J. Org. Chem. 1986, 51, 2093–2098 2093

Mechanism of the Superoxide Anion Radical ($O_2^{-}\bullet$) Mediated Oxidation of Diarylmethanes

Aryeh A. Frimer,* Tova Farkash-Solomon, and Gladis Aljadeff

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52100, Israel

Received December 19, 1985

Variously substituted diphenylmethanes (**2a–l**) were prepared and reacted competitively with $O_2^{-}\cdot$ (generated from KO_2/18-crown-6 polyether) in benzene. The relative rate constants (k_{rel}) correlated best ($r = 0.993$) with σ^-, giving a ρ value of 3.96 ± 0.16. For the corresponding oxygenation mediated by *tert*-butoxide, the ρ obtained was 1.77 ± 0.41 ($r = 0.950$). The primary deuterium isotope effects (k_H/k_D) on the superoxide reaction of diphenylmethane and its 4,4′-dichloro analogue were 2.36 and 2.14, respectively. The rate of reaction was found to be linearly proportional to the crown ether concentration, and no reaction occurred in its absence. These results indicate that the reaction is homogeneous and is first order in superoxide and diphenylmethane. The correlation with σ^- and the magnitudes of ρ and the primary isotope effect are interpreted as requiring a reaction sequence in which a proton is first transfered from substrate to superoxide in the rate-determining step, with the resulting benzylic anion undergoing subsequent oxygenation to the corresponding ketones **1**. A Brønsted analysis of the deprotonation reaction yields an α value of 0.69, suggesting a late transition state. The discrepancy between these results obtained in benzene and those of others for Me_2SO studies raises the possibility of a solvent-dependent duality of mechanism.

Introduction

The heated debate on the role of superoxide anion radical ($O_2^{-}\cdot$) in oxygen toxicity[1-3] has generated a good deal of interest in the organic chemistry of this active oxygen species.[4] Early researchers in the field generally assumed that superoxide-mediated oxidations of hydrocarbons proceeded via an initial abstraction of labile hydrogen atoms from the substrate by the radical anion (eq 1). The resulting carbon based radical then combined with

$$RH + O_2^{-}\cdot \rightarrow R\cdot + HOO^- \qquad (1)$$

$$R\cdot + O_2 \rightarrow ROO\cdot \qquad (2)$$

$$ROO\cdot + O_2^{-}\cdot \rightarrow ROO^- + O_2 \qquad (3)$$

$$ROO^- \rightarrow\ \rightarrow \text{Oxidation products} \qquad (4)$$

molecular oxygen[5] to produce peroxy intermediates which decompose in turn yielding the observed oxidation products (eq 2–4). Sawyer[6] subsequently posited that $O_2^{-}\cdot$ can promote proton transfer from substrates to an extent equivalent to that of a conjugate base of an acid with a pK_a of ~ 24. In light of this, a general consensus has been developing that C–H linkages with low pK_a values ($\lesssim 20$) react with $O_2^{-}\cdot$ via initial proton transfer[4] (eq 5). The

$$RH + O_2^{-}\cdot \rightarrow R^- + HO_2\cdot \qquad (5)$$

$$R^- + O_2 \rightarrow R\cdot + O_2^{-}\cdot \qquad (6)$$

resulting carbanion is converted to the corresponding carbon-based radical (eq 6) and subsequently oxygenated (eq 2–4) along the lines elucidated by Russell and coworkers for base-catalyzed autoxidations.[7]

In the case of substrates with pK_a values greater than 20, there is no such unanimity on the question of mechanism. Although Sawyer has shown that even weakly acidic *oxygen* acids such as *n*-butanol (pK_a of 33 in DMF)[6d] are efficiently deprotonated by $O_2^{-}\cdot$, this may have little relevance to the corresponding *carbon* acids, for it is wellknown[8a] that the deprotonation of oxygen and nitrogen heteroacids is kinetically a much more facile process than that of carbon acids of corresponding pK_a. It is this dichotomy, then, between equilibrium acidity (pK_a) and kinetic acidity which again raises the question of whether deprotonation predominates over radical hydrogen abstraction in superoxide-mediated oxidations of weak carbon acids.

A survey of the literature reveals that various diarylmethanes have been oxidized by $O_2^{-}\cdot$ to the corresponding ketones including anthrone, 9,10-diphenylanthracene, fluorene (pK_a = 23),[8b] xanthene, diphenylmethane (pK_a = 34),[8b] and distyrylmethane.[9] Hydrogen atom abstraction has indeed been proposed by many authors[9] as the initial step in these $O_2^{-}\cdot$-induced processes. However, we note that bona fide base-catalyzed autoxidations have also been reported for each of these compounds with other bases.[7,9,10] Furthermore, recent calculations by Liebman

---

(1) See the articles of I. Fridovich and J. Fee and the subsequent extensive discussion in "Oxygen and Oxy-Radicals, in Chemistry and Biology"; Rodgers, M. A. J., Powers, E. L., Eds.; Academic Press: New York, 1981; pp 197–239.

(2) See the exchange of correspondence between Fridovich and Sawyer and Valentine: Fridovich, I.; Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1982**, *15*, 200.

(3) Baum, R. M. *Chem. Eng. News* **1984** (April 9), 20–26.

(4) For recent reviews see: (a) Frimer, A. A. In "The Chemistry of Functional Groups: Peroxides"; Patai, S., Ed.; Wiley: Chichester, 1983; pp 429–461. (b) Frimer, A. A. In "Superoxide Dismutase"; Oberley, L. W., Ed.; Chemical Rubber Co.: Boca Raton, Florida, 1982; Vol. 2, pp 83–125.

(5) Radical coupling between $O_2^{-}\cdot$ and neutral free radicals has not been observed.[4]

(6) (a) Sawyer, D. T.; Gibian, M. J. *Tetrahedron* **1979**, *35*, 1471. (b) Sawyer, D. T.; Gibian, M. J.; Morrison, M. M.; Seo, E. T. *J. Am. Chem. Soc.* **1978**, *100*, 627, footnote 20. (c) Gibian, M. J.; Sawyer, D. T.; Ungermann, T.; Tangpoonpholvivat, R.; Morrison, M. M. *J. Am. Chem. Soc.* **1979**, *101*, 640. (d) Nanni, E. J.; Stallings, M. D.; Sawyer, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 4481.

