gem-Dialkali Derivatives of Certain Functionally Substituted Organic Compounds[1,2]

Edwin M. Kaiser,*[3a,b] Lance E. Solter,[3b] Richard A. Schwarz,[3c]
Robert D. Beard,[3b,d] and Charles R. Hauser[3c,e]

Contribution from the Departments of Chemistry, University of Missouri, Columbia, Missouri 65201, and Duke University, Durham, North Carolina 27706.
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Abstract: Certain nitriles, sulfones, and related compounds have been rapidly and conveniently converted to their corresponding *gem*-polyalkali derivatives by means of excess *n*-butyllithium in THF–hexane. The relative ease of formation of the *gem*-dialkali salts of nitriles is attributed to a sesquiazacetylene type of structure while those of sulfones and related compounds are ascribed to d_π–p_π resonance interactions. Despite resonance stabilization, the subsequent reactions with electrophiles like deuterium oxide, alkyl halides, and esters were observed to occur only on the α-carbon atoms of such reagents. The condensation reactions of these polyalkali derivatives not only illustrate their usefulness in synthesis, but also are taken as evidence for their existence.

Although few in number, *gem*-dialkali and -dialkaline earth derivatives have generally been prepared by reductions of appropriate halides or by metalations of certain active hydrogen compounds. For example, those prepared by reduction include the following. Methylenedimagnesium diiodide and dibromide have been formed in poor to good yields;[4a,b] however, solubility problems precluded reaction of these reagents with any electrophile other than water.[4b,5] Methylenedilithium has been proposed as a product in the pyrolysis of methyllithium,[6] and as an intermediate in the reaction of methylene bromide with lithium and chlorotrimethylsilane to give bistrimethylsilylmethane in low yield.[7] The dimagnesium dibromide derivative of bisphenylsulfonylmethane has been prepared from the corresponding dibromide as evidenced by a correct elemental analysis, but only single condensation reactions were realized with benzoyl chloride and bromodiphenylmethane.[8] More recently, dipotassiodiphenylmethane, prepared in good yield by a Wolff–Kishner type of reduction performed on dipotassiobenzophenone hydrazone, has been formed as demonstrated by deuteration experiments.[9]

The second method of preparing *gem*-dialkali organometallics, *via* metalation, appears to be more versatile than the reductions described above. For example, dipotassiodiphenylmethane was apparently prepared by the action of potassium on the parent hydrocarbon since a twofold aroylation was subsequently realized with benzoyl chloride to give 1-benzoyloxy-1,2,2-triphenylethene.[10] Multiple metalations of acetylenes to afford organometallics with more than one metal atom on a given carbon atom have been reported,[11a–e] although one research group described inconvenient reaction periods and yields which were poor or not reported.[11c,e] Functionally substituted organic compounds like phenylacetonitrile,[2a] acetonitrile,[12] acetomesitylene,[2a] and benzyl phenyl sulfone[2b] have been geminate dimetalated as evidenced by deuterations and alkylations. Finally, toluene has been polymetalated and subsequently trimethylsilyated to afford interesting intermediates.[13]

Two other types of *gem*-dialkali derivatives deserve brief mention. Various monofunctional organonitrogen compounds have been geminate dimetalated, then diaroylated to conveniently give triaroylamines.[14] Certain *gem*-diorganoboranes and -alanes, prepared by hydroboration or hydroalumination of acetylenes, have been converted to 1-alkali-1-boron (or aluminum) derivatives or ate complexes by means of *n*-butyllithium and other strong bases.[15a,d] Such species have been carbonated,[15a,d] alkylated,[15b,d] and caused to react with various carbonyl compounds.[1c,5d]

Our interest in this area, described in preliminary form,[2] originally stemmed from the observation that a tetrahydrofuran (THF) solution of phenylacetonitrile, upon treatment with *n*-butyllithium in hexane, underwent a color change from yellow to brown as the solution was treated with a second equivalent of the base. This report describes the results of the subsequent investigation illustrating that not only can various functional groups facilitate the formation of *gem*-dialkali compounds, but also that such geminate diorganome-

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(1) Supported at the University of Missouri by the Petroleum Research Fund, administered by the American Chemical Society on Grant 959-G, and at Duke University by the National Science Foundation.

(2) Preliminary reports: (a) E. M. Kaiser and C. R. Hauser, *J. Amer. Chem. Soc.*, **88**, 2348 (1966); (b) E. M. Kaiser and C. R. Hauser, *Tetrahedron Lett.*, 3341 (1967).

(3) (a) Author to whom correspondence should be addressed; (b) University of Missouri; (c) Duke University; (d) NDEA Fellow, 1966–1969; (e) deceased, Jan 6, 1970.

(4) (a) G. Emschwiller, *C. R. Acad. Sci.*, **183**, 665 (1926); (b) D. A. Fidler, J. R. Jones, S. L. Clark, and H. Strange, *J. Amer. Chem. Soc.*, 77, 6634 (1955).

(5) D. Y. Chang and C.-L. Tseng, *Trans. Sci. Soc. China*, 7, 243 (1932); *Chem. Abstr.*, **26**, 5544 (1932).

(6) G. Wittig and G. Harborth, *Chem. Ber.*, 77, 306 (1944).

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(9) E. M. Kaiser, F. E. Henoch, and C. R. Hauser, *ibid.*, 90, 7287 (1968).

(10) M. O. Saint Pierre, *Bull. Soc. Chim. Fr.*, **5**, 292 (1891).

(11) (a) R. West, P. A. Carney, and I. C. Mineo, *J. Amer. Chem. Soc.*, **87**, 3788 (1965); (b) J. E. Mulvaney, T. L. Folk, and D. J. Newton, *J. Org. Chem.*, **32**, 1674 (1967); (c) J. Klein and S. Brenner, *J. Amer. Chem. Soc.*, **91**, 3094 (1969); (d) R. West and P. C. Jones, *ibid.*, **91**, 6156 (1969); (e) J. Klein and E. Gurfinkel, *J. Org. Chem.*, **34**, 3952 (1969).

(12) G. A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, **93**, 1714 (1971).

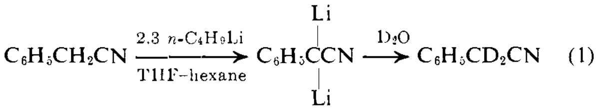
(13) R. West and P. C. Jones, *ibid.*, 90, 2656 (1968).

