to the established "radical-pair" theory. Subsequently, we realized[2] that our model and the radical-pair theory would differ in one important respect. The radical-pair theory predicts that the semiquinone radical and the counter radical, which arises from the H atom abstraction, would have *opposite* electron polarization.[4] Our model predicts the *same* spin polarization. To the best of our knowledge, there has been no reported experimental observation on the CIDEP behavior of both radicals. In this communication we report such experimental observations; the results indicate that the semiquinone and the counter radical have the *same* polarization.

In the photochemical system of 1,4-naphthoquinone in 2-propanol, the short-lived $(CH_3)_2COH$ counter radical has eluded experimental detection. One of the reasons that the 2-propanol radical is difficult to detect is that it readily reacts with quinones to form semiquinones.[5] Thus, it may be possible to observe a more "stable" counter radical if there were a hydrogen donor which would react *rapidly* with the spin-polarized triplet quinone.

In order to arrive at definite conclusions about the spin polarization of both the semiquinone radical and the counter radical, it is necessary to monitor both radicals simultaneously. Consequently, the esr spectra of the radical pair must have some nonoverlap components so that their decay can be measured separately at different magnetic fields.

With the previous considerations in mind, we chose to carry out our investigation in a photochemical system of duroquinone in acetic acid in the presence of a highly reactive hydrogen donor, namely, the 2,6-di-*tert*-butylphenol. For this system we observed CIDEP in both the durosemiquinone radical and the 2,6-di-*tert*-butylphenoxy radical. We established that all hyperfine components of *both* radicals exhibit the same emissive behavior. A typical decay curve for the phenoxy counter radical is shown in Figure 1. This observation confirms a prediction of our earlier theoretical model.[3] We also carried out control experiments to confirm that the phenoxy radicals were not generated by direct photolysis of the phenol in our present system using all Pyrex optics and cells.

In addition to finding both the semiquinone radical and the counter phenoxy radical in the emissive mode, we also observed the following. The initial emission of the phenoxy radicals was enhanced by increasing concentration; this is due to the increase of hydrogen abstraction rate when the spin depolarization rate is relatively constant in the given system. In acetic acid, the photochemical reaction gives a steady-state concentration of phenoxy radicals which is greater than that of the semiquinone radicals. However, the reverse is obtained when *tert*-butyl alcohol is used as solvent.

We have observed that the CIDEP behavior of the semiquinone radical and the phenoxy counter radical is to some degree dependent on solvents. At present we cannot explain the effect of solvents on actual photochemical reactions. Nonetheless, the present results do suggest that our previously discussed model[2,3] is at least qualitatively correct. Further detailed and systematic studies will follow.

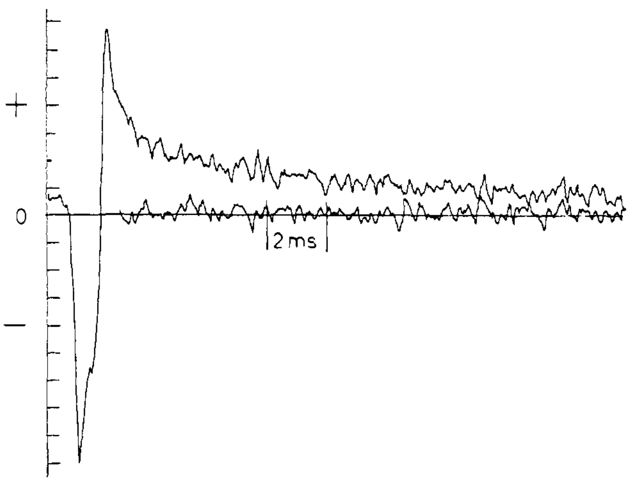

Figure 1. Time dependence of the esr signal intensity at constant magnetic field of the 2,6-di-*tert*-butylphenoxy radicals produced from the photolysis of duroquinone and the parent phenol in acetic acid: absorption mode (+), emission mode (−).

Acknowledgments. This research is supported by the National Research Council of Canada.

