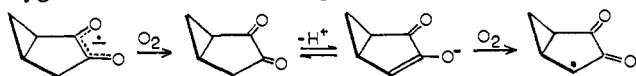
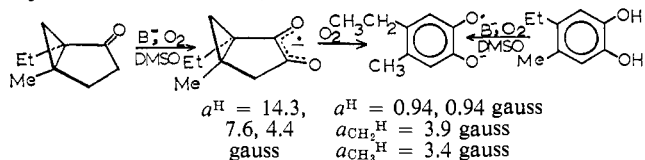


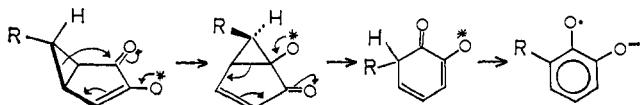
Another molecular rearrangement that has been observed is the conversion of bicyclo[3.1.0]hexane semidiones into *o*-benzosemiquinones by exposure to excess oxygen. This is a rearrangement which we associate



with either the enolate anion of the diketone or the α,β -diketo radical. The rearrangement is not a simple cyclopropane ring opening since the carbon originally C-6 in the bicyclohexane finally occupies a position adjacent to the carbonyl carbon atoms.



In a similar fashion the 6-ethylbicyclo[3.1.0]hexane semidione is converted to 3-ethyl-*o*-benzosemiquinone ($a^H = 3.5, 2.6,$ and 1.0 gauss; $a_{CH_3^H} = 1.0$ gauss). The rearrangement can be readily envisioned as involving a cyclopropanol ring opening (* = radical or carbanion).



(7) A ring flip is observed at quite low temperatures for *syn*-6-hydroxybicyclo[3.1.0]hexene-2 on neutral alumina: U. Schillkopf and J. Paust, *Ber.*, **98**, 2221 (1965). Isomerization is much slower on acidic alumina. The 2-methylbicyclo[2.1.0]pentane system will also undergo a ring inversion thermally: J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 3250 (1962). A similar type of ring flip is observed for the cyclopropyl group of benzonorcaradiene at 180° : E. Vogel, D. Wendisch, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964); E. Vogel, R. Erb, G. Lenz, and A. A. Bothner-By, *Ann.*, **682**, 9 (1965).

(8) National Aeronautics and Space Administration Predoctoral Fellow, 1965-1967.

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Received August 21, 1967

Radical Cyclization of an Acetylene

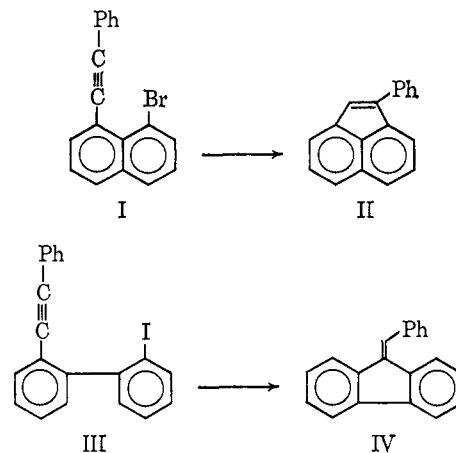
Sir:

Intramolecular additions of carbonium ions, carbocations, and free radicals to olefins are clearly established phenomena. By contrast, reports of cyclizations involving acetylenic bonds are scarce. Kandil and Dessy¹ have described the isolation of cyclized products of the reaction of *n*-butyllithium with substituted naphthalenes (I) and biphenyls (III) to give acenaphthylene (II) and fluorene (IV) derivatives. In these systems, halogen-metal interchange would produce an organometallic group which is locked in direct proximity to the triple bond.

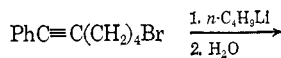
It is one of the purposes of this communication to report that such steric coercion is not a requirement for the cyclization of acetylenes. Treatment of 6-bromo-1-phenyl-1-hexyne (V) with excess *n*-butyllithium in hexane-ether (5:1),² followed by hydrolysis, gave benzylidenecyclopentane in 60% yield (the alternative cyclization product, 1-phenylcyclohexene, if

(1) (a) S. A. Kandil and R. E. Dessy, *J. Org. Chem.*, **30**, 3857 (1965); (b) *J. Am. Chem. Soc.*, **88**, 3027 (1966).

