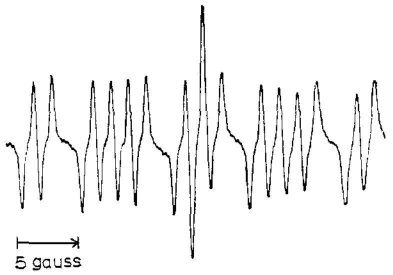
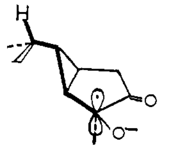


Figure 1. First-derivative esr spectrum obtained by exposure of phototestosterone to a trace of oxygen in dimethyl sulfoxide solution containing potassium *t*-butoxide.

phototestosterone (**9**) and dihydrolumisantoin (**10**) (Figure 1). The *trans* coplanar arrangement required for a maximum in this long-range hyperfine splitting is illustrated by the fact that only one of the γ-methylene hydrogen atoms interact in **10**.



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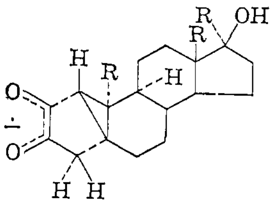
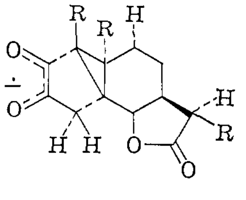


9, R = CH_3
a^{H} = 13.9, 7.6, 4.8, 1.5 gauss



10, R = CH_3
a^{H} = 14.3, 7.6, 1.1 gauss

Semidiones **7**, **9**, and **10**, as well as numerous other derivatives, have been observed to undergo the stereospecific hydrogen–deuterium exchange at C-4.

The application of esr spectroscopy as a tool in the proof of structure of bicyclic ketones is obvious.

Acknowledgment. β-Dihydroumbellulone was graciously supplied by Professor R. H. Eastman. The esr spectrum of **9** was obtained by Dr. E. R. Talaty and spectra of additional derivatives of **9** and **10** have been obtained by Dr. R. S. Givens.

[7] National Aeronautics and Space Administration Predoctoral Fellow, 1965–1967.

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Received August 21, 1967

Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation.
XII. Molecular Rearrangements in the Bicyclo[3.1.0]hexane Semidiones[1]

Sir:

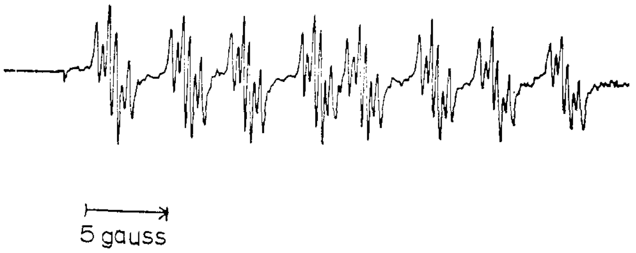
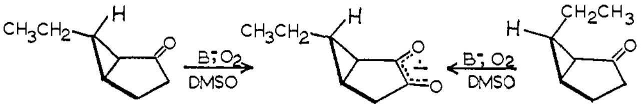


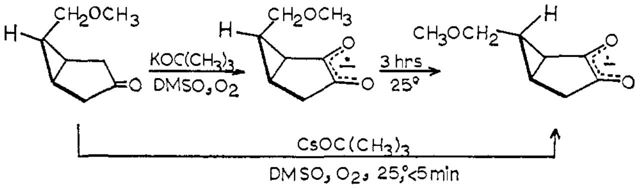
Figure 1. First-derivative esr spectrum of radical anion produced by exposure of *syn*- or *anti*-4-ethylbicyclo[3.1.0]hexan-2-one to a trace of oxygen in dimethyl sulfoxide solutions containing potassium *t*-butoxide.

Oxidation of *syn*- or *anti*-6-ethylbicyclo[3.1.0]hexan-2-one[2,3] in basic dimethyl sulfoxide (DMSO) solution yields the same semidione whose hyperfine splitting constants[4] are consistent with the more stable *anti* structure (Figure 1).

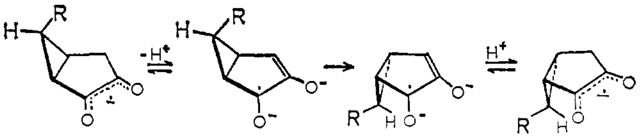
Oxidation of *syn*-6-(methoxymethyl)bicyclo[3.1.0]hexan-3-one[3,5] in DMSO containing potassium *t*-butoxide initially yields a complex esr signal that slowly (3 hr) converts to a pure signal whose hfsc are consistent with the *anti* structure (a^{H} = 14.65, 7.75, 4.22, 0.75 (2 H), and 0.35 gauss). It is tempting to assume that the mixture of radical anions first observed consists of the *anti* semidione and its unrearranged C-6 epimer. Oxidation in the presence of the stronger base cesium *t*-butoxide, forms the *anti* semidione with no indication of the formation of an initial mixture of radicals (spectrum recorded 5–10 min after oxygenation).



a^{H} = 14.7, 7.8, 4.2, 0.35 gauss
$a_{CH_2}^{H}$ = 0.75 gauss



The 6-ethylbicyclo[3.1.0]hexan-2-ones do not epimerize under the reaction conditions if oxygen is excluded. An epimerization mechanism involving ionization of the cyclopropyl hydrogen atoms apparently can be eliminated since the semidione of bicyclo[3.1.0]hexan-3-one in DMSO-d_6 does not show any hydrogen–deuterium exchange at the cyclopropyl positions.[6] Epimerization at C-6 may involve a ring flip at either the diketone, radical-anion, or the radical-dianion state. The effect of base seems most consistent with the radical dianion. Of course the ring flip depicted must involve the uncoupling and re-formation of the C-1–C-5 bond.[7] Alternately the rupture and closure of the C-1–C-6 or C-5–C-6 bonds can be involved.



