

with the estimate (8.6 eV) yielded by perturbation of isobutylene using the procedure reported in studies of silabenzene<sup>8</sup> and 1-silatoluene.<sup>9</sup>

The adiabatic ionization potential, reported recently by Gusel'nikov and Nanetkin<sup>10</sup> ( $7.5 \pm 0.3$  eV), lies below the onset of the band in our observed spectra (8.0 eV). Their value could be correct if the Frank-Condon factors for formation of the adiabatic ionic state are of negligible intensity. Such could be the case if the ionic ground state has a perpendicular geometry. The broad gross shape of the presently observed photoelectron band is not inconsistent with such a geometrical change, but the lack of vibrational resolution prevents any definite predictions of the nature of the geometric change accompanying ionization. We hope the present results may stimulate examination of the ionic states of **1** by reliable theoretical methods.

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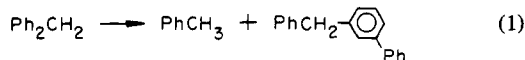
### A Possible Nucleophilic Ipso-Aromatic Substitution with a Benzyl Anion as the Leaving Group<sup>1</sup>

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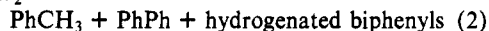
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We report here two examples of ipso-aromatic substitution when diphenylmethane alone, eq 1, or diphenylmethane plus benzene,



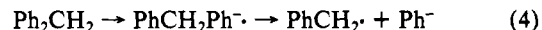
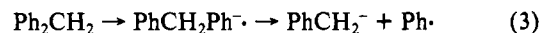
eq 2, are treated with NaK at 0 °C for 3 h in a mixture of glyme  $\text{C}_6\text{H}_6 + \text{Ph}_2\text{CH}_2 \rightarrow$



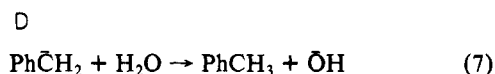
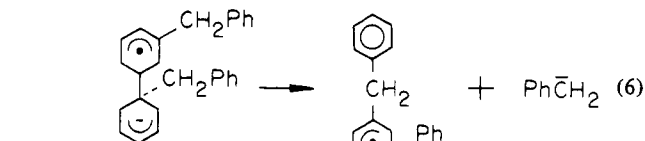
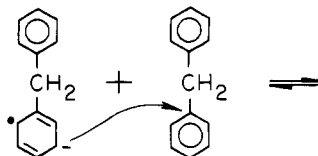
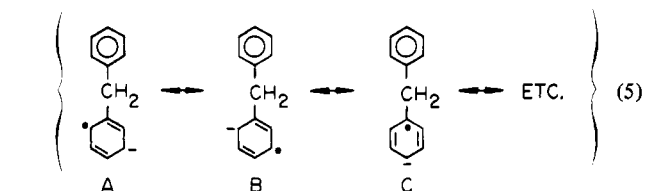
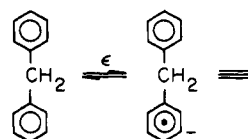
and triglyme. That the latter reaction is indeed an ipso reaction between benzene and diphenylmethane and the biphenyl and hydrogenated biphenyls are not produced through dimerization of benzene<sup>2</sup> was shown by labeling the diphenylmethane with carbon-14 (in the phenyl) and demonstrating that the  $\text{C}_{12}$  products obtained from the labeled reactant contain carbon-14. The biphenyl was also labeled when the reaction was carried out with benzene-<sup>14</sup>C and diphenylmethane.