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An Approach to Tetrahedrane. Pyrolysis of the Dilithium Salt of *trans*-Butenedial Bistosylhydrazone

Sir:

As a possible precursor of tricyclo[1.1.0.0^{2,4}]butane (IV, tetrahedrane), the title compound (Ia) has been prepared. Pyrolysis of Ia, by immersion of the pyrolysis vessel, under evacuation through a series of traps cooled at −80° and with liquid nitrogen, into a bath held at 140°, was complete within 1–1.5 min. This procedure is a modified version of that of Kaufman, *et al.*[1]

The condensate at −80° was entirely THF, in which Ia was prepared. The absence of butenyne, benzene, cyclooctatetraene, and *syn*-$\Delta^{3,7}$-tricyclo[4.2.0.0^{2,5}]octadiene was verified by glpc. It is therefore clear that cyclobutadiene is not formed.[2] The material condensable with liquid nitrogen, but not at −80°, contained acetylene[3] and 1–1.5% ethylene. In later experiments with Ib, the ethylene was collected by preparative glpc and found to contain no deuterium. Thus, acetylene is the *only* volatile product of pyrolysis of Ia. The residue was not examined in detail; however, it was apparent that some polymerization had occurred.

To investigate the intermediate(s) responsible for acetylene, deuterium labeling experiments were performed. 2,5-Furan-d_2, from deuterolysis[4] of 2,5-

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[4] F. J. Adrian, *J. Chem. Phys.*, **54**, 3918 (1971).

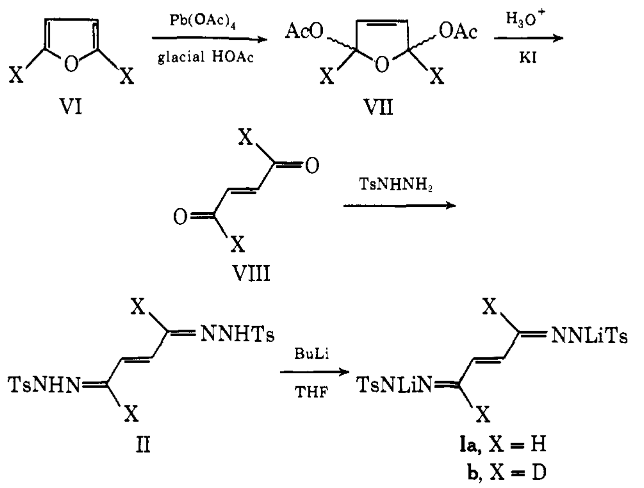
[5] F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962).

[1] G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Schechter, *J. Amer. Chem. Soc.*, **87**, 935 (1965).

[2] E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *ibid.*, **91**, 1875 (1969).

[3] A 20–30% variable yield which seemed to be dependent on the fineness of subdivision of powdered Ia.

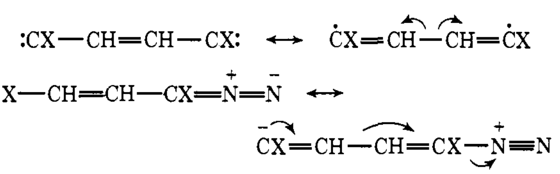
[4] B. Bak, L. Hansen, and J. Rastrup-Andersen, *Discuss. Faraday Soc.*, **19**, 30 (1955).



dichloromercurifuran,[5] was employed as shown for the preparation of Ib. The deuterium content (±1%) at each stage, as determined by nmr, was: VI, X = 88% D; VII, X = 87% D; and VIII, X = 87% D.[6] Positions 3 and 4 of VII, X = D, relative to acetate as an internal reference, had 99.8 ± 0.8% H. Accurate analysis of II, X = D was not possible. However, the *total* deuterium content of VIII was 43.5% and that of the acetylenes obtained from Ib averaged 43.3%. Thus, the isotopic compositions of Ib, II (X = D), and VIII (X = D), were considered identical.

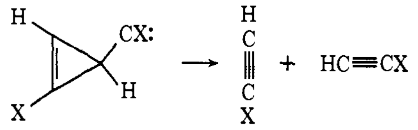
Conceivable pathways for the production of acetylene are depicted in reactions 1–4. Reaction 3 is a cheletropic fragmentation for which there is a reported analog.[7] The labeling experiments may provide four possible limiting results. (i) Only C_2HD will be produced by Ib *via* reactions 1–3. (ii) Path a, reaction 4, will yield a 1:4:1 distribution of C_2D_2:C_2HD:C_2H_2. (iii) Path b will provide a 1:6:1 ratio if b is irreversible, or (iv) a 1:4:1 distribution if III-d_2 and V-d_2 equilibrate at least four to five times faster than the rate of acetylene formation. Cases iii and iv provide for the possibility that the formation of tetrahedrane is precluded because of impossibly high strain.

