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Received July 27, 1979

Carbon-Carbon Cleavage during Birch-Hückel-Type Reductions[1]

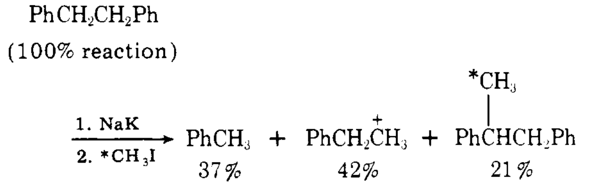
Sir:

Recently it was reported[2] that the action on coal (Westerholt Mine, Robert Seam, 24% volatile) of potassium in a mixture of glyme and triglyme, followed by quenching with water, (a) reduced the coal in three passes from $C_{100}H_{63}O_{3.2}$ to fractions of composition $C_{100}H_{144}O_{1.8}$ (soluble) and $C_{100}H_{91}O_{3.4}$ (insoluble) and (b) diminished the molecular weight of the soluble sample from $>10^5$ to values of 3000-5000. It further appeared, from spectral (NMR and quantitative IR) data, that the methyl-group content of the product increased with increased hydrogen uptake; i.e., ~40% of the hydrogen uptake was related to the increase in methyl-group content. This is a surprising conclusion, for it implies the cleavage of *aliphatic* carbon-carbon bonds in the coal structures and is contrary to the commonly held concept of the Birch-Hückel reduction,[3,4] in which aromatic rings are reduced to cycloalkenes.

Not only protic solvents, but also ethers[4] and alkyl halides, may be used[5,6] as quenchers, with the formation, e.g., from naphthalene, of methyl-[5] and isopropylnaphthalenes.[6] A less drastic reduction prior to the alkylation procedure has been applied to coal by Sternberg and co-workers.[7] However, this reduction method may be seen as being related to the Birch-Hückel reduction. Sternberg and co-workers explained the high solubility of the product by (a) cleavage of ether linkages to form phenolate anions, (b) C-alkylation of the aromatic anions, and (c) O-alkylation of the phenolate anions. A similar reduction procedure by direct insertion of potassium has been reported,[8] and the formation of the potassium graphite intercalation compound by treating graphite with potassium naphthalene[9] links these unconventional reduction methods to the more common Birch-Hückel method.

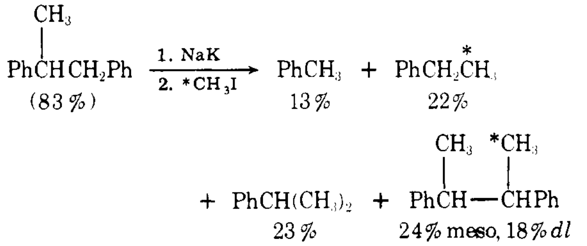
There is some evidence for cleavage of aliphatic carbons during Birch-Hückel reductions in highly substituted, hindered compounds,[3b,10-12] and Langendijk and Swarc[13] reported spectral evidence for cleavage of 1,2-di(α-napthyl)ethane by sodium in THF, THP, DME, and HMPA.[14] However, other authors[12c,15] found that 1,2-diphenylethane cannot be cleaved in ether. (In unpublished work,[16] Grovenstein and co-workers have found that cesium-sodium-potassium alloy will cleave bibenzyl and several of its derivatives.)

For the reasons mentioned above we studied the reactions of sodium-potassium alloy in the solvent system glyme-triglyme[2] on a series of model compounds to determine whether, in fact, the Birch-Hückel reduction can be used in this solvent system to cleave carbon-carbon bonds. In the first series of experiments—to simplify product analysis—methyl-^{14}C iodide[17] was used to quench the solutions. The reactions were all carried out at the same temperature (0 °C) and concentrations and for the same lengths of time (3 h).[18] Conditions were not optimized. Since the products were analyzed by GC,[18] the yields are reported as percent composition of the components which pass through the chromatograph. The reactants, products, and yields[18] are shown (reactions 1-5). *meso-* and *dl-*