We demonstrated earlier<sup>3</sup> that NaK in glyme-triglyme for 3 h at 0 °C cleaves bibenzyl (water quench) to yield toluene. Similarly, 1,2-diphenylpropane yields toluene and ethylbenzene. There are other minor products formed by interaction of the

organic reactants with solvent.<sup>4</sup> Remarkably, diphenylmethane under the same conditions yields toluene<sup>3</sup> (43%) and another product (33%) which we have now definitely identified by independent synthesis as 3-benzylbiphenyl<sup>5</sup> (eq 1). Phenyl-*p*-tolylmethane undergoes a completely analogous reaction to yield *p*-xylene and 4-methylbenzylbiphenyl. In neither of the latter two reaction products could we find a trace of benzene, even with <sup>14</sup>C-ring-labeled diphenylmethane as the starting material (the carbon-14 provides a sensitive method for the detection of benzene, if it were present). This observation rules out a mechanism involving direct fragmentation of the  $\text{sp}^3\text{-sp}^2$  bond such as shown in eq 3 or 4 followed by attack of  $\text{Ph}^\cdot$  or  $\text{Ph}^-$  on diphenylmethane



to produce 3-benzylbiphenyl, since it would be expected that either phenyl radical<sup>6</sup> or phenyl anion should react with solvent to produce benzene. Further, the highly selective formation of 3-benzylbiphenyl provides another argument against attack of  $\text{Ph}^\cdot$  on diphenylmethane, since such attack should produce a mixture of the *o*-, *m*-, and *p*-biphenyls.<sup>7</sup> The mechanism shown in eq 5-8



is consistent with all of the facts.<sup>8</sup> Another possibility, suggested by Professor E. Grovenstein, is dimerization of two radical anions, which for convenience can be written in their resonance forms

(4) In addition to toluene (85%), bibenzyl yielded<sup>3</sup> 11% of a second product which has now been identified (<sup>1</sup>H, <sup>13</sup>C NMR) as 1,2-diphenylbutane.

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(1) Research sponsored by the Division of Chemical Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

(2) Grovenstein, E. Jr.; Longfield, T. H.; Quest, D. E. *J. Am. Chem. Soc.* 1977, 99, 2800. When the reaction is carried out with benzene alone (NaK, glyme-triglyme, 0 °C, 3 h), there are only traces of reaction products of benzene detectable. For a discussion of ipso reactions with radicals see: Tiecco, M. *Pure Appl. Chem.* 1981, 53, 239.

(3) Collins, C. J.; Hombach, H.-P.; Maxwell, B.; Woody, M. C.; Benjamin, B. M. *J. Am. Chem. Soc.* 1980, 102, 851.

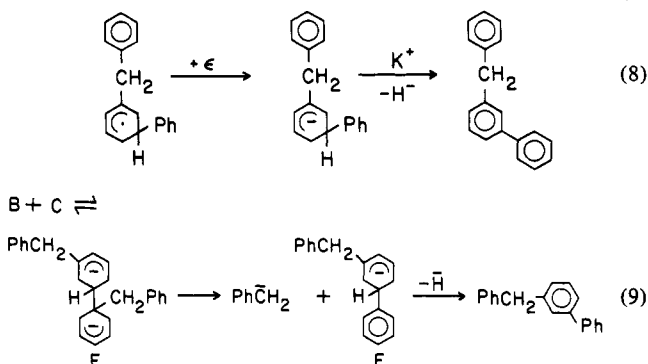
(5) The method of synthesis was 3-methylbiphenyl-<sup>14</sup>C. 3- $\text{PhC}_6\text{H}_4\text{CH}_2\text{Br}$   $\xrightarrow{\text{DMF}}$  3- $\text{PhC}_6\text{H}_4\text{CHO}$   $\xrightarrow{\text{PhMgBr}}$  3- $\text{PhC}_6\text{H}_4\text{CH(OMe)Ph}$   $\xrightarrow{\text{SOCl}_2}$  3- $\text{PhC}_6\text{H}_4\text{CH}_2\text{Ph}$ . The proton and <sup>13</sup>C NMR spectra were identical with those of the product from eq 1. 3-Benzylbiphenyl (mp 47 °C) has been previously synthesized by: Chel'tsova, M. A.; Petrov, A. D.; Lubuzh, E. D.; Ereemeeva, T. E. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* 1965, 14, 107.

(6) Kryger, R. D.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* 1977, 99, 7589.

(7) For a discussion of partial rate factors for attack of phenyl radicals on aromatic substrates, see: Perkins, M. J. *Free Radicals* 1973, 2, 231.

