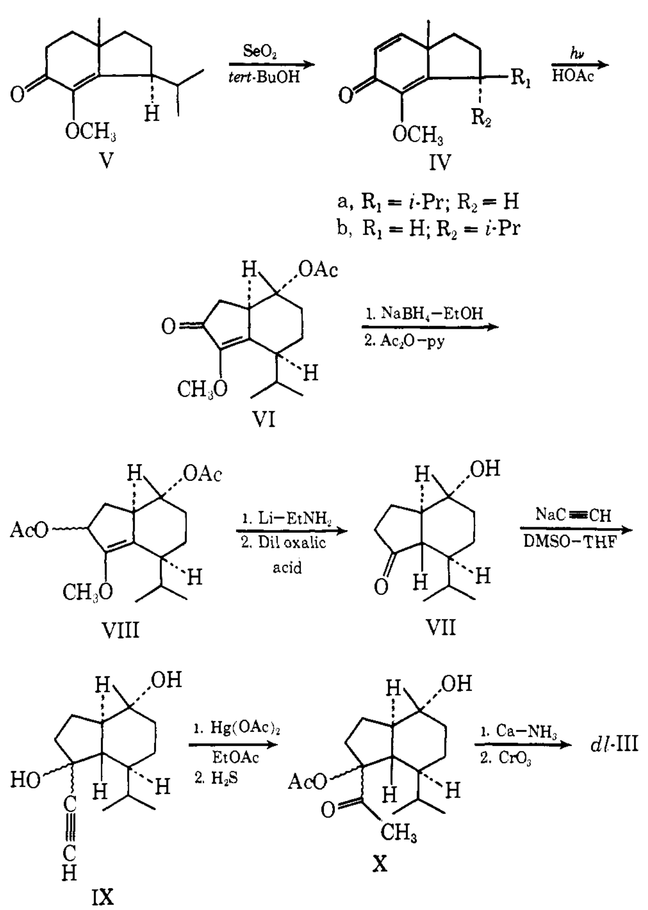

quartet, J_{AB} = 10 Hz, 2 H, C-1 and C-2 H); ir (film) 1659 (C=O), 1608 cm^{-1} (C=C). The minor isomer (IVb) showed bp 94–97° (0.07 mm); nmr (CCl_4) δ 0.68 and 0.97 (d of d, J = 7 Hz, C-6 $(CH_3)_2CH$–), 1.22 (s, 3 H, C-1 CH_3), 3.69 (s, 3 H, OCH_3), 5.99 and 6.94 ppm (AB quartet, J_{AB} = 10 Hz, 2 H, C-1 and C-2 H); ir (film) 1661 (C=O), 1609 cm^{-1} (C=C). Examination of models of IVa and IVb suggests that $A^{1,3}$ strain should be less in the fomer, and thus IVa should be the more stable isomer. The stereochemical assignment of IVa was borne out by its subsequent conversion into *dl*-oplopanone (III).

Irradiation of IVa under the conditions described for Ib gave the acetoxy ketone VI: 91% yield; mp 73–74.5°; nmr (CCl_4) δ 0.88 and 0.97 (d of d, J = 6 Hz, 6 H, C-6 $(CH_3)_2CH$–), 1.22 (s, 3 H, C-9 CH_3), 1.91 (s, 3 H, Ac), 2.18 (d, J = 4.5 Hz, 2 H, C-2 CH_2), 3.01 (t, J = 4.5 Hz, 1 H, C-1 H), 3.84 ppm (s, 3 H, OCH_3); ir (CCl_4) 1738 (acetate C=O), 1714 (C=O), 1630 cm^{-1} (C=C).[10] The nmr absorption for the C-1 and C-2 protons indicated that the stereochemistry of VI at C-1 and C-9 was the same as that present in IIb (X = Ac).

A procedure similar to that described by Ireland and coworkers[11] and by us[12] was employed for the conversion of VI into VII, a degradation product of oplopanone.[6] Treatment of VI with sodium borohydride in ethanol followed by acetylation of the allylic hydroxyl group with acetic anhydride in pyridine gave the diacetate VIII (94%), mp *ca.* 20°,[13] as a mixture of C-2 isomers. The mixture showed nmr (CCl_4) δ 0.89 and 0.93 (d of d, J = 6 Hz, 6 H, C-6 $(CH_3)_2CH$'s), 1.27 and 1.33 (singlets for the C-9 CH_3's of the two isomers), 1.89 (s, 3 H, C-2 Ac's), 2.01 (s, 3 H, C-9 Ac's), 3.51 (s, 3 H, OCH_3's), 5.63–5.92 ppm (m, 1 H, C-3 H's); ir (film) 1720 cm^{-1} (acetate C=O).

Treatment of VIII with lithium in ethylamine (inverse addition) at −78° led to cleavage of the allylic acetate and reduction of the tertiary acetate grouping to give a hydroxy enol ether which was converted into VII (50%) by hydrolysis with 0.25 equiv of oxalic acid in aqueous methanol for 2 hr. The hydroxy ketone VII showed the same nmr and ir spectral properties as those reported[6] for the hydroxy ketone from the natural source.