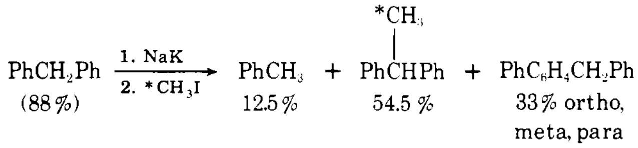
$$\underset{\text{(100\% reaction)}}{\text{PhCH}_2\text{CH}_2\text{Ph}} \xrightarrow[\text{2. *CH}_3\text{I}]{\text{1. NaK}} \underset{37\%}{\text{PhCH}_3} + \underset{42\%}{\text{PhCH}_2\overset{+}{\text{C}}\text{H}_3} + \underset{21\%}{\text{Ph}\overset{\text{*CH}_3}{\overset{|}{\text{C}}}\text{HCH}_2\text{Ph}}$$

(1)



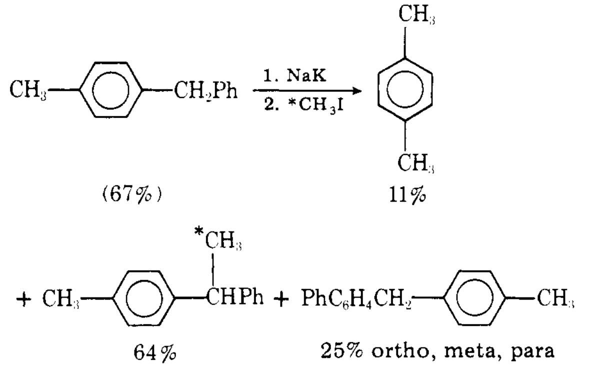
$$\underset{(83\%)}{\text{Ph}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{HCH}_2\text{Ph}} \xrightarrow[\text{2. *CH}_3\text{I}]{\text{1. NaK}} \underset{13\%}{\text{PhCH}_3} + \underset{22\%}{\text{PhCH}_2\overset{*}{\text{C}}\text{H}_3} + \underset{23\%}{\text{PhCH(CH}_3)_2} + \underset{24\%\ \text{meso},\ 18\%\ dl}{\text{Ph}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{H}-\overset{\text{*CH}_3}{\overset{|}{\text{C}}}\text{HPh}}$$

(2)

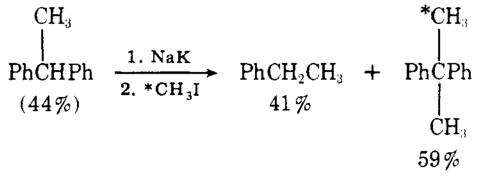


$$\underset{(88\%)}{\text{PhCH}_2\text{Ph}} \xrightarrow[\text{2. *CH}_3\text{I}]{\text{1. NaK}} \underset{12.5\%}{\text{PhCH}_3} + \underset{54.5\%}{\text{Ph}\overset{\text{*CH}_3}{\overset{|}{\text{C}}}\text{HPh}} + \underset{33\%\ \text{ortho, meta, para}}{\text{PhC}_6\text{H}_4\text{CH}_2\text{Ph}}$$

(3)



(4)



$$\underset{(44\%)}{\text{Ph}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{HPh}} \xrightarrow[\text{2. *CH}_3\text{I}]{\text{1. NaK}} \underset{41\%}{\text{PhCH}_2\text{CH}_3} + \underset{59\%}{\text{Ph}\underset{\text{CH}_3}{\underset{|}{\overset{\text{*CH}_3}{\overset{|}{\text{C}}}}}\text{Ph}}$$

(5)

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Table I. Yields of Cleavage Products for Four Typical Reactants (NaK in Glyme-Triglyme, 0 °, 4-h Water Quench)

no.	reactant	products	yield, %[a]	total recovery, %[b]	recovered reactant, %
1	bibenzyl	toluene	85	96	35
		unidentified	11		
2	1,2-diphenylpropane	toluene	44		
		ethylbenzene	40	89	23
		2-phenylbutane[c]	5		
3	diphenylmethane	toluene	43		
		benzylbiphenyl	33	76	86
4	phenyl-*p*-tolylmethane	*p*-xylene	33		
		4-methylbenzylbiphenyl	28	61	81

[a] Based on unrecovered reactant and corrected for (multiplied by) fraction of total recovery. [b] As measured against biphenyl, the internal GC standard. [c] Identified through ^{1}H and ^{13}C NMR.