(7) (a) Russell, G. A.; Janzen, E. G.; Bemis, A. G.; Geels, E. J.; Moye, A. J.; Mak, S.; Strom, E. T. *Adv. Chem. Ser.* **1965**, No. 51, 112. (b) Russell, G. A. *Pure Appl. Chem.* **1967**, *15*, 185. (c) Russell, G. A.; Bemis, A. G.; Geels, E. J.; Janzen, E. G.; Moye, A. J. *Adv. Chem. Ser.* **1968**, No. 75, 174.

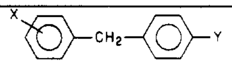
(8) (a) Crooks, J. E. In "Proton-Transfer Reactions"; Caldin, E., Gold, V., Ed.; Chapman and Hall: London, 1975; pp 153–177. (b) Streitweiser, A., Jr.; Heathcock, C. H. "Introduction to Organic Chemistry"; Macmillan: New York, 1976; Appendix IV, p 1191.

(9) (a) Galiani, G.; Rindone, B. *Tetrahedron* **1981**, *37*, 2313. (b) Moro-oka, Y.; Chung, P. J.; Arakawa, H.; Ikawa, T. *Chem. Lett.* **1976**, 1293. (c) Tezuka, M.; Ohkatsu, Y.; Osa, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1471. (d) Lee-Ruff, E.; Timms, N. *Can. J. Chem.* **1980**, *58*, 2138. (e) Top, S.; Jaoven, G.; McGlinckey, M. *Chem. Commun.* **1980**, 643. (f) Dietz, E.; Peover, M. E.; Rothbaum, P. *Chem. Ing. Tech.* **1970**, *42*, 185. (g) Ruddock, G. W.; Raleigh, J. A.; Greenstock, C. L. *Biochem. Biophys. Res. Commun.* **1981**, *102*, 554.

(10) (a) Hawthorne, J. O.; Schowalter, K. A.; Simon, A. W.; Wilt, M. H.; Morgan, M. S. *Adv. Chem. Ser.* **1968**, *75*, 203. (b) DiBiase, S. A.; Gokel, G. W. *J. Org. Chem.* **1978**, *43*, 447. (c) Neumann, R.; Sasson, Y. *J. Org. Chem.* **1984**, *49*, 1282. (d) Artamkina, G. A.; Grinfel'd, A. A.; Beletskaya, I. P. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1983**, 345. (e) Artamkina, G. A.; Grinfel'd, A. A.; Beletskaya, I. P. *Tetrahedron Lett.* **1984**, *25*, 4989.

0022-3263/86/1951-2093$01.50/0 © 1986 American Chemical Society

Table I. Relative Rate Constants and Reaction Parameters for the Reaction of Diphenylmethanes with Superoxide and *tert*-Butoxide

					k_{rel}[c]	
X	Y	compd	$\sigma(\sigma^-)$[a]	ΔpK_a[b]	$O_2^-\cdot$[d]	t-$C_4H_9O^-$[e]
4-CH_3O	H	**2b**	−0.27 (−0.20)	−1.14	0.129	
4-CH_3	H	**2c**	−0.17	−0.97	0.450	
4-F	F	**2d**	0.12 (−0.04)[f]	−0.23	0.745	
H	H	**2a**	[0][g]	[0][g]	[1][g]	
4-Cl	H	**2e**	0.227	1.29	10.5	
4-Br	H	**2f**	0.232	1.32	15.4	[1][g]
4-Cl	Cl	**2g**	0.454[f]	2.59	154	6.177
3-NO_2	H	**2i**	0.71	4.05	696	9.963
4-CN	H	**2j**	0.66 (0.90)	5.13	6610	17.904
4-NO_2	H	**2k**	0.78 (1.24)	7.07	34600	

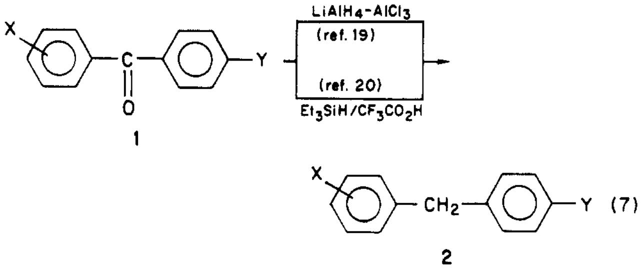
[a] σ and σ^- values from ref 21. [b] Calculated from ρ in Me_2SO[22] (see Discussion). [c] Values are precise to ± 5%. [d] In benzene. [e] In toluene. [f] Twice the value of the monosubstituted analogue. [g] Reference value.

and Valentine[11] raise serious doubts as to any possible role for $O_2^-\cdot$ as a general initiator of oxidative processes via hydrogen atom abstraction. This is because hydrogen atom abstractions occur at appreciable rates only when the bond energy of the bond being made exceeds the bond energy of the bond being broken.[11] Liebman and Valentine calculate a H–O bond dissocation energy for HO_2^- of approximately 66 kcal mol^{-1}. A quick scan of any table of bond dissociation energies[12] reveals that only a handful of substrates bear R–H bonds remotely that weak. Fluorene, for example, is estimated[13] to have a homolytic bond dissociation energy of approximately 80 ± 5 kcal mol^{-1}.

Somewhat surprisingly, however, Benson and O'Neil[14] report a C–H bond energy of only 66 ± 6 kcal mol^{-1} for diphenylmethane. This low value is a bit problematic for two major reasons. Firstly, the stabilization of free radicals by a vicinal phenyl or vinyl group is nearly identical,[15a] and 1,4-pentadiene[15b] and 1,4-heptadiene[16] have bond strengths of 80 and 76.5 kcal/mol, respectively. Furthermore, as noted by Howard and Ingold and co-workers,[17] triphenylmethane has a D(R–H) of 75. These authors prefer a higher value of 81 for diphenylmethane which is more in line with their observation of a good correlation between radical autoxidation propagation rate constants and carbon–hydrogen bond strengths. Most recently Rossi et al.[18] have confirmed this prediction and report a C–H bond energy of 81.4 kcal/mol. Nevertheless, if Benson and O'Neil are correct, diphenylmethane should be an ideal candidate for an $O_2^-\cdot$-induced radical process. We, therefore, decided to study the substituent effect parameters of the $O_2^-\cdot$-mediated oxidation of diphenylmethane in order to elucidate whether such a process is radical or anionic in nature.