(8) For evidence that radicals are converted to anions in glyme in the presence of alkali metals, see: Garst, J. E. *Acc. Chem. Res.* 1971, 4, 400.

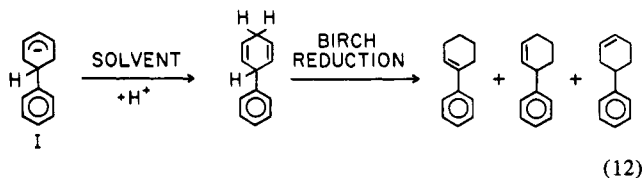
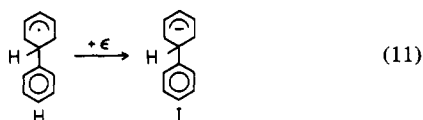
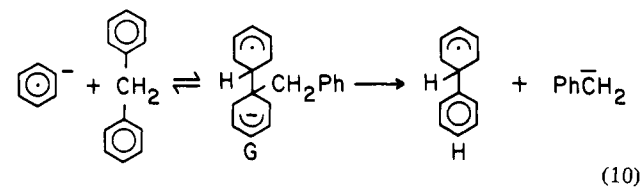
B and C, to yield the dianion E (eq 9), which then loses a benzyl



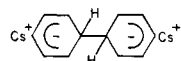
anion to produce the anion F; on loss of a hydride anion F yields 3-benzylbiphenyl. In both mechanisms the reaction is an ipso-aromatic substitution, and the leaving group is a benzyl anion.<sup>9</sup>

Gerson and Martin<sup>10</sup> showed that the diphenylmethane radical anion ( $-70^\circ\text{C}$ ) possesses predominant and equal charges in the ortho and meta positions. If we assume a steric effect at the ortho position for attack by the radical anion, then the predominant meta attack, eq 1 and 6, appears reasonable.

In order to determine whether we were dealing with an isolated case, we repeated the reaction of diphenylmethane with NaK in glyme-triglyme ( $0^\circ\text{C}$ , 3 h) in the presence of 1.1 molar equiv of benzene. We reasoned that the benzene radical anion should undergo the ipso reaction with diphenylmethane to yield toluene and biphenyl. After being quenched with water, the reaction mixture was subjected to GC (and GC/MS) analysis. The molar percentages of products for a typical run were toluene 56, biphenyl plus the hydrogenated biphenyls<sup>11</sup> 38, 3-benzylbiphenyl 2, and dihydro-3-benzylbiphenyl 6. Forty-eight percent of the diphenylmethane was recovered unchanged. The reaction between benzene and diphenylmethane can be formulated as an ipso nucleophilic substitution reaction which proceeds through the benzene radical anion as shown in eq 10-14. If the initial attack of the



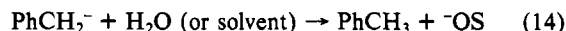
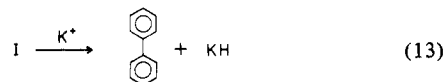
(9) Grovenstein and co-workers<sup>2</sup> formulate the dimerization of benzene in Cs K Na in THF at  $-70^\circ\text{C}$  as proceeding through the benzene radical anion to produce



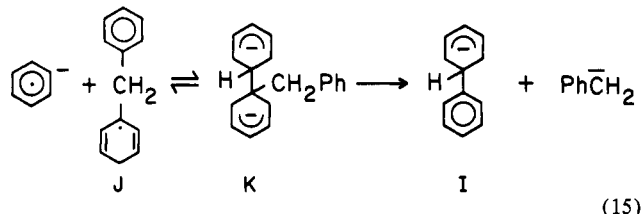
which on quenching with water yields 1,1',4,4'-tetrahydrobiphenyl.

(10) Gerson, F., Martin, W. B., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 1883.

