dioxetanes, respectively. The literature[8,9] provides support for the excited states generated to be heavily n-π^* triplets.

With this in mind, we find it remarkable that the efficiency of the Type A rearrangement is so slightly dependent on the dioxetane reactant structure, or, equivalently, on the second ketonic product (i.e., **5a, 5b,** or **5c**) generated. In particular, one might have expected that in the case of β-acetonaphthone formation from the β-naphthyl dioxetane **1c,** the reaction transition state would sense the availability of a low (i.e., 59 kcal/mol) β-acetonaphthone triplet and would avoid generating the 68.5 kcal/mol 4,4-diphenylcyclohexadienone triplet. This is *not* the case.[10]

We can conclude that the dioxetane decomposition is controlled by the energetics leading to n-π^* excited species. Here we have experimental evidence in support of literature theoretical suggestions[9] for preferential generation of the n-π^* triplet. Our observation of the system's inability to generate β-acetonaphthone π-π^* triplets suggests that dienone π-π^* triplets are similarly inaccessible. The lack of energy drainage to the 59 kcal/mol β-acetonaphthone triplet implies a lack of inter- and intramolecular equilibration between the states of dienone and β-acetonaphthone. The nonequilibration between dienone n-π^* and π-π^* configurations has independently been advanced by Schuster.[12a] Considering the extreme rapidity of the rearrangement of 4,4-diphenylcyclohexadienone triplet,[5b] these conclusions seem reasonable.

Thus, n-π^* triplet 4,4-diphenylcyclohexadienone, when generated specifically, gives the usual Type A rearrangement. Although this configurational assignment is somewhat controversial,[12b] our conclusion is in agreement with the postulate we made many years ago.[5a]

The 4,4-diphenylcyclohexadienone system has proven unique in that both vertical and nonvertical photochemistry without light have been accessible. Thus we have now been able to place a molecule both midway on the hypersurface leading from excited state to product and also at the origin corresponding to initial excited state itself.

Acknowledgment. Support of this research by the National Science Foundation and by the U.S. Army Research Office (Durham) is gratefully acknowledged.

References and Notes

(1) This is Paper 95 of our series. For Paper 94 see H. E. Zimmerman, F. X. Albrecht, and M. J. Haire, *J. Am. Chem. Soc.*, in press.
(2) (a) H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **88**, 5352 (1966); (b) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968).
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(4) T. R. Darling and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 1625 (1974).
(5) (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); **84**, 4527 (1962); (b) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 1436 (1964); **89**, 906 (1967).
(6) Synthetic and experimental detail will be reported in our full paper. Satisfactory elemental analyses were obtained on all thermally stable compounds and spectral data were used for the dioxetanes.
(7) The unimolecular rate of cleavage of methyl phenyl dioxetane **1a** at 71.4° was determined by NMR following to be 4.5×10^{-4} sec^{-1} (CCl_4). This is remarkably similar to the reported[8a] rate of 4.0×10^{-4} sec^{-1} (70°, benzene) for 3,3,4,4-tetramethyl-1,2-dioxetane.
(8) (a) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **94**, 2886 (1972); **95**, 264 (1973); (b) N. J. Turro et al., *ibid.*, **96**, 1627 (1974); (c) H. C. Steinmetzer, A. Yekta, and N. J. Turro, *ibid.*, **96**, 284 (1974); (d) P. D. Wildes and E. H. White, *ibid.*, **93**, 6286 (1971); (e) T. Wilson and A. P. Schaap, *ibid.*, **93**, 4126 (1971).
(9) A variety of theoretical considerations predict formation of n-π^* triplet products: (a) D. Kearns, *Chem. Rev.*, **71**, 345 (1971); (b) D. R. Roberts, *J. Chem. Soc., Chem. Commun.*, 683 (1974); (c) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 7578 (1974); (d) M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, *ibid.*, **96**, 7579 (1974).
(10) Reaction of β-naphthyl dioxetane **4c** in the presence of 0.10 *M* cyclohexadiene triplet scavenger led to no diminution of bicyclic ketone product, establishing absence of complicating chain processes and free β-acetonaphthone triplet.
(11) The mirror image situation has been reported by N. J. Turro, G. Schuster, J. Pouliquen, R. Pettit, and C. Mauldin, *J. Am. Chem. Soc.*, **96**, 6797 (1974), who concluded that π-π^* triplet excitation generated from Dewar acetophenone was not readily convertible to n-π^* excitation.
(12) (a) D. I. Schuster and K. V. Prabhu, *J. Am. Chem. Soc.*, **96**, 3511 (1974). (b) Interestingly, the same study[12a] arrived at the conclusion that it is the π-π^* excited state which rearranges. However, the 3,4-dimethyl-4-trichloromethylcyclohexadienone system studied was a particularly difficult one. It is possible that piperylene free radical chain inhibition is superimposed on the normal excited state quenching which, as a result of varying chain length, would lead to spurious Stern-Volmer slopes and data derived therefrom such as lifetime, self-quenching rates, and state equilibration.

