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Chemistry of Dianions. Formation and Reactivity of Anionic Species Derived from Tetraphenylbutatriene

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1,1,4,4-Tetraphenylbutatriene (I) reacts with alkali metals in ethereal solvents to form the corresponding anion-radical II and dianion III. A quantitative study of the influence of reaction conditions on the nucleophilicity of the dianion has been made. New acetylenic compounds and some unusual n.m.r. spectra are described and a molecular orbital account of the configuration of the anionic species is reported.

The reaction of alkali metals with aromatic olefins and other electron-accepting unsaturated compounds to form reactive adducts has been known since 1914.^{1,2}

In recent years, electron spin resonance measurements have been widely used in elucidation of these adducts.³ In many cases, however, the structure of the adducts is not necessarily that of the starting organic substrate.^{4,5} Studies by electron spin resonance, therefore, are frequently insufficient to determine the course of reaction between alkali metals and electron acceptors unless accompanied by parallel chemical investigation, especially in those cases where two electrons are transferred to form diamagnetic dianions.

Little is known about the formation and the detailed chemical behavior of the latter species,⁶ although three modes of reactivity are generally recognized: (1) They may react as strong bases removing protons from any weaker bases present including solvent. (2) They may engage in nucleophilic displacements. (3) They may transfer their extra electrons to an acceptor, returning to starting material and metal cation.

Although few alkali metal adducts of cumulenes have been reported, 1,1,3,3-tetraphenylallene (IV) has been found to react with up to two moles of metal. The adduct, however, upon further reaction yielded products so varied and complex that its nature could not be fully established.^{2,7} In this study tetraphenylbutatriene (I) was chosen for investigation. Although the reduction potential and ultraviolet spectrum of the mono and di-negative ions of I have been reported,⁸ the chemical nature of these species has not been investigated.

In the present investigation Compound I was found to react with sodium or potassium in 1,2-dimethoxyethane (DME) to give a purple solution. Electron spin resonance of this solution showed a

strong single peak, approximately 17.5 gauss wide with no evidence of hyperfine splitting. This signal lasted for somewhat more than one week under nitrogen, in a sealed tube at room temperature. When these solutions were freshly prepared and treated with excess methyl iodide, compound I was regenerated in good yield. This appears, therefore, to be an electron transfer process from the anion radical to the halide (see Chart I).

In diethyl ether, however, Compound I reacted with sodium or potassium to give a brown suspension. Electron spin resonance study of this reaction showed the same signal (17.5 gauss wide, no hyperfine splitting) though considerably weaker, which disappeared within 2 to 3 hours. Reaction of this suspension with methyl iodide gave, in addition to starting material, 2,2,5,5-tetraphenyl-3-hexyne (V) isolated in 33% yield. These results show that different products are obtained under different reaction conditions and confirm the polarographic reduction studies⁸ which indicate that Compound I may add one or two electrons from alkali metals in discrete stages.

An independent synthesis of the 1,1,4,4-tetraphenylbutyne-1,4-dianion (III) was attempted by an ether cleavage reaction of 1,4-dimethoxy-1,1,4,4-tetraphenyl-2-butyne (VI) with potassium in DME. A similar reaction was described by Bergmann⁹ who reported dianion formation from VI with sodium in ether. According to Bergmann, protonation of the dianion gave two unidentified hydrocarbons, m.p.'s 97° and 167°. We obtained a solution having a strong electron spin resonance signal identical with that obtained from the 1,1,4,4-tetraphenylbutatriene anion-radical. Hence, we postulate that I is formed by bisdemethoxylation of the starting material (*cf.* Chart II) by the alkali metal; Compound I could then undergo further reaction with metal to form II.

The apparently large change in the rate of formation and reactivity of the metal-tetraphenylbutatriene adducts with change of solvent, as demonstrated by the electron spin resonance studies, and the known^{10,11} influence of the cation on the course of reactions of organometallic reagents prompted a thorough analysis of the products of alkylation of tetraphenylbutatriene under a variety of conditions. An analytical method based on the

(1) W. Schlenk, J. Appenrodt, A. Michael and A. Thal, *Ber.*, **47**, 437 (1914).

(2) W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

(3) D. Lipkin, E. D. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953); D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

(4) A. K. Hoffmann and A. G. Tesch, *ibid.*, **81**, 5519 (1959).

(5) A. K. Hoffmann, W. G. Hodgson and W. H. Jura, *ibid.*, **83**, 4675 (1961); R. L. Ward, *ibid.*, **83**, 3623 (1961).

(6) The alkali metal adducts of stilbene, azobenzene and related compounds have been investigated in detail by J. W. B. Reesor, J. G. Smith and G. F. Wright, *J. Org. Chem.*, **19**, 940 (1954); J. W. B. Reesor and G. F. Wright, *ibid.*, **22**, 375 (1957).

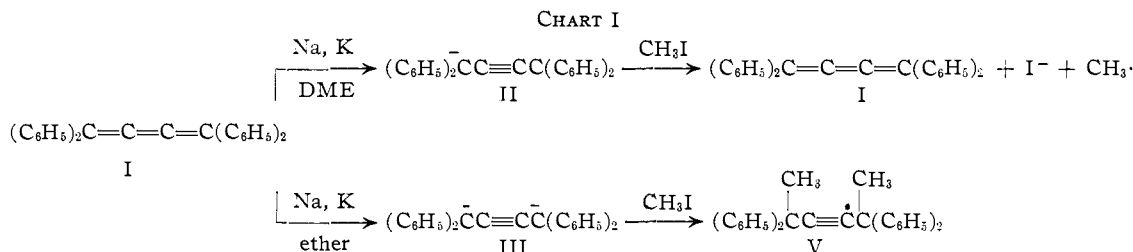
(7) C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.*, **56**, 1133 (1934).