(14) For example, see E. M. Kaiser, R. L. Vaulx, and C. R. Hauser, *J. Org. Chem.*, **32**, 3640 (1967); E. M. Kaiser and H. H. Yun, *ibid.*, **35**, 1348 (1970).

(15) (a) G. Cainelli, G. Dal Bello, and G. Zubiani, *Tetrahedron Lett.*, 3429 (1965); (b) G. Cainelli, G. Dal Bello, and G. Zubiani, *ibid.*, 4315 (1966); (c) G. Zweifel and H. Arzoumanian, *ibid.*, 2535 (1966); (d) G. Zweifel and R. B. Stelle, *ibid.*, 6021 (1966).

tallics are synthetically useful intermediates in the synthesis of other organic molecules.

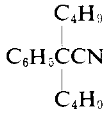
The results obtained with nitriles will be reported first. Thus, phenylacetonitrile (**1**) is rapidly and conveniently converted to its *gem*-dialkali salt **1′′** [16] by means of excess *n*-butyllithium in THF–hexane as evidenced by deuterations, certain condensations, and infrared spectroscopy. For example, stirring nitrile **1** in THF with 2.3 equiv of *n*-butyllithium in hexane at 25° for 1 hr followed by addition of excess deuterium oxide afforded nitrile **1** containing 1.78 benzylic deuterium atoms per molecule in 90% yield (eq 1). Similar metalations effected at 0° or upon heating (64°) likewise gave **1′′** since subsequent deuterations gave **1**-d_2 containing 1.60 and 1.65 benzylic deuterium atoms per molecule, respectively.



$$\mathrm{C_6H_5CH_2CN} \xrightarrow[\text{THF-hexane}]{2.3\ n\text{-}\mathrm{C_4H_9Li}} \mathrm{C_6H_5}\overset{\overset{\mathrm{Li}}{|}}{\underset{\underset{\mathrm{Li}}{|}}{\mathrm{C}}}\mathrm{CN} \xrightarrow{\mathrm{D_2O}} \mathrm{C_6H_5CD_2CN} \qquad (1)$$

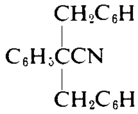
1 **1′′** **1**-d_2

Dialkali salt **1′′** also readily entered into twofold condensations with certain alkyl halides. Thus, treatment of **1′′** with 2.25 equiv of *n*-butyl bromide and with benzyl chloride gave dialkyl derivatives **2** and **3** in yields of 68 and 81%, respectively, after 3 hr reaction periods at 25°. The corresponding monoalkyl derivatives **4** and **5** were side products in the above reactions and were present in yields of 17 and 12%, respectively. That such alkylations occur rapidly was demonstrated by achieving a 67% yield of dibutyl derivative **2** after only a 10-min alkylation period at 0°.



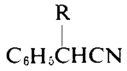
$$\mathrm{C_6H_5}\overset{\overset{\mathrm{C_4H_9}}{|}}{\underset{\underset{\mathrm{C_4H_9}}{|}}{\mathrm{C}}}\mathrm{CN}$$

2



$$\mathrm{C_6H_5}\overset{\overset{\mathrm{CH_2C_6H_5}}{|}}{\underset{\underset{\mathrm{CH_2C_6H_5}}{|}}{\mathrm{C}}}\mathrm{CN}$$

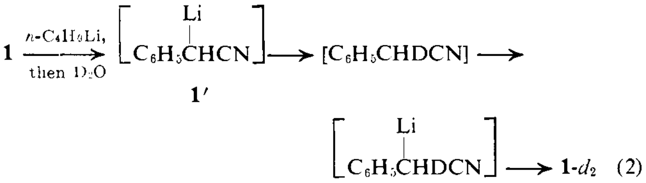
3



$$\mathrm{C_6H_5}\overset{\overset{\mathrm{R}}{|}}{\mathrm{C}}\mathrm{HCN}$$

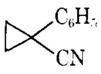
4, R = n-$\mathrm{C_4H_9}$
5, R = $\mathrm{CH_2C_6H_5}$

Since the above deuteration and alkylation products could also be explained by sequential monometalations–monocondensations, thereby resulting only in the intermediacy of monocarbanions (eq 2), certain experiments were performed to demonstrate that dianion **1′′** was indeed formed in these metalation reactions. First, the infrared spectrum of **1′′** contained a band at 1905 cm^{-1} but none at 2160 or 2130 cm^{-1}. On the other hand, the spectrum of the corresponding monolithio salt **1′**, prepared as above in THF–hexane using only 1 equiv of *n*-butyllithium, possessed the latter bands, but not the former one. Such spectra are comparable to those recently reported for lithio- and dilithioacetonitrile and related compounds.[12] Second, in those cases where **1′′** was prepared at 64°, no base sufficiently strong to ionize **1** was present when the electrophilic coreagents like alkyl halides were added. Thus, when a solution of 2.3 equiv of *n*-butyllithium in THF–hexane was refluxed for 1 hr and the resulting solution then treated with **1**, followed after 1 hr by deuterium oxide, **1** was recovered which contained only a trace of benzylic deuterium. Third, correct theoretical amounts of butane gas were evolved within 30 min when *n*-butyllithium was added either to THF alone or to THF containing **1** and the mixtures were then heated. Incidentally, the benzylic hydrogens of **1** do not undergo exchange with deuterium oxide under the conditions employed for deuteration of **1′′**.

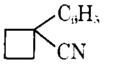


$$\mathbf{1} \xrightarrow[\text{then } \mathrm{D_2O}]{n\text{-}\mathrm{C_4H_9Li},} \left[\mathrm{C_6H_5}\overset{\overset{\mathrm{Li}}{|}}{\mathrm{C}}\mathrm{HCN}\right] \longrightarrow [\mathrm{C_6H_5CHDCN}] \longrightarrow$$
$$\qquad\qquad\mathbf{1'}$$
$$\left[\mathrm{C_6H_5}\overset{\overset{\mathrm{Li}}{|}}{\mathrm{C}}\mathrm{HDCN}\right] \longrightarrow \mathbf{1}\text{-}d_2 \qquad (2)$$

Certain other condensations were also performed on *gem*-dialkali salt **1′′** including cyclizations effected on dihaloalkanes. Thus, slow addition of ethylene chloride to **1′′** followed by 4- or 16-hr reaction periods afforded 1-cyano-1-phenylcyclopropane (**6**) in yields of 50 and 65%, respectively. Also, the use of 1,3-dichloropropane and 1,4-dibromobutane gave the corresponding cyclobutyl and cyclopentyl derivatives **7** and **8** in yields of 41 and 47%, respectively.



