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Carbon-Carbon Cleavage during Birch-Hückel-Type Reductions¹

Sir:

Recently it was reported² 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 C₁₀₀H₆₃O_{3.2} to fractions of composition C₁₀₀H₁₄₄O_{1.8} (soluble) and C₁₀₀H₉₁O_{3.4} (insoluble) and (b) diminished the molecular weight of the soluble sample from >10⁵ 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 ethers⁴ and alkyl halides, may be used^{5,6} as quenchers, with the formation, e.g., from naphthalene, of methyl-⁵ and isopropyl-naphthalenes.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

naphthalene⁹ 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 Swarc¹³ reported spectral evidence for cleavage of 1,2-di(α-naphthyl)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 (In unpublished work,¹⁶ Grovenstein and co-workers have found that cesium-sodium-potassium alloy will cleave dibenzyl and several of its derivatives.)

For the reasons mentioned above we studied the reactions of sodium-potassium alloy in the solvent system glyme-triglyme² 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-¹⁴C iodide¹⁷ 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 yields¹⁸ are shown (reactions 1-5). *meso*- and *dl*-

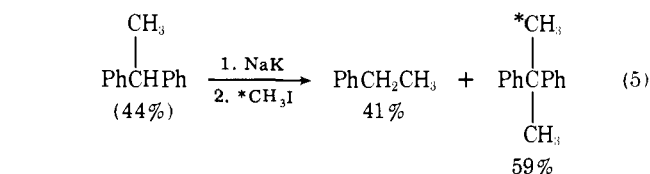
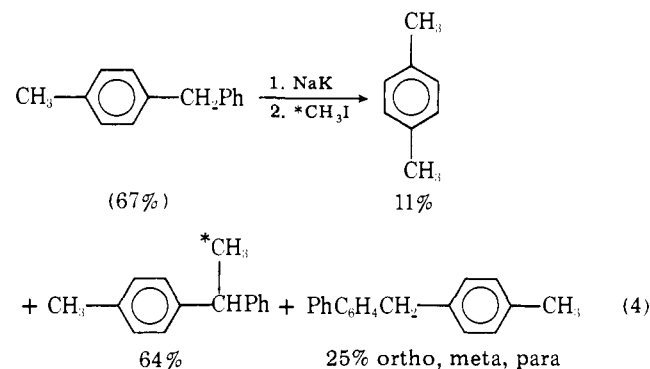
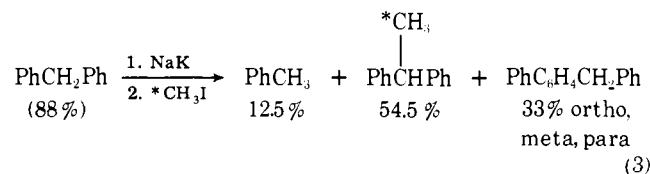
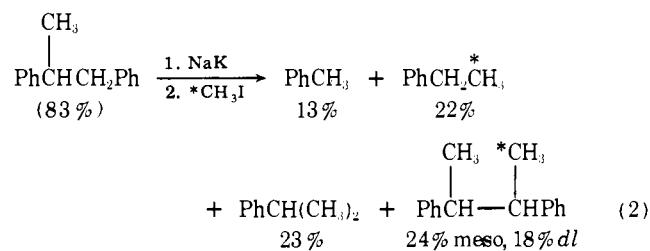
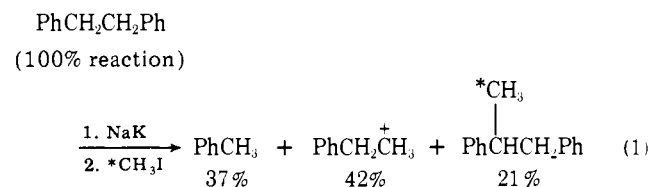


Table I. Yields of Cleavage Products for Four Typical Reactants (NaK in Glyme-Triglyme, 0 °, 4-h Water Quench)

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

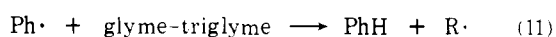
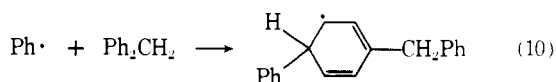
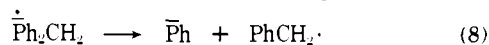
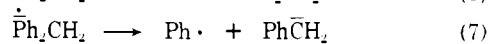
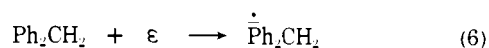
^a Based on unrecovered reactant and corrected for (multiplied by) fraction of total recovery. ^b As measured against biphenyl, the internal GC standard. ^c Identified through ¹H and ¹³C NMR.

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 ¹H and ¹³C 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 ¹H and ¹³C 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-¹⁴C-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.

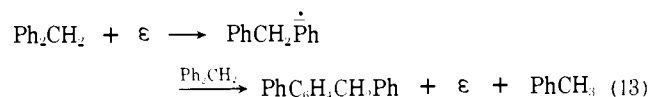
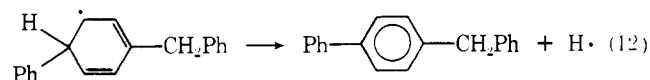
One would expect the yields of toluene and benzylbiphenyls (reaction 3) and *p*-xylene and *p*-tolylbiphenylmethane (reaction 4), contrary to observation, to be the same. When a water quench is used (Table I), the yields of toluene and *p*-xylene are slightly greater than those of the substituted biphenyls. 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_N2 reaction between solvent and the 2-phenyl-1-propyl carbanion.

Reactions 1 and 2 portray the splitting of sp³-sp³ carbon-carbon bonds, and are explainable in conventional¹³ mechanistic terms. In each of the reactions 3-5, however, sp²-sp³ 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 rea-

sonable 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.



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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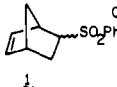


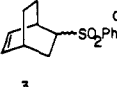


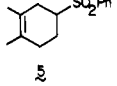


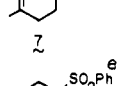

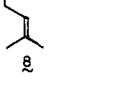


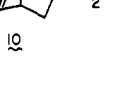

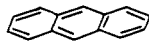
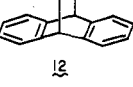
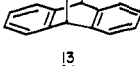
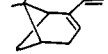
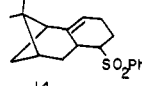
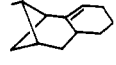
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An Ethylene and Terminal Olefin Equivalent in [4 + 2] π Cycloadditions. General Synthetic Application of Phenyl Vinyl Sulfone to the Construction of Functionalized Six-Membered Rings

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 regioselective (for terminal olefinic synthons) alternative has yet been devised. In this communication, we demonstrate that phenyl vinyl sulfone⁷ can serve very conve-

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

diene	reactn conditions	adduct structure	cyclo-addn yield, % ^a	desulfonyln product ^b	yield, % ^a
	25°C , 110 hr.		100		80
	125°C , 17 hr.		89		78
	135°C , 32 hr.		94		76
	120°C , 28 hr.		93	-----	
	155°C , 22 hr.		98		92
	135°C , 18 hr.		68		91
	155°C , 100 hr.		96		94
	150°C , 28 hr.		98		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**. ^e 18% exo, 82% endo (syn to double bond) mixture.

niently 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 regioselective 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.

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