Results

For the purpose of this study we prepared diphenylmethanes **2b–l** by reduction of the corresponding benzophenones **1** with either lithium aluminum hydride–aluminum trichloride according to the procedure Nystrom and Berger[19] (for **2b–h**) or with triethylsilane in trifluoroacetic acid media following Doyle and co-workers[20] (for **2i–l**) (eq 7). The dideuterio analogues of **2a**, **2g**, and **2h** (Ar_2CD_2)



1

2

(7)

a: X=Y=H
b: X=p-OCH_3, Y=H
c: X=p-CH_3, Y=H
d: X=Y=p-F
e: X=p-Cl, Y=H
f: X=p-Br, Y=H
g: X=Y=p-Cl
h: X=Y=p-OCH_3
i: X=m-NO_2, Y=H
j: X=p-CN, Y=H
k: X=p-NO_2, Y=H
l: X=p-$N(CH_3)_2$, Y=H

were also prepared by replacing $LiAlH_4$ in these syntheses with $LiAlD_4$.

The substituted diphenylmethanes were reacted competitively at ambient temperature in benzene solutions of $O_2^-\cdot$, generated from potassium superoxide and 18-crown-6 polyether. Relative rate constants of reaction (k_{rel}) were determined by following the disappearance of the competing substrates by GLC using diphenylacetylene as the internal standard (see Experimental Section) in conjunction with the equation

$$k_{rel} = \frac{k_A}{k_B} = \frac{\log (A_0/A_t)}{\log (B_0/B_t)} \qquad (8)$$

where A_0, A_t, B_0 and B_t are the GLC peak areas of diphenylmethanes A and B (normalized by the peak area of the inert internal standard) prior to the addition of $O_2^-\cdot$ (t = 0) and at time t. If it is a valid competition experiment, and if the reaction is first order in substrates A and B as assumed in eq 8, then k_{rel} will not be a function of the extent of the reaction. Within experimental error (less than ± 5%) this was indeed found to be the case in these competition experiments. In order to assure conveniently measurable rates, the initial ratio of KO_2:crown ether: substrate was 12:10:1. Even under these conditions, however, compounds **2h** and **2l** reacted too slowly to give reliable values. Table I presents the relative rate constant data (k_{rel}) obtained, based on an arbitrarily assigned value

---

(11) Liebman, J. F.; Valentine, J. S. *Isr. J. Chem.* **1983**, *23*, 439.

(12) See for example, "Handbook of Chemistry and Physics", 61st ed.; Weast, R. C., Ed.; Chemical Rubber Co.: Boca Raton, FL, 1980; p F-233.

(13) McMahon, T. D.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 3399, 3405, Table VI.

(14) Benson, S. W.; O'Neil, H. E. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1970**, *No. 21.*

(15) (a) O'Neil, H. E.; Benson, S. W. *Int. J. Chem. Kinet.* **1969**, *1*, 221. (b) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

(16) Egger, K. W.; Jola, M. *Int. J. Chem. Kinet.* **1970**, *2*, 265.

(17) Korcek, S.; Chenier, J. H. B.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1972**, *50*, 2285.

(18) (a) Rossi, M. J.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493, Table III cited a value of 84.

(19) (a) Nystrom, R. F.; Berger, C. R. A. *J. Am. Chem. Soc.* **1958**, *80*, 2896. (b) Blackwell, J.; Hickinbottom, W. J. *J. Chem. Soc.* **1961**, 1405.

(20) West, C. T.; Donnelly, S. J.; Kooistra, D. A.; Doyle, M. P. *J. Org. Chem.* **1973**, *38*, 2675.

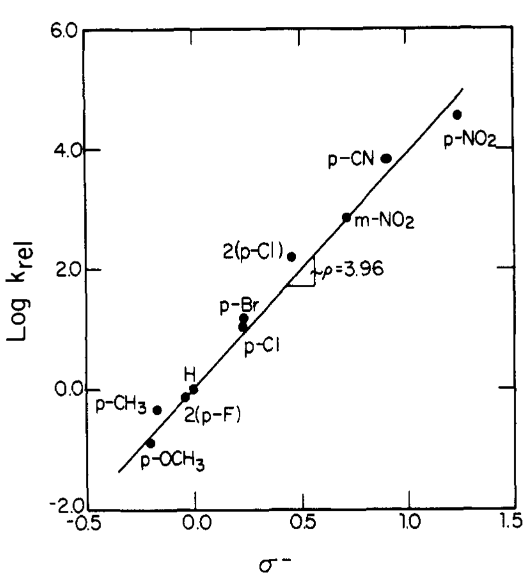


Figure 1. Hammett-type plot of log k_{rel} vs. σ^- for the $O_2^-\cdot$-mediated oxidation of substituted diphenylmethanes.

of 1.0 for unsubstituted diphenylmethane **2a**. Figure 1 shows the corresponding $\sigma\rho$ Hammett plot. As seen, a very good linear least squares fit ($r = 0.993$) is obtained with σ^- values,[21] giving a ρ value of 3.96 ± 0.16. σ Values[21] produced a much poorer fit ($r = 0.965$) with a ρ of 4.99 ± 0.47.

For the purpose of comparison, diarylmethane **2f**, **2g**, **2i**, and **2j** were reacted competitively in toluene solutions with *tert*-butoxide, generated from the corresponding potassium salt and 18-crown-6. Because of the extremely fast rate of reaction, it was necessary to lower the temperature of the reaction solution to 0 °C and utilize an initial ratio of $KOC(CH_3)_3$:crown:substrate of 2:1:1. The relative rates were determined as before (see Table I), and the ρ value obtained using σ^- was 1.77 ± 0.41 ($r = 0.950$).

Returning now to the superoxide system, the primary isotope effect (k_H/k_D) for diphenylmethanes **2a** and **2g** were determined by allowing the protio (Ar_2CH_2) and dideuterio (Ar_2CD_2) analogues to react in competition in the presence of hexamethylbenzene as the internal standard. ^1H NMR analysis of the mixture prior and following 2.5 h of reaction (see Experimental Section) yielded the k_H/k_D values of 2.36 and 2.14 for **2a** and **2g** respectively. Both these values had a precision of $<\pm 10\%$.

