of the 2-aryloxy moiety, an effect which is not operative in the α anomer. The same chloro sugar VIII was obtained from either VIIa or VIIb. Reaction of VIII with chloromercuri-6-benzamidopurine gave 9-(2,3,5-tri-O-benzoyl-2-C-methyl-β-D-ribofuranosyl)-6-benzamidopurine (IX) as an amorphous solid. The blocked intermediate IX was purified by chromatography on silica gel. Removal of the benzoyl blocking groups from IX in the methanolic sodium methoxide gave crystalline 2′-C-methyladenosine (II);[6] mp 257–258°; $\lambda_{\max}^{H_2O}$ mμ ($\epsilon \times 10^{-3}$) 258 at pH 1 (15.1), 260 at pH 7 (15.1), 260 at pH 13 (14.9); $\tau^{\text{deuteriopyridine}}$ 3.10 (singlet, H-1′) and 4.93 ppm (doublet, H-3′) ($J_{3',4'}$ = 8.8 cps); $[\alpha]_D$ $-21°$ (c 0.5, H_2O); $[\phi]$ $-2500°$ at λ_{278}, $[\phi]$ $+10{,}000°$ at λ_{247} (c 5.16×10^{-3}, H_2O).[7]

[6] The product was assigned the β-anomeric configuration on the basis of the "*trans*" rule and the optical rotational data.

[7] We wish to thank Dr. J. J. Wittick of these laboratories for the ORD determination. Nmr spectra were measured with a Varian A-60 spectrometer.

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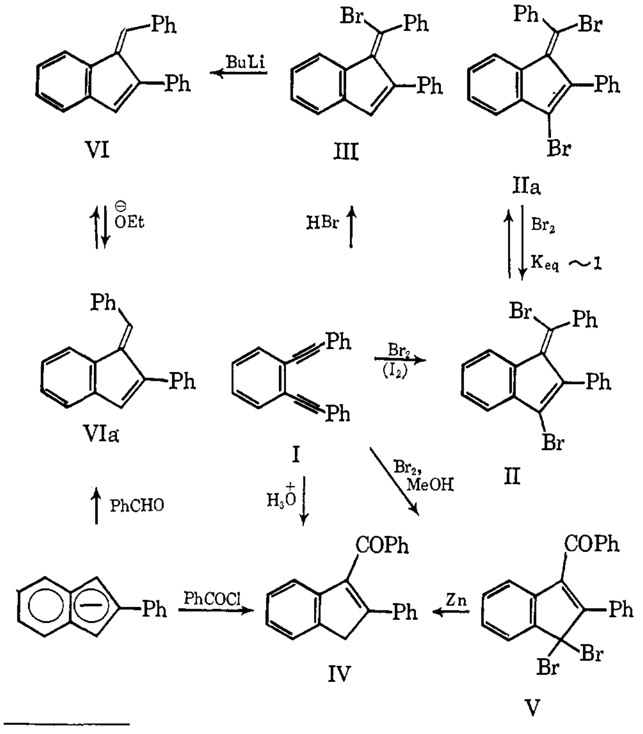
Received August 22, 1966

An Example of Alkyne–Alkyne Interaction

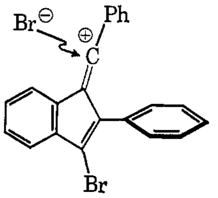
Sir:

In marked contrast with its behavior on reaction with iron pentacarbonyl or on irradiation,[1] *o*-bis(phenylethinyl)benzene[2] (I) exhibits pronounced interaction between its triple bonds when confronted with electrophilic, nucleophilic, or radical reagents.

Addition of bromine to I in chloroform afforded a single yellow-orange dibromide II, mp 139–141°.[3]



Comparison of its ultraviolet spectrum ($\lambda_{\max}^{EtOH}$ 247 mμ (log ϵ 4.22), 277 (4.19), 340 (4.12)) with those of similar[4] benzofulvenes of known or herein determined structure points to the presence of this π system in II and eliminates from consideration 2,3-diphenylnapthalene or 1,2-dibenzylidenebenzocyclobutene[5] derivatives. The bromination satisfies the standard criteria of a concerted stereoselective reaction. Competitive bromination of I and tolane produces II exclusively; no tolane dibromide could be detected. Equilibration of II with an orange isomer, IIa, mp 114–117°, $\lambda_{\max}^{EtOH}$ 250 mμ (ϵ 4.18), 274 (4.19), and 337 (4.10), $K_{eq} \sim 1$, could be achieved by allowing II to stand in chloroform containing small amounts of bromine, but IIa could not be detected as a primary product of the bromination. Both stereoisomeric diiodides could be isolated on iodination of I. They closely resembled II spectrally. On the basis of recent work[6-8] on resonance-stabilized vinyl cations, II is assigned the stereochemistry arising from least hindered attack of bromide ion on ion VII.