Compound VII was converted into *dl*-oplopanone by reaction with excess sodium acetylide in dimethyl sulfoxide–THF[14] to give an ethynyl carbinol (IX), reaction of this compound with mercuric acetate in ethyl acetate[15] to give an α-acetoxy ketone (X), and removal of the acetoxyl grouping with calcium in liquid ammonia followed by oxidation with Jones reagent.[16] Although intermediates IX and X were not purified and fully characterized, they exhibited spectral properties consistent with the indicated structures. The synthetic oplopanone exhibited nmr, ir, and glc properties identical with those of an authentic sample of the natural product.[17]

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[10] That epimerization at C-6 did not occur during irradiation was shown by the fact that pure IVa gave pure VI, while irradiation of the 5:1 mixture of IVa and IVb gave a 5:1 mixture of VI and the corresponding C-6α isopropyl compound.

[11] R. E. Ireland, D. R. Marshall, and J. W. Tilley, *J. Amer. Chem. Soc.*, **92**, 4754 (1970).

[12] D. Caine and J. B. Dawson, *Chem. Commun.*, 1232 (1970).

[13] Purification of VIII was carried out by recrystallization from ether–hexane at −20°.

[14] J. Kříž, M. J. Beneš and J. Peška, *Tetrahedron Lett.*, 2881 (1965).

[15] H. B. Kagan, A. Marquet, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1079 (1960).

[16] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[17] We wish to express our deep appreciation to Dr. H. Minato for supplying us with an authentic sample of oplopanone.

[18] NDEA Title IV Fellow, 1966–1967; Union Camp Fellow, 1969–1970.

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On the Geometry of Tetraphenylethylene Dianion

Sir:

Reductions of arylethylenes, like tetraphenylethylene (:TPE), by two electrons lead to arylethylene dianions. Indirect evidence suggests, but does not de-

$$:\text{TPE} \xrightarrow{2\text{Na}} :\text{TPE}:^{2-},2\text{Na}^{+} \qquad (1)$$

mand, that the dianions have substantially different geometries from the parent hydrocarbons.[1–7] One

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[1] D. W. Ovenall and D. H. Whiffen, *Chem. Soc., Spec. Publ.*, No. 12, 139 (1958), and ensuing discussions by M. J. S. Dewar, N. S. Hush, and P. Gray, *ibid.*, 164, 166 (1958).

[2] N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

[3] J. F. Garst, E. R. Zabolotny, and R. S. Cole, *J. Amer. Chem. Soc.*, **86**, 2257 (1964).

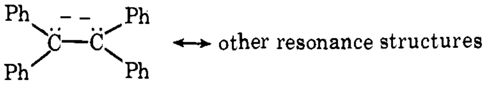
[4] J. F. Garst, J. G. Pacifici, and E. R. Zabolotny, *ibid.*, **88**, 3872 (1966).

[5] R. C. Roberts and M. Szwarc, *ibid.*, **87**, 5542 (1965).

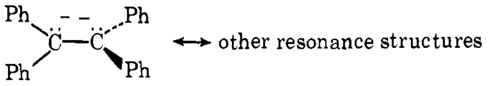
[6] A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **91**, 1892 (1969).

[7] M. Szwarc, "Carbanions, Living Polymers, and Electron Transfer Processes," Interscience, New York, N. Y., 1968, pp 361 ff.

hypothesis invokes "twisted" structures for the dianions, in which the general planes of the two ends of the ions are not coincident, but perhaps perpendicular.[8]



planar[8]



twisted[8]

Spectroscopic data have been interpreted recently as favoring a "nearly planar" structure for :TPE:$^{2-}$.[10] The arguments leading to this conclusion are spurious, and the data on which they are based are not relevant to the question.

Three experimental facts were made the basis for choosing between essentially planar and twisted structures for :TPE:$^{2-}$.[10] (1) The nmr spectrum of :TPE:$^{2-}$ indicates magnetic equivalency of the four phenyl groups. (2) The esr spectrum of :TPE·$^{-}$ implies that all the spin density is in the phenyl rings. (3) The ir spectrum of :TPE:$^{2-}$ exhibits a shift of aryl vibration frequencies which is suggestive of substantial delocalization of charge into the phenyl groups. All three of these facts are consistent with an essentially planar structure for :TPE:$^{2-}$, but *none of them is inconsistent with twisted structures*. Thus, they cannot be made grounds for choosing between these possibilities.

The consistency of twisted structures with facts 1 and 3 is obvious. (1) For many nonplanar, static geometries of :TPE:$^{2-}$, including twisted ones, the phenyl groups are geometrically equivalent; hence, they are magnetically equivalent. An even wider variety of mobile structures would give magnetic equivalency through averaging. (3) Twisting about the central C-C bond in :TPE:$^{2-}$ would not destroy the effectiveness of conjugation within each half the molecule. To a first approximation, each half of a twisted (90°) :TPE:$^{2-}$ would resemble a diphenylmethyl anion. The infrared spectrum of triphenylmethyl anion shows a band at 1559 cm^{-1},[10] similar to that of :TPE:$^{2-}$ (1556 cm^{-1}). In view of the similarity expected for diphenylmethyl and triphenylmethyl anions, this is perfectly consistent with a twisted structure for :TPE:$^{2-}$.[11]

Fact 2, which is poorly supported,[12] is irrelevant to the question of the structure of :TPE:$^{2-}$ because the data actually refer to another species (:TPE·$^{-}$). By virtue of this irrelevancy, fact 2 is consistent with any structure for :TPE:$^{2-}$, twisted, planar, or otherwise.[17]

Therefore the problem of the structure of arylethylene dianions remains very much an open question.