It was also of interest to determine the effect of $O_2^-\cdot$ concentration on the rate of the reaction. To this end, three reaction solutions were prepared containing 4-chlorodiphenylmethane, **2e**, crown ether, and KO_2 in the molar ratios 1:10:12, 1:7.5:12 and 1:5:12. We assumed that the dissolved $O_2^-\cdot$ concentration is directly proportional to the crown ether concentration. The reactions commenced upon the addition of substrate simultaneously to each of the solutions which also contained diphenylacetylene as internal standard. GLC analysis indicated that increasing the crown ether concentration, and presumably the dissolved $O_2^-\cdot$ concentration, by factors of 2.0 and 1.33, increased the rate of reaction experimentally by factors of 2.11 and 1.39, respectively, with a precision of ±10% in each case. No reaction occurs in the absence of crown ether.

Discussion

Our primary concern in this research has been to gain insight into the role played by $O_2^-\cdot$ in the oxidation of diarylmethanes which it mediates. To this end, we were first interested in determining the kinetic order of superoxide and substrate in these reactions.

Since no reaction occurs in the absence of crown ether, we can safely assume the absence of any heterogeneous reaction occurring on the surface of the benzene insoluble KO_2. The data further indicate that the reaction is first-order in substrate. This is clear from the fact that eq 8, derived for competition reactions first-order in substrate, yields k_{rel} values which are essentially invariant throughout the duration of the reaction.

The question of the kinetic order of $O_2^-\cdot$ is a bit more problematic. This is because the solubilized $O_2^-\cdot$ may either be paired with the potassium cation–crown ether complex [$C(K^+)$], or exist as a free ion (eq 9 and 10, respectively). In the former case, the concentration of the

$$C + KO_2 \rightarrow C(K^+)O_2^-\cdot \qquad (9)$$

$$C + KO_2 \rightarrow C(K^+) + O_2^-\cdot \qquad (10)$$

solubilized superoxide will be linearly proportional to the initial concentration of crown ether. Equation 10, on the other hand, requires the concentration of $O_2^-\cdot$ to be proportional to the *square root* of the initial crown ether concentration.[23]

Of these two possibilities, we favor the former for two reasons. Firstly, ion pairing is the expected state of aggregation in a nonpolar aprotic medium such as benzene. More importantly, however, we find that increasing the crown ether concentration by factors of 1.33 and 2.0 increases the rate of reaction (within experimental error) by the same amount. This linear proportionality between the rate and the crown ether concentration is readily accommodated by equation 9 if the rate of reaction is first-order in superoxide. For equation 10 to be operative, the reaction would have to be second-order in superoxide in order to compensate for the aforementioned square root relationship between the superoxide and crown ether concentrations. However, as will be shown later, the physical data (substituent and isotope effects) are inconsistent with a mechanism in which two molecules of $O_2^-\cdot$ are involved up to the rate-determining step. We conclude, therefore, that the reaction is homogeneous, takes place in the benzene phase, and is first order in each of the reactants superoxide and diarylmethane.

We turned our attention next to the question of mechanism. The excellent correlation ($r = 0.993$) between log k_{rel} and σ^- with a ρ of nearly 4 strongly suggests the involvement of a carbanion at the benzylic carbon. For the purpose of comparison, ρ values for benzylic hydrogen abstraction from toluenes by radicals are generaly negative (−0.09 to −1.96). The sole exception is the *tert*-butyl radical which yields a ρ of +0.99 using regular σ values.[24]

Several mechanistic schemes are consistent with the observed substituent effect on the reaction and are outlined below.

---

[21] Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323, Table I, and references cited therein. Where σ^- values are unavailable we have assumed that $\sigma^- = \sigma$.

[22] Algrim, D.; Bares, J. E.; Branca, J. C.; Bordwell, F. G. *J. Org. Chem.* **1978**, *43*, 5024, Table I.

[23] The equilibrium equation for eq 10 is

$$\frac{[C(K^+)][O_2^-\cdot]}{[C][KO_2]} = K_{eq}$$

However $[KO_2]$ remains constant in the solid phase and $[C(K^+)] = [O_2^-\cdot]$. This equation simplifies therefore to $[O_2^-\cdot]^2 = K'_{eq}[C]$.

[24] (a) Pryor, W. A.; Davis, W. H., Jr.; Stanley, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 4754. (b) Pryor, W. A.; Lin, T. H.; Stanley, J. P.; Henderson, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 6993.

mechanism 1

$$\mathrm{RH} + \mathrm{O_2}^{-}\cdot \overset{\text{fast}}{\rightleftharpoons} \mathrm{R}\cdot + \mathrm{HOO}^-$$

$$\mathrm{R}\cdot + \mathrm{O_2}^{-}\cdot \xrightarrow{\text{slow}} \mathrm{R}^- + \mathrm{O_2}$$

mechanism 2

$$\mathrm{RH} + \mathrm{O_2}^{-}\cdot \overset{\text{fast}}{\rightleftharpoons} \mathrm{R}^- + \mathrm{HOO}\cdot$$

$$\mathrm{R}^- + \mathrm{O_2} \xrightarrow{\text{slow}} \text{products}$$

mechanism 3

$$\mathrm{RH} + \mathrm{O_2}^{-}\cdot \xrightarrow{\text{slow}} \mathrm{R}^- + \mathrm{HOO}\cdot$$

$$\mathrm{R}^- + \mathrm{O_2} \xrightarrow{\text{fast}} \text{products}$$

The first mechanism involves a preequilibrium in the first step in which $O_2^{-}\cdot$ functions as a radical by abstracting a hydrogen atom from the substrate. This is followed by a slow rate-determining electron transfer from $O_2^{-}\cdot$ to the substrate radical generating a carbanion. Mechanisms 2 and 3 both envision $O_2^{-}\cdot$ functioning as a base; however, in the former the proton abstraction occurs in a preequilibrium step, while in the latter, proton removal is the rate-determining process.