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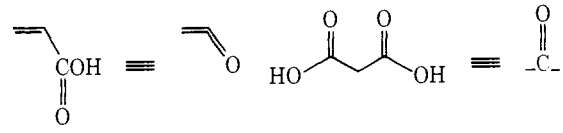
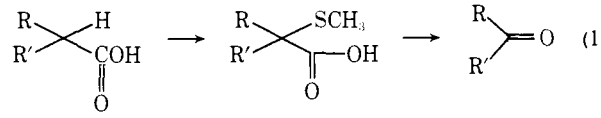
New Synthetic Reactions. Oxidative Decarboxylation

Sir:

The conversion of a carboxylic acid (or derivative) to a ketone with loss of one carbon atom plays an important role in organic chemistry.[1] This degradation is an important tool in the structural elucidation of natural products.[2] It also allows carboxylic acid derivatives to serve as synthetic equivalents of other structural fragments. For example, acrylic acid becomes an equivalent of ketene,[3] carboxylic acids become acyl anion equivalents, and malonic acid becomes an



equivalent of a carbonyl dianion. We wish to report a particularly convenient new two-step method (see eq 1) which utilizes a novel oxidative decarboxylation as the key step.[4]



(1)

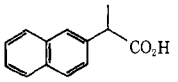
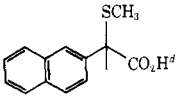
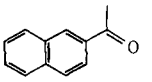
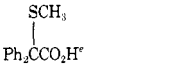
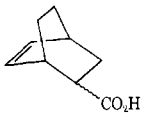
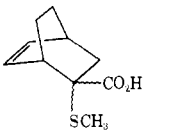
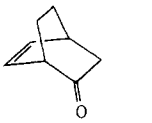
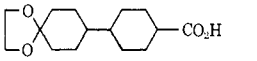
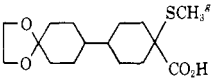
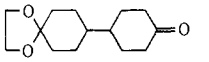
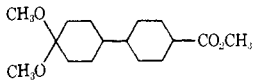
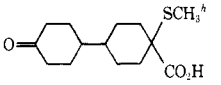
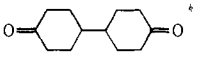
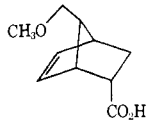
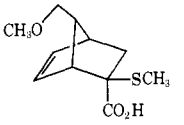
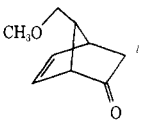
1

The sulfenylation of the dianions of carboxylic acids[5] generated utilizing 2 equiv of lithium diisopropylamide followed by addition of dimethyl disulfide proceeds practically quantitatively.[6] For dialkylcarboxylic acids (i.e., **1,** R and R′ are alkyl), addition of HMPA for the metalation and sulfenylation is recommended.

To a mixture of the sulfenylated acid and sodium bicarbonate in alcohol solution (methanol, ethanol, or *tert*-butyl alcohol) is added solid *N*-chlorosuccinimide at room temperature. Gas evolution (carbon dioxide) occurs immediately. Aqueous work-up allows isolation of the initial product, the ketal, which is readily hydrolyzed to the ketone with aqueous hydrochloric acid. Table I summarizes various applications. The yields have not been optimized in any case. Successful results have been obtained with an α,α-diaryl, an aryl alkyl, and dialkyl carboxylic acids. It is interesting to note that a double bond (entries 3 and 6) and a ketone (entry 5) do not interfere in the oxidative elimination step. Entry 5 demonstrates the availability of the requisite intermediate by hydrolysis of the sulfenylated ester.[6a,c] However, the stringent conditions required for such a hydrolysis makes it much less attractive than the direct sulfenylation of the acid.