(8) G. J. Hoijtink and P. H. van der Meij, *Z. physik. Chem.*, **20**, 1 (1959).

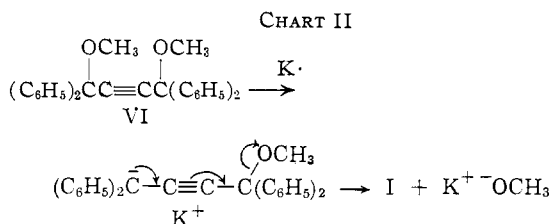
(9) E. Bergmann, *Ber.*, **63B**, 2593 (1930).

(10) W. I. O'Sullivan, F. W. Swamer, W. J. Humphlett and C. R. Hauser, *J. Org. Chem.*, **26**, 2306 (1961).

(11) A. A. Morton and A. E. Brachman, *J. Am. Chem. Soc.*, **76**, 2973 (1954).



use of nuclear magnetic resonance proved to be most suitable.



In its nuclear magnetic resonance spectrum, I had only an aromatic multiplet absorption centered at 2.75 τ . The di-alkylation product, 2,2,5,5-tetraphenyl-3-hexyne (V) had a similar aromatic multiplet and also a single sharp peak at 8.10 τ properly characteristic of the methyl hydrogens. The integrated ratios of the two peak areas were 10.0:3.0 as expected. The percentage methylation product in a mixture derived from I readily can be calculated from the areas of the aromatic (Ar) and aliphatic (Al) peaks. It is

$$\% \text{ methylation} = \frac{\text{Al(obs.)} / \text{Al(theo.)}}{\text{Ar(obs.)} / \text{Ar(theo.)}} \times 100 = \frac{\text{Al(obs.)} / \text{Ar(obs.)} \times 100}{0.3}$$

since Al (theo.)/Ar (theo.) = 6/20 = 0.3 for the fully methylated product. Similarly, the percentage solvent cleavage could be estimated by the relative area of the peak at 3.40 τ characteristic of the protonated material, 1,1,4,4-tetraphenyl-1,3-butadiene (VII). The percentage methylation thus calculated will be correct to the extent of the accuracy of the method ($\pm 5\%$) regardless of what the methylated species are. No evidence of significant quantities of other methylated species could be detected by n.m.r.; nevertheless, a careful chromatographic separation of the alkylation products in a room temperature run was made and indicated that only V and I were present after solvent; unreacted methyl iodide and salts were removed.

The results of a study of the product distribution as a function of solvent and metal is reported in Table I. The results indicate that under the conditions employed, the dianion III is most nucleophilic in DME with potassium as the cation. It is apparent that even under the most favorable conditions investigated, charge-transfer to methyl iodide still competes with nucleophilic attack. The absence of solvent cleavage products even after extended periods of time at room temperature is notable and reflects the ability of the added electrons to be delocalized on the benzene rings with a resultant lowering of the basicity of the anionic species.

When Compound I was treated with a single equivalent of potassium in DME and the anion-

TABLE I
PRODUCTS OF ALKYLATION OF II AND III WITH METHYL IODIDE (BY N.M.R.)

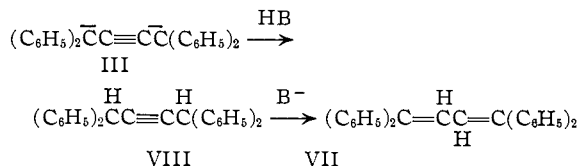
Run	Species and conditions	Alkylation, %	Electron transfer, %	Solvent cleavage, %
1	Dianion III, K, DME, RT	83.2	16.8	0 ^a
2	Dianion III, Na, DME, RT	47.5	52.5	0 ^a
3	Dianion III, K, Et ₂ O, RT	60.5	39.5	0 ^a
4	Dianion III, Na, Et ₂ O, RT	66.7	33.3	0 ^a
5	Dianion III, K, DME, 85°	10	...	35
6	Dianion III, K, DME, 0°	60	...	0 ^a
7	Anion-radical II, K, DME, RT	0 ^a	100	0 ^a

^a No signal at the expected position could be detected, indicating less than 5% of this product. ^b Since the amount of the metal consumed was not known in these runs, the amount of electron transfer could not be ascertained since unreacted I could also have been present.

radical solution alkylated with methyl iodide, the product was pure I as determined by mixed m.p. and n.m.r. spectrum (*cf.* Table I). Thus, the anion-radical acts exclusively as an electron transfer agent and not as a nucleophile toward methyl iodide.

The effect of temperature was also examined. After 48 hours at 0°, methylation of the reaction product of I and potassium in DME gave a mixture which had an exceptionally clean n.m.r. spectrum and indicated 60% alkylation. This is consistent with the view that less dianion was present; hence, reaction of I with metal to form dianion was slower at 0° than at room temperature.

When I and excess potassium were allowed to react in refluxing (85°) DME for 24 hr., solvent cleavage became the most significant reaction (35%) and only 10% of the product was methylated. The initial acetylenic product (VIII) arising from protonation of III by solvent or by some other proton donor is isomerized to 1,1,4,4-tetraphenylbutadiene (VII). This isomerization is known to proceed in the presence of bases.¹²



Reaction of I with lithium was also investigated. While no reaction could be detected in ether after 7 days, after a long (2 days) induction period Compound I did react with lithium in DME. After 4 days of further reaction with excess lithium, reaction of the product with methyl iodide resulted in traces of alkylation (by n.m.r.). This indicates

(12) K. Brand, *Z. Elektrochem.*, **16**, 669 (1910).