(11) A 168-mg sample of one peak (Dexsil 300 on 90/100 Anachrom Q) was isolated (preparative GC). <sup>1</sup>H and <sup>13</sup>C NMR spectra indicated the sample was a mixture of biphenyl and the phenylcyclohexenes in about equal amounts. Catalytic hydrogenation (Pd/C) afforded phenylcyclohexane (<sup>13</sup>C NMR spectrum identical with authentic sample) and biphenyl. The GC/MS (OV101) column afforded better separation and indicated that a spectrum of hydrogenated biphenyls has been produced—in addition to biphenyl.



benzene radical anion on diphenylmethane (eq 10) to form G is reversible,<sup>12</sup> then the driving force for the reaction could be the production of the stable benzyl anion and the phenylcyclohexadienyl radical<sup>13</sup> H by fragmentation of G. The Grovenstein mechanism<sup>2,9</sup> may also be written for the reaction of benzene with diphenylmethane and involves the formation of I through the intermediates J and K as shown in eq 15; I then follows the same



reaction scheme<sup>14</sup> (eq 12 and 13) previously postulated for the mechanism involving nucleophilic aromatic substitution.<sup>15</sup>

In summary, we have observed two cases of ipso-aromatic substitution. A choice between alternative mechanisms (e.g., eq 10 and 11 or eq 15) must await further evidence.

**Acknowledgment.** We thank Mr. L. L. Brown for determining the <sup>13</sup>C NMR spectra and Dr. E. W. Hagaman for their interpretation. C.J.C. acknowledges helpful discussions with Professor E. Grovenstein, Jr., Dr. M. Poutsma, and Professor F. Schell.

(12) The best models for the intermediates (or transition states) D and G are Meisenheimer complexes whose formation have been shown to be reversible under certain conditions. See: Servis, K. L. *J. Am. Chem. Soc.* **1965**, *87*, 5495; **1967**, *89*, 1508. Also, see a series of papers by Bernasconi and co-workers: Bernasconi, C. F.; Gandler, J. R. *Ibid.* **1978**, *100*, 8117.

(13) DeTar, D. F. *J. Am. Chem. Soc.* **1967**, *89*, 4058.

(14) For examples of further reductions of initial Birch-Hückel reduction products, see: Schlenk, W.; Bergman, E. *Liebigs Ann. Chem.* **1928**, *463*, 90. Hückel, W.; Breitschneider, H. *Ibid.* **1939**, *540*, 157. Birch, A. J. *J. Chem. Soc.* **1944**, 430. Krauch, H.; Kunz, W. "Reaktionen der Organische Chemie", 4th ed., Huthig Verlag: Heidelberg, 1969. Birch, A. J.; Subba Rao, G. *Adv. Org. Chem.* **1972**, *8*, 1. Hückel, W.; Vevera, E. *Chem. Ber.* **1956**, *89*, 2105. Hückel, W.; Cramer, R.; Laufer, S. *Liebigs Ann. Chem.* **1960**, *630*, 89.

(15) A referee points out that Young and Bauld (Young, J. D.; Bauld, N. L. *Tetrahedron Lett.* **1971**, 2251) found that the diphenylmethane radical anion (DPM<sup>-</sup>) is considerably more stable than the benzene radical anion (B<sup>-</sup>) and that the proposed reaction 10 thus conflicts with the Young and Bauld results. If, however, DPM<sup>-</sup> is more stable, then B<sup>-</sup> should be more reactive. Young and Bauld do not specify the temperature employed, and they point out that radical anions "are not generated in high concentrations when the crown ether is omitted". We did not, in the experiments reported here, use crown ether as a solvent. In the one case in which glyme and 18-crown-6 were employed, the reaction did not proceed. We observed, in addition, a dependence of product upon temperature in several of the NaK reductions between  $-40$  and  $0^\circ\text{C}$ .

### Interaction of Pyruvate-Thiamin Diphosphate Adducts with Pyruvate Decarboxylase. Catalysis through "Closed" Transition States<sup>1</sup>

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The enzymic decarboxylation of pyruvate has been proposed to proceed via the enzyme-bound adduct of the substrate with the coenzyme thiamin diphosphate (TDP, 1).<sup>2-4</sup> This adduct,  $\alpha$ -

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