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[1] This work was supported by grants from the National Science Foundation (GP-6402X) and the Army Research Office (Durham) (DA-ARO-D-31-124-G867).

[2] Prepared by ring closure reactions of *cis*- and *trans*-$CH_3CH_2CH{=}CHCH_2CH_2COCHN_2$.

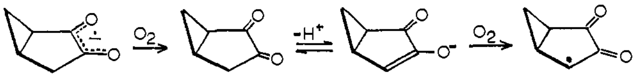
[3] Satisfactory analyses and spectral data were obtained for all new compounds.

[4] G. A. Russell, P. R. Whittle, J. McDonnell, *J. Am. Chem. Soc.*, **89**, 5515 (1967).

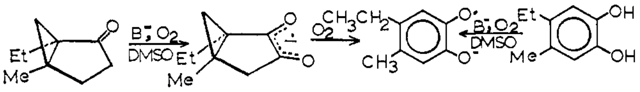
[5] Prepared from the *syn*-6-carboxaldehyde of bicyclo[3.1.0]hexene: J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Am. Chem. Soc.*, **85**, 582 (1963).

[6] Epimerization at C-6 appears to require a steric driving force since no significant amount of epimerization for the *syn*-6-deuterio semidione is detected within 10 hr.

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



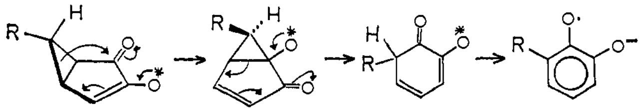
with either the enolate anion of the diketone or the α,β-diketo radical. The rearrangement is not a simple cyclopropane ring opening since the carbon originally C-6 in the bicyclohexane finally occupies a position adjacent to the carbonyl carbon atoms.



a^H = 14.3, 7.6, 4.4 gauss

a^H = 0.94, 0.94 gauss
$a_{CH_2}{}^H$ = 3.9 gauss
$a_{CH_3}{}^H$ = 3.4 gauss

In a similar fashion the 6-ethylbicyclo[3.1.0]hexanesemidione is converted to 3-ethyl-*o*-benzosemiquinone (a^H = 3.5, 2.6, and 1.0 gauss; $a_{CH_2}{}^H$ = 1.0 gauss). The rearrangement can be readily envisioned as involving a cyclopropanol ring opening (* = radical or carbanion).



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(7) A ring flip is observed at quite low temperatures for *syn*-6-hexoxybicyclo[3.1.0]hexene-2 on neutral alumina: U. Schöllkopf 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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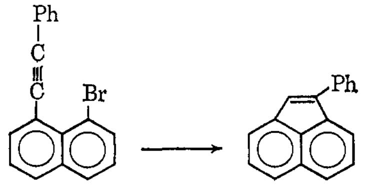
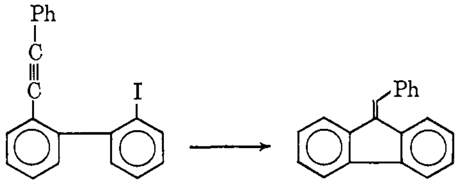
Radical Cyclization of an Acetylene

Sir:

Intramolecular additions of carbonium ions, carbanions, and free radicals to olefins are clearly established phenomena. By contrast, reports of cyclizations involving acetylenic bonds are scarce. Kandil and Dessy[1] 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.



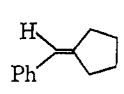
I II



III IV

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 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

$$\underset{\text{V}}{PhC{\equiv}C(CH_2)_4Br} \xrightarrow[2.\ H_2O]{1.\ n\text{-}C_4H_9Li}$$



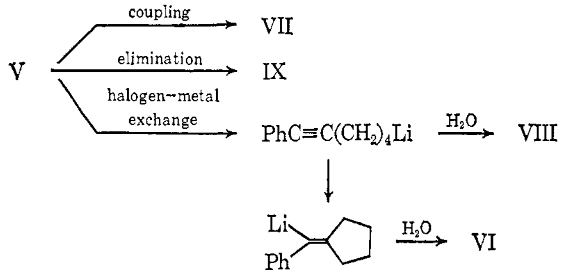
$$+ \ \underset{\text{VII, 20\%}}{PhC{\equiv}C(CH_2)_7CH_3} \ +$$

VI, 60%

$$\underset{\text{VIII, 3\%}}{PhC{\equiv}C(CH_2)_3CH_3} \ + \ \underset{\text{IX, 1\%}}{PhC{\equiv}C(CH_2)_2CH{=}CH_2}$$

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 Dessy[1] 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



X

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 hexane[2] 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

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(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 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.