TABLE II

No.	Name	R	ALKYLATION PRODUCT		Analyses, %		N.m.r.		
			M.p., °C.	Yield, %	Theor.	Fd.	Position ^a	Theor.	Ratio Fd.
1	2,2,5,5-Tetraphenyl-3-hexyne	-CH ₃	82.5-83.5	33	C 93.22	93.36	2.65	10.0	10.0
2	3,3,6,6-Tetraphenyl-4-octyne	-CH ₂ -CH ₃	128-129	66	C 92.71	92.88	2.65	10.0	10.0
					H 7.29	7.19	7.65	2.0	2.06
3	1,2,2,5,5,6-Hexaphenyl-3-hexyne	-CH ₂ -C ₆ H ₅	132-133	61	C 93.64	93.59	2.65	15.0	15.12
					H 6.36	6.36	6.66	2.0	2.0
4	4,4,7,7-Tetraphenyl-1,9-decadiene-5-yne	-CH ₂ -CH=CH ₂	105-106	51	C 93.11	92.96	2.65	10.0	10.0
					H 6.89	6.84	5.0	3.0	3.4
5	1,1,4,4-Tetraphenyl-1,3-butadiene	-H ^b	193-194	90	C 93.81	93.38	2.85	10.0	10.0
					H 6.19	6.45	3.40	1.0	0.96
6	1,4-Bis-(diphenylphosphinyl)-1,1,4,4-tetraphenylbutyne	-(C ₆ H ₅) ₂ P → O ^c	348 d.	30	C 82.30	81.83	.. ^d
					H 5.31	5.50
7	1,1,4,4-Tetraphenyl-3-hexynedioic acid	-COOH	194-195 ^f	63	C 80.70	80.70	2.65 ^e
					H 4.97	5.07

^a Tau values, run at 56.4 mc. ^b The product is the isomer 1,1,4,4-tetraphenyl-1,3-butadiene (X). ^c The alkylating agent was (C₆H₅)₂PCl. ^d The product was insoluble in common solvents used for n.m.r. ^e The product could be dissolved in CD₃OD; however, the acidic proton was obscured in the n.m.r. spectrum by this solvent and only the aromatic multiplet could be observed. ^f Decomposed at its m.p. with gas evolution.

that dianion formation with lithium is either very slow or that the lithium salt of III acts almost exclusively as an electron transfer agent. The system was not further investigated.

Treatment of dianion III with alkylating agents other than methyl iodide produced a new series of symmetrically substituted acetylenic compounds. These compounds and their physical properties are reported in Table II.

A brief investigation of the reaction of 1,1,3,3-tetraphenylallene (IV) with alkali metal was made to see whether the nature of the dianion could be determined. Polarographic reduction in DMF indicated a single *two*-electron reduction at -2.092 v., then no further reduction through a potential of -2.9 v.

When IV was treated with potassium metal in DME at room temperature a deep purple solution was obtained which on alkylation with methyl iodide gave an oil which could not be crystallized. The n.m.r. spectrum of this oil showed aromatic, olefinic and saturated hydrogens in a non-integral ratio indicating a mixture. As the olefinic hydrogens probably arose from proton abstraction from solvent, the initially formed anionic species is a considerably stronger base than the dianion III. This fact is also apparent from a comparison of the polarographic reduction potentials, -2.092 and -1.73 v., respectively.

An unexpected effect was uncovered in the n.m.r. spectra of I and the derivatives reported in Table II. It is reported¹³ that the induced field set up by an acetylenic linkage contributes to the shielding of neighboring protons. As this shielding falls off by the cube root of the distance, the different aromatic protons have different chemical

shifts resulting in multiple splittings of the aromatic hydrogens. This effect has been noted in phenylacetylenes, but there have been no previous reports of this effect either in compounds where the aromatic ring is one carbon removed from the acetylene or where a cumulene rather than an acetylene is responsible for the n.m.r. splitting.

The n.m.r. spectra of compounds 1-4 and 7 in Table II as well as tetraphenylbutatriene (shown in Fig. 1) all exhibit a broad multiplet in the region 2.3-3.0 τ . Significantly, neither benzonitrile nor 1,1,3,3-tetraphenylallene (IV) shows this type of fine structure, suggesting that the presence of two connected sp-hybridized carbon atoms is required for this splitting effect to be observed.

Molecular Orbital Calculations.—It is of interest to consider the geometry of I and its derivatives the anion-radical II and the dianion III, since the stereoelectronic configuration of a transient ionic species is important in determining its ultimate chemical behavior.¹⁴