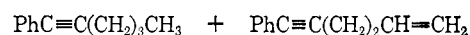
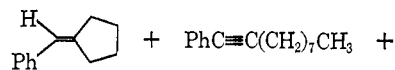
(2) The same reaction occurs in the absence of ether, but at a much lower rate. Rate acceleration by addition of ethers to *n*-butyllithium



formed at all, is present in less than 0.05%), and products of coupling (VII), reduction (VIII), and elimination (IX) in smaller amounts. The reaction at room



V

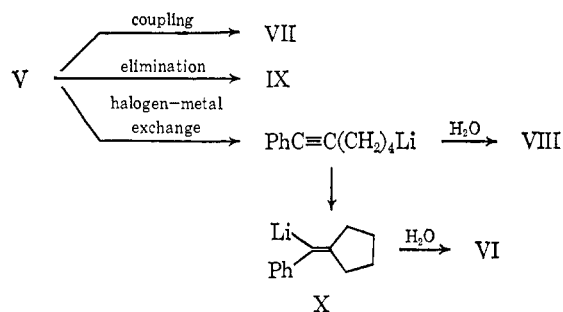


VIII, 3%

IX, 1%

temperature is complete in less than 5 min. Other organolithium compounds, ethyllithium and *t*-butyllithium, for example, give the cyclization in similar yields. The reaction of V with magnesium also gives cyclized product,³ apparently by two parallel mechanistic routes.

Kandil and Dessy¹ postulated that the cyclizations of compounds I and III proceeded through an aryllithium intermediate, and thus constituted the first carbanionic cyclization of an acetylene. A similar reaction scheme can be constructed for the products formed from V. However, several aspects of this

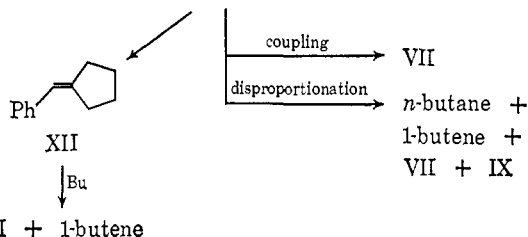
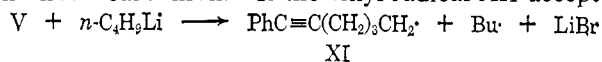


mechanism do not seem to be consistent with certain characteristics of the reaction. If D_2O is used to hydrolyze the reaction mixture, deuterium is found in only 7% of VIII and 25% of VI. The organolithium intermediate, X, would have been expected to be stable under the reaction conditions and to be fully deuterated by D_2O addition. If *n*-butyllithium in hexane² is mixed with V and sealed in an nmr tube, the absorption of the vinyl proton of VI can be clearly seen before the tube is reactions is a well-known effect: J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171 (1963); C. G. Screttas and J. F. Eastham, *ibid.*, **88**, 5668 (1966).

(3) Cyclizations in similar systems have been observed by J. K. Crandall, private communication.

opened for hydrolysis. Addition of D_2O in this case gives only 11% deuterium in VI. Further, if the acetylene VIII is treated with *n*-butyllithium under the same conditions where V reacts completely in 3 min, less than 10% of VIII reacts in 1 hr. Clearly the (intermolecular) addition of a primary organolithium to the phenylacetylene moiety is relatively slow. Even the halogen-metal exchange might not be expected to occur in this system. In an analogous example, Applequist⁴ observed no exchange between *n*-propyllithium and ethyl bromide.

These inconsistencies are largely obviated by a reaction scheme in which the cyclizing species is a radical⁵ and not a carbanion. If the vinyl radical XII accepted



a hydrogen atom from the butyl radical to give VI and 1-butene, the facts that VI was present in the reaction mixture before hydrolysis and that it incorporated little deuterium on D_2O hydrolysis are explained. The small amount of deuterium incorporation in VI could result from further electron transfer to give the vinyl carbanion by a competing direct carbanionic cyclization or by metalation of VI. 1-Butene is indeed formed in this reaction, and the accompanying communication⁶ reports compelling proof (the observation of chemically induced dynamic nuclear polarization CIDNP) that it results from the butyl radical. Further, and by similar proof, the 1-phenyl-5-hexen-1-yne (IX) must result from a radical intermediate, and the presence of XI in the reaction solution is established. These facts strongly suggest that cyclization proceeds by a radical pathway.