6



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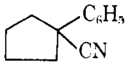
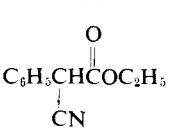


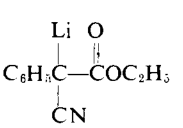
8

Dilithiophenylacetonitrile (**1′′**) was also monoacylated with 1.25 equiv of diethyl carbonate to afford cyano ester **9** in 79% yield (based on **1′′**); an identical carbethoxylation on monolithiophenylacetonitrile (**1′**) gave compound **9** in only 39% yield. Similarly, benzoylations with methyl benzoate on the di- and monoalkali salts of this nitrile afforded ketonitrile **10** in yields of 71 and 35%, respectively. It is interesting, but not surprising, that such acylations on **1′′** proceed in yields that are over twice as great as those realized on **1′**. It is well known[17] that acylations on monocarbanions proceed only to the extent of 50% reaction (based on carbanion) since the acylated product undergoes further ionization by the original carbanion to afford an anion like **9′** and the conjugate acid of the original carbanion. The lattice species, of course, is incapable of undergoing acylation. Such a loss of carbanion is avoided with reagents like **1′′** since monoacylation leads directly to anions like **9′**.



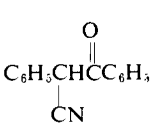
$$\mathrm{C_6H_5}\underset{\underset{\mathrm{CN}}{|}}{\mathrm{C}}\mathrm{H}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OC_2H_5}$$

9



$$\mathrm{C_6H_5}\overset{\overset{\mathrm{Li}}{|}}{\underset{\underset{\mathrm{CN}}{|}}{\mathrm{C}}}\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OC_2H_5}$$

9′



$$\mathrm{C_6H_5}\underset{\underset{\mathrm{CN}}{|}}{\mathrm{C}}\mathrm{H}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{C_6H_5}$$

10

Two other nitriles were briefly investigated as potential sources of geminate dianions. Thus, β-naphthylacetonitrile (**11**) was converted to **11′′** by means of *n*-butyllithium. Subsequent treatment of **11′′** with deuterium oxide gave the deuterated nitrile which contained 1.45 benzylic deuterium atoms per molecule. Interestingly, attempts to prepare the geminate dianion of *p*-tolunitrile (**12′′**) by means of *n*-butyllithium resulted in addition of the base across the nitrile linkage. Thus, the only product obtained from this reaction was *p*-toluvalerophenone (**13**) which probably arose from hydrolysis of the corresponding imine (**14**).

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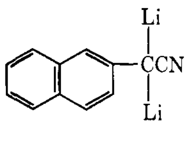
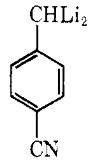
(16) Although compounds like **1′′** would be expected to possess delocalized charges (see Discussion), for convenience, only the canonical forms which lead to observed products will be shown in the Results.

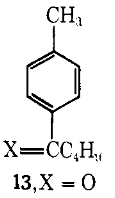
(17) For example, see C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. React.*, **8**, 113 (1954).



11''



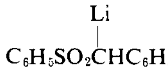
12''



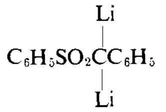
13,X = O
14,X = NH

Next, certain sulfur-containing compounds possessing labile α-hydrogens were also treated with *n*-butyllithium in THF–hexane to afford *gem*-dialkali derivatives. For example, benzyl phenyl sulfone (**15**) has been converted to dilithio salt **15''** as evidenced by infrared spectroscopy and condensation reactions. Thus, while the infrared spectrum of the yellow THF–hexane solution of the monoanion **15'** showed only a broadening of the S–O stretching frequencies at 1325 and 1150 cm^{-1}, that of the orange solution of **15''** contained no bands at the above frequencies. Instead, two broad bands were present at lower energies, namely at 1275 and 1100 cm^{-1}.

As expected, **15''** underwent deuteration with deuterium oxide to afford the dideuterated derivative **15**-d_2 in 95% yield. Similarly, dialkylations were realized on **15''** with *n*-butyl bromide and benzyl chloride to give derivatives **16** and **17** in yields of 72 and 83%, respectively. An acylation on **15''** was also realized with 1 equiv of methyl benzoate to afford β-ketosulfone **18** in 63% yield.


$C_6H_5SO_2\overset{Li}{C}HC_6H_5$

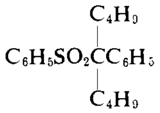
15'


$C_6H_5SO_2\underset{Li}{\overset{Li}{C}}C_6H_5$

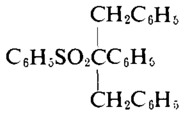
15''

$C_6H_5SO_2CD_2C_6H_5$

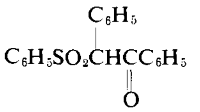
15-d_2


$C_6H_5SO_2\underset{C_4H_9}{\overset{C_4H_9}{C}}C_6H_5$

16

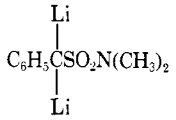

$C_6H_5SO_2\underset{CH_2C_6H_5}{\overset{CH_2C_6H_5}{C}}C_6H_5$

17

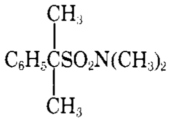

$C_6H_5SO_2\overset{C_6H_5}{C}H\underset{O}{\overset{}{C}}C_6H_5$

18

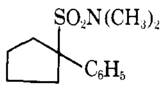
Similar treatment of *N*,*N*-dimethyl-α-toluenesulfonamide (**19**) with 2.2 equiv of *n*-butyllithium in THF–hexane gave the corresponding α,α-dilithio derivative **19''**. Deuteration of **19''** gave recovered sulfonamide containing 1.6 benzylic deuterium atoms per molecule in 81% yield. Similarly, treatment of **19''** with methyl iodide and with 1,4-dibromobutane gave compounds **20** and **21** in yields of 75 and 90%, respectively.


$C_6H_5\underset{Li}{\overset{Li}{C}}SO_2N(CH_3)_2$

19''


$C_6H_5\underset{CH_3}{\overset{CH_3}{C}}SO_2N(CH_3)_2$

20



21

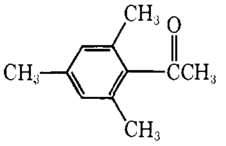
Surprisingly, attempted diionization of bissulfone **22** with *n*-butyllithium in THF–hexane apparently afforded only monolithio salt **22'** since subsequent deuteration with deuterium oxide gave **22** which contained only 0.8 deuterium atom on the methylene carbon. Alkylation with benzyl chloride also afforded only the monobenzyl derivative **23**. The failure of bissulfone **22** to afford a geminate dianion can be attributed to the very low solubility of the monoanion **22'** since a very voluminous white suspension was formed upon reaction of **22** and 1 equiv of *n*-butyllithium. The suspension did not appear to change upon addition of more base.