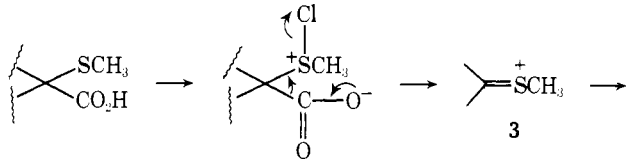
The accompanying equations provide a mechanistic rationale for the oxidative decarboxylation. Chlorination at

Table I. Oxidative Decarboxylation

Entry no.	Acid	Sulfenylation[a] temp (°C), time (min)	Sulfenylated acid	Oxidation time (hr)	Ketone	% yield[o]
1		−20, 20[b] 0, 30		1.25[i]		64[m]
2	Ph_2CHCO_2H	−20, 25[b] 0, 25		1.5[i]	Ph_2CO	57[m]
3		0, 40[c]		1.5–2.5[i]		44[n]
4		0, 30[c]		1.5[i]		78[m]
5		−20, 30[b] 0, 30 *p*, 5		3[i]		69[m]
6		0, 50[c]		2[i]		62–76[n]

[a] Dianion generation accomplished utilizing 2 equiv of lithium diisopropylamide at between 0 and −20° for 1–3 hr. [b] Solvent: THF. [c] Solvent: THF–HMPA. [d] Isolated sample had mp 109–114°. [e] Isolated sample had mp 178–179°. [f] Isolated sample had mp 104–113°. [g] Isolated sample had mp 149–150°. [h] Work-up of the sulfenylation reaction effected hydrolysis of the ketal. Hydrolysis of the ester was accomplished by utilizing aqueous potassium hydroxide in refluxing ethylene glycol. [i] Solvent: ethanol. [j] Solvent: *tert*-butyl alcohol. [k] Identified by comparison to an authentic sample. [l] Vpc analysis indicates greater than 97% purity of indicated isomer. [m] Intermediate sulfenylated acid purified prior to oxidative elimination. [n] Intermediate sulfenylated acid not purified prior to oxidative elimination. [o] Overall isolated yield from starting acid. [p] Room temperature.

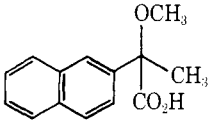
sulfur rather than at the carboxylate anion[7] initiates the reaction.



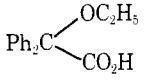
2

3

This intermediate **2** is supported by the observation of alkoxy displacement products **4** and **5** obtained when the more