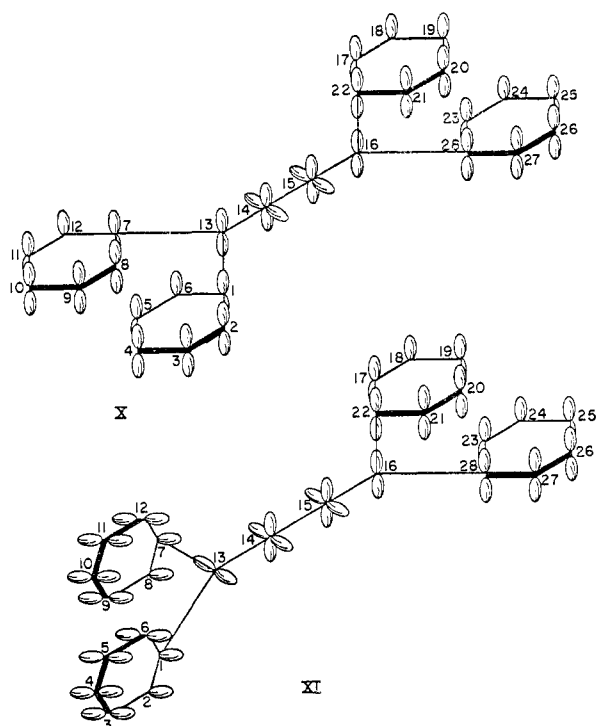
Valence bond theory predicts that the planar molecular configuration of tetraphenylbutatriene (X) would, in the ground state, be more stable than the higher energy rotamer XI, a diradical. This is further indicated by our observation that I shows no e.s.r. signal and by the report that I is diamagnetic¹⁵; there is, however, no reason to feel, *a priori*, that the configuration of II and III must be the same as the neutral molecule.

To obtain some indication in a theoretical sense of the configuration of II and III, molecular orbital calculations employing the Hückel approximation have been made on the tetraphenylbutatriene molecule and the diphenylvinylmethyl radical XII. Details are given in the section on calcu-

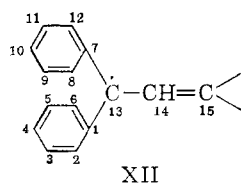
(13) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 178.

(14) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

(15) R. Kuhn and K. Wallenfels, *Ber.*, **71B**, 783 (1938).



lations. The radical XII is of importance since it represents the π -orbital system in one plane of the rotamer XI of tetraphenylbutatriene. Two iden-



tical planes perpendicular to each other with essentially the π -configuration of XII exist in XI.

The results of the calculations are summarized in the molecular orbital diagram, Fig. 2. For tetraphenylbutatriene in configuration X the total energy of the filled molecular orbitals in the 28-electron plane is 38.79 $|\beta|$. Considering the electrons in the perpendicular π -orbital at C_{14} and C_{15} to have the energy of ethylene in the ground state, 2.00 $|\beta|$, the total π -orbital energy of the molecule becomes 40.79 $|\beta|$.

For the diphenylvinylmethyl radical XII the total energy of the 15 electrons in the delocalized π -molecular orbitals is 20.39 $|\beta|$. In a molecular system represented by XI, there are 2 of these molecular orbital systems in the same molecule, perpendicular to each other. Since the assumption is made that there is no resonance interaction between the two orthogonal systems, the total π -orbital energy of the molecule XI is 40.78 β . This is coincidentally the same as the π -orbital energy of X, indicating that the configuration of the neutral molecule is due to subtle effects neglected in the Hückel calculation. The calculations are not without significance for the neutral molecule, however, since they account qualitatively for the ready *cis-trans* isomerism of disubstituted tetraphenyl-

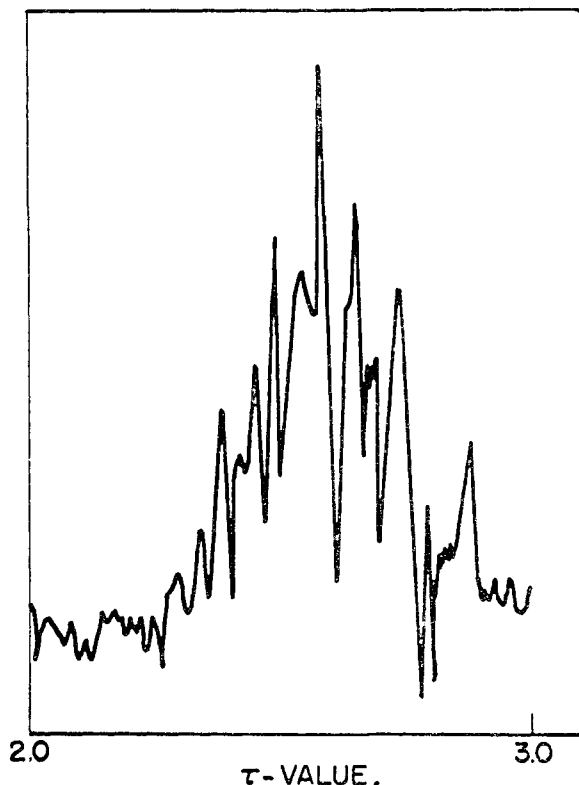


Fig. 1.—Tetraphenylbutatriene aromatic n.m.r. spectrum.

butatrienes.¹⁶ The barrier to rotation should be low when the half-rotated species is similar in energy to the original conformation.

It can be seen readily from the molecular orbital diagram that any additional electrons (marked by an asterisk) added to XI will go into a non-bonding orbital. If, however, additional electrons are added to X they will go into a slightly (+0.286 $|\beta|$) anti-bonding orbital. Thus the simple Hückel approximation slightly favors the non-planar rotamer XI for II and III and this preference increases with the number of electrons added. Since the Hückel method involves gross approximations, it is apparent that the choice of configurations for these species cannot be resolved by this type of molecular orbital calculation alone.¹⁷ From the above considerations and the reported spectral data,¹⁸ however, it appears most probable that III has configuration XI

(16) R. Kuhn and K. L. Scholler, *Chem. Ber.*, **87**, 598 (1954); R. Kuhn and D. Blum, *ibid.*, **92**, 1483 (1959).