$(C_6H_5SO_2)_2CH_2$ **22** $(C_6H_5SO_2)_2CHLi$ **22'** $(C_6H_5SO_2)_2CHCH_2C_6H_5$ **23**

Next, interaction of benzyl phenyl sulfoxide (**24**) with excess *n*-butyllithium in THF–hexane afforded dilithio salt **24''** since subsequent treatment with deuterium oxide afforded sulfoxide **24** containing 1.51 methylene deuterium atoms per molecule. No deuterium exchange on **24** was realized with lithium deuteroxide and deuterium oxide under conditions similar to those employed for the deuteration of **24''**.

$C_6H_5SOCH_2C_6H_5$ **24** $C_6H_5SOCLi_2C_6H_5$ **24''**

Finally, acetomesitylene (**25**) was apparently converted to its geminate dianion since subsequent treatment with deuterium oxide afforded **25** which contained 2.02 acetylmethyl deuterium atoms. In a blank experiment of **25** with lithium deuteroxide and deuterium oxide, no exchange was observed to occur.

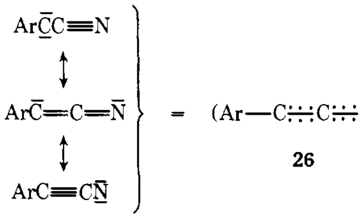


25

Discussion

The *gem*-polyalkali derivatives reported above represent the first examples of a presumably general class of unique organometallic reagents arising from ionization of two hydrogen atoms from the same carbon atom α to a single nonhydrocarbon functional group. Previously, the small number of related compounds had been obtained only from hydrogen compounds activated by adjacent aromatic or acetylenic functional groups.

Although all of the active hydrogen compounds in this study have previously been converted to their monoalkali salts, one would anticipate at first glance that ionization of a second geminate type of hydrogen atom would be both thermodynamically and kinetically unfeasible. In the case of phenyl- and β-naphthylacetonitriles, though, geminate diionization leads to the first examples of sesquiazacetylenes,[11c] systems whose potential syntheses were predicted after the appearance of our initial disclosure.[2a] Such compounds, pictured as consisting of sp-hybridized atoms (see **26** blow), are thought to impart special stabilization to these multiple anions because of their relatively high degree of s character.[18]



26

In the case of benzyl phenyl sulfone (**15**) and *N*,*N*-dimethyl-α-toluenesulfonamide (**19**), the geminate dianions are capable of stabilization by d_π–p_π interactions[19] re-

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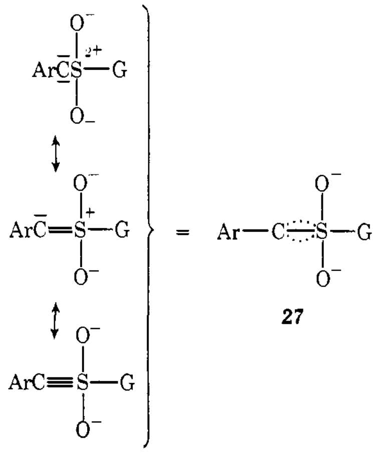
(18) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 48–50.

(19) See ref 18, pp 71–84.

sulting in a resonance hybrid which could be drawn as in **27**. As above, **27** contains an sp-hybridized carbon atom. The infrared spectrum of **15''** (G = C_6H_5) is consistent with **27** since the positive charges on sulfur are diminished resulting in reduced force constants for the S–O bonds, thereby causing a shift in the stretching frequencies to lower energies.



27

Such polymetalations and subsequent condensations should be capable of extension to many other active hydrogen compounds, particularly those which contain hydrogen atoms α to atoms possessing vacant d orbitals. The recently reported two-base technique of Mao, Hauser, and Miles[20] should be of particular interest for the ionization of those compounds containing functional groups which have a propensity for undergoing addition reactions with strong bases like *n*-butyllithium.

Experimental Section[21]

1,1-Dilithiophenylacetonitrile (1''). **A. Preparation.** To 70.3 ml (0.11 mol) of 1.6 *M* *n*-butyllithium in hexane, at room temperature or at 0°, was added rapidly 70.0 ml of anhydrous THF followed by a solution of 5.85 g (0.05 mol) of phenylacetonitrile in 50 ml of THF added during 5 min. The solution refluxed spontaneously. After 1 hr, the brown solution was assumed to contain 0.05 mol of 1,1-dilithiophenylacetonitrile (**1''**). As evidenced by certain of the deuteration and alkylation reactions described below, compound **1''** was similarly prepared by adding the *n*-butyllithium during 5 min to a THF solution of phenylacetonitrile, or by running the metalation reactions from 0 to 65° for 1–12 hr; however, the longer reaction periods resulted in diminished yields of **1''**.

B. Deuterations. To 0.05 mol of **1''**, prepared as in part A, at 0°, was added all at once 5.4 ml (0.3 mol) of deuterium oxide in 20 ml of THF. The resulting suspension was filtered by suction, the filtrate was dried ($MgSO_4$) and concentrated, and the residue was distilled to afford 5.28 g (90%) of deuterated phenylacetonitrile: bp 77–78° (3.8 mm) (lit.[22] bp 234° (760 mm)); nmr (neat) δ 7.16 (s, 5, ArH), 3.47 (m, 0.22, Ar*CH*). Thus, the nitrile contained 1.78 benzylic deuterium atoms per molecule.

Similar deuterations were effected on **1''** prepared under different conditions as follows (time, temperature of preparation, amount of benzylic deuterium atoms, per cent yield of phenylacetonitrile): 12 hr at 65°, 1.5, 78%; 1 hr at 65°, 1.65, 79%; 1 hr at 0°, 1.6, 80%.

In a blank experiment, a solution of 70.3 ml (0.11 mol) of 1.6 *M* *n*-butyllithium in hexane and 70 ml of THF was refluxed for 1 hr causing the correct amount of butane to be evolved within 30 min. Upon cooling to 25°, the solution was treated with 5.85 g (0.05 mol) of phenylacetonitrile (**1**) in 50 ml of THF. After stirring for 1 hr, this solution was cooled to 0°, then deuterated as above to give 5.5 g (94%) of nitrile **1** whose nmr indicated the presence of no more than 0.1 benzylic deuterium atom per molecule.