To distinguish between the various possibilities, deuterated analogues of **2a** and **2g** were prepared and the isotope effects for their reaction with $O_2^{-}\cdot$ were found to be 2.36 and 2.14 respectively. The magnitude of the isotope effect (~ 2.25) rules out the rapid preequilibria required by mechanisms 1 and 2 which should be much less sensitive to deuteration. Thus the kinetic data, namely the correlation with σ^-, the magnitudes of ρ, and the primary deuterium isotope effect, are only consistent with the reaction sequence described in mechanism 3 in which a proton is transferred from substrate to $O_2^{-}\cdot$ in the rate-determining step.

It should be noted that mechanism 3 is basically the first steps of the base-catalyzed autoxidative process outlined by the sequence of equations 5, 6, 2–4. For the purpose of comparison, we oxygenated several diphenylmethanes in the presence of another base, *tert*-butoxide. As expected the log k_{rel} values again correlated best with σ^- yielding a ρ of 1.77. This reaction constant is less than half of that observed for $O_2^{-}\cdot$ and is consistent with the Hammond postulate[25] which predicts an earlier transition and therefore a lower selectivity for the more reactive *tert*-butoxide.

Additional information regarding the transition state structure in the superoxide reactions can be gleaned from a Brønsted analysis[26] of this acid base process. In order to perform such an analysis, the pK_{a} values for the variously substituted diphenylmethane carbon acids must be known. This is a simple matter since Bordwell and coworkers[22] report a ρ of 5.7 for the equilibrium acidity of substituted diphenylmethanes in Me_2SO. The ΔpK_{a} for the various substituted diphenylmethanes can be determined from $\Delta pK_{\mathrm{a}} = \sigma^-\rho$. Since Bordwell[27] has shown that the relative pK_{s} for acids forming delocalized anions do no differ much with solvent, we assume the applicability of these values, listed in Table I, to benzene as well.

A plot of log k_{rel} vs. ΔpK_{a} (Figure 2) yields a Brønsted α value of 0.69 (r = 0.993). The magnitude of α suggests

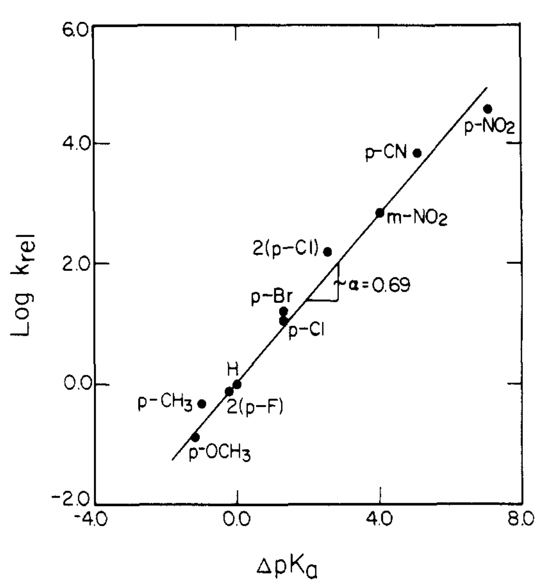


Figure 2. Brönsted plot of log k_{rel} vs. ΔpK_{a}.

that the proton abstraction involves a late transition state.[28] In this regard it should be noted that the aforementioned deuterium isotope effect of ~ 2.25 could a priori be consistent with either an early or late transition state. The α value, however, demonstrates that the latter is indeed the case.

All these results indicate that, at least in benzene, the $O_2^{-}\cdot$-mediated oxidation of diphenylmethane (and presumably that of other diarylmethanes) proceeds via an initial rate determining deprotonation by $O_2^{-}\cdot$ generating a benzylic carbanion. Clearly these results are at odds with the data of Lee-Ruff and co-workers[9d] who report that in Me_2SO diarylmethanes undergo oxygenation with $O_2^{-}\cdot$ via an initial hydrogen atom abstraction (eq 1). The source of this glaring discrepancy is not clear. It should be pointed out that Rosenthal and Frimer as well as Arudi et al.[29] have noted that Me_2SO is not inert to $O_2^{-}\cdot$. Indeed, many of the purported superoxide reactions carried out in this solvent may in fact result from the dimsyl anion or hydroperoxy radical formed according to eq 11. This

$$\mathrm{CH_3SOCH_3} + \mathrm{O_2}^{-}\cdot \rightarrow \mathrm{CH_3SOCH_2}^- + \mathrm{HOO}\cdot \quad (11)$$

should be taken into consideration when evaluating the results of the Canadian group[9d] who utilized Me_2SO as their solvent.

If we, however, accept the Lee-Ruff mechanism for Me_2SO solutions, it is possible that the variance between our mechanism and that of Lee-Ruff stems from the difference in polarity of the media in which the reactions were performed. The potential of $O_2^{-}\cdot$ as a hydrogen abstractor should increase on going to a more polar solvent; as seen from eq 1, the negative charge which is initially smeared over the two oxygen atoms of $O_2^{-}\cdot$ now becomes more concentrated in the HOO^- product, residing on a single oxygen atom. The basicity of superoxide, on the other hand, is expected to increase drastically upon going to nonpolar solvents such as benzene which are poor solvating

---

(25) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(26) Alder, R. W.; Baker, R.; Brown, J. M. "Mechanism in Organic Chemistry"; Wiley-Interscience: London, 1971.

(27) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

(28) (a) While the bulk of the literature supports Leffler's[28b–d] suggestion that the parameter α may be utilized as a measure of the transition state structure, this has recently been the subject of some scrutiny.[28e] (b) Leffler, J. E. *Science (Washington, D.C.*, 1883-) **1953**, *117*, 340. (c) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963. (d) See also Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3907; *Ibid.* **1975**, *97*, 3417. (d) Pross, A. *J. Org. Chem.* **1984**, *49*, 1811.

(29) (a) Rosenthal, I.; Frimer, A. *Tetrahedron Lett.* **1975**, 3731. (b) Arudi, R. L.; Allen, A. O.; Bielski, B. H. J. *FEBS Lett.* **1981**, *35*, 265. (c) Arudi, R. L., personal communication, 1983.

media for charged species. These two effects may well result in a solvent-dependent duality of mechanism for the reaction of $O_2^-\cdot$.

Further investigations along these lines are presently in progress in our laboratory.

