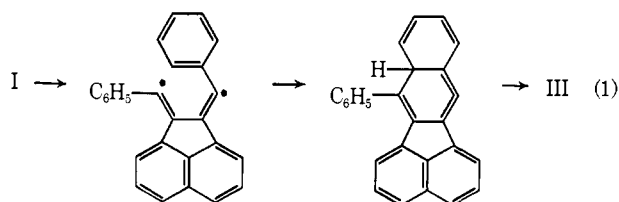
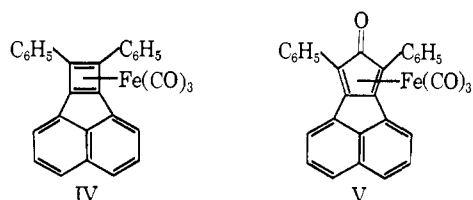


A diradical process for formation of III which allows the geometric changes necessary and involves hydrogen rearrangement is summarized in eq 1. Related concerted, dipolar, acid-catalyzed, or more complicated mechanisms can also be envisaged. The gross chemical



changes in conversion of the *parallel* acetylene I to III are analogous to formation of 9-phenyldibenz[*a,c*]anthracene by irradiation of the *crossed* acetylene, 2,2'-bis(phenylethynyl)biphenyl.^{3,7} Cyclobutadiene and other intermediates may be involved in the present systems; however they are not yet isolable. Attempts to lock I with iron pentacarbonyl⁸ as its cyclobutadiene-iron tricarbonyl (IV) gives acetyliron tricarbonyl (V, mp 205°, tan) and III. Compound V is identified by



its keto and metal carbonyl absorptions (6.13 and 4.87, 5.02, and 5.05 μ) and its decomposition to acetylone. The novel 1,4-transannular insertion reaction of I with iron pentacarbonyl differs from that for 1,2-bis(phenylethynyl)benzene.⁹

Bromination of I occurs by transannular 1,4-addition to yield 1,2-bis(α -bromobenzylidene)acenaphthene (VI, eq 2, mp 149°); adducts VII–XI and their geometric isomers were not isolated. Bromination of I is strikingly different from the collapsing domino process in conversion of 1,2-bis(phenylethynyl)benzene by bromine to 3-bromo-1-(α -bromobenzylidene)-2-phenylindene.⁹

Compound VI is white, shows no acetylenic absorption, gives a negative silver nitrate test, is oxidized by sodium dichromate to acenaphthenequinone, and, of particular interest, reacts with magnesium to give I. Its ultraviolet spectrum ($\lambda_{\text{max}}^{\text{ethanol}}$ 210 (ϵ 41,800), 239 (65,900), and 328 m μ (13,000)) is similar to that of acenaphthylene derivatives and indicates that its exocyclic double bonds are highly twisted.¹⁰ Structure VIa or VIb agrees with the nmr in that the phenyl groups ($\tau \sim 2.80$) are not extensively shielded.

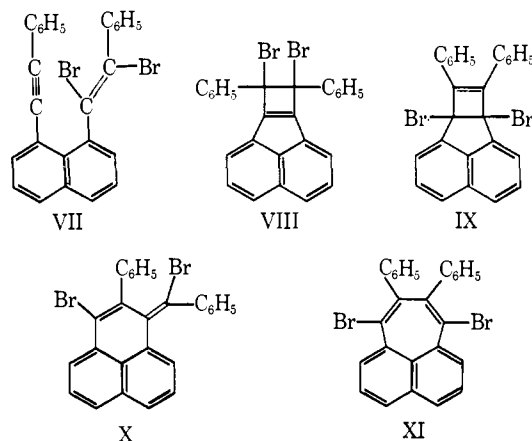
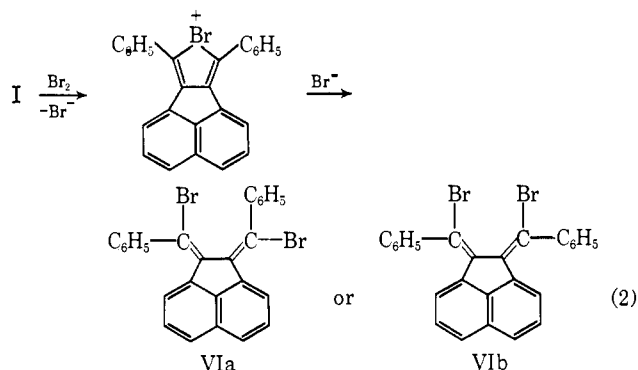
Compound VI dehydrobrominates to 7-bromo-12-phenylbenzo[*k*]fluoranthene (XII, 78%, mp 138°) when warmed or photolyzed, possibly as in eq 3. The structure of XII is confirmed from its spectra and its reaction with magnesium and hydrolysis to give III.