Finally, a solution of 5.85 g (0.05 mol) of nitrile **1** in 120 ml of THF and 70 ml of hexane at 0° was treated with 1.25 g (0.05 mol) of lithium deuteroxide and 0.91 ml (0.05 mol) of deuterium oxide. The mixture was allowed to warm to 25° during the next 30 min, filtered, and worked up as above to afford 4.36 g (75%) of nitrile **1**, bp 92–93° (6 mm). The nmr spectrum of the product suggested that no deuterium had been incorporated into **1**.

C. Butylation. To 0.05 mol of **1''** at 25° was added during 5 min a solution of 15.4 g (0.11 mol) of *n*-butyl bromide in 50 ml of THF. After 3 hr, the suspension was hydrolyzed by 100 ml of water, the layers were separated, and the aqueous layer was extracted with three 50-ml portions of ethyl ether. The combined extracts were dried ($CaSO_4$) and concentrated and the residue was distilled to give 1.5 g (17%) of α-*n*-butylphenylacetonitrile (**4**), bp 105–106° (4.5 mm) (lit.[23] bp 152–155° (20 mm)), and 7.8 g (68%) of α,α-di-*n*-butylphenylacetonitrile (**2**), bp 139–141° (4.5 mm) (lit.[24] bp 135–140° (1.5 mm)). The infrared spectra and vpc retention times of **2** and **4** were identical with those of authentic samples.

D. Benzylation. To 0.05 mol of **1''** at 25° was added during 10 min a solution of 14.2 g (0.11 mol) of benzyl chloride in 50 ml of THF. After 3 hr, the mixture was hydrolyzed and worked up as above to give 1.4 g (12%) of 2,3-diphenylpropionitrile (**5**), bp 150–152° (2 mm) (lit.[25] bp 134–150° (0.6 mm)), and 11.0 g (81%) of 1,2,3-triphenyl-2-cyanopropane (**3**), bp 207–209° (2 mm) (lit.[25] bp 185–186° (0.6 mm)). The infrared spectra of **3** and **5** were identical with those of authentic samples.

E. Cyclizations. To 0.05 mol of **1''** at 25° was added during 40 min a solution of 4.95 g (0.05 mol) of ethylene chloride in 100 ml of THF. After 16 hr, the mixture was hydrolyzed by 100 ml of 3 *N* hydrochloric acid and worked up as above to afford 4.61 g (65%) of 1-phenyl-1-cyanocyclopropane (**6**): bp 89–90.5° (2.5 mm) (lit.[26] bp 98–100° (1 mm)); ir (neat) 2220 (CN), 685 and 748 cm^{-1} (ArH); nmr (neat) δ 7.2 (s, 5, ArH), 1.3 (m, 4, cyclopropyl); mass spectrum (70 eV) m/e 143 (molecular ion). When the reaction was repeated for 4 hr instead of 16 hr, 3.50 g (50%) of cyclopropane **6** was obtained.

Similarly, treatment of 0.05 mol of **1''** with a solution of 5.65 g (0.05 mol) of 1,3-dichloropropane in 100 ml of THF during 1 hr followed by stirring for 4–22 hr gave, upon work-up, 2.85–3.2 g (36–41%) of 1-phenyl-1-cyanocyclobutane (**7**): bp 113–115° (3 mm) (lit.[27] bp 90–128° (4 mm)); nmr (neat) δ 7.62 (m, 5, ArH), 1.75 (m, 6, cyclobutyl).

Likewise, addition of a solution of 12.8 g (0.05 mol) of 1,4-dibromobutane in 100 ml of THF during 10–12 min to **1''** followed by stirring for 9 hr gave, upon work-up, 4.1 g (47%) of 1-phenyl-1-cyanocyclopentane (**8**): bp 157–160° (24 mm) (lit.[28] bp 148–153° (20 mm)); nmr (neat) δ 7.33 (m, 5, ArH), 1.96 (m, 8, CH_2).

F. Acylations. Treatment of 0.05 mol of **1''** during 6 min with a solution of 5.9 g (0.05 mol) of diethyl carbonate in 50 ml of THF afforded a yellow solution which was refluxed for 2 hr. Upon cooling, the resulting suspension was treated with 100 ml of 3 *N* hydrochloric acid and worked up to give 7.45 g (79%) of ethyl 2-cyano-2-phenylacetate (**9**): bp 106–107° (1.5 mm) (lit.[29] bp 165.5° (20 mm)); ir (neat) 2250 (CN), 1745 (C=O), 1245 (CO stretch), 735 and 696 cm^{-1} (aromatic).

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[20] C. Mao, C. R. Hauser, and M. L. Miles, *J. Amer. Chem. Soc.*, **89**, 5303 (1967).

[21] All lithiations were performed under nitrogen in 500-ml round-bottomed three-necked flasks fitted with a mechanical stirrer and a reflux condenser. The THF employed was freshly distilled from lithium aluminum hydride. The *n*-butyllithium, supplied by the Foote Mineral Co., Exton, Pa., was introduced directly into the reaction mixtures *via* a hypodermic syringe. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were determined on Perkin-Elmer spectrometers, Models 137 or 237. Nmr spectra were obtained with a Varian Associates A-60 spectrometer using tetramethylsilane as internal standard. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

[22] "Tables for Identification of Organic Compounds," The Chemical Rubber Co., Cleveland, Ohio, 1964, p 266.

[23] L. H. Baldinger and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **55**, 2851 (1933).

[24] N. Sperber, D. Papa, and E. Schwenk, *ibid.*, **70**, 3091 (1948).

[25] C. R. Hauser and W. R. Brasen, *ibid.*, **78**, 494 (1956).

[26] E. C. Knowles and J. B. Cloke, *ibid.*, **54**, 2028 (1932).

[27] F. H. Case, *ibid.*, **55**, 2927 (1933).

[28] C. H. Tilford, M. G. van Campen, Jr., and R. S. Shelton, *ibid.*, **69**, 2902 (1947).

[29] J. C. Hessler, *Amer. Chem. J.*, **32**, 122 (1904).

When the reaction was repeated on 0.05 mol of monolithiophenylacetonitrile employing 5.9 g (0.05 mol) of diethyl carbonate in THF, cyano ester **9** was obtained in only 39% yield.