Experimental Section

The spectrometers used for ^{1}H NMR, IR, and mass spectra were Varian T-60, Perkin-Elmer Model 257, and Hitachi Perkin-Elmer RMU-6, respectively. Gas chromatograms were obtained using a Packard 7300 gas chromatography system combined with a Spectra-Physics SP 4100 computing integrator. 18-Crown-6 polyether (Fluka), potassium *tert*-butoxide (Fluka), and powdered potassium superoxide (Callery) were used as supplied and stored in a desiccator. Benzene and toluene were dried over sodium wire.

Preparation of Diphenylmethanes 2b–h. The title compounds were synthesized by reducing the corresponding commercially available (Aldrich) benzophenones **1b–h** with $LiAlH_4$–$AlCl_3$ following either method 2 (for **1b**, **1e**, and **1f**) or method 3 (**1c**, **1d**, **1g**, and **1h**) of Nystrom and Berger.[19] In the case of **1d**, **1g**, and **1h**, the ketones were introduced to the reducing medium via extraction from a soxhlet thimble by refluxing solvent (ether). Reactions were generally carried out on 0.05 mol of ketone. Although the literature[19] reports yields of 80–90%, in our hands the desired products were isolated in only 60–80% yields. The corresponding dideuterio analogues of **2a**, **2g**, and **2h** were prepared with $LiAlD_4$.

2b: prepared in a 60% yield; bp 48 °C (0.06 torr) [lit.[19b] 166 °C (13 torr); lit.[31] 162 °C (13 torr)]; ^{1}H NMR (CCl_4) δ 7.1 (s, 5 H), 7.0 (d, J = 8.5 Hz, 2 H), 6.67 (d, J = 8.5 Hz, 2 H), 3.83 (s, 2 H), 3.67 (s, 3 H) [lit.[30] ($CDCl_3$) 3.81, 3.66]; IR (neat) 3020, 3005, 2910, 2840, 1610, 1500, 1455, 1445, 1305, 1250, 1180, 1110, 1040, 845, 805, 775, 735, 705 cm^{-1}; MS (70 eV), *m/e* 198 (M^+), 183 ($M^+ - CH_3$), 167 ($M^+ - OCH_3$), 166, 165, 153, 121 ($CH_3OC_6H_4CH_2$), 91 ($C_6H_5CH_2$).

2c: prepared in a 60% yield; ^{1}H NMR (CCl_4) δ 7.3–6.95 (m, 9 H), 3.9 (s, 2 H), 2.3 (s, 3 H); bp, MS, and IR are consistent with literature values.[31]

2d: purified from ketone **1d** by dissolving in hexane yielding the desired product in a 66% yield; ^{1}H NMR (CCl_4) 7.8–6.65 (m, 8 H), 3.83 (s, 2 H) [lit.[32] (acetone-d_6) 3.876]; MS (70 eV), *m/e* 204 (M^+), 203, 183 ($M^+ - F - 2$ H), 170, 165, ($M^+ - 2$ F $-$ H) 157, 151, 133, 99.

2e: prepared in 60% yield; bp 138 °C (4 torr) [lit.[19b] 160 °C (11 torr)]; ^{1}H NMR (CCl_4) δ 7.13 (s, 9 H), 3.86 (s, 2 H); IR (neat) 3015, 2905, 1490, 1455, 1435, 1410, 1180, 1095, 1020, 845, 795, 750, 705 cm^{-1}; MS (70 eV), *m/e* 204 ($M^+ + 2$), 202 (M^+), 167 ($M^+ - Cl$), 166, 165, 152, 124, 90, 88.

2f: obtained in a 62% yield; bp 120 °C (4 torr) [lit.[19b] 164 °C (14 torr)]; ^{1}H NMR (CCl_4) δ 7.4–6.75 (m, 9 H), 3.87 (s, 2 H); IR—identical with spectrum 615H in Pouchert;[33] MS (70 eV), *m/e* 248 ($M^+ + 2$), 246 (M^+), 167 ($M^+ - Br$), 166, 165, 152, 90, 88.

2g: isolated in a 60% yield; mp (hexane) 55.5 °C [lit.[19b,34] 55–56 °C]; ^{1}H NMR (CCl_4) δ 7.08 (AA′BB′, m, 8 H), 3.87 (s, 2 H) [lit.[32] (acetone-d_6) 3.869]; IR and MS identical with literature.[34]

Deuterio-2g: purified by column chromatography on silica with 1:1 hexane–CH_2Cl_2 as eluent; ^{1}H NMR same as protio analog but lacking 3.87 singlet; MS (70 eV), *m/e* 240 ($M^+ + 2$), 238 (M^+), 236 ($M^+ - D$), 202 ($M^+ - Cl$), 168 ($M^+ - 2$ Cl), 167, 166, 141, 139, 111.

2h: synthesized in an 83% yield; mp (hexane) 52 °C [lit.[32] 51–52 °C]; ^{1}H NMR (CCl_4) δ 6.95 (d, J = 9 Hz, 4 H), 6.67 (d, J = 9 Hz, 4 H), 3.77 (s, 2 H), 3.67 (s, 6 H), [lit.[32] (acetone-d_6) 3.820]; MS (70 eV), *m/e* 228 (M^+), 213 ($M^+ - CH_3$), 197 ($M^+ - OCH_3$), 165 ($M^+ - 2$ (OCH_3) $-$ H), 153, 141, 121 ($CH_3OC_6H_4CH_2$), 119, 117, 91, 82, 76.

Table II. GLC Conditions and Results of Competition Studies

relative rate constants[a]	Δt between samples	column[b] (temp, °C)
$k_{2f}/k_{2e} = 1.46$	10 h	A (165)
$k_{2e}/k_{2a} = 10.5$	24 h	A (150)
$k_{2g}/k_{2f} = 10.0$	9 h	A (165)
$k_{2d}/k_{2a} = 0.745$	24 h	A (150)
$k_{2c}/k_{2a} = 0.450$	24 h	A (150)
$k_{2b}/k_{2c} = 0.288$	30 h	A (155)
$k_{2i}/k_{2g} = 4.53$	7.5 min	A (program[c])
$k_{2j}/k_{2i} = 9.49$	4 min	B (215)
$k_{2k}/k_{2j} = 5.23$	1 min	B (225)

[a] Values are precise to ±5% and differ from those of Table I in which k_{2a} has been arbitrarily assigned a value of unity. [b] Column A: 4.5 ft × $^1/_8$ in. glass column packed with 10% FFAP on Chromosorb PAW DMCS; column B: 6 ft × $^1/_8$ in. glass column packed with 10% OV-17 on Chromosorb P. Injector and detector temperatures set 25 °C above column temperature. Flow rate = 40 mL/min. [c] Column temperature increased at 1.5 °C/min from 180 to 230 °C and held at 230 °C for 20 min.

