbonyl bands in the residue and sublimate were nearly identical) and Girard's T reagent did not separate the ketone from the carbonate. Finally, a series of fractional crystallizations, using aqueous acetone, separated the less soluble V from the crude carbonate, m.p. 182–190°. Recrystallization from 50% ethanol (Darco) provided an analytical sample of *cis*-1,2-diphenylacenaphthenediol carbonate, m.p. 196.5–197.5°, which did not depress the melting point of authentic VI, whose preparation by another method is described below.

Anal. Calcd. for $C_{25}H_{16}O_3$: C, 82.40; H, 4.43. Found: C, 82.39; H, 4.33.

The yields of product in this reaction were 60% V and 27% VI, although some material may have been lost in separation of the two. Considerable amounts of VI were also obtained in duplicate runs with potassium acetate, and also with added sodium acetate, although the ketone:carbonate ratio was much greater in this instance. Spectral data for VI is given in Table II.

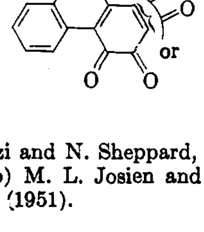
An alternative synthesis of VI involved the reaction of *cis*-1,2-diphenylacenaphthenediol[39] with diethyl carbonate and sodium ethoxide. The diol (0.5 g.) was dissolved in excess diethyl carbonate, containing a small piece of sodium, and the mixture heated for 3 hr. at 140–180° in an oil bath. Samples of the distillate were periodically withdrawn and tested with ceric nitrate reagent until a negative alcohol test resulted, the mixture being treated with fresh portions of diethyl carbonate after each sample of distillate was taken. The reaction mixture was then poured into 50% ethanol which contained 2–3 ml. of acetic acid (to neutralize the sodium hydroxide), causing precipitation of crude VI, m.p. 168–183°, which was recrystallized from 50% ethanol: m.p. 194–196.5°. A mixed m.p. with VI obtained by oxidation of IV, m.p. 196.5–197.5°, was 193–196°. The infrared spectra of the two samples were superimposable.

Oxidation of diphenylenediphenylethylene. The general procedure for oxidation in acetic acid-acetic anhydride, using potassium acetate, was followed. One gram (3 mmoles) of the olefin and 3.0 g. (30 mmoles) of potassium acetate. were oxidized by 0.60 g. of chromium trioxide in 110 ml. of acetic acid and 38 ml. of acetic anhydride. The addition of 150 ml. of water and cooling afforded 0.57 g. (48%) of crude carbonate, m.p. 187–192°, whose infrared spectrum was identical with that of pure diphenylenediphenylethylene carbonate, m.p. 228–228.5°, obtained by extensive recrystallization from 75% ethanol. No other products resulted from this purification, nor was any starting material recovered. The infrared spectrum was taken and the pertinent peaks recorded in Table II.

Anal. Calcd. for $C_{27}H_{18}O_3$: C, 83.06; H, 4.65. Found: C, 82.65; H, 4.79.

From the mother liquors, after filtration of the carbonate, was obtained an additional 0.05 g. of colorless crystals, m.p. 137–143°, the infrared spectrum of which showed a ketonic carbonyl band at 6.04 μ, in addition to the equal intense 5.55 μ carbonate band. The ketone is probably 9-benzoyl-9-phenylfluorene, one of the reported oxidation products,[33] rather than 10,10-diphenyl-9-phenanthrone, which has the carbonyl stretching band at 5.9 μ. After removal of the 137–143° product, the filtrate was concentrated and extracted with benzene, as above, yielding eventually an orange oil from which crystalline fluorenone, m.p. and mixed m.p. 82.5–83°, was obtained.

Oxidation of 9,10-diphenylphenanthrene. Using the usual proportions of hydrocarbon (3 mmoles), potassium acetate (30 mmoles), and chromic anhydride (6 mmoles), the oxidation was carried out in acetic acid–anhydride. Some starting material was recovered upon diluting the reaction mixture. Further addition of water afforded an amorphous, flesh-colored solid, m.p. 90°. The infrared spectrum showed strong carbonate absorption (5.52 μ), and other carbonyl bands at 5.66 μ (?) and 6.05 μ (quinone). Chromatography over alumina, with benzene eluant, followed by recrystallization separated this solid into starting material, crude carbonate, as feathery white flakes which could not be obtained analytically pure by recrystallization from dilute ethanol, and a bright, orange-red crystalline solid, m.p. 256–257°, which was virtually insoluble in absolute ethanol. This latter product had a strong carbonyl band at 6.05 μ, with a shoulder at 6.07 μ and a medium intensity band at 6.16 μ. Not enough material was available for further study, but a possible formulation is an "extended" *para*-quinone or an *ortho*-quinone such as that shown below. The position of the infrared bands are in accord with a polynuclear quinone[40] of either type.