(17) The results do indicate the possibility of an equilibrium between the rotamers. The position of such an equilibrium might be sensitive to external factors such as solvent or counter-ion. If the rotamers had different reactivity, the sensitivity of the reaction course to counter-ion and solvent described in Table I would be accounted for. Thus configuration X might favor electron transfer reaction while configuration XI would favor nucleophilic reaction.

(18) Additional evidence for dianion III existing predominantly in the XI configuration can be found in the published ultraviolet spectra.⁹ The spectrum of the anion-radical II shows a strong absorption peak at 800 $m\mu$, not found in I, which is presumably due to a low energy transition arising from the added electron moving to the next higher molecular orbital. The absence of this peak in the spectrum of III indicates that the molecular orbitals for III differ appreciably from II. We wish to thank Prof. H. B. Gray for his helpful discussion on this point.

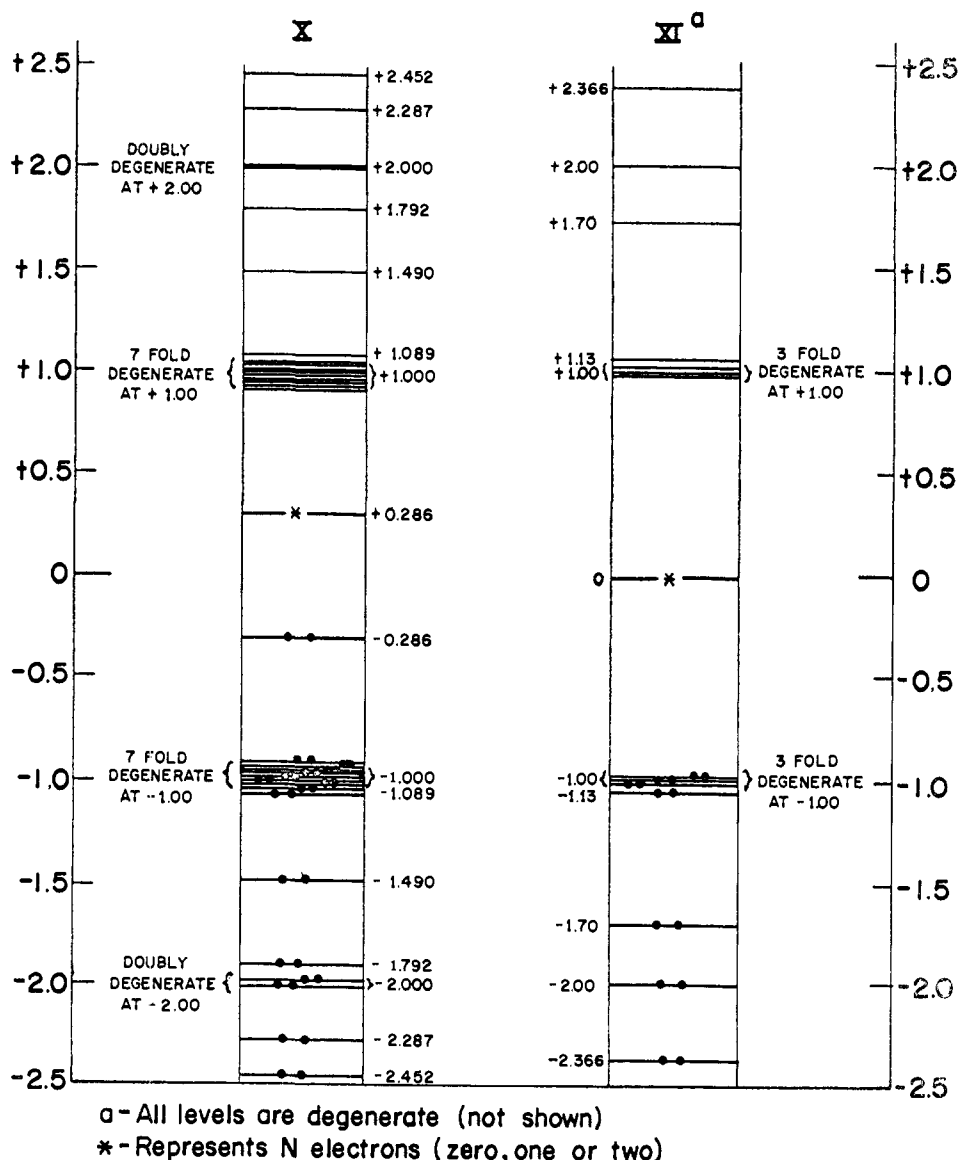


Fig. 2.—Molecular orbital diagram.

rather than X. In addition, electrostatic repulsion between the two paired non-bonded electrons of dianion III should lead to their maximal separation,¹⁹ favoring configuration XI and further supporting the prediction based on the Hückel calculation.

Experimental²⁰

1,1,4,4-Tetraphenylbutyne-1,4-diol.—A solution of ethylmagnesium bromide was prepared from 24.3 g. (1.0 g.-atom) of magnesium turnings and 120 g. (1.1 moles) of ethyl bromide in 600 ml. of dry ether. Into this solution was passed purified acetylene²¹ at a moderate rate, with stirring, at room temperature, for 18 hr. At this point, a solution of 200.2 g. of benzophenone in 600 ml. of dry benzene was added with rapid stirring, over 1 hr. The reaction mixture after remaining overnight was decomposed by pouring into excess acidified ice-water. The benzene-ether layer was

separated and the remaining aqueous solution and solids were extracted with ether. These extracts were combined with the previously separated ether-benzene mixture and concentrated to give a slurry of fine white solid. Filtration gave 110 g. (28%) of the diol, m.p. 191–192° (reported²² 193°). Recrystallization from toluene gave 102 g., m.p. 193.0–193.5°.