Deuterio-2h: purified by column chromatography on silica with 1:1 hexane–CH_2Cl_2 as eluent; mp (hexane) 52–53 °C; ^{1}H NMR—same as protio but lacking 3.77 singlet; MS (70 eV), *m/e* 230 (M^+), 215 ($M^+ - CH_3$), 199 ($M^+ - OCH_3$), 168 ($M^+ - 2$ (OCH_3)), 155, 143, 123 ($CH_3OC_6H_4CD_2$), 121, 119, 117, 85, 83, 81.

Preparation of Diphenylmethanes 2i–2l. These analogues were prepared according to the procedure of Doyle et al.[20] by reducing the corresponding ketone **1i–1l** with triethylsilane in trifluoroacetic acid media. While **1k** and **1l** are commercially available (Aldrich), benzophenones **1i** and **1j** were prepared by Friedel–Crafts acylation of benzene with the corresponding acid chlorides.[35a] The latter were prepared in turn by thionyl chloride treatment of the carboxylic acids.[35b]

***m*-Nitrobenzoyl chloride**: isolated in a 50% yield; bp 86–87 °C (0.5 torr), solidifies upon standing [lit.[35b] bp 153–154 °C (12 torr); mp 33 °C].

1i: obtained in 50% yield; mp (absolute EtOH) 93 °C (lit.[36] 95–95.5 °C); ^{1}H NMR (CCl_4) δ 8.6–7.3 (m); MS (CI) *m/e* 228 ($M^+ + 1$); MS (EI, 30 eV), 225 ($M^+ - 2$, probably formation of 3-nitrofluorenone), 208, 207, 179 ($M^+ - NO_2$), 149 ($M^+ - NO_2C_6H_4CO - H^+$), 104 (C_6H_4CO), 77 (C_6H_5).

2i: obtained pure (TLC) in a 90% yield by distilling off lower boiling fractions at 72–74 °C (6 torr). NMR and MS were consistent with literature values.[37]

***p*-Cyanobenzoyl chloride**: prepared in a 91% yield; bp 110 °C (2 torr). Distillate solidifies with mp 78.5 °C [lit.[38] 65 °C].

1j: synthesized in a 50% yield; mp 112–113 °C [lit.[36] 113–113.5 °C]; ^{1}H NMR (CCl_4) δ 7.72 (s, 5 H), 8.2–7.2 (m, 4 H); MS (70 eV), *m/e* 204 (M^+), 129 (*p*-$CNC_6H_4CO - H^+$), 104 (C_6H_4CO), 77 (C_6H_5).

2j: the residue, remaining after removal of the more volatile fractions at 60 °C (10 torr), was partially soluble in hexane. Rotary evaporation of the hexane solution gave the desired product in a 60% yield. The product was a low melting solid [lit.[39] mp 51–52; bp 120–125 °C (0.1 torr)]; ^{1}H NMR (CCl_4) δ 7.1 (bs, 5 H), 7.25 (m [AA′BB′] 4 H), 4.0 (s, 2 H); MS (70 eV), *m/e* 193 (M^+), 192, 167 ($M^+ - CN$), 166, 165, 116 ($NCC_6H_4CH_2$), 105, 91 ($C_6H_5CH_2$).

2k: bp, NMR, and MS are consistent with the literature values;[20,37,40] the diarylmethylene group appears at 3.97 ppm in CCl_4; IR (neat) 3025, 2905, 1595, 1450, 1340, 1180, 1105, 1072, 1015, 860, 740, 705 cm^{-1}.

2l: prepared in a 60% yield; bp 106–108 °C (0.5 torr) [lit.[39] 180–181 °C (20–21 torr)]; solidifies slowly at room temperature [lit.[39] mp 33–34 °C]; ^{1}H NMR (CCl_4) δ 7.05 (bs, 5 H), 6.73 (m,

---

(30) Nakai, Y.; Yamada, F. *Org. Mag. Reson.* **1978**, *11*, 607.

(31) Grasselli, J. G.; Ritchey, W. M. "Atlas of Spectral Data and Physical Constants of Organic Compounds", 2nd ed.; CRC Press Inc: Cleveland, 1975; Vol. III; p 599, compound m370.

(32) Gronowitz, S.; Konar, A.; Hornfeldt, A.-B. *Org. Mag. Reson.* **1977**, *9*, 213.

(33) Pouchert, C. J. "The Aldrich Library of Infrared Spectra", 3rd ed.; The Aldrich Chemical Co.: Milwaukee, 1981.

(34) Reference 31, p 587, compound m253.

(35) (a) Scheifele, H. J., Jr.; Detar, D. F. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 34. (b) Murch-Peterson, J., ref. 35a, p 715.

(36) Nishida, S. *J. Org. Chem.* **1967**, *32*, 2692.

(37) Robinson, G. E.; Thomas, C. B.; Vernon, J. J. *J. Chem. Soc. (B)* **1971**, 1273.

(38) Ashley, J. N.; Barber, H. J.; Ewins, A. J.; Newberry, G.; Self, A. D. H. *J. Chem. Soc.* **1942**, 103.

(39) Gribble, G. W.; Kelly, W. J.; Emery, S. E. *Synthesis* **1978**, 763.

(40) Gehring, D. G.; Reddy, G. S. *Anal. Chem.* **1965**, *37*, 868.

4 H), 3.8 (s, 2 H), 2.9 (s, 6 H); MS (70 eV), *m/e* 211 (M^+), 193, 167 ($M^+ - N(CH_3)_2$), 166, 165, 152, 134 [$CH_2C_6H_4N(CH_3)_2$], 91 ($C_6H_5CH_2$).