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[39] G. Witting, M. Leo, and W. Weimer, *Ber.*, **64**, 2405 (1940).

[40] (a) D. Hadzi and N. Sheppard, *J. Am. Chem. Soc.*, **73**, 5460 (1951). (b) M. L. Josien and N. Fuson, *J. Am. Chem. Soc.*, **73**, 478 (1951).

Oxidation of cis- and trans-1,2-bis(p-chlorophenyl-1,2-diphenylethylene. (A) *The trans isomer.* Seven-tenths of a gram of the olefin in 25 ml. of acetic acid and 15 ml. of acetic anhydride was oxidized by a solution of 0.4 g. of chromium trioxide in 25 ml. of acetic acid and 10 ml. of the anhydride, in the usual manner. The addition of 30 ml. of hot water and cooling produced 0.16 g. (22%) of crystalline solid, m.p. 197–205° which gave a melting point depression upon mixing with starting olefin. This material, which was a mixture of diastereomeric epoxide, was fractionally crystallized from ethanol-benzene. The less-soluble isomer, presumed to be the *dl*-racemate, had m.p. 218–220° (long needles); the infrared spectrum had the following bands, among others, which were not present in the spectrum of the *meso* isomer: 13.20, 13.55, 14.32, and 15.50 μ.

Anal. Calcd. for $C_{26}H_{18}OCl_2$: C, 74.82; H, 4.35. Found: C, 74.84; H, 4.31.

After several more crops of solid were collected from the ethanol-benzene solution, the pure *meso*-1,2-bis(*p*-chlorophenyl)-1,2-diphenylethylene oxide separated as chunky prisms, m.p. 165.5–167.5°. Infrared bands unique for this diastereomer appeared at 11.76, 11.92, 12.70, 13.00, 13.88, 14.20, and 15.38 μ.

Anal. Found: C, 74.40; H, 4.50.

The oxidation mixture, after removal of the epoxide fraction, was again diluted with 25 ml. of hot water and cooled. An amorphous white solid, weighing 0.43 g. and with m.p. 53–70°, was obtained. Infrared examination of this mixture indicated that it consisted of the diastereomeric carbonates (53% yield), slightly contaminated with *p*-chlorobenzophenone (weak absorption at 6.02 μ). The latter impurity was removed by chromatography over alumina and the isomeric carbonates submitted for analysis.

Anal. Calcd. for $C_{27}H_{18}O_3Cl_2$: C, 70.29; H, 3.93. Found: C, 70.76; H, 4.02.

By means of an extensive series of fractional crystallizations from aqueous ethanol the less-soluble isomer, presumably *dl*-1,2-bis(*p*-chlorophenyl)-1,2-diphenylethylene carbonate, was separated as colorless needles, m.p. 164–166°. Pertinent infrared bands, not found in the spectrum of the *meso* form, appeared at 7.73, 8.40, 9.45, 9.95, 11.10, 12.80, and 14.32 μ.

Anal. Found: C, 70.10; H, 3.90.

Nearly pure *meso*-1,2-bis(*p*-chlorophenyl)-1,2-diphenylethylene carbonate was obtained from the filtrates, after a number of intermediate crops of crystals had been collected. This diastereomer had m.p. 142–144° (mixed m.p. with *dl* was 119–124°) and crystallized as small cubes. Its characteristic infrared bands, among others, appeared at 9.65, 10.04, 11.05, 12.35, 12.60, 13.28, 14.00, and 14.26 μ; small shoulders at 9.45 and 9.95 μ suggested some contamination by racemic carbonate.

Anal. Found: C, 70.22; H, 3.86.

A synthetic 50:50 mixture of the diasteromeric carbonates gave an infrared spectrum almost superimposable with those of the crude carbonate mixtures isolated from oxidation of each isomeric olefin.

No effort was made to isolate the *p*-chlorobenzophenone.

(B) *The cis isomer.* Using the same conditions and ratios of reactants and solvent, 0.36 g. of the *cis* olefin was oxidized and the reaction mixture worked up as above. The crude epoxide, m.p. 175–189°, weighed 0.09 g. (24%) and was again separable into the *meso* and racemic forms. Further dilution afforded 0.21 g. (51%) of mixed carbonate, m.p. 52–71°, whose infrared spectrum was identical with the isomeric carbonate mixture obtained from the *trans* olefin, there being a trace of *p*-chlorobenzophenone again present. This spectrum was also very similar to that of the 50:50 carbonate mixture.