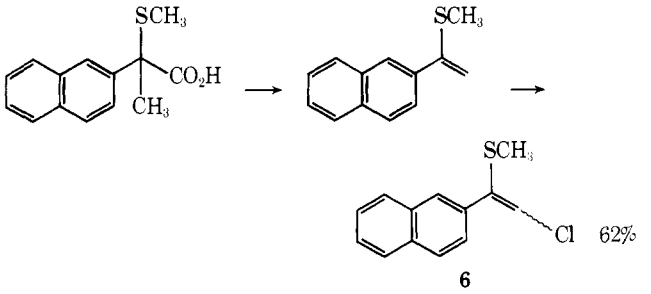


4



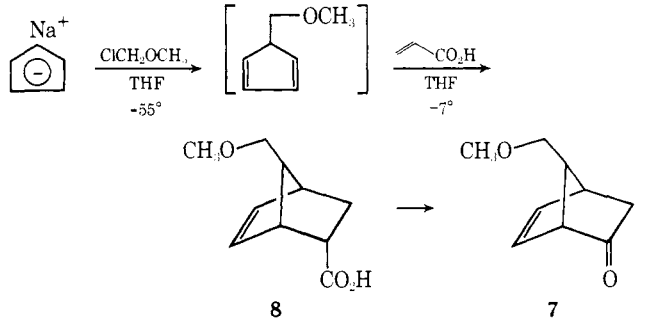
5

nucleophilic alcohols were employed as solvents. In the case of the naphthyl system switching to ethanol precluded this process, whereas the benzhydryl system required *tert*-butyl alcohol as solvent to fully suppress this type of product. The use of a somewhat nucleophilic alcohol to trap the sulfonium ion **3** is required when an α-carbon bears hydrogen. Thus, carrying out the elimination of the naphthyl system in *tert*-butyl alcohol led to deprotonation of the intermediate corresponding to **3** followed by subsequent chlorination of the reactive vinyl sulfide to form **6.** Considering these factors, ethanol appears to be the best solvent for most cases.



6

The advantages of this method are clearly indicated by the synthesis of the important Corey prostaglandin intermediate **7** (see Table I, entry 6) utilizing acrylic acid as the ketene equivalent. The preparation of the bicycloheptane **8**



8 7

recognizes the excellent dienophilic properties of acrylic acid and minimizes base catalyzed isomerization of the intermediate 5-monoalkylated cyclopentadiene.[8] Chromatographic analysis (silicon oil DC 710 column) of **7** indicates greater than 97% isomeric purity.

Acknowledgment. We wish to thank the Wisconsin Alumni Research Foundation, the National Science Foundation, and the National Institutes of Health for support of this work.

References and Notes

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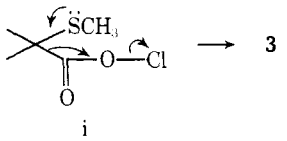
(3) For related work see S. Ranganathan, D. Ranganathan, and A. K. Mehrotra, *J. Am. Chem. Soc.*, **96**, 5261 (1974); D. A. Evans, W. L. Scott, and L. K. Truesdale, *Tetrahedron Lett.*, 121 (1972); E. J. Corey, T. Ravindranathan, and S. Terashima, *J. Am. Chem. Soc.*, **93**, 4326 (1971); P. S. Wharton and B. T. Aw, *J. Org. Chem.*, **31**, 3787 (1966); P. K. Freeman, D. M. Balls, and D. J. Brown, *ibid.*, **33**, 2211 (1968); J. Paasivirta and H. Krieger, *Suom. Kemstilehti B*, **38**, 182 (1965); J. Paasivirta, *Suom. Kemstilehti A*, **39**, 120 (1966); H. Krieger and S. E. Masar, *Ibid.*, **39**, 119 (1966); P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, **78**, 2473 (1956).

(4) For a related independent study for conversion of nitriles to ketones see D. S. Watt, *J. Org. Chem.*, **39**, 2799 (1974); S. J. Selikson and D. S. Watt, *Tetrahedron Lett.*, 3029 (1974). This method is limited to aryl substituted systems.

(5) P. L. Creger, *J. Am. Chem. Soc.*, **89**, 2500 (1967); P. E. Pfeffer, L. S. Silbert, and J. M. Chirinko, Jr., *J. Org. Chem.*, **37**, 451 (1972); P. L. Creger, *ibid.*, **37**, 1907 (1972).

(6) (a) B. M. Trost and T. N. Salzmann, *J. Am. Chem. Soc.*, **95**, 6840 (1973); (b) B. M. Trost, K. Hiroi, and S. Kurozumi, *Ibid.*, **97**, 438 (1975); (c) B. M. Trost and T. N. Salzmann, *J. Org. Chem.*, **40**, 148 (1975).

(7) The fragmentation of i also could form the intermediate **3**. This reaction



i

can be considered analogous to the decarboxylative elimination of β-halo acids. For leading references see H. E. Zaugg, *Org. React.*, **8**, 305 (1954).

(8) The use of thallium salts in the alkylation or catalysts in the Diels–Alder reactions are precluded by this approach. See E. J. Corey, U. Koelliker, and J. Neuffer, *J. Am. Chem. Soc.*, **93**, 1489 (1971).