Bryce-Smith's proposal⁷ that the products of the reaction of *n*-butyl bromide with *n*-butyllithium in benzene are best explained by free-radical reactions provides precedence for the suggestion of radical intermediates in the case at hand. Indeed, preliminary investigation of the *n*-butyl bromide-*n*-butyllithium system⁶ shows that it also exhibits CIDNP, firmly supporting Bryce-Smith's mechanism. Attempts are in progress, utilizing this effect, to define the generality of this mechanism in other reactions of organometallic compounds.

Acknowledgment. Helpful conversations with R. G. Lawler are gratefully acknowledged. The nmr and mass spectrometers used in the investigation were provided by the National Science Foundation.

(4) D. E. Applequist and D. F. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963).

(5) Kandil and Dessy^{1b} suggest that radical cyclizations occur with copper derivatives of I and III.

(6) H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518, (1967).

(7) D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

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Received August 3, 1967

Nuclear Magnetic Resonance Emission and Enhanced Absorption in Rapid Organometallic Reactions

Sir:

We report here the observation of large positive and negative dynamic polarizations of protons in simple olefins during conventional 60-MHz nmr studies of rapid reactions of organometallic compounds. Although all of the features of the spectra which we have observed are not yet understood, we make this preliminary report because even a simplified analysis¹ of this novel effect, which is appropriately named chemically induced dynamic nuclear polarization (CIDNP), shows that it promises to be of considerable importance in studying reactions involving free-radical intermediates.^{1a}

Figures 1 and 2 show two nmr spectra, selected from a number obtained (using a Varian A-60A spectrometer), which clearly show the inverted lines which are a manifestation of stimulated nmr emission. Figure 1b shows a scan of the nmr region from δ 4.5 to 6.3 obtained from 0.5 ml of a hexane solution which is 1.6 *M* in *n*-butyllithium (Foote Mineral Co.), 0.9 *M* in *n*-butyl bromide, and 0.8 *M* in diphenylacetylene.² Figure 1c is a scan of the same region 2 min after the addition of 0.2 ml of diethyl ether.^{3,4} Repeated scanning of this region shows that the absorption and emission lines of Figure 1c rapidly approach a maximum intensity and slowly decrease, after about 6 min giving the weak absorption spectrum shown in Figure 1d. The spectrum in Figure 1d is consistent with that of the 1 (δ 4.8) and 2 (δ 5.8) protons of 1-butene. The striking correspondence between the positions of the enhanced lines and those of 1-butene (Figure 1a) suggests strongly that this is the chemical species responsible for the intense absorption and emission lines. It is notable, however, that the absorption spectrum arising from the proton at the 2 position in 1-butene consists of four triplets (to first order) while the lines which are enhanced in Figure 1c correspond only to the two outermost triplets. This is an important observation since it shows that the absorption lines are not simply due to an initial surge in 1-butene concentration which then falls to a low value. If this were the case one would reasonably expect to see all of the absorption lines of the olefinic protons.⁵

The spectrum shown in Figure 2b was obtained 30 sec after preparing a pentane solution which was 1.54 *M* in *t*-butyllithium (Lithium Corp. of America) and 0.9 *M* in *n*-butyl bromide. The intensity of absorption

(1) R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5519 (1967).

(1a) NOTE ADDED IN PROOF. Nmr emission has also been observed from the products of thermal decomposition of peroxides and azo compounds by J. Bargon and H. Fischer. We wish to express our gratitude for communication of their results prior to publication.

(2) The presence of a compound containing carbon-carbon unsaturation seems to be necessary to observe CIDNP in this case. When the unsaturated compound is 2-pentyne, the absorption lines shown in Figure 1c become emission lines, and *vice versa*.

(3) The reported time is that at which the scan was started; the scan time for the region of interest was 65 sec.

(4) Ether is known to markedly increase the reactivity of *n*-butyllithium: J. K. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171 (1963).

(5) The chemical logic of such a rapid change in 1-butene concentration might also be questioned in view of the finding that the addition of an olefin such as *cis*-2-pentene, which would compete with 1-butene in most reactions that it might undergo, has little effect on the rate of the reaction and the relative intensities of enhanced absorption and emission.