In a similar reaction, 0.05 mol of **1''** was treated during 5 min with a solution of 6.80 g (0.05 mol) of methyl benzoate in 50 ml of THF. After stirring at reflux for 2 hr, the solution was worked up to give 7.85 g (71%) of benzoylphenylacetonitrile (**10**): mp 93–95.5° (lit.[30] mp 94–95°); ir (mull) 2250 (CN), 1678 (C=O), 750 and 695 cm^{-1} (ArH); nmr (CF_3CO_2H) δ 7.75 (m, 10, ArH), 6.08 (s, 1, ArCH).

When the reaction was repeated on 0.05 mol of monolithiophenylacetonitrile employing 6.80 g (0.05 mol) of methyl benzoate, ketonitrile **10** was obtained in 35% yield.

1,1-Dilithio-β-naphthylacetonitrile. Preparation and Deuteration. To 70.3 ml (0.11 mol) of 1.6 *M n*-butyllithium in hexane and 70 ml of THF, mixed as in part A above, was added during 5 min a solution of 8.36 g (0.05 mol) of β-naphthylacetonitrile (**11**) in 50 ml of THF. After 1 hr, the deep red-brown solution was cooled to 0° and deuterated by the addition of 5.4 ml (0.3 mol) of deuterium oxide as above. Work-up gave 6.6 g (79%) of nitrile **11**: bp 160–164° (3.5 mm) (lit.[31] mp 79–81°); nmr (neat) δ 6.91 (m, 7, ArH), 3.0 (broad s, 0.56, benzylic). Thus, the nitrile possessed 1.44 benzylic deuterium atoms per molecule.

Attempted Polylithiation of *p*-Tolunitrile. This reaction was effected essentially as described for β-naphthylacetonitrile above using 70.3 ml (0.11 mol) of *n*-butyllithium, 5.85 g (0.05 mol) of *p*-tolunitrile (**12**), and 4 ml (0.2 mol) of deuterium oxide. The resulting yellow solution was then treated with 100 ml of 3 *N* hydrochloric acid and heat was applied for 2 hr. Upon cooling, the mixture was worked up in the usual fashion to give 7.1 g (81%) of *p*-toluvalerophenone (**13**): bp 100–102° (2.5 mm) (lit.[32] bp 266–267°; nmr (neat) δ 7.46 (d, 2, ArH), 6.75 (d, 2, ArH), 2.36 (t, 2, $ArCOCH_2$), 1.83 (s, 3, $ArCH_3$), 0.87 (m, 7, CH_2, CH_3).

1,1-Dilithiobenzyl Phenyl Sulfone (15). A. Preparation. To a suspension of 11.6 g (0.05 mol) of benzyl phenyl sulfone (**15**) in 78 ml of THF was added, during 14 min, 78 ml (0.125 mol) of 1.6 *M n*-butyllithium in hexane to afford a yellow mixture which turned orange as the second equiv of the base was added. After 1 hr, the resulting solution was assumed to contain 0.05 mol of dilithiobenzyl phenyl sulfone (**15''**).

B. Deuteration. To 0.05 mol of **15''** at 0° was added all at once a solution of 3 ml (0.15 mol) of deuterium oxide in 25 ml of THF to give a voluminous white suspension. Solid product was collected by suction, combined with that obtained by concentrating the organic phase, and washed thoroughly with water. Drying afforded 11.0 g (95%) of benzyl phenyl sulfone: mp 145–146°; nmr ($CDCl_3$) δ 7.37 (m, 10, ArH), 4.3 (s, 0, $ArCH_2$). Thus, the recovered sulfone contained 2.0 benzylic deuterium atoms per molecule.

C. Alkylations. Dilithio salt **15''** (0.05 mol) was treated during 12 min with a solution of 17.2 g (0.125 mol) of *n*-butyl bromide in 50 ml of THF. After refluxing the resulting solution for 24 hr, the mixture was hydrolyzed by 100 ml of water and worked up to give an oil which crystallized from absolute ethanol to afford 12.25 g (72%) of α,α-di-*n*-butylbenzyl phenyl sulfone (**16**): mp 106–106.2°; nmr ($CDCl_3$) δ 7.21 (m, 10, ArH), 1.58 (m, 18 aliphatic CH).

Anal. Calcd for $C_{21}H_{28}SO_2$: C, 73.22; H, 8.19; S, 9.29. Found: C, 73.36; H, 8.35; S, 9.50.

Similarly, 0.05 mol of **15''** was treated during 5 min with a solution of 16.0 g (0.123 mol) of benzyl chloride in 50 ml of THF. Heat was applied for 22 hr and the suspension was then worked up to give 17.18 g (83%) of α,α-dibenzylbenzyl phenyl sulfone (**17**): mp 182–184°; nmr ($CDCl_3$) δ 7.1 (m, 20, ArH), 3.93 (q, 4, $ArCH_2$).

Anal. Calcd for $C_{26}H_{24}SO_2$: C, 78.62; H, 5.86; S, 7.76. Found: C, 78.56; H, 5.78; S, 7.66.

D. Benzoylation. To 0.025 mol of **15''** was added during 10 min a solution of 3.4 g (0.025 mol) of methyl benzoate in 50 ml of THF. The resulting solution was refluxed for 4 hr, cooled, and hydrolyzed by pouring it into ice–water–hydrochloric acid. The mixture was worked up to give a solid which was recrystallized from 95% ethanol to afford 5.3 g (63%) of α-benzoylbenzyl phenyl sulfone (**18**): mp 138–140°; nmr ($CDCl_3$) δ 7.72 (m, 15, ArH), 5.87 (s, 1, ArCH).

Anal. Calcd for $C_{20}H_{16}SO_3$: C, 71.43; H, 4.75; S, 9.49. Found: C, 71.46; H, 4.84; S, 9.37.

When the reaction was repeated using a reflux period of only 1 hr, ketosulfone **18** was obtained in only 24% yield.

Preparation of *N,N*-Dimethyl-α-toluenesulfonamide (19). Excess gaseous dimethylamine was passed into a solution of 5.0 g (0.026 mol) of α-toluenesulfonyl chloride. After washing the solution and drying ($MgSO_4$), removal of the solvent gave, upon recrystallization from aqueous ethanol, 4.40 g (84%) of *N,N*-dimethyl-α-toluenesulfonamide (**19**), mp 99–100.5° (lit.[33] mp 102–103°).

α,α-Dilithio-*N,N*-dimethyl-α-toluenesulfonamide (19''). A. Preparation. To a solution of 1.0 g (0.005 mol) of *N,N*-dimethyl-α-toluenesulfonamide in 20 ml of THF at 0° was added, during 5 min, 6.7 ml (0.011 mol) of 1.6 *M n*-butyllithium in hexane. After removing the ice bath and stirring for 45 min, the pale yellow solution was assumed to contain 0.005 mol of **19''**.