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Received January 20, 1975

Electrochemical Detection of Conformational Equilibria in Tetraalkylhydrazines

Sir:

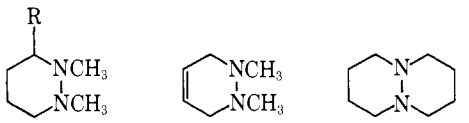
The potential at which electrochemical oxidation or reduction of a compound occurs is controlled by the E^0, rate of the heterogeneous electron transfer reaction, the rates of chemical reactions of the reactant preceding electron transfer, and rates of reactions of the product following electron transfer. Structural effects on observed oxidation/reduction potentials can appear through all of these factors. In particular, heterogeneous electron transfer rates have been discussed in terms of conformational and solvation changes accompanying electron transfer.[1] When it is considered, however, that different conformations of reactant species will often exist, and that these conformations could have different E^0 values and electron transfer rates, it seems possible that different electrochemistry for different conformations might be detectable.

Table I. Cyclic Voltammetry Data[a] for Hydrazines **1–4**

Compound	Temp (°C)	Scan rate (mV/sec)	E_p^{ox} (mV)	E_p^{red} (mV)	ΔE_p (mV)	$E_p^{ox'}$ (mV)
1	+23	100	352	273	79	unobsd
	−47	20	336	240	96	*a*
	−47	50	*a*	228		503
	−47	200	*a*	197		550
	−72	100	*a*	106		738
2	+23	100	372	292	80	unobsd
	−85	50	363	195	168	*a*
	−85	100	389	173	216	*a*
	−85	200	423	138	285	640
3	+23	100	468	380	88	unobsd
	−55	20	440	334	106	*a*
	−55	50	467	330	137	(ca. 700)
	−55	200	*a*	298		774
	−85	200	*a*	217		907
4	+23	100	418	341	77	unobsd
	−65	50	483	250	233	unobsd
	−65	200	578	205	373	unobsd

[a] Distortion due to this wave is apparent, but a clear maximum was not observed.

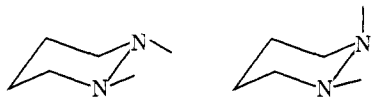
A variety of tetraalkylhydrazines show electrochemically reversible (or nearly reversible) oxidation at room temperature.[2] We have discovered that lowering the temperature allows the detection of two separate oxidation peaks by slow scan cyclic voltammetry (cv) in some cases. The cv of the six-ring hydrazines **1–4**, which illustrate this phenomenon, are discussed here.



1, R = CH_3 3 4
2, R = H

When **1–3** were oxidized at a gold electrode in butyronitrile (an excellent low temperature electrochemical solvent[3]), they showed nearly reversible behavior[4] (Table I). At −47°, 20 mV/sec scan rate, for **1**, in addition to the wave observed at room temperature,[5] distortion was apparent at higher potential (Figure 1b), and at faster scan rates this grew into a clearly resolved peak (Figure 1c), designated as $E_p^{ox'}$ in Table I. At the faster scan rates, the first peak (E_p^{ox}) had greatly decreased in size, and $E_p^{ox'}$ had shifted to significantly higher values. Dimethylhexahydropyridazine (**2**) showed similar behavior, although appearance of distortion for the $E_p^{ox'}$ peak only became apparent at lower temperatures, and the $E_p^{ox'}$ peak remained clearly smaller than the E_p^{ox} peak, even at low temperatures and fast scan rates. Dimethyltetrahydropyridazine (**3**) showed behavior qualitatively similar to **1**, the E_p^{ox} peak becoming far smaller than the $E_p^{ox'}$ peak at fast scan rates and low temperatures. In contrast, diazadecalin **4** showed no sign of an $E_p^{ox'}$ wave at any temperature or scan rate.

These effects were all completely reversible, disappearing when the temperature was raised. We suggest that the only plausible cause for observing the $E_p^{ox'}$ peak is that a more difficultly oxidizable conformation of **1–3** is being oxidized at low temperature and/or fast scan rates than under slow passage, room temperature conditions. Different conformations must show different electrochemical behavior. We suggest that the conformations responsible for E_p^{ox} and $E_p^{ox'}$ may be assigned to ee and ae respectively,[6] on the



ee ae