(7) (a) E. H. White and A. A. F. Sieber, *Tetrahedron Letters*, 2473 (1966). (b) B. Bossenbroek, Ph.D. Thesis, The Ohio State University, 1967, independently concluded that 2,2'-bis(phenylethynyl)biphenyl photolyzes to 9-phenyldibenz[*a,c*]anthracene.^{7a}

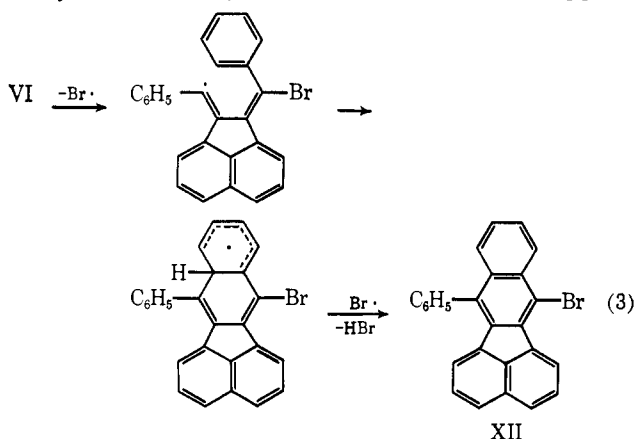
(8) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3253 (1965).

(9) H. W. Whitlock, Jr., and P. E. Sandvick, *ibid.*, **88**, 4525 (1966).

(10) N. Maxim, *Bull. Soc. Chim. France*, **45**, 1137 (1929), reports that 1,2-bis(benzylidene)acenaphthene is red-orange.



The reactivity of VI apparently stems from its twisted exocyclic structure, and conversion to XII appears



more favorable from VIa, the product of *trans* addition to I, than from VIb.

Acknowledgment. This research was supported by Petroleum Research Fund 451-A1.

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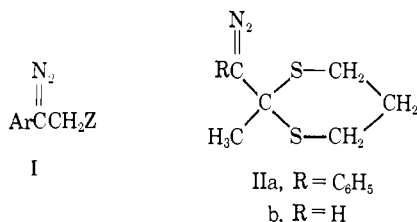
The Effects of Neighboring Heteroatoms in Rearrangement to Divalent Carbon

Sir:

The abilities of the indicated groups to migrate to divalent carbon in decomposition of diazo compounds are: hydrogen > aryl > methyl.¹ Photolysis of 1-

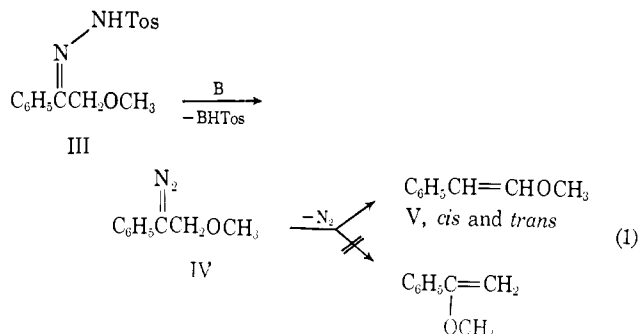
(1) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961); (b) H. Phillip and J. Keating, *Tetrahedron Letters*, 523 (1961); (c) G. Kaufmann, The Ohio State University, 1963–1966.

diazo-2-methoxy-2-methylpropane yields 1-methoxy-1-methylcyclopropane by insertion and *cis*- and *trans*-2-methoxy-2-butenes by methyl migration; rearrangement of the methoxy group to give 1-methoxy-2-methylpropene is very minor.² We wish to summarize the intramolecular reactions of diazo compounds having ether, amine, and thioether substituents in β positions (I, Z = OCH₃, OC₆H₅, N(CH₃)₂, SC₂H₅, and SC₆H₅) and of representative 2-diazomethyl-2-methyl-1,3-dithianes (II). These systems provide information



concerning atomic and participative factors which allow rearrangement of β substituents to divalent carbon.