VII

Reaction of I with hydrogen bromide in chloroform or hydrobromic acid in acetic acid affords a single hydrobromide, III, mp 144–145°, $\lambda_{\max}^{EtOH}$ 252 mμ (ϵ 4.34), 274 (4.38), and 339 (3.99). Reaction of III with butyllithium in ether at 0° followed by protonation gave diphenylbenzofulvene VI. Fulvene VI was identified as the less stable of the two isomers produced on *t*-butoxide-catalyzed condensation of 2-phenylindene and benzaldehyde. The two isomers, VI, mp 129–131°, and VIa, an oil, could be separated by chromatography and interconverted on being allowed to stand with potassium ethoxide in ethanol; VIa was considerably the more stable. Their sterochemistry is assigned from the consideration of models. Hydration of I could be effected by acetic acid–sulfuric acid. The product, IV, mp 92–93°, was identical with that arising from lithium 2-phenylindenide and benzoyl chloride. The rate constant for hydration of I in aqueous 95% ethanolic sulfuric acid (1:1:2) at 48.9° ($k = 2.04 \times 10^{-5}$ sec^{-1}) was 36 times that ($k = 5.68 \times 10^{-7}$ sec^{-1}) for hydration of tolane under the same conditions. Bromination of I in methanol gave, in addition to starting material and a 12% yield of II, a 72% yield of dibromo ketone V, mp 116–117°. Brief reaction of V with zinc in acetic acid gave IV. Both IV and V are considered as arising from facile electrophilic attack on alkoxy- and acetoxyfulvene precursors.

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[1] E. Müller, M. Sauerbier, and J. Heiss, *Tetrahedron Letters*, 2473 (1966).

[2] Mp 51–52°; from bromination–dehydrobromination of *o*-distyrylbenzene.

[3] All new compounds have been characterized by elemental analysis and afford the various spectra appropriate for the assigned structure.

[4] N. Campbell, P. S. Davidson, and M. G. Heller, *J. Chem. Soc.*, 993 (1963).

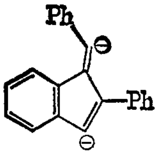
[5] A. T. Blomquist and V. J. Hruby, *J. Am. Chem. Soc.*, **86**, 5041 (1964).

[6] C. A. Grob, J. Csapilla, and G. Cseh, *Helv. Chim. Acta*, **47**, 1590 (1964).

[7] C. A. Grob and G. Cseh, *ibid.*, **47**, 194 (1964).

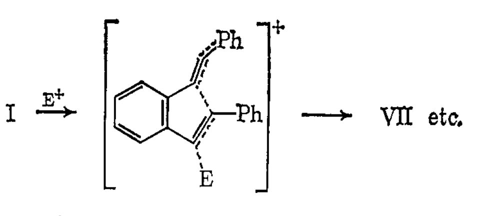
[8] D. S. Noyce, M. A. Matesich, O.P., M. D. Schiavelli, and P. E. Peterson, *J. Am. Chem. Soc.*, **87**, 2295 (1965).

The domino folding of the triple bonds in I is not limited to attack of electrophiles. Irradiation of I and thiophenol gave an unstable yellow 1:1 adduct identified spectrally as a benzofulvene. Reaction of I with lithium or lithium naphthalenide in tetrahydrofuran gave after protonation fulvene VIa.[9] Addition of deuterium oxide to the reaction mixture afforded doubly deuterated VIa, but whether or not the fulvene dianion VIII is the kinetic or thermodynamic product of this metallation is presently unclear. Reduction in the presence of proton donors (lithium in methanol and ammonia) led only to the uncyclized products *o*-bis(2-phenylethyl)benzene and *o*-styrylbibenzyl.[10]