1,1,4,4-Tetraphenylbutatriene.—To a refluxing solution of 16.0 g. (0.041 mole) of 1,1,4,4-tetraphenylbutyne-1,4-diol and 16.6 g. (0.10 mole) potassium iodide in 60 ml. of ethanol was added, dropwise, over 15 min., a solution of 4.0 g. of concd. sulfuric acid in 40 ml. of ethanol. Refluxing was continued for 1 hr., the mixture was allowed to cool to room temperature, and was filtered and washed with ethanol.

Golden yellow crystals, 11.5 g. (79%), m.p. 233–235° (reported²³ m.p. 235°) were obtained. Recrystallization from acetic acid, then xylene, brought the m.p. to 235–236°.

1,4-Dimethoxy-1,1,4,4-tetraphenylbutyne.—Into a 250-ml. flask was placed 10.0 g. (0.036 mole) of 1,1,4,4-tetraphenylbutyne-1,4-diol and 120 ml. of anhyd. methyl alcohol. The diol was dissolved by slight warming. To the warm (50–60°) solution was added 1.5 ml. of concd.

(19) For a discussion of electrostatic repulsion in dianions, see N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

(20) All melting points are uncorrected.

(21) Acetylene was purified by successively passing through a Dry Ice-acetone trap, concd. sulfuric acid, sodium hydroxide pellets and finally a column of Linde 4A molecular sieves.

(22) G. Du Pont, *Compt. rend.*, **150**, 1524 (1910).

(23) J. Wolinski, *Roczniki Chem.*, **31**, 1189 (1957); *C. A.*, **52**, 10024 (1958).

sulfuric acid in 10 ml. of methanol. The mixture was shaken, then allowed to stand at room temperature for 24 hr. The crystalline product was filtered and washed successively with methanol, aqueous ammonia then methanol again. Recrystallization from benzene-hexane gave an almost quantitative yield; 10.4 g., m.p. 111–112°; reported 111–112.5°,²⁴ 115–116°.⁹

Electron Spin Resonance Analyses.—A 23-cm. piece of 4-mm. Pyrex glass tubing, closed at one end, was sealed to a 23-cm. length of 10-mm. tubing. The combined tube was flamed under vacuum then flushed with nitrogen. Under a stream of nitrogen *ca.* 25 mg. of 1,1,4,4-tetraphenylbutatriene (I), *ca.* 25 mg. of alkali metal, several broken glass chips and 5 ml. of dry solvent were added to the tube. The tube was evacuated until the solvent began to boil, then cooled in a Dry Ice-acetone-bath, evacuated on the vacuum pump and sealed off. Upon shaking the sealed tube, reaction between 1,1,4,4-tetraphenylbutatriene and the alkali metal quickly occurred. The solution then was examined in the 4 mm. section of the tube in the electron spin resonance spectrometer.

2,2,5,5-Tetraphenyl-3-hexyne.—To a slurry of 3.56 g. (0.010 mole) of I in 100 ml. of dry ether under nitrogen was added 0.46 g. (0.02 g. atom) of sodium. The reaction mixture was stirred for 18 hours after the first appearance of a brown color. Methyl iodide then was added dropwise until a bright yellow color appeared. The product was filtered, dissolved in chloroform and washed with water. The chloroform was removed under reduced pressure and the resulting gum taken up in 50 ml. of refluxing xylene. When the xylene solution was cooled to room temperature, 1.59 g. of 1,1,4,4-tetraphenylbutatriene, m.p. 235°, mixed m.p. 235°, separated. The remaining material was concentrated at reduced pressure and chromatographed on a 72 × 2.4 cm. column of silica gel slurry packed in 5% ether in hexane. Elution with 1 l. of 2.5% ether in hexane gave no material. A second liter of 2.5% ether in hexane eluent contained a trace of solid. The next 500 ml. of 2.5% ether in hexane eluent contained 1.55 g. of solid, m.p. 80–82°, from which 0.91 g. of 2,2,5,5-tetraphenyl-3-hexyne, m.p. 82–83°, was obtained by recrystallization from petroleum ether. Further elution with increasing amounts of ether up to 10% in hexane gave only 1,1,4,4-tetraphenylbutatriene (I); total I recovered from the chromatograph was 0.76 g.

In a second preparative run, 4.0 g. (0.011 mole) of I and 0.60 g. (0.026 g.-atom) of sodium in 100 ml. of ether was allowed to react for 24 hr. and was then treated with excess methyl iodide.

After the usual work-up, a semi-solid material was obtained which partially dissolved when treated with benzene. The undissolved portion consisted of bright yellow crystals. Filtration gave 0.77 g. of 1,1,4,4-tetraphenylbutatriene, m.p. 235°, mixed m.p. undepressed. Concentration of the mother liquor gave 1.42 g. (33%) of yellow tinged plates of V, m.p. 80–82°. Six recrystallizations from hexane gave white crystals of V, 0.61 g., m.p. 82.5–83.5°. The analysis is reported in Table II.

Reactions of 1,1,4,4-Tetraphenylbutatriene with Alkali Metals.—All reactions studied were run in 250-ml. heavy-walled erlenmeyer flasks under a slight positive head of ketyl-purified nitrogen.²⁵ The flasks were purged with nitrogen and flamed before use. Stirring was with a glass-covered magnetic stirring bar in the presence of some broken glass chips which aided in exposing fresh surfaces of the alkali metal. 1,2-Dimethoxyethane was distilled from lithium aluminum hydride immediately before use and diethyl ether was stored over sodium wire. The alkali metal was weighed under a petroleum solvent, cut into the smallest pieces practical and introduced into the flask in a stream of nitrogen. 1,1,4,4-Tetraphenylbutatriene, thoroughly dried in a vacuum desiccator, was normally added last.