Competition Studies. Relative Rate Constants. The relative rate constants for the reaction of $O_2^{-}\cdot$ with diphenylmethanes **2** were determined by a series of competition reactions. Potassium superoxide (1.5 mmol) wad added to a benzene solution (30 mL, Na-dried) containing 0.125 mmol of each competitor, crown ether (1.25 mmol), and the internal standard diphenylacetylene (0.125 mmol). The reaction vessel was capped with a septum, and the reaction mixture was magnetically stirred at ambient temperature. For each pair of reactants, four or five samples were removed at appropriate intervals during the course of the reaction and quenched with 10% HCl. The organic phase of each sample was then analyzed by GLC at least thrice with the relative rate constants for the disappearance of the competitors calculated from their respective GLC peak areas using equation 8. Table II shows the VPC conditions and the results of these competitions.

Isotope Effects. The isotope effects for diphenylmethanes **2a** and **2g** were determined by ^1H NMR analysis of competition reactions between the protio ($ArCH_2$) and deuterio ($ArCD_2$) analogues, as follows. A mixture of **2** (**a** or **g**), its deuterio analogues and hexamethylbenzene in an appropriate molar ratio of 5:5:1 was prepared and analyzed by ^1H NMR. The relative integrations of the benzyl methyls of the standard, the diarylmethylene hydrogens of the protio compounds, and the aromatic hydrogens due to both the protio and deuterio species permitted a determination of the ratio of standard:protio analogue:deuterio analogue prior to reaction ($t = 0$). An aliquot of this mixture, containing 1.25 mmol of each competitor, 0.25 mmol of standard, and 12.5 mmol of 18-crown-6 polyether was dissolved in 300 mL of sodium-dried benzene to which 15 mmol of KO_2 were subsequently added. After 2-3 h, the reaction mixture was quenched with 10% HCl, neutralized with $NaHCO_3$, washed 4 times with water (to remove all traces of crown ether), and dried over $MgSO_4$. The solvent was evaporated and the residue, containing unreacted starting materials, internal standard, and products, was dissolved in CCl_4 and analyzed again by ^1H NMR. The relative integrations of the benzylic methyl absorption of the standard versus the diarylmethylene absorption of the protio species indicated the extent of reaction of the latter. The unreacted starting material was collected by preparative GLC (3 ft × $^1/_4$ in. copper column packed with 10% FFAP on chromosorb PAW DMCS) and analyzed by ^1H NMR. The relative integrations of the methylene and aromatic absorptions indicated the relative amounts of unreacted protio and deuterio analogues. Combining the information from the two NMR analyses following workup permitted the determination of the ratio of standard:protio analogue;deuterio analogue following reaction. The isotope effect (k_H/k_D) was then calculated using the equation

$$k_H/k_D = \frac{\log (H_i/H_f)}{\log (D_i/D_f)}$$

where H_i, H_f, D_i, D_f are the relative initial and final amounts of protio and deuterio compounds.

Concentration Effects. Three 50-mL round-bottomed flasks were each charged with 20 mL of sodium-dried toluene and 110 mg (1.5 mmol) of KO_2 but differing amounts of 18-crown-6, namely 330 mg (1.25 mmol), 247 mg (0.938 mmol), and 165 mg (0.675 mmol), respectively. The reaction vessels were capped with rubber septa and magnetically stirred for 1 h to assure saturation. In addition, a stock solution was prepared containing equimolar amounts of 4-chlorodiphenylmethane (**2e**) and diphenylacetylene (as internal GLC standard). Reaction commenced simultaneously in each flask upon addition of an aliquot of this stock solution containing 0.125 mmol of **2e** and 0.125 mmol of diphenylacetylene. For each concentration, samples were removed from the reaction vessels at time $t = 0$, 24, 48 and 72 h, and the reaction in each sample was quenched with 10% HCl. The organic phase of each sample was then analyzed at least thrice by GLC (3 ft × $^1/_2$ in. glass column packed with 15% FFAP on chromosorb PAW DMCS at 200 °C) to determine the relative rate of disappearance of starting material. These were then compared to the results obtained for similar reaction times at other concentrations. These series of simultaneous reactions were repeated 4 times, and the results obtained had a precision of ±10%.

Note Added in Proof: In the closing paragraph of the Introduction we noted the low *D*(R-H) value of 66 kcal/mol reported by Benson and O'Neil[14] of diphenylmethane. Professor Benson has recently communicated to us that this value was based on pyrolysis data for diphenylacetic acid which was undoubtedly in error by about 10 kcal. He agrees, therefore, with the current[17,18] value of 81 kcal/mol. This revised *D*(R-H) value will affect the predicted electron affinity of the diphenylmethyl radical reported by McMahon and Kebarle.[13]

Acknowledgment. We would like to express our heartfelt gratitude to Professor Shmaryahu Hoz for sharing with us his creative and insightful thoughts on the issues raised in this paper.

Registry No. 1i, 2243-80-3; **1j**, 1503-49-7; **2a**, 101-81-5; **2b**, 834-14-0; **2c**, 620-83-7; **2d**, 457-68-1; **2e**, 831-81-2; **2f**, 2116-36-1; **2g**, 101-76-8; **2g**-deutero, 101419-03-8; **2h**-deutero, 56652-42-7; **2i**, 5840-41-5; **2j**, 23450-31-9; **2k**, 1817-77-2; D_2, 7782-39-0; superoxide, 11062-77-4.

The Nickel Promoted 1,3-Migration of an sp^2 Center: Ring Expansion of a Vinylcyclobutene

Dale DiFrancesco and Allan R. Pinhas*

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172

Received November 14, 1985

The nickel tetracarbonyl promoted rearrangement of dimethyl 3-vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate (1) to dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate (2) proceeds in two distinct steps involving dimethyl 3-vinylcyclobutene-1,2-dicarboxylate (5) as an isolable intermediate. Both steps require the presence of the transition metal. Deuterium labeling shows that it is an sp^2 center and not an sp^3 center of the vinylcyclobutene which undergoes the migration.

Introduction

Due to our interest in transition metal promoted rearrangements, we became intrigued by a report in which dimethyl 3-vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate (1) undergoes a ring expansion, with concomitant loss of the chlorines, to give dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate, (2) upon treatment with nickel tetracarbonyl in refluxing benzene/dimethylformamide.[1] The net result of this ring expansion reaction, regardless of its mechanism, is a nickel promoted 1,3-sigmatropic shift. Although there

---

[1] Scharf, H.-D.; Korte, F. *Chem. Ber.* **1966**, *99*, 1299, 3925.

0022-3263/86/1951-2098$01.50/0 © 1986 American Chemical Society