B. Deuteration. To a solution of 0.005 mol of **19''** was rapidly added 0.25 ml (0.014 mol) of deuterium oxide in 10 ml of THF. After stirring for 15 min, the mixture was treated with 20 ml of water and worked up as usual to give 0.99 g of solid which, upon recrystallization from chloroform–ligroin, afforded 0.81 g (81%) of deuterated *N,N*-dimethyl-α-toluenesulfonamide, mp 101.5–103.0°. The nmr indicated incorporation of 80% deuterium in the benzylic position, using the *N*-methyl peak as an internal standard.

C. Methylation. A solution of 0.005 mol of **19''** was treated with a solution of 1.56 g (0.011 mol) of methyl iodide in 20 ml of THF added dropwise. After stirring for 16 hr, the solution was hydrolyzed by 20 ml of water. The usual work-up gave a powder which was recrystallized from chloroform–ligroin to afford 0.85 g (75%) of *N,N*-dimethyl-2-phenyl-2-propanesulfonamide (**20**): mp 102–104°; ir (KBr) 3010 (arom CH), 2990, 2975, 2860 and 2820 (CH_3), 1600, 1500 and 1450 (arom CH), 1300 and 1120 (SO_2N), and 780, 725, and 700 cm^{-1} (arom); nmr ($CDCl_3$) δ 7.75–7.25 (m, 5, ArH), 2.54 (s, 5.8, NCH_3), and 1.83 (s, 6.3, α-CH_3).

Anal. Calcd for $C_{11}H_{17}NO_2S$: C, 58.12; H, 7.54; N, 6.16. Found: C, 57.99; H, 7.85; N, 5.99.

D. Dialkylation with 1,4-Dibromobutane. To a stirred solution of 0.01 mol of **19''** in 50 ml of THF was added during 30 min a solution of 2.16 g (0.01 mol) of 1,4-dibromobutane in 20 ml of THF. The solution was stirred for 5 hr, treated with 20 ml of water, and worked up as usual to give 2.29 g (90%) of crude 1-(*N,N*-dimethylsulfamyl)-1-phenylcyclopentane (**21**), mp 123–126°. Vacuum sublimation of this material at 100° (0.15 mm) afforded 1.97 g (86%) of pure **21**: mp 126–128°; ir (KBr) 3060 (arom CH), 2950 and 2875 (aliph CH), 1600, 1500 and 1450 (arom C=C), 1300 and 1130 (SO_2N), 770 and 710 cm^{-1} (arom); nmr ($CDCl_3$) δ 7.78–7.23 (m, 5, ArH), 2.49 (s), and 2.30–1.40 (m) (14.3, NCH_3, cyclopentane).

Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.62; H, 7.55; N, 5.52; S, 12.65. Found: C, 61.86; H, 7.49; N, 5.56; S, 12.67.

Attempted Preparation of *gem*-Dilithiobisphenylsulfonylmethane. To a solution of 7.4 g (0.025 mol) of the disulfone **22** in 70 ml of THF was added 35 ml (0.056 mol) of 1.6 *M n*-butyllithium in hexane. After 1 hr, the resulting yellow suspension was cooled to 0° and treated with 5 ml (0.25 mol) of neat deuterium oxide added all at once. The solution was stirred briefly, then it was treated with 100 ml of 3 *N* hydrochloric acid. The mixture was worked up as usual to give 6.23 g (84%) of recovered disulfone **22**: mp, mmp 114–116°; nmr ($CDCl_3$) δ 7.63 (m, 10, ArH), 4.75 (s, 1.2 aliph CH). Thus, only 0.8 atom of deuterium was incorporated per molecule.

The above reaction was repeated except that the purported dianion was treated during 5 min with a solution of 8.0 g (0.061 mol) of benzyl chloride in 50 ml of THF. After refluxing for 22 hr, the suspension was worked up to give, in addition to recovered disulfone **22**, 1.7 g (18%) of 1,1-diphenylsulfonyl-2-phenylethane (**23**): mp 140–142°; nmr ($CDCl_3$) δ 7.13 (m, 15, ArH), 4.53 (t, 1, SO_2CH), and 3.35 (d, 2, CH_2Ar).

Anal. Calcd for $C_{20}H_{18}S_2O_4$: C, 62.17; H, 4.66; S, 16.58. Found: C, 62.27; H, 4.70; S, 16.38.

1,1-Dilithiobenzyl Phenyl Sulfoxide. Preparation and Deuteration. To a solution of 5.4 g (0.025 mol) of benzyl phenyl sulfoxide (**24**) in 100 cm^3 of THF at 0° was added 40 ml (0.065 mol) of *n*-butyllithium in hexane, causing the mixture to become yellow, then brown. After 15 min, the mixture was treated with 5 ml (0.25 mol) of deuterium oxide causing the color to quickly change from brown to white. Filtering the suspension and stripping the filtrate gave 5.6 g of a light yellow solid, mp 100–115°. Recrystallization of a

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(30) C. J. Eby and C. R. Hauser, *J. Amer. Chem. Soc.*, **79**, 723 (1957).

(31) O. Blank, *Chem. Ber.*, **29**, 2373 (1896).

(32) E. E. Blaise, *C. R. Acad. Sci.*, **133**, 1217 (1901).

(33) T. B. Johnson and J. A. Ambler, *J. Amer. Chem. Soc.*, **36**, 372 (1914).

portion of the solid from carbon tetrachloride gave pure benzyl phenyl sulfoxide (**24**): mp 123–125°; nmr (CCl_4) δ 7.11 (m, 10, ArH) and 4.0 (s, 0.49, CHSO). Thus the compound contained 1.51 deuterium atoms per molecule.

In a blank run, a mixture of 40 ml (0.065 mol) of *n*-butyllithium in hexane and 5 ml (0.25 mol) of deuterium oxide in 100 ml of THF at 0° was treated with 5.4 g (0.025 mol) of benzyl phenyl sulfoxide. The reaction was worked up as above to give starting material, mp 123–125° after recrystallization from CCl_4, in which no detectable exchange had occurred.