Oxidation of trans-α,α′-dimethylstilbene. A mixture of 2.5 g. of the olefin, 11 g. of potassium acetate, 90 ml. of acetic acid, and 40 ml. of acetic anhydride was heated on the steam bath while a solution of 2.0 g. of chromium trioxide in 2 ml. of water, 60 ml. of acetic acid, and 70 ml. of acetic anhydride was gradually added (1.25 hr.). After stirring for 30 min. more, 125 ml. of water was added and the solution allowed to cool. Nine-tenths of one gram of starting material, m.p. 100–102°, was recovered. As no more crystalline material was obtained upon further dilution of the filtrates, they were concentrated *in vacuo* and extracted several times with ether. Work-up of the ether extracts gave an orange oil, smelling like acetophenone, whose infrared spectrum showed hydroxyl absorption at 2.87 μ and four carbonyl bands, at 5.59, 5.78, 5.93, and 6.05 μ. In previous runs it had not been possible to separate the carbonate, using chromatography and crystallization methods, since it was always contaminated with the 6.05-μ absorbing component. Accordingly the oily product mixture was treated overnight with Girard's T reagent, yielding material from which most of the carbonyl components, including the 6.05-μ product, has been removed (by infrared). This oil was then chromatographed over alumina, using benzene as eluent, and the fractions which were richest in carbonate (as judged from infrared spectra) were combined and triturated with 60% ethanol. Thirteen milligrams (0.6%) of pure *dl*-α,α′-dimethylhydrobenzoin carbonate, m.p. 118–120°, was obtained. A mixed melting point determination with authentic *dl*-carbonate (preparation below), m.p. 120.5–121°, was undepressed and the two samples had identical infrared spectra.

Preparation of dl- and meso-α,α′-dimethylhydrobenzoin carbonates. These two carbonates were prepared by the same procedure as VI (see above) except that dimethyl carbonate was used instead of diethyl carbonate. Recrystallization of the crude carbonates from dilute ethanol removed the more soluble, unreacted glycols.

dl-α,α′-Dimethylhydrobenzoin carbonate was obtained as colorless needles in 80% yield, from the *dl*-pinacol[30]: m.p. 120.5–121° (from 60% ethanol). The infrared spectrum showed bands, characteristic of this diastereomer only, at 8.12, 9.50, and 9.86 μ.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.14; H, 5.96.

The *meso* isomer was obtained in 87% yield as colorless flakes from dilute ethanol, m.p. 129.5–130°, by reaction of *meso*-acetophenone pinacol[31] with dimethyl carbonate. A lower melting form, m.p. 106.5–107°, was also obtained. This had an infrared spectrum identical with that of the 130° form. Characteristic infrared bands were present at 8.85, 8.32, 9.75, and 14.10 μ.

Anal. Found: C, 76.20; H, 5.90.

Each of the isomeric carbonates was subjected to the action of chromic anhydride in hot acetic acid–anhydride. The recovery of pure *dl*-carbonate, m.p. 119–119.5°, was 94%, and that of the *meso* isomer, m.p. 129.5–130°, was 96%.

Oxidation of tetraphenylethylene with potassium permanganate. In small portions, 0.79 g. (5 mmoles) of powdered potassium permanganate was added (30 min.) to a hot stirred solution of I (3 mmoles) in 150 ml. of acetic acid and 50 ml. of acetic anhydride. The dark brown solution was then stirred for 15 min. more, diluted with 100 ml. of water, and allowed to cool. The colorless crystalline product which settled out proved to be II, m.p. 200.5–203°, weight 0.20 g. (19% yield). The filtrate was concentrated under reduced pressure, poured into water and extracted with ether. Work-up of the ether extracts yielded a yellow oil which did not deposit any carbonate when triturated with dilute ethanol. Treatment of the oil with excess 2,4-dinitrophenylhydrazine reagent produced 1.64 g. of the benzophenone derivative (corresponding to 75% yield of benzophenone).

In another run, carried out exactly as above except that 30 mmoles of potassium acetate was added, a pale yellow solution resulted, from which 0.27 g. (26%) of II, m.p. 201–204°, crystallized. Concentration of the filtrate, followed by ether extraction and work-up in the usual manner, produced an oil whose infrared spectrum was essentially that of benzophenone but also showed weak carbonate absorption (5.60 μ).

When benzpinacol (3 mmoles) was oxidized with potassium permanganate (5 mmoles) in acetic acid and acetic anhydride, with added potassium acetate, no crystalline product was obtained from the diluted reaction mixture. Concentration of the solution and extraction with benzene gave an oil which was shown to be benzophenone (infrared).

