and $C_{17}H_{14}O$, respectively, tabulated by Benyon[17] and then making provision for the fact that the oxygen-18 content is going to be variable in this case, rather than having the normal isotopic abundance used in calculating the tables in Benyon's book. The reliability of this method of determining P for the alcohol samples was verified by comparing the value of P for a sample of *p*-methylbenzhydrol determined in this way with the value determined by the method of Doering and Dorfman.[16] Within experimental error the results were the same.

The rate of ^{18}O equilibration between alkyl and acyl oxygens in the thiocarbonate was determined by plotting log $(P - P_\infty)/(P_0 - P_\infty)$ *vs.* time, where P_0 is the atom per cent oxygen-18 for a sample at $t = 0$, and $P_\infty = (P_0 + 0.204)/2$.

(17) J. H. Benyon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier, Amsterdam, 1960, pp 521, 537.

Registry No.—**1a**, 3326-54-3; (±)-**1b**, 38379-31-6; (+)-**1b**, 38379-32-7; **1b**-^{18}O, 38379-33-8; (±)-**1c**, 38379-34-9; (+)-**1c**, 38379-35-0; **1c**-^{18}O, 38379-36-1; *p*-methylbenzhydrol-^{18}O, 38379-37-2; *p*-methylbenzophenone, 134-84-9; α-naphthylphenylcarbinol-^{18}O, 38379-39-4; α-naphthyl phenyl ketone, 642-29-5; α-naphthyl phenyl ketone-^{18}O, 38379-41-8; (+)-*p*-methylbenzhydrol acid phthalate, 38379-42-9; (+)-*p*-methylbenzhydrol, 75832-67-4; (−)-α-naphthylphenylcarbinol, 1517-61-9; (±)-*p*-methylbenzhydrol, 38379-45-2; (±)-α-naphthylphenylcarbinol, 38379-46-3.

Protonation of Fumaric and Maleic Acids and Their Diethyl Derivatives

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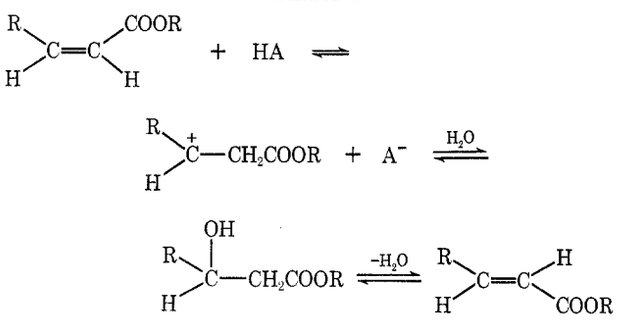
Strong acid media were employed to protonate maleic and fumaric acid and their diethyl ester derivatives. Nuclear magnetic resonance (nmr) showed that preferential oxygen protonation was occurring. In none of the compounds studied could protonation of the carbon–carbon double bond be observed.

As part of our continuing studies[1] of carbocations in strongly acidic solvents, we have investigated the thermodynamics of diprotonation of a series of diacids, diesters, and diketones. In light of the long-standing controversy regarding the site of protonation of the isomeric maleic and fumaric acids,[2] it was necessary to verify the structure of the protonated species in strong acid systems. That structure is the subject of this paper.

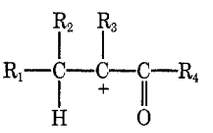
Many cis–trans isomerizations of α,β-unsaturated carboxylic acids are acid catalyzed. The mechanism of these reactions has been thoroughly studied. From their results Noyce and coworkers[3] detailed the mechanism as an addition–elimination in which the first step was protonation of the ethylenic linkage followed by the hydration of the resulting carbocation (Scheme I).