Dilithioacetomesitylene. Preparation and Deuteration. To a solution of 102 ml (0.163 mol) of 1.6 *M* *n*-butyllithium in hexane was rapidly added 100 ml of THF followed by a solution of 8.1 g (0.05 mol) of acetomesitylene (**25**) in 50 ml of THF, added during 5 min. After 1 hr, the solution was treated with 2.9 ml (0.16 mol) of deuterium oxide in 22 ml of THF added all at once. The resulting suspension was filtered and the solid was washed thoroughly with anhydrous ether. After drying ($CaSO_4$) and concentrating the filtrate, the residual liquid was distilled to give 5.36 g (66%) of deuterated acetomesitylene (**25**): bp 75–76° (2 mm) (lit.[34] bp 237 (758 mm); nmr (neat) δ 6.73 (s, 2, ArH), 2.25 (m, 0.95, $COCH_3$), 2.18 (s, 3, *p*-CH_3), 2.10 (s, 6, *o*-CH_3).

In a blank experiment, a solution of 8.1 g (0.05 mol) of acetomesitylene in 150 ml of THF and 100 ml of dry hexane was treated with 4.0 g (0.16 mol) of lithium deuteroxide and 2.9 ml (0.16 mol) of deuterium oxide. After stirring for several minutes, the mixture was filtered and worked up as above to afford 7.72 g (96%) of acetomesitylene, bp 82–84° (3.5 mm). The ir and nmr spectra were identical with those of authentic undeuterated acetomesitylene.

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[34] A. Behal and V. Auger, *Bull. Soc. Chim. Fr.*, **9**, 703 (1893).

High-Pressure Studies. VIII. Thermal Decomposition of Isomeric *tert*-Butyl Vinyl Peresters in Solution[1]

Robert C. Neuman, Jr.,* and Gary D. Holmes[2]

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. *Received October 21, 1970*

Abstract: The effects of pressure on the rates and decomposition products of the cis and trans isomers of *tert*-butyl 2-propyl-2-peroxypentenoate were determined using the solvent cumene. The data indicate that both isomers decompose by one-bond O–O scission to yield geminate vinylcarboxy and *tert*-butoxy radicals. The isomeric vinylcarboxy radicals appear to have different reactivities. The data indicate that the initially formed geminate pairs recombine to regenerate starting material in competition with disproportionation and separative diffusion. The apparent activation volumes for the two isomers are different (cis, +6.8 ± 0.4 cm^3/mol; trans, +9.0 ± 1.0 cm^3/mol) and this suggests that recombination of the radical pair derived from the *trans*-perester is more competitive with disproportionation and separative diffusion than that for the other isomer. Disproportionation to form 3-heptyne and 3,4-heptadiene is more favorable from the *cis*-vinylcarboxy radical and it also appears that this radical undergoes unimolecular decarboxylation more rapidly than the corresponding isomer. The isomeric vinyl radicals ultimately formed from these peresters equilibrate rapidly at atmospheric pressure, but the data suggest that application of pressure permits preequilibrium trapping.

Effects of pressure on decomposition rates and products of free-radical initiators have been used to probe their decomposition mechanisms.[1a,3] Observed activation volumes for one-bond scission initiators are substantially larger than those for two-bond initiators (Table I)[1a,3,4] and this has been rationalized as the kinetic result of cage return of the primary radical products in the former systems.[1a,3,5] We have obtained the majority of the pressure data for two-bond initiators, but our results for one-bond systems were limited to a cursory study of *tert*-butyl perbenzoate.[3c] We report here a more detailed pressure study of two isomeric *tert*-butyl vinyl peresters which we presumed would fall within this latter class of initiators.[6] The kinetic and product data for *cis*- and *trans*-*tert*-butyl 2-propyl-2-peroxypentenoate (**1** and **2**)[7] in cumene: (1) support the one-bond scission decomposition

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[1] (a) Parts VI and VII: R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 654, 657 (1971). (b) Support by the National Science Foundation (GP-8670) is gratefully acknowledged. (c) Presented at the ACS-CIC Joint Meeting, Toronto, Canada, May 24–29, 1970, Abstracts, Phys 056.

[2] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research through a graduate student fellowship to G. D. H. (1969–1970).

[3] (a) R. C. Neuman, Jr., and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970); (b) R. C. Neuman, Jr., *Intra-Sci. Chem. Rep.*, **3**, 269 (1969); (c) R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **91**, 6024 (1969); (d) R. C. Neuman, Jr., and R. J. Bussey, *Tetrahedron Lett.*, 5859 (1968); (e) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, 3281 (1968); (f) R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **89**, 4549 (1967).

[4] (a) A. E. Nicholson and R. G. W. Norrish, *Discuss. Faraday Soc.*, **22**, 97 (1956); (b) A. E. Nicholson and R. G. W. Norrish, *ibid.*, **22**, 104 (1956); (c) C. Walling and J. Pellon, *J. Amer. Chem. Soc.*, **79**, 4786 (1957); (d) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, Jr., *ibid.*, **87**, 518 (1965); (e) C. Walling and G. Metzger, *ibid.*, **81**, 5365 (1959); (f) C. Walling and H. P. Waits, *J. Phys. Chem.*, **71**, 2361 (1967); (g) A. H. Ewald, *Discuss. Faraday Soc.*, **22**, 138 (1965).

[5] For the general homolytic scission mechanism below, ΔV_{obsd}^*

$$\text{initiator} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{cage radicals} \xrightarrow{k}$$

equals $\Delta V_1^* + RT\,\partial \ln (1 + k_{-1}/k)/\partial P$. The latter term should be positive since k includes k_d which is greatly pressure retarded. For two-bond scission, $k_{-1} = 0$; hence if values of ΔV_1^* are similar for one- and two-bond scission, ΔV_{obsd}^* for the former would be greater than for the latter.[1a,3]

[6] See (a) L. A. Singer and J. Chen, *Tetrahedron Lett.*, 4849 (1969); (b) L. A. Singer and N. P. Kong, *J. Amer. Chem. Soc.*, **89**, 5251 (1967); (c) R. M. Fantazier and J. A. Kampmeier, *ibid.*, **88**, 5219 (1966); (d) L. A. Singer and N. P. Kong, *ibid.*, **88**, 5213 (1966); (e) J. A. Kampmeier and R. M. Fantazier, *ibid.*, **88**, 1959 (1966).

[7] (a) Structural assignments are consistent with nmr positions of vinyl proton signals[6b,d] and independent syntheses of the carboxylic acid precursors from the corresponding vinyl iodides;[7b] complete details are outlined in G. D. H.'s Ph.D. Dissertation, University of California, Riverside, Calif., 1970; (b) R. C. Neuman, Jr., and G. D. Holmes, *J. Org. Chem.*, 33, 4317 (1968).