2,3-diphenylbutane (reaction 2) were identified through their NMR spectra. Both *o*- (mp 54 °C) and *p*- (mp 85 °C) benzylbiphenyls (reaction 3) were described by Goldschmidt;[20] our product, based on ^{1}H and ^{13}C NMR, GC-mass spectrometry, and C and H analyses, must be a mixture of the three isomers. Vernon and Robinson[21,22] prepared *p*-methylbenzylbiphenyl, and the ^{1}H and ^{13}C NMR spectrum of our product (reaction 4) is consistent with that structure. When reaction 3 was carried out with *phenyl*-labeled diphenylmethane we found no evidence (GC and radioactivity monitor) for the production of benzene; a portion of the solvent, however, was labeled, indicating reaction of diphenyl-^{14}C-methane with glyme, triglyme, or both. No benzene was produced as well during reactions 4 or 5.

A second series of reactions was carried out in which water was used as the quencher. The NaK was first stirred 4 h in glymes at −15 °C; reaction time after addition of reactant was 3 h at 0 °C. Percentage yields were calculated against an internal standard (biphenyl). The results are given in Table I.

One would expect the yields of toluene and benzylbiphenyls (reaction 3) and *p*-xylene and *p*-tolylbiphenylmethane (reaction 4), contrary to observation, to be the same. When a water quench is used (Table I), the yields of toluene and *p*-xylene are slightly greater than those of the substituted biphenyls. The discrepancies in reactions 3 and 4 may be due to reaction of diphenylmethane and phenyl-*p*-tolylmethane with solvent to yield materials not observable by GC. Certainly the 2-phenylbutane (reaction 2, Table I) produced from 1,2-diphenylpropane must be formed by an S$_N$2 reaction between solvent and the 2-phenyl-1-propyl carbanion.

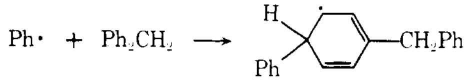
Reactions 1 and 2 portray the splitting of sp^3–sp^3 carbon–carbon bonds, and are explainable in conventional[13] mechanistic terms. In each of the reactions 3-5, however, sp^2–sp^3 carbon–carbon bonds are broken, but the mechanisms are not clear. Using reaction 3 as an example, the cleavage can be imagined as taking place through either reaction 7 or reaction 8. If reaction 7 occurs, then the absence of benzene is difficult to explain, for the rate at which a phenyl radical extracts hydrogen from solvent (reaction 9) should be faster than the rate (reaction 10) of its addition to diphenylmethane,[23] and we would expect benzene (reaction 11) to be formed in reasonable yield compared with the benzylbiphenyls (reactions 10 and 12). The same reasoning could be applied to reaction 8; a phenyl anion might also be expected to extract hydrogen from solvent to yield benzene. Consequently we believe it possible that a nucleophilic aromatic substitution is taking place (reaction 13), and we are presently investigating this likelihood.

$$\text{Ph}_2\text{CH}_2 + \varepsilon \longrightarrow \overset{\bullet}{\overline{\text{Ph}}}{}_2\text{CH}_2 \qquad (6)$$

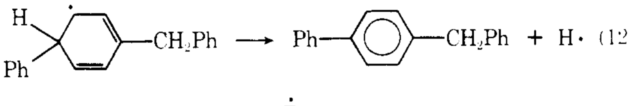
$$\overset{\bullet}{\overline{\text{Ph}}}{}_2\text{CH}_2 \longrightarrow \text{Ph}\cdot + \text{Ph}\bar{\text{C}}\text{H}_2 \qquad (7)$$

$$\overset{\bullet}{\overline{\text{Ph}}}{}_2\text{CH}_2 \longrightarrow \overline{\text{Ph}} + \text{PhCH}_2\cdot \qquad (8)$$

$$\text{Ph}\cdot + \text{glyme} \longrightarrow \text{C}_6\text{H}_6 + \text{glyme}\cdot \qquad (9)$$