In a typical reaction, 0.20 g. (0.00056 mole) of 1,1,4,4-tetraphenylbutatriene was stirred with 0.085 g. (0.0037 g.-atom) of sodium in 50 ml. of diethyl ether under nitrogen. The reaction mixture turned purple, then reddish-brown within a few minutes. Stirring was continued for 91 hr. then 2.0 ml. of methyl iodide was added in a stream of nitrogen decolorizing the solution. The solution was

then concentrated at reduced pressure, redissolved in hot chloroform, filtered and reconcentrated at reduced pressure. The reconcentrated material then was analyzed by nuclear magnetic resonance.

Methylation of 1,1,4,4-Tetraphenylbutatriene-Alkali Metal Adducts.—Preliminary experiments demonstrated that two moles of sodium or potassium would completely react with one mole of 1,1,4,4-tetraphenylbutatriene in DME or ether within 18–20 hr. under the reaction conditions described. Subsequent reactions, where the dianion was to be studied, employed excess alkali metal and time periods greater than 20 hr.

In runs 1–4 in Table I, 0.20 g. (0.00056 mole) of 1,1,4,4-tetraphenylbutatriene (I) was treated with 0.0037 g. atom of alkali metal for 91 hr. Alkylation was with 2.0 ml. of methyl iodide. In runs 5 and 6 the same quantities of materials were used. In no. 5, potassium was the alkali metal and the DME solution was refluxed for 24 hr. then alkylated with 2.0 ml. of methyl iodide. In run 6 with the same metal and solvent, the reaction flask was kept at 0° with intermittent stirring for 48 hr. before reaction with 2.0 ml. of methyl iodide. In run 7, 0.50 g. (0.0014 mole) reacted with 0.055 g. (0.0014 g. atom) of potassium in DME for 48 hr.; alkylation was with 1.0 ml. of methyl iodide.

Treatment of 1,1,4,4-Tetraphenylbutyne-1,4-dianion with Alkylating Agents other than Methyl Iodide.—The hydrocarbon compounds described in Table II were each prepared by treating 0.50 g. (0.0014 mole) of I with 0.36 g. (0.0092 g. atom) of potassium for 48 hours then alkylating with excess (2.0 ml.) of the appropriate reagent (ethyl iodide, benzyl chloride, allyl bromide). The products were recrystallized from ethanol to constant m.p. The dicarboxylic acid was prepared by pouring the solution of dianion III onto powdered Dry Ice. Acidification and the usual work up gave 0.95 g. of I, identified by mixed m.p. from ethanol. The ethanolic mother liquor was concentrated at reduced pressure and the residue crystallized from hexane to give the dicarboxylic acid. Recrystallizations were made from heptane-chloroform.

1,4-Bis-(diphenylphosphinyl)-1,1,4,4-tetraphenylbutyne was prepared from 2.00 g. (0.0056 mole) of I and 0.277 g. (0.012 g. atom) of sodium in 50 ml. of ether to form III, followed by addition of 2.5 g. (0.011 mole) of chlorodiphenylphosphine. The product was recrystallized from xylene to give 0.51 g. of I (identified by mixed m.p.). Concentration of the xylene mother liquor led to the isolation of 1.25 g. of material melting at 348° dec. Infrared and microanalysis established the compound as the bisphosphine oxide.

1,1,3,3-Tetraphenylallene was prepared from benzalacetophenone by the five-step synthesis reported by Schlenk and Bergmann.² From 100.0 g. (0.48 mole) of benzalacetophenone, 18.9 g. (11.5% over-all) of 1,1,3,3-tetraphenylallene (IV) was obtained, m.p. 164–165°, reported² 164–166°. The nuclear magnetic resonance spectrum showed only a sharp peak at 2.72 τ .

In the stirring apparatus described previously, 3.44 g. (0.01 mole) of IV was allowed to react with 0.78 g. (0.2 g. atoms) of potassium in DME for 96 hours. Treatment with 2.0 ml. of methyl iodide discharged the purple color. Work-up gave a viscous oil which we were unable to crystallize. N.m.r. indicated a complex mixture.

Nuclear Magnetic Resonance Spectra.—Spectra were run as solutions in carbon disulfide with tetramethylsilane as an internal standard on a Varian HR-60 instrument run at 56.4 mc. The results are included in Table II.

Ultraviolet Absorption Data.—The following were run in cyclohexane: 2,2,5,5-tetraphenyl-3-hexyne, 260 $m\mu$ peak ($\log \epsilon$ 2.98), shoulders at 253, 263, 269 $m\mu$; 1,2,2,5,5,6-hexaphenyl-3-hexyne, 260 $m\mu$ peak ($\log \epsilon$ 3.16), shoulders at 254, 265, 270 $m\mu$; 3,3,6,6-tetraphenyl-4-octyne, 259 $m\mu$ peak ($\log \epsilon$ 2.52), shoulders at 254, 263, 274 $m\mu$; 4,4,7,7-tetraphenyl-1,9-decadiene-5-yne, 259 $m\mu$ peak ($\log \epsilon$ 3.42), shoulders at 253, 263, 270 $m\mu$. 1,1,4,4-Tetraphenylbutatriene, 270 $m\mu$ peak ($\log \epsilon$ 4.57), 318 $m\mu$ peak ($\log \epsilon$ 3.55), 417 $m\mu$ peak ($\log \epsilon$ 4.64).