The acetylene obtained upon pyrolysis of Ib was purified by preparative glpc[8] to avoid analytical[9] interference by ethylene. The results from three runs are presented in Table I. Table II provides the distributions calculated for the limiting pathways discussed above.

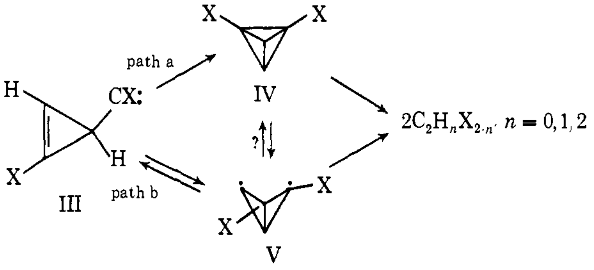


(1)

(2)



(3)



(4)

Table I. Acetylenic Distribution from Ib

Acetylene	Run 1, %	Run 2, %	Run 3, %	Av, %
C_2D_2	4.4	4.3	4.7	4.5
C_2HD	77.1	78.3	77.7	77.7
C_2H_2	18.5	17.4	17.6	17.8

Table II. Calculated Acetylenic Distributions[a]

Acetylene	No scrambling, %	1:4:1, %	1:6:1, %
C_2D_2	0	13	9.5
C_2HD	87	62	68
C_2H_2	13	25.5	22

[a] Based on deuterium content of Ib, X = 87% D.

Although the results of Table I correspond to none of the limiting cases discussed, the scrambling observed does indicate intervention of the processes of reaction 4. Thus, although the nonscrambling reactions 1–3 are predominant, it can be shown that tetrahedrane (IV) and the bicyclobutyl diradical (V) are indicated precursors for 37% (case ii or iv) to 47% (case iii) of the acetylenes. If only V has formed, its percentage formation lies within the range 37–47%; the exact value depends on the rate of equilibration of III and V relative to the rate of fragmentation, if such equilibration occurs. Any distinction between path a and a combination of paths a and b is obviated by the then necessary inclusion of the reversible arrows between IV and V, reaction 4.

In any event, and in the absence of additional viable scrambling mechanisms, either a tetrahedrally symmetric intermediate (or transition state) has been produced in the pyrolysis of I or, given the opportunity, the bicyclobutyl diradical, V, has formed and abstained from closing the last bond to provide tetrahedrane.[10]

It seems probable that the question of whether tetrahedrane is a bound structure with respect to C–C stretch, or is even attainable on the C_4H_4 energy surface, must await the results of low-temperature experiments which are in progress.[11]

Acknowledgments. We wish to thank Dr. Conrad Cone for aid in the mass spectral analyses. Our gratitude is extended to the National Minister of

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(5) H. Gilman and G. F. Wright, *J. Amer. Chem. Soc.*, **55**, 3302 (1933).

(6) In the absence of KI, significant amounts of *cis*-VIII are produced. As employed, VIII was free of the cis isomer, as shown by nmr and by the lack of formation of detectable quantities of pyridazine when VIII was allowed to react with hydrazine.

(7) P. B. Shevlin and A. P. Wolf, *J. Amer. Chem. Soc.*, **88**, 4735 (1966).

(8) 12 ft × 0.25 in. stainless-steel column, 80–100 Porpak N (55°).

(9) Low voltage measurements, with no fragmentation, of *m/e* 26, 27, and 28 were performed on a CEC Model 21-102 mass spectrometer. An accuracy of ±0.5% absolute was established by control experiments.

(10) For discussions of the energetics of this process, see N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 3966 (1967); and R. J. Buenker and S. D. Peyerimhoff, *ibid.*, **91**, 4342 (1969).

(11) The support of the Robert A. Welch Foundation is gratefully acknowledged. The mass spectrometer was purchased with funds provided by NSF Grant No. GP-8509.

Education and to Kyung-Pook National University, Taegu, Korea, for extension of Dr. Lee's leave of absence.

