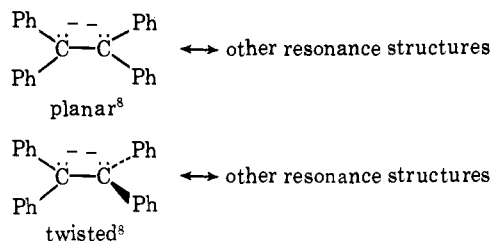hypothesis invokes "twisted" structures for the dianions, in which the general planes of the two ends of the ions are not coincident, but perhaps perpendicular.[8]

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.

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

(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·$^-$.[8] 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

(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.

under the methyl protons. It was, therefore, 1-*p*-tolyl-1,3-propanediol diacetate (bp 131° (2 mm)).

Similarly, metalation and subsequent hydroboration of 1-phenylbut-2-ene[5] gave after acetylation in 60% yield (bp 100–110° (1 mm)) the mixture of the two diacetates of the diastereoisomeric 1-phenylbutane-1,3-diols and less than 10% of other distillable products. The isomers (3:4 ratio) were separated by glpc. The first isomer showed the benzylic proton at δ 5.81 (t, $J = 7$ Hz), the other proton α to acetate at 5.0 (q, $J = 6$ Hz), a methyl at 1.20 (d, $J = 6$ Hz), and the protons of the two acetoxy groups at 1.93 (s) and 1.96 (s); the corresponding signals for the diastereoisomer were at 5.76 (t, $J = 7$ Hz), 4.76 (q, $J = 6$ Hz), 1.20 (d, $J = 6$ Hz), 1.96 (s), and 2.0 (s).

A mixture of positional isomers was obtained only in the reaction with 3-phenylbut-1-ene.[6] The products in the last reaction consisted of 3-phenylbutane-1,3-diol and the diastereoisomeric 3-phenylbutane-1,2-diols in a 1.6:1 ratio. Acetylation of the mixture of diols gave a mixture (bp 130–140° (2 mm)) of a monoacetate of the 1,3-diol and diacetates of the 1,2-diols. The monoacetate showed the methyl α to the hydroxyl group at δ 1.5 (s), the methylene α to the acetoxy group at 4.06 (t, $J = 6$ Hz), the other methylene at 2.13 (m), and the acetoxy protons at 1.66 (s). The 1,2-diacetates showed three protons α to acetoxy groups, six protons of the acetoxy groups, and a methyl as a doublet. The pmr was not well resolved, since the diastereoisomers were not separated. All the compounds showed correct elemental analyses. The separations were performed by glpc on a 5 m $\times$ $^1/_4$ in. column of 15% diethylene glycol succinate on Chromosorb W.

The reaction of phenylallyllithium with borane takes place either at the 1 or the 3 position of the allylic system to give a four-coordinated boron complex. It is possible that this complex transfers a hydride ion to excess borane present in the solution, forming a borohydride ion and an allylic borane. This allylborane, or the initial complex, is hydroborated in a regiospecific[7] manner to give predominantly the product with the two boron atoms in the molecule separated by three carbon atoms.

The attachment of the first boron atom to the phenylallyllithium system probably did not occur at the carbon next to the phenyl group. The collapse ratio during the protonation[8] of the phenylallylic anion was reported to be 2.4:1 for the 3 and 1 positions, respectively. The reaction of the anion with borane is less exothermic than protonation (and perhaps also reversible) and should give a larger amount of the more stable conjugated product than protonation. This was supported by the reaction of phenylallyllithium with trimethyl borate, that gave cinnamyl alcohol after oxidation of the product with hydrogen peroxide. The reaction of borane with the lithium derivative obtained from 3-phenylbut-1-ene should also give the allylic borane I in the first step, since even protonation has shown in this case a collapse ratio[6] of 40:1 in favor of the conjugated product. The second boron atom has a choice

between a secondary and tertiary carbon and the last was preferred, contrarily to what is observed generally during hydroborations.[4] The first introduced boron

I   II
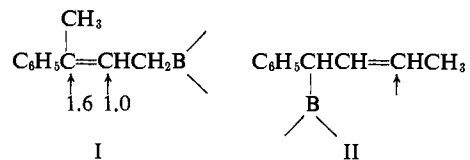
atom is certainly responsible for this effect. The position of the introduction of the first boron atom into 1-phenyl-3-methylallyllithium is less certain. Stabilization of the charge by the phenyl and of the double bond by the methyl group[6] will favor attack at the benzylic position. Further attack by borane of the possible intermediate II occurs almost entirely at only one of the two secondary carbons, the one further from the first boron atom.

The following procedure was used. Allylbenzene (2 g) was added to 23 ml of 1.6 M butyllithium in ether; the solution was left overnight[9] at room temperature and then added dropwise to 50 ml of a cooled solution (ice) of 2 M borane in THF. The solution was stirred for 5 hr, excess diborane decomposed slowly with 40 ml of water, and the product was oxidized by 40 ml of NaOH (3 N), dropwise addition of 40 ml of hydrogen peroxide, and subsequent stirring for 3 hr. Extraction of the product from the mixture (saturated with K_2CO_3) with three portions of 30 ml of ether and acetylation overnight with 16 ml of acetic anhydride–pyridine (1:1) gave 2.6 g of the diacetate, bp 125° (0.5 mm).

A reaction of ethyllithium with diborane was reported by Schlesinger and Brown to give lithium borohydride.[10] Recently a number of base-catalyzed reactions of borane were observed and were assumed to proceed via carbanions.[11]

(9) For 2 days in the case of 3-phenylbut-7-ene.

(10) H. I. Schlesinger and H. C. Brown, *J. Amer. Chem. Soc.*, 62, 3429 (1940).

(11) H. C. Brown, *et al.*, *ibid.*, 91, 2146, 2147, 4303, 6852, 6854, 6855 (1969).

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A Model for Alcohol Dehydrogenase. The Zinc Ion Catalyzed Reduction of 1,10-Phenanthroline-2-carboxaldehyde by *N*-Propyl-1,4-dihydronicotinamide

Sir:

Zinc ion is essential for the catalytic activity of horse liver alcohol dehydrogenase;[1-4] one zinc ion appears to be present[5-7] at each of the two active sites of the enzyme. The most likely location of the metal ion within the active site is at or near the binding sites of the nico-

(1) H. Theorell, A. P. Nygaard, and R. Bonnichsen, *Acta Chem. Scand.*, 9, 1148 (1955).

(2) B. L. Vallee and F. L. Hoch, *J. Biol. Chem.*, 225, 185 (1957).

(3) A. Akeson, *Biochem. Biophys. Res. Commun.*, 17, 211 (1964).

(4) D. E. Drum, T.-K. Li, and B. L. Vallee, *Biochemistry*, 8, 3783 (1969).

(5) T. Yonetani, *Biochem. Z.*, 338, 300 (1963).

(6) D. S. Sigman, *J. Biol. Chem.*, 242, 3815 (1967).

(7) D. E. Drum and B. L. Vallee, *Biochemistry*, 9, 4079 (1970).

(5) K. W. Wilson, J. D. Roberts, and W. Young, *J. Amer. Chem. Soc.*, 71, 2019 (1949).

(6) D. J. Cram, *ibid.*, 74, 2137 (1952).

(7) A. Hassner, *J. Org. Chem.*, 33, 2684 (1968).

(8) S. W. Ela and D. J. Cram, *J. Amer. Chem. Soc.*, 88, 5777, 5791 (1966).