Potassium permanganate oxidation of trans-1,2-bis(p-chlorophenyl)-1,2-diphenylethylene. The *trans* olefin (0.70 g.) was oxidized with potassium permanganate in the same manner as I. Work-up of the dark brown mixture afforded 0.12 g. (16%) of diastereomeric epoxides, m.p. 193–206°, whose infrared spectrum showed that both *meso-* and *dl*-epoxides were present, the latter in greater amount.

Chromyl chloride oxidation of tetraphenylethylene. A solution of 1.9 g. (12.3 mmoles) of chromyl chloride in 75 ml. of acetic acid and 25 ml. of acetic anhydride was added dropwise (1 hr.) to a hot (90–95°) stirred solution of 1.66 g. (5 mmoles) of I in 85 ml. of acetic acid and 15 ml. of acetic anhydride. After 10 min. more, 100 ml. of water was added (highly exothermic) and the dark green solution allowed to cool. Filtration afforded 0.49 g. of an ochre-yellow, low melting (100°) solid, which gave a positive Beilstein test). Chromatography over alumina, with benzene as eluant, produced white crystals, m.p. 162–174°; this material was shown to be a mixture of mainly II and the corresponding chlorohydrin (?) by infrared examination, there being no carbonyl absorption and only four peaks not found in the spectrum of pure II. When the filtrate was concentrated and extracted with benzene in the usual manner, and the oily residue examined by infrared, no carbonate absorption (5.60 μ) was detected, benzophenone being the sole component. The presence of small amount of tetraphenylethylene chlorohydrin in the solid products (above) was inferred from the positive halogen test and the fact that refluxing the 162–174° solid briefly with ethanolic potassium hydroxide gave fairly pure II, m.p. 197–201°, which did not depress the melting point of authentic tetraphenylethylene oxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Structure of Distyrinic Acid

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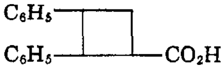
Distyrinic acid (I), the chief saturated acidic product from the treatment of cinnamic acid with 50% sulfuric acid at reflux, had previously been assigned the structure 2,3-diphenylcyclobutanecarboxylic acid (IA). We wish to report that the correct structure is IB, the compound being the mechanistically reasonable 1-phenyl-2-carboxy-3-methylindane.

In 1882 Fittig and Erdmann[1] reported that treatment of cinnamic acid with hot 50% sulfuric acid yielded a mixture of saturated acids, which they called "distyrenic acid." In 1923 Stoermer and Becker[2] reinvestigated this substance and separated it into two pure compounds, a major component, distyrinic acid, and a minor isomer, distyranic acid. Their structural investigation was confined to distyrinic acid, available in 2.6% over-all yield from cinnamic acid, and the evidence they report seems unambiguous. They found that drastic oxidation of the compound yielded benzil, establishing that there are two unsubstituted phenyl rings on adjacent carbons, and that pyrolysis of the calcium salt of the compound yielded ethylstilbene, again supporting the idea that there are adjacent phenyl groups. Both the pyrolysis product and the analytical data establish the presence of a ring, furthermore, and on the basis of this evidence they assigned distyrinic acid the structure (Ia).



Ia

We have reinvestigated this substance for two reasons: (1) the mechanism by which this compound might be formed is intriguing, since any simple scheme would predict the predominant 1,3-arrangement of phenyls, electrophilic attack being expected of course on the β-carbon of a styrene system; (2) the reaction offers a fairly convenient route to an otherwise difficultly accessible cyclobutane derivative. Accordingly, we repeated the procedure of Stoermer and Becker and obtained distyrinic acid in an over-all yield of 3.4%, confirming at least this aspect of their report. There is no doubt that we have obtained their substance, since the preparation was repeated according to their description and fractional distillation of the mixed methyl esters from the acidic reaction product, as they described, gave the methyl ester of distyrinic acid, m.p. 72.5–73° (lit., m.p. 73°). Hydrolysis afforded distyrinic acid, m.p. 153–154° (lit., m.p. 147°). We have also prepared the corresponding amide, m.p. 208° (lit., m.p. 205°). Furthermore, our analytical data correspond to those reported for both the acid and the ester. However, it soon became obvious that the previously assigned structure is incorrect.

The most convincing evidence that structure (Ia) cannot be correct comes from our studies on nitric acid oxidation of methyl distyrinate. Thus oxidation with refluxing 30% nitric acid, conditions which would certainly not rearrange a compound which had been prepared by three days' refluxing in 50% sulfuric acid, furnished *o*-benzoylbenzoic acid.

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