(10)

$$\text{Ph}\cdot + \text{glyme–triglyme} \longrightarrow \text{PhH} + \text{R}\cdot \qquad (11)$$


(12)

$$\text{Ph}_2\text{CH}_2 + \varepsilon \longrightarrow \text{PhCH}_2\overset{\bullet}{\overline{\text{Ph}}}$$

$$\xrightarrow{\text{Ph}_2\text{CH}_2} \text{PhC}_6\text{H}_4\text{CH}_2\text{Ph} + \varepsilon + \text{PhCH}_3 \qquad (13)$$

It now appears that the repeated action of sodium–potassium alloy in glyme–triglyme followed by quenching with methyl iodide or with water can be an efficient low-temperature method for degrading coal by cleavage of aliphatic as well as aromatic–aliphatic carbon–carbon bonds.

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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 Corporation. Preliminary reports of this work were presented by H.-P. Hombach at the 26th DGMK Meeting in Berlin, Germany, Oct 6, 1978, and by C. J. Collins at the ACS/CSJ Chemical Congress, Honolulu, Hawaii, April 1-6, 1979.

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(18) The general procedure was as follows. NaK (0.5 g) was added to a mixture of 20 mL of glyme and 20 mL of triglyme in a 300-mL round-bottom flask (argon sweep) which had been cooled to −40 °C. The mixture was stirred until a constant blue color was achieved. The solution was warmed to 0 °C and 1 g of substrate was added. The mixture was stirred at 0 °C for 3 h. Methyl-^{14}C iodide[13] (1–2 mL) was added dropwise until the solution was clear yellow. The mixture was cooled to <20 °C and excess NaK was removed mechanically. Pentane (or benzene, depending on substrate) (20 mL) was added, followed by 100 mL of H_2O. After separation of organic layer, it was concentrated and subjected to GC (with carbon-14 monitor) analysis (Barber-Coleman Model 5000). The products were identified by preparative GC (Varian Aerograph Series 2860) separation followed by NMR analysis (both ^{1}H and ^{13}C)
(19) (a) Ott, E. *Ber. Dtsch. Chem. Ges.* **1928,** *61,* 2139. (b) ^{1}H NMR spectra of *meso-* and *dl*-1,2-diphenylbutane: the methyl resonance of the meso isomer was a doublet centered at 1.03 ppm, whereas the methyl doublet of the *dl* isomer was centered at 1.29 ppm downfield from the meso isomer as expected; the methine hydrogen of both isomers was a poorly resolved multiplet centered at 2.90 ppm; both isomers had broadened aromatic resonance at 7.15 ppm.
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(22) *p*-Benzylbiphenyl was prepared by the Friedel-Crafts alkylation of biphenyl with benzyl bromide and $AlCl_3$. The para isomer (mp 84 °C) exhibited ^{1}H and ^{13}C NMR spectra similar to, but not identical with, those of the substances isolated from reaction 3. From the spectra of the mixture of ortho and meta isomers of benzylbiphenyl left after isolation of the para isomer, we conclude that the substances isolated from reaction 3 are mixtures of all three isomers. Independent syntheses of the ortho and meta isomers are now underway. Friedel-Crafts acylation of biphenyl with *p*-toluyl chloride followed by reduction of the ketone yielded the *p*-(*p*-methylbenzyl)biphenyl (mp 86–87 °C) whose ^{1}H and ^{13}C NMR spectra were identical with those of the substances isolated from reaction 4. Once again, a mixture of all three isomers seems likely. Details will be published later.
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(24) Visiting Scientist, May–Sept 1978. Correspondence can be addressed to this author at the Max-Planck Institut für Kohlenforschung, 4330 Mülheim (Ruhr), Kaiser-Wilhelm Platz 1, West Germany.