Decomposition of 2-methoxyacetophenone *p*-tosylhydrazone³ (III, mp 103°) by butyllithium, sodium methoxide, or lithium methoxide (1.1–3.1 equiv)⁴ in diglyme at 130° or pyrolysis of the lithium salt of III gives only *cis*- and *trans*- β -methoxystyrenes (52% *trans*) (V, 90% yield, eq 1) as intramolecular products.⁵ 2-Phenoxyacetophenone *p*-tosylhydrazone



(mp 125°) is converted similarly to *cis*- and *trans*- β -phenoxystyrenes⁵ (90%). Thermolyses of 1-diazo-2-methoxy-1-phenylethane (IV) and 1-diazo-2-phenoxy-1-phenylethane (VI) thus result in carbenic rearrangement of β -hydrogen rather than of methoxy or phenoxy groups.

1-Diazo-2-dimethylamino-1-phenylethane (VIII), prepared *in situ* from 2-dimethylaminoacetophenone *p*-tosylhydrazone hydrochloride (VII, mp 171°, eq 2) and sodium methoxide or butyllithium (1.1–3.0 equiv), decomposes in inert environments to *cis*- and *trans*- β -dimethylaminostyrenes (IX).⁵ The β -dimethylamino group does not rearrange carbenically in competition with hydrogen.

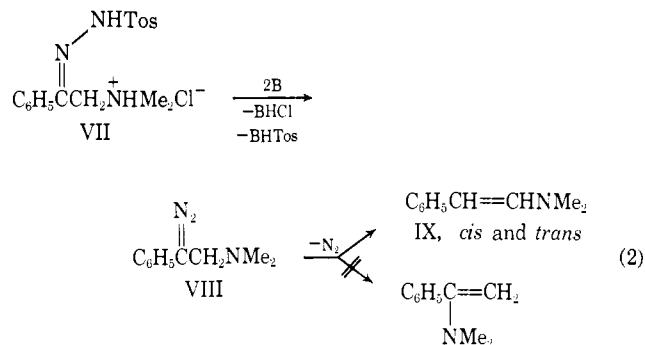
The carbenic behavior of 1-diazo-1-phenyl-2-thioethoxyethane (XI) is quite different from that of IV, VI,

(2) (a) W. Kirmse and M. Buschhoff, *Angew. Chem.*, 77, 681 (1965). (b) Irradiation of diazoacetaldehyde diethyl acetal yields ketene diethyl acetal and *cis*- and *trans*-1,2-diethoxyethylenes;^{2a} the relative abilities for hydrogen and β -ethoxyl to migrate were not reported however.

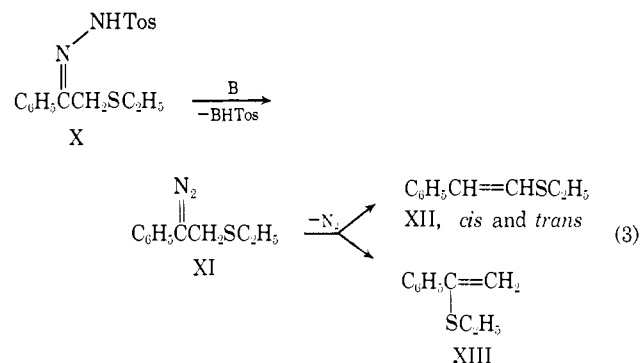
(3) (a) *p*-Tosylhydrazones presently described were prepared from *p*-tosylhydrazine and the corresponding ketones or aldehyde. (b) All new compounds reported have proper analyses.

(4) The decompositions were studied systematically over the range of equivalents indicated.

(5) Identified (a) by their gas chromatographic properties and/or (b) their conversion in high yields to phenylacetaldehyde 2,4-dinitrophenylhydrazone by 2,4-dinitrophenylhydrazone reagent.



and VIII. Reaction of 2-ethylmercaptoacetophenone *p*-tosylhydrazone (X, mp 124°) with sodium methoxide (1.1–3.1 equiv) or butyllithium (1.1–1.3 equiv) in decalin or diglyme at 130° or pyrolysis of the lithium salt of X efficiently yields (eq 3) *cis*- and *trans*- β -thioethoxystyrenes (XII, 9–15%) and α -thioethoxystyrene^{3a,6} (XIII, 91–85%). Similar decomposition of 1-diazo-1-phenyl-



2-thiophenoxyethane (XIV) from 2-phenylmercaptoacetophenone *p*-tosylhydrazone (mp 98°) gives *cis*- and *trans*- β -thiophenoxystyrenes (0–8%) and α -thiophenoxystyrenes^{3a,6} (100–92%).