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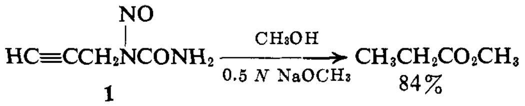
Intramolecular Reactions of Propargyl Diazotates. A Novel Approach to the Favorskii Rearrangement

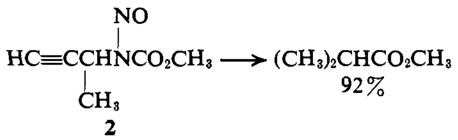
Sir:

Aliphatic diazotates, generated from nitrosoamides and base, have been trapped by intramolecular reaction with epoxide[1] and allene[2] groups. We report here on the intramolecular addition of propargyl diazotates to the carbon–carbon triple bond which initiates a reaction sequence closely related to the Favorskii rearrangement.[3]

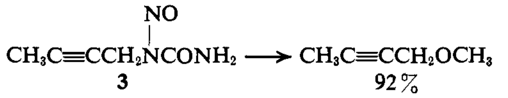
N-Nitroso-*N*-propargylureas and carbamates afford propargyl and allenyl ethers when treated with weakly alkaline methanol.[4] In 0.5 *N* $NaOCH_3$, however, some of the nitrosoamides produce esters in high yield, as shown below.



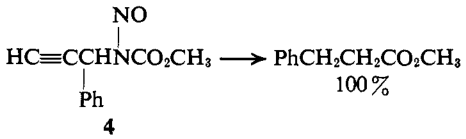
$$\underset{\mathbf{1}}{HC{\equiv}CCH_2\overset{\overset{NO}{|}}{N}CONH_2} \xrightarrow[0.5\ N\ NaOCH_3]{CH_3OH} \underset{84\%}{CH_3CH_2CO_2CH_3}$$



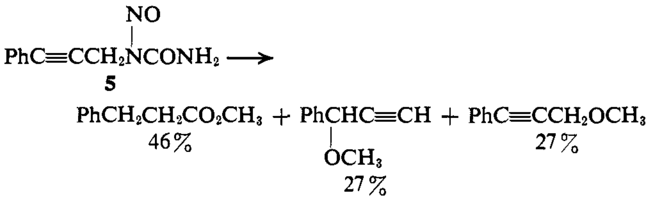
$$\underset{\mathbf{2}}{HC{\equiv}C\underset{\underset{CH_3}{|}}{C}H\overset{\overset{NO}{|}}{N}CO_2CH_3} \longrightarrow \underset{92\%}{(CH_3)_2CHCO_2CH_3}$$



$$\underset{\mathbf{3}}{CH_3C{\equiv}CCH_2\overset{\overset{NO}{|}}{N}CONH_2} \longrightarrow \underset{92\%}{CH_3C{\equiv}CCH_2OCH_3}$$



$$\underset{\mathbf{4}}{HC{\equiv}C\underset{\underset{Ph}{|}}{C}H\overset{\overset{NO}{|}}{N}CO_2CH_3} \longrightarrow \underset{100\%}{PhCH_2CH_2CO_2CH_3}$$

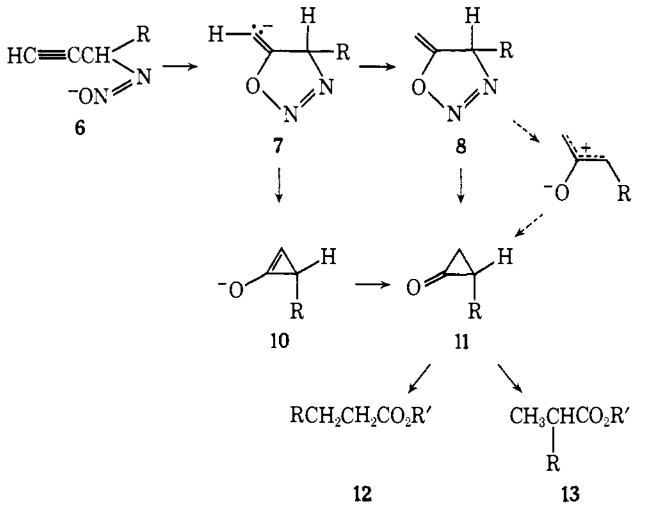


$$\underset{\mathbf{5}}{PhC{\equiv}CCH_2\overset{\overset{NO}{|}}{N}CONH_2} \longrightarrow$$