Richards, *et al.*,[2] recently concluded from secondary kinetic isotope effects and isotopic exchange experiments on the fumarase-catalyzed isomerization of *l*-malate to fumarate that the same type of carbocation intermediate is involved. This mechanism is quite different from that proposed by Fahey and Schneider[4] for the addition of HCl to diethyl maleate and fumarate in acetic acid. In compounds like XCH=CHY where X has positive character and is itself a base (*e.g.* O=COEt), protonation on carbon may not be the most favorable process. Fahey and Schneider have proposed that the interconversion of malate to fumarate might proceed *via* a modification of the 1,4-addition mechanism originally proposed by Ogg and Nozaki.[5] As they point out, formation of a carbocation adjacent to a carbonyl group is surprising. However, the data of Hansen, *et al.*,[2] seem to require this intermediate in the enzyme-catalyzed reaction.

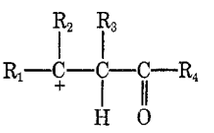
SCHEME I



Observation of the carbocation from malate or fumarate in strong acid, in conjunction with deuterium incorporation, would present strong evidence in favor of protonation of the –C=C– bond. α,β-Unsaturated carboxylic acids and carbonyl compounds have previously been shown to protonate on oxygen in superacid media.[6] However, no studies of maleic and fumaric acids or their derivatives appear to have been published. Previous attempts to prepare cations of the type **1** and **2**



1



2

by treating α- or β-halo ketones or aldehydes in strong acid have proven unsuccessful.[7] However, Kuta and

(1) J. W. Larsen, *J. Amer. Chem. Soc.*, **93**, 5107 (1971); J. W. Larsen, P. A. Bouis, M. W. Grant, and C. A. Lane, *ibid.*, **93**, 2067 (1971); J. W. Larsen, *ibid.*, **92**, 5136 (1970); J. W. Larsen, S. Ewing, and M. Wynn, *Tetrahedron Lett.*, 539 (1970).

(2) R. A. Alberty, W. G. Miller, and H. F. Fisher, *J. Amer. Chem. Soc.*, **79**, 3973 (1957); D. E. Schmidt, Jr., W. G. Nigh, C. Tanzer, and J. H. Richards, *ibid.*, **91**, 5849 (1969); R. C. Fahey and H. Schneider, *ibid.*, **92**, 6885 (1970); J. N. Hansen, E. L. Dinova, and P. D. Boyer, *J. Biol. Chem.*, **244**, 6270 (1969).

(3) D. S. Noyce, H. S. Avarbock, and W. L. Reed, *J. Amer. Chem. Soc.*, **84**, 1647 (1962); D. S. Noyce, P. A. King, F. B. Kirby, and W. L. Reed, *ibid.*, **84**, 1632 (1962).

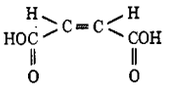
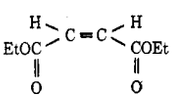
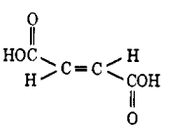
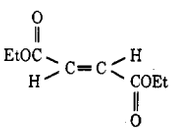
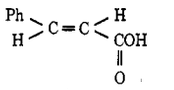
(4) R. C. Fahey and H. Schneider, *ibid.*, **92**, 6885 (1970).

(5) K. Nozaki and R. Ogg, Jr., *ibid.*, **63**, 2583 (1941).

(6) For a general review see G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970).

(7) G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *J. Amer. Chem. Soc.*, **94**, 3554 (1972).

TABLE I[h]

Registry no.	Compd	Temp, °C	OH	α-CH_2	β-CH_3	H_β of $X_2C{=}C(H_\alpha)Y$	H_α of $X_2C{=}C(H_\alpha)Y$	Solvent
110-16-7		37	12.9			6.27		DMSO-d_6
		37				7.05		D_2SO_4
		−80				7.13[g]		FSO_3H, FSO_3H–SbF_5[f]
141-05-9		37		4.11[a]	1.21[b]	6.10		CCl_4
		37		4.76	1.72	6.94		D_2SO_4
		−80		4.80	1.72	7.09		FSO_3H
		0		5.31	1.80	7.34		FSO_3H–SbF_5[f]
		−60	13.86	5.31	1.80	7.34		FSO_3H–SbF_5[f]
110-17-8		37	12.28				6.68	DMSO-d_6
		37					7.12	D_2SO_4
		−80					7.53	FSO_3H, FSO_3H–SbF_5[f]
623-91-6		37		4.16[a]	1.25[b]		6.70	CCl_4
		37		4.81	1.74		7.26	D_2SO_4
		−80		5.20	1.81		7.65	FSO_3H
		0, −60		5.32	1.84		7.69	FSO_3H–SbF_5[f]
		−60	13.77	5.32	1.84		7.69	FSO_3H–SbF_5[f]
140-10-3		37	13.21				6.46[α] 7.83[β]	DMSO-d_6[c]
		37					6.65[α] 8.35[β]	D_2SO_4[d]
		−80					6.78[α] 8.60[β]	FSO_3H[e]