Carbenic decomposition of XI and XIV thus involves major rearrangement of thioether groups rather than hydrogen. The much greater tendency of thioether than of ether or amine substituents to migrate is rationalizable in terms of the greater participative ability of covalent sulfur than of oxygen or nitrogen.⁷ In carbenic rearrangement of a diazo compound such as XI it is also possibly significant that 3d orbital delocalization involving the rearranging sulfur group leads to an ylide-like transition state (XV)⁸ which is not as available to the oxygen (XVI) or nitrogen (XVII) analogs.^{8a}

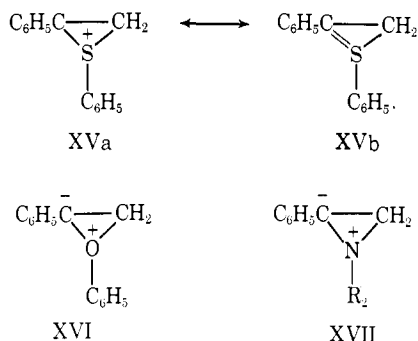
Carbenic decomposition of 2-ethylmercaptoacetophenone *p*-tosylhydrazone (X, mp 124°) is altered greatly when greater than 1 equiv of butyllithium is

(6) These products were converted efficiently by acidic 2,4-dinitrophenylhydrazine to acetophenone 2,4-dinitrophenylhydrazone.

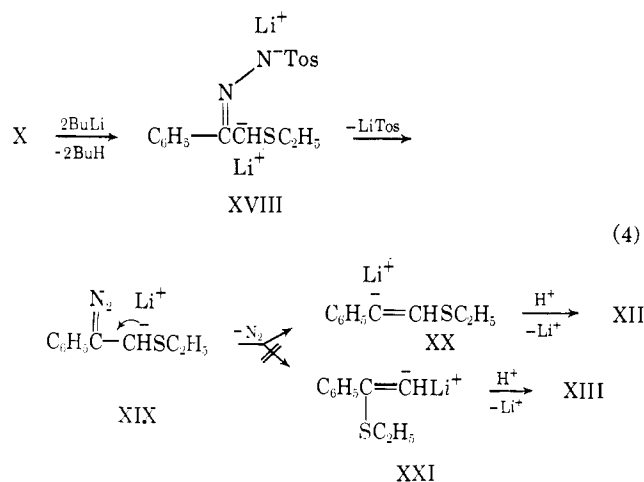
(7) For discussion of participation of oxygen-, nitrogen-, and sulfur-containing substituents in intramolecular nucleophilic processes, see S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, 70, 828 (1948), and P. D. Bartlett, S. D. Ross, and C. G. Swain, *ibid.*, 71, 1415 (1949).

(8) Sulfonium alkylides (R₃S=CR₂) related to XV have been reviewed by A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, Chapter 9.

(8a) NOTE ADDED IN PROOF. Decompositions of XI and of 1-diazo-1-phenylethane in diglyme at 85° occur by first-order processes with rate constants of 1.44 × 10⁻⁴ and 1.51 × 10⁻⁴ sec⁻¹, respectively. Rearrangement of the thioethoxy group does not appear to result in kinetic acceleration in thermolysis of XI. Bond breaking involving expulsion of nitrogen thus is a principal feature in the rate-determining step for decomposition of XI and migration of the thioethoxy group occurs in a transition state having extensive carbenic character or derived from the intermediate carbene.

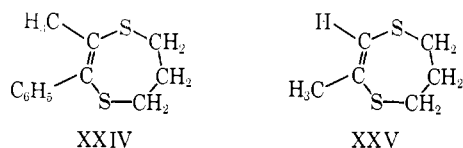


used.⁹ Reaction of X with butyllithium (2.1–3.1 equiv) in decalin at 120° and neutralization result in exclusive formation of XII; the thioethoxy group does not migrate. It is probable that X, in the presence of excess butyllithium, collapses primarily as its dianion (XVIII, eq 4) to XIX which then decomposes to XX rather than to XXI.⁹ Conversion of X to XVIII is indicated by its reaction with butyllithium (3.0 equiv) in tetrahydro-



furan at 0° and neutralization by deuteriotrifluoroacetic acid (3 equiv) to give N,2-dideuterio-2-ethylmercaptoacetophenone *p*-tosylhydrazone¹⁰ (99% isotopic purity). Further evidence for the mechanism sequence proposed is derived by demonstration that the dry salt obtained from 3 equiv of butyllithium and X decomposes thermally to an intense red intermediate which loses nitrogen and then gives XII after neutralization.