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(8) The phenyl groups are expected to exhibit the usual "propellering" with respect to the general plane of the planar structure and the general plane of each half the ion in twisted structures.[9]

(9) G. Favini and M. Simonetta, *Theor. Chim. Acta*, **1**, 294 (1963).

(10) D. H. Eargle, Jr., *J. Amer. Chem. Soc.*, **93**, 3859 (1971).

(11) In ref 10, the discussion of the charge delocalization consideration is muddled by the unusual view that sp^3 hybridization would apply to the ethylenic carbon atoms of a twisted :TPE:$^{2-}$ and to certain planar structures as well; see Figure 1, ref 10. It is considered therein that sp^2 hybridization would apply for a special planar structure, somehow distinguished from the ordinary planar structure. Apparently, the author had in mind variations in the weights of contributions of various canonical forms to the resonance hybrid. Insofar as hybridization is concerned, an sp^3 description might be applied legitimately to a family of structures not considered here, but which are also possibilities, those in which the geometries about the ethylenic carbon atoms are pyramidal.

(12) Fact 2 rests on measurements of the hyperfine coupling constants of the phenyl protons in :TPE·$^{-}$.[6] The sum of these is 24.32. This is about the same absolute magnitude as McConnell's Q,[13] so the sum of spin densities at the carbon atoms to which the phenyl protons are attached is one, assuming that all relevant spin densities are positive.[10] A calculation by the method of McLachlan[14] for a completely planar :TPE·$^{-}$ leads to the prediction of *negative* spin density at the "meta" carbon atoms of the phenyl rings.[15] This, coupled with the fact that the appropriate value for Q is somewhat uncertain,[16] casts suspicion on the conclusion that there is no significant spin density at the ethylenic carbon atoms of :TPE·$^{-}$.[10]

(13) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(14) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(15) Unpublished calculations. See J. F. Garst and R. S. Cole, *J. Amer. Chem. Soc.*, **84**, 4352 (1962), for other parameters derived from the same calculations.

(16) See discussion of J. R. Bolton in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, p 9 ff.

(17) From fact 2, it is reasoned in ref 10 that the total π-bond order for the central C-C bond is approximately the same (near one) for planar versions of :TPE, :TPE·$^{-}$, and :TPE:$^{2-}$. Even if this were true, it would not imply that :TPE:$^{2-}$ is planar. To reach such a conclusion, one needs to consider the *energies* of planar *and* twisted structures. It will not suffice to consider an ancillary "property" like bond order for only one of the possible structures under consideration.

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Metalation Reactions. XI.[1] Preparation of 1,3-Diols by Hydroboration of Allyllithium Derivatives

Sir:

We wish to report a new method for the preparation of 1,3-diols from unsaturated hydrocarbons. In this method the two hydroxyl groups are introduced in a molecule containing only one double bond.

Allylbenzene was readily metalated[2] with butyllithium in ether to give phenylallyllithium. Treatment of the solution of this lithium derivative with a solution of borane in THF[3] and subsequent oxidation with alkaline hydrogen peroxide in water[4] gave a single product (65% yield by isolation of the diacetates) characterized as 1-phenyl-1,3-propanediol by its analysis, the ir spectrum showing a strong band at 3300–3400 cm^{-1} and the pmr spectrum exhibiting five aromatic protons at δ 7.23 (s), one benzylic proton α to a hydroxyl at 4.76 (t, J = 6 Hz), two protons α to a hydroxyl at 3.65 (t, J = 6 Hz), two additional protons at 1.85 (q), and two protons of the hydroxyl groups. The diacetate of this diol was prepared and characterized in a similar manner.

An analogous reaction was obtained with *p*-methylallylbenzene. The single diol product of metalation–hydroboration was converted to the diacetate (80% by isolation). The pmr spectrum of this compound showed the phenyl protons at δ 7.15 (s), the methyl group on the aromatic rings at 2.33 (s), one benzylic proton α to an acetoxy group at 5.78 (t, J = 6 Hz), two diastereotopic protons α to an acetoxy group at 4.0 (m), two singlets at 2.0 and 1.9, each of three protons of the acetyl groups, and two additional protons hidden

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(1) Also: Borane Reactions. VIII. Preceding paper in this series: J. Klein and D. Lichtenberg, *J. Org. Chem.*, **35**, 2654 (1970).

(2) H. F. Herbrandson and D. S. Mooney, *J. Amer. Chem. Soc.*, **79**, 5809 (1957).

(3) H. C. Brown and P. A. Tierney, *ibid.*, **80**, 1552 (1958).

(4) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.