[a] Quartet, J = 7.5 Hz. [b] Triplet, J = 7.5 Hz. [c] Ph multiplet 7.45. [d] Ph multiplet 7.58. [e] Ph multiplet 7.63. [f] 11.5 mol % SbF_5 in FSO_3H. [g] Protonated anhydride form. [h] Chemical shifts are in δ values.

Pospisil[8] examined the protonation of fumaric acid and reported that in D_2SO_4 the ratios of hydroxylic protons to protons bound to carbon is 2:3. This evidence led them to propose that fumaric acid is protonated on carbon in sulfuric acid. Chemical shifts for their spectra were not reported.

Results and Discussion

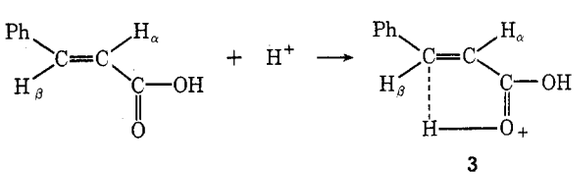
In order to substantiate the claim of preferential –C=C– protonation,[8] maleic and fumaric acid and their diethyl derivatives were dissolved in strong acids, and their proton nmr (pmr) spectra were investigated. Table I gives a summary of the chemical shifts. There is no evidence in the nmr spectra for carbon protonation. If a small amount of reversible carbon protonation were occurring in D_2SO_4, the signal due to the vinyl protons should diminish with time. Noyce, *et al.*,[3] have reported that incorporation of deuterium occurs with *trans*-cinnamic acid. This did not occur with maleic or fumaric acid and their diethyl derivatives. The spectra were unchanged after 48 hr in D_2SO_4 at 25°.

Brower[9] has shown that the carbocations formed upon monoprotonation of malonic acid and its methyl ester have the same structure $(H)MeO(C{=}O)CH_2C(=O)OHMe(H)^+$. Assuming similar behavior, fumaric and maleic acids and their diethyl derivatives would provide an intramolecular internal standard, since the ethyl groups are not subject to exchange with the solvent. The result of this investigation shows a proton ratio of 2:4:6 between the ethylene, methylene, and methyl groups, also indicating no protonation of the ethylene group in diethyl maleate and fumarate.

In strong acid media it has been demonstrated that the proton on the carbonyl group can be observed at low temperature.[6] However, even at −80°, no $-OH^+$ signal could be observed in FSO_3H or FSO_3H–SbF_5 for the acids listed in Table I. Brower reported the same behavior for malonic acid derivatives. Evidently, under the acidic conditions used, the solute ions rapidly exchange protons with the solvent and are thus not observed.

The diesters show markedly different behavior. The chemical shift data (Table I) indicate that in FSO_3H diethyl maleate is monoprotonated while the fumarate is diprotonated. In FSO_3H–SbF_5 both are diprotonated. Under conditions of diprotonation the $-OH^+$ signal of diethyl fumarate appears as a slightly broadened singlet at −13.77 ppm. Presumably this could be the result of unresolved coupling. The spectrum of diethyl maleate appears as a much broader singlet. The detection of the hydroxylic protons in the diesters can be attributed to the added stability provided by the presence of the ethyl group. Apparently the ethyl group stabilizes the protonated ester sufficiently to slow down the rapid exchange of the acidic proton with the solvent.