Salts of 2-benzoyl-2-methyl-1,3-dithiane *p*-tosylhydrazone (XXII, mp 145°) and 2-formoyl-2-methyl-1,3-dithiane *p*-tosylhydrazone (XXIII, mp 123°) decompose to 2-methyl-3-phenyl-1,4-dithia-2-cycloheptene (XXIV) and 2-methyl-1,4-dithia-2-cycloheptene (XXV), respec-



(9) (a) W. Kirmse, B. G. von Bülow, and H. Schepp, *Ann.*, **691**, 41 (1966), also report that decomposition of salts of *p*-tosylhydrazones is altered in excess (7–8 equiv) sodium amide or sodium hydride. For additional description and discussion of the effects of excess butyllithium on the decomposition of *p*-tosylhydrazones, see R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967); G. Kaufmann, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967). (b) The present mechanism involving *p*-tosylhydrazone dianions differs from that of Kirmse, *et al.*

(10) The deuterium content and positions were established by nmr methods.

tively. Ring expansion rather than methyl migration in these systems again reflects the marked ability of β -thioether groups to undergo carbenic rearrangement. The structure of XXIV is assigned from its nmr and its hydrogenation over nickel to 1-phenylpropane; XXV is established from its nmr signals (τ) at 8.15 (doublet, area 3, $J \sim 1$ cps), 7.85 (multiplet, area 2), 6.55 and 6.60 (superimposed triplets, area 4), and 4.32 (quartet, area 1).

The effects of other neighboring groups in carbenic rearrangement are being investigated.

Acknowledgment. This research was supported by the National Science Foundation.

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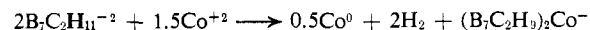
Received August 28, 1967

New Polyhedral Transition Metal Complexes Containing the $\text{B}_7\text{C}_2\text{H}_9^{-2}$ Ligand

Sir:

The recent discovery of polyhedral transition metal complexes in which the metal is "sandwich" bonded to two 11-particle icosahedral carborane fragments¹ (dicarbollide ion, $\text{B}_9\text{C}_2\text{H}_{11}^{-2}$) led us to investigate routes to similar structures which contain smaller $\text{B}_n\text{C}_2\text{H}_{n+2}^{-2}$ ligands. In this and the accompanying communication we report the synthesis of representative polyhedral species which contain the $\text{B}_7\text{C}_2\text{H}_9^{-2}$ and $\text{B}_6\text{C}_2\text{H}_8^{-2}$ ligands coordinated to transition metals.

The previously described $\text{B}_7\text{C}_2\text{H}_{13}$ carborane² reacts with 2 moles of sodium hydride in diethyl ether to produce the $\text{B}_7\text{C}_2\text{H}_{11}^{-2}$ ion. Treatment of this ion with cobalt(II) chloride in diethyl ether solvent results in the formation of hydrogen, cobalt metal, and the very stable complex $(\text{B}_7\text{C}_2\text{H}_9)_2\text{Co}^-$ (I), which contains cobalt in the formal oxidation state +3. Yields of I were 51%. The salts of $\text{Co}^{III}[\text{B}_7\text{C}_2\text{H}_9]_2^-$ are brown [λ_{max} m μ (ϵ): 224 (16,000), 261 (sh) (8950), 290 (sh) (7900), and 373 (5050)]. *Anal.* Calcd for $(\text{CH}_3)_4\text{N}(\text{B}_7\text{C}_2\text{H}_9)_2\text{Co}$:



C, 27.41; H, 8.63; B, 43.15; N, 4.00; Co, 16.81; equiv wt, 351. Found: C, 27.12; H, 8.60; B, 43.22; N, 4.30; Co, 16.93; equiv wt, 340. The formula weight of the tetraethylammonium salt was determined: calcd for $(\text{C}_2\text{H}_5)_4\text{N}(\text{B}_7\text{C}_2\text{H}_9)_2\text{Co}$, 405; found, 407 (osmometric), assuming 100% dissociation in acetone solution.

The 60-Mc/sec ^1H nmr spectrum of the tetramethylammonium salt of I contained a sharp singlet of intensity 12 at τ 6.22 and two broad singlets, each of intensity 2, at τ 3.40 and 4.80. The former resonance was assigned to the methyl protons of the cation and the two smaller resonances to two dissimilar sets of protons attached to the carbon atoms of the complex. The 32-Mc/sec ^{11}B nmr spectrum of I consisted of a low-field doublet and an overlapped array of six distinct doublets which correspond to seven distinct types of B atoms in the complex.

(1) (a) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965); (b) M. F. Hawthorne and T. D. Andrews, *Chem. Commun.*, 443 (1965).

(2) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 607 (1966).