Calculations.—For X and XII, the corresponding secular determinants were written and equated to zero employing the standard Hückel approximation.²⁶ Overlap integrals between adjacent as well as non-adjacent orbitals were taken

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(25) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957, p. 299.

(26) E. Hückel, *Z. Physik*, **70**, 204 (1931); C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947).

as zero in setting up the determinant. For purposes of evaluating the related exchange integrals, they were not taken as zero.

The resonance or exchange integrals, the non-diagonal elements, were taken as zero for all orthogonal adjacent p-orbitals and all nonadjacent orbitals, and were taken as 1.00 (in units of beta) between all adjacent p-orbitals in the same plane except for the adjacent orbitals 13-14, 14-15 and 15-16. Because in the latter cases the hybridizations and interatomic distances differ from the usually encountered sp^2-sp^2 interaction, a correction was made. The method of Mulliken²⁷ was used to determine the overlap of the adjacent orbitals 13-14, 14-15 and 15-16 in I. The interatomic distance 13-14 = 15-16 was taken as 1.34 Å, while the 14-15 distance was taken as 1.20 Å. From the tables,²⁷ $S_{13-14} = S_{15-16} = 0.273$ and $S_{14-15} = 0.338$.

The exchange integrals used in the determinants were

(27) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

evaluated by making use of the equation $(H_{ij}/H_{kl}) = (S_{ij}/S_{kl})(1 + S_{kl})/(1 + S_{ij})$, relating exchange to overlap integrals.²⁸ In this case, k and l were taken to refer to a pair of adjacent benzene carbon atoms; thus $H_{kl} = \beta$ and $S_{kl} = 0.247$. The values (in units of beta) of the exchange integrals obtained were $H_{13-14} = H_{15-16} = 1.08\beta$ and $H_{14-15} = 1.27\beta$. The molecular orbitals available for delocalization in X and XI (in terms of beta) are indicated in Fig. 2.

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[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C.]

ortho Effects in Reactions of Nucleophiles with Benzyl Chlorides¹

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Rates of reactions of LiOCH_3 , LiSC_6H_5 , KI and $(\text{CH}_3)_3\text{N}$ with benzyl chloride and its *o*-methyl and *o*-bromo derivatives have been measured; ΔH^\ddagger and ΔS^\ddagger values have been determined. The reagents of higher polarizability (I^- and $\text{C}_6\text{H}_5\text{S}^-$) are especially reactive, relative to CH_3O^- , with substrates carrying *ortho* substituents of higher polarizability. London interactions in the transition state are tentatively judged to be responsible. Experimental $\Delta\Delta\Delta F^\ddagger$ values agree rather well with $\Delta\Delta\Delta H^\ddagger$ values reckoned from London theory. In the case of trimethylamine reagent, steric interaction with *ortho* substituents obscures the effects of London forces.

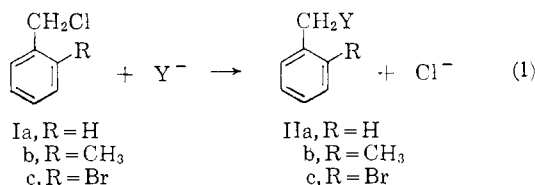
An earlier paper⁴ called attention to an interesting relationship: nucleophiles of high polarizability are, relative to those of low polarizability, especially reactive with substrates carrying high-polarizability substituents near the reaction site. This trend was discerned in the reactions of $\text{C}_6\text{H}_5\text{S}^-$ (*vs.* CH_3O^-) with 1-halo-2,4-dinitrobenzenes (1-substituent varied),⁵ of Br^- (*vs.* Cl^-) and I^- (*vs.* Br^-) with alkyl halides (displaced halogen varied), and in the reactions of $\text{C}_6\text{H}_5\text{S}^-$ or I^- (*vs.* CH_3O^-) with α -substituted methyl halides (α -substituent or displaced halogen varied).⁴ This regularity was then sought and found in the reactions of $\text{C}_6\text{H}_5\text{S}^-$ (*vs.* CH_3O^- or OH^-) with 2-substituted 1-fluoro-4-nitrobenzenes (2-substituent varied).⁶

This relationship is thought to represent reduction of transition state free energy by London forces acting between attacking nucleophile and nearby substrate substituents.^{4,6} On that view, the energetic advantage should be proportional to the polarizabilities of the reagent and the substituent and inversely proportional to the sixth power of their distance of separation.⁷ Accordingly, this factor should be negligible in the initial

state where the reagent and substrate are widely separated, and should benefit the transition state the more as the polarizabilities of reagent and substituent are greater.

Spinner⁸ has also discussed London forces as a factor affecting nucleophilic displacement rates.

This paper describes the search for, and discovery of, this regularity in some $\text{S}_\text{N}2$ displacements in *o*-substituted benzyl chlorides (eq. 1). The nucleophiles concerned are the methoxide, thio-



phenoxide and iodide ions and the trimethylamine molecule. The *o*-substituents are hydrogen, methyl and bromine. We confess that, before experimental work was commenced, data already in the literature⁹ were extrapolated to a promise of success in this search.

Experimental

Benzyl chloride was a commercial product re-distilled through a good column; b.p. 61.9° (12 mm.).

***o*-Xylyl chloride** was prepared by sulfuryl chloride chlorination of *o*-xylene.¹⁰ The *o*-xylene was purified by sulfonation, recrystallization of the sodium salt of the sulfonic acid, and

(8) E. Spinner, *Austral. J. Chem.*, **13**, 218 (1960).

(9) Reference 4, Table IV.

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