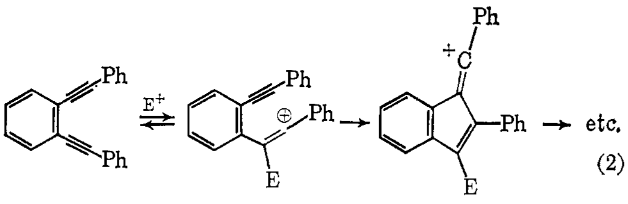


VIII

We tentatively suggest that the behavior of I toward electrophiles represents a concerted ring closure *via* the transition state represented in eq 1. The main evidence for this lies in the observed rate enhancement of electrophilic attack on I compared to tolane which, considering the inductively deactivating effect of the neighboring acetylene,[11] is substantial. If one abandons the restrictions imposed by a rate-determining irreversible initial attack of the electrophile,[8,12] however, an equally plausible mechanism involving intramolecular siphoning off of a reversibly formed intermediate as in eq 2 can be formulated. We cannot presently decide between these.

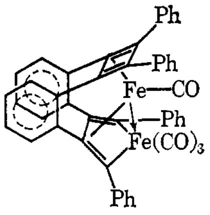


(1)



(2)

Probably the most interesting feature of the above reactions is their contrast with the behavior of I on irradiation[1] and on reaction with iron pentacarbonyl. The latter affords several related dimeric complexes, one of which possesses[13] structure IX, while the former affords a product apparently derived from a closely related carbon skeleton. The difference in the two sets of reaction probably results from: (1) in the absence of capturing agents, domino folding can only lead to polymerization, and (2) the yields of the dimeric products are relatively low.



IX

Acknowledgment. Partial support by the National Science Foundation and National Institutes of Health is gratefully acknowledged.

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Received July 25, 1966

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[9] As expected, according to the investigation of D. Y. Curtin and W. J. Koehl, *J. Am. Chem. Soc.*, **84** (1967) (1962).

[10] S. A. Kandil and R. E. Dessy, *ibid.*, **88**, 3027 (1966), have recently reported similar examples of intramolecular anionic attack on acetylenes.

[11] P. E. Peterson and R. J. Kamat, *ibid.*, **88**, 3152 (1966).

[12] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.*, 394 (1965).

[13] L. F. Dahl, personal communication.

[14] A. P. Sloan Fellow.

The Kinetics of the Basic Hydrolysis of Difluoramine

Sir:

Difluoramine has been found to undergo basic hydrolysis in aqueous solution to yield difluorodiazine (N_2F_2).[1,2] Early speculations on the mechanism of this reaction suggested that ionization of HNF_2 to yield H^+ and NF_2^- was involved. We have analyzed the products of the reactions of difluoramine with a variety of anions and have found HNF_2 is quite susceptible to anionic attack in general.

The reaction of difluoramine with excess hydroxyl ion in water yields approximately 60% N_2F_2 and 20% nitrogen. The remainder of the nitrogen-containing products are varying amounts of N_2F_4, N_2O, NO_3^-, and NO_2^-. Preliminary experiments with a variety of anions gave rate data which indicate that the reaction is generally base catalyzed (see Table I). The kinetics of the reactions with these anions are currently being studied in greater detail. In this communication we report the detailed results with hydroxyl ion.

Table I. Approximate Rate Constants for the Attack of Anions on HNF_2

Anion	K_2, M^{-1} sec^{-1}
CN^-	4.6×10^{-2}
NCS^-	1.8×10^{-2}
Br^-	$\sim 8 \times 10^{-3}$
$H_2PO_4^-$	5.8×10^{-3}
Cl^-	$\sim 5 \times 10^{-4}$
OAc^-	4.7×10^{-5}

The reaction of HNF_2 was studied over the range of pH 7 to 9.3. The concentration of HNF_2 in solution was measured accurately as a function of time by means of the polarographic reduction of HNF_2.[3]

Polarograms were recorded with a Sargent Model XXI polarograph. A standard H cell and saturated calomel reference electrode were used, and the polaro-

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[1] G. A. Ward and C. M. Wright, *J. Am. Chem. Soc.*, **86**, 4333 (1964).

[2] K. J. Martin, *ibid.*, **87**, 394 (1965).

[3] G. A. Ward, C. M. Wright, and A. D. Craig, *ibid.*, **88**, 713 (1966).