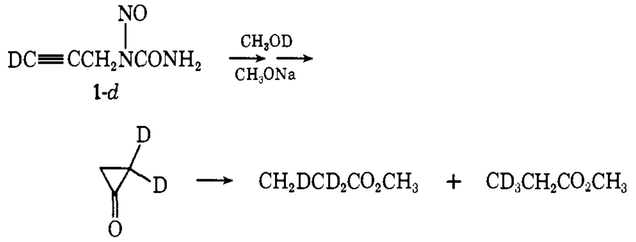
$$\underset{46\%}{PhCH_2CH_2CO_2CH_3} + \underset{27\%}{Ph\underset{\underset{OCH_3}{|}}{C}HC{\equiv}CH} + \underset{27\%}{PhC{\equiv}CCH_2OCH_3}$$

Ester formation proceeds readily with terminal triple bonds; it is completely eliminated, however, by substitution of the ethynyl hydrogen by methyl (**3** reacts to give ethers exclusively). Phenyl substitution, as in **5**, causes a decrease but no complete elimination of ester formation. The substituent effects are suggestive of nucleophilic attack on the triple bond as the initial step. The two isomeric phenyl compounds **4** and **5** give rise to the same ester whereas the structurally related α-methyl and α-phenyl compounds (**2** and **4**, respectively) produce structurally different esters. The pattern of ester structures is rationalized by assuming a cyclopropanone as the immediate percursor of the esters (Scheme I). Both α- and γ-substituted nitrosoamides afford the same cyclopropanone **11**. If R stabilizes a neighboring negative charge, as in the case of phenyl,[5] alkoxide opens the cyclopropanone to give ester **12**. If R destabilizes a neighboring negative charge, as in the case of methyl, the result of alkoxide attack is a branched-chain ester **13**.

Scheme I



Scheme I is fully confirmed by the distribution of deuterium in methyl propionate obtained from **1**-*d*

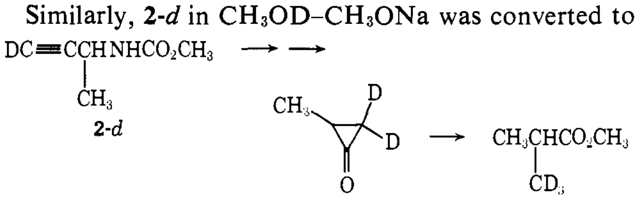


$$\underset{\mathbf{1}\text{-}d}{DC{\equiv}CCH_2\overset{\overset{NO}{|}}{N}CONH_2} \xrightarrow[CH_3ONa]{CH_3OD}$$

$$\longrightarrow CH_2DCD_2CO_2CH_3 + CD_3CH_2CO_2CH_3$$

in CH_3OD. The deuterium-decoupled pmr spectrum of the product mixture displayed sharp singlets for the α and β protons. Obviously, the components of the mixture carry hydrogen either in the α or in the β position, but not in both positions. The integral of the undecoupled spectrum yielded an α:β proton ratio of 43:57. The deviation from 50:50 should be attributed to a slow exchange of the α protons of methyl propionate in 0.5 *N* CH_3ONa–CH_3OD rather than to an isotope effect.

Similarly, **2**-*d* in CH_3OD–CH_3ONa was converted to



$$\underset{\mathbf{2}\text{-}d}{DC{\equiv}C\underset{\underset{CH_3}{|}}{C}HNHCO_2CH_3} \longrightarrow \longrightarrow$$

$$\longrightarrow CH_3\underset{\underset{CD_3}{|}}{C}HCO_2CH_3$$

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(1) A. Padwa, N. C. Das, and D. Eastman, *J. Amer. Chem. Soc.*, **91**, 5178 (1969); A. Padwa, P. Cimiluca, and D. Eastman, *J. Org. Chem.*, **37**, 805 (1972).

(2) D. J. Northington and W. M. Jones, *Tetrahedron Lett.*, 317 (1971).

(3) Reviews: A. A. Achrem, T. K. Ustynjuk, and J. A. Titov, *Usp. Khim.*, **39**, 1560 (1970); A. S. Kende, *Org. React.*, **11**, 261 (1960).

(4) W. Kirmse and J. Heese, *Chem. Commun.*, 258 (1971).

(5) Both 1-chloro-1-phenyl-2-propanone and 1-chloro-3-phenyl-2-propanone afforded methyl 2-phenylpropionate on treatment with sodium methoxide in methanol: W. D. McPhee and E. Klingsberg, *J. Amer. Chem. Soc.*, **66**, 1132 (1944).