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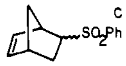
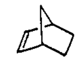
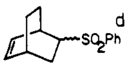
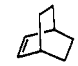
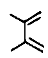
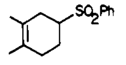
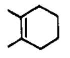
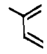
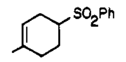
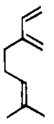
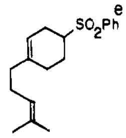
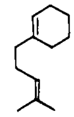
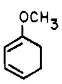
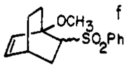
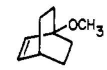
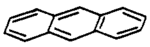
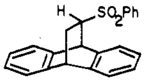
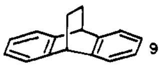
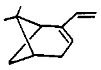
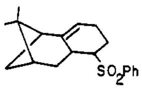
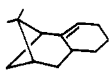
Received May 21, 1979

An Ethylene and Terminal Olefin Equivalent in [4 + 2] π Cycloadditions. General Synthetic Application of Phenyl Vinyl Sulfone to the Construction of Functionalized Six-Membered Rings

Sir:

The widespread use of the Diels–Alder reaction in synthetic organic methodology stems in large part from the frequent need to elaborate six-membered rings and the customarily high efficiency of such cycloadditions. A long-standing restriction to the universal application of this chemistry materializes when the diene and dienophile have no π-donor–acceptor complementarity. This phenomenon is witnessed perhaps most acutely in the case of ethylene,[1–4] although allyl compounds in general also exhibit slight dienophilic reactivity.[5,6] Despite the serious constraints caused by the natural reluctance of such olefinic partners to enter into concerted cycloaddition,[1c] no general, suitably mild, and regiospecific (for terminal olefinic synthons) alternative has yet been devised. In this communication, we demonstrate that phenyl vinyl sulfone[7] can serve very conveniently as an ethylene equivalent in [4 + 2] cycloadditions. Furthermore, since **1** is captured by unsymmetrical dienes with high regioselectivity, the α-sulfonyl carbanion centers in the adducts are available for the regiospecific attachment of appendages and/or functional groups. As a result, these intermediates are utilizable in manifold ways as terminal olefin equivalents. Exploitation of these results should serve to augment our ability to elaborate complex cyclohexane derivatives more expeditiously.

Table I. Ethylene Equivalency. Cycloadditions of Phenyl Vinyl Sulfone and Reductive Desulfonylation of the Adducts

diene	reactn conditions	adduct structure	cycloaddn yield, %[a]	desulfonyln product[b]	yield, %[a]
	25°C, 110 hr.	 [c] 1	100	 2	80
	125°C, 17 hr.	 [d] 3	89	 4	78
	135°C, 32 hr.	 5	94	 6	76
	120°C, 28 hr	 7	93	-----	
	155°C, 22 hr.	 [e] 8	98	 9	92
	135°C, 18 hr.	 [f] 10	68	 11	91
	155°C, 100 hr.	 12	96	 13	94
	150°C, 28 hr.	 14	98	 15	97

[a] The yields are based upon quantities of pure material isolated after column chromatography except in the cases of **2, 4,** and **6** which were purified by distillation. [b] All products exhibited satisfactory IR, NMR, mass, and microanalytical data unless known previously; in these circumstances, direct spectral comparisons with authentic samples were made. [c] 22% exo, 78% endo mixture (see ref 8i). [d] 19% exo, 81% endo mixture. Regiochemistry assigned on the basis of analogy to **7.** i[f] 18% exo, 82% endo (syn to double bond) mixture.

The concept of utilizing simple α,β-unsaturated sulfones as dienophiles is not new. Isolated examples of their use by various investigators have been reported.[8] The objectives of the past studies range from comparisons of relative rate ratios and analyses of exo–endo stereoselectivities to the incorporation of a sulfone group for chemical purposes. Because symmetrical dienes were always employed, no information has been previously uncovered concerning the regiochemistry of these