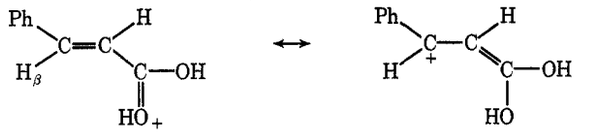
The pmr spectrum of protonated *trans*-cinnamic acid was also investigated, since Brand and Fleet[10] proposed structure **3** as a result of their polarographic studies. However, from the pmr data it can be seen that the β hydrogen in protonated cinnamic acid is appreciably deshielded in comparison to the α



3

(8) L. Pospisil and J. Kuta, *Collect. Czech. Chem. Commun.*, **34**, 742 (1969).
(9) D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87**, 225 (1968).
(10) M. J. Brand and B. Fleet, *J. Electroanal. Chem.*, **16**, 341 (1968).

hydrogen, suggesting a significant amount of positive charge on the β carbon. Further studies into the



hindered rotation about the C–O partial double bond are being pursued in this laboratory.

Thus there is no evidence for protonation of the –C=C– of maleic and fumaric acids in strong acids. The relationship of this observation to the path of enzymatic catalyzed cis–trans isomerization is not clear. It does seem that, if the enzyme-catalyzed reaction is indeed proceeding *via* carbon protonation, then there must be in the enzyme a highly specific arrangement of the active site, forcing the proton onto carbon rather than onto the more basic carboxyl group.

Experimental Section

Materials.—All compounds were commercially available and were distilled or recrystallized before use. All compounds were dried thoroughly, liquids over 4 Å molecular sieves and solids over P_2O_5 under vacuum.

Spectra.—Room-temperature nmr spectra were recorded on a Varian A-60 spectrometer. All chemical shifts (δ) are reported in parts per million relative to internal tetramethylamonium bromide taken as δ 3.2.

Low-temperature spectra were recorded on a Varian HA-100 spectrometer equipped with a variable-temperature probe.

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Notes

Reaction of Nitroxyl Radicals with Metal Carbonyls

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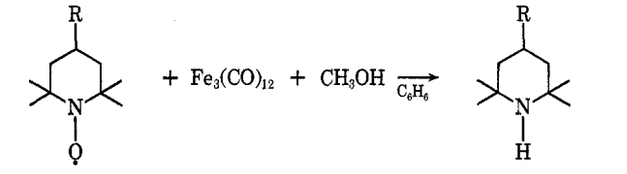
Deoxygenation reactions have been observed from treatment of sulfoxides,[1] amine oxides,[2] azoxy compounds,[2,3] nitrones,[2] and *C*-nitroso compounds[2,3] with iron pentacarbonyl [$Fe(CO)_5$]; nitro compounds with $Fe(CO)_5$,[2,4] diiron enneacarbonyl [$Fe_2(CO)_9$],[4] or triiron dodecacarbonyl [$Fe_3(CO)_{12}$–methanolic benzene];[5] *N*-nitroso compounds with $Fe(CO)_5$[2] or group VI metal carbonyls;[6] and *N*-phenyl-2-oxa-3-azabicyclo-[2.2.2]octene-5 with $Fe_2(CO)_9$.[7] There have been no reports, to the author's knowledge, of the reaction of metal carbonyls with nitroxyl radicals, an important group of compounds[8,9] potentially capable of undergoing deoxygenation to amino radicals. This note describes the reaction of iron carbonyls and group VI metal carbonyls with nitroxyl radicals.

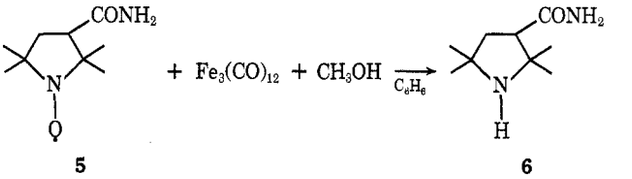
Reaction of 2,2,6,6-tetramethylpiperidine-1-oxyl (**1**) with either $Fe(CO)_5$ in hot benzene or $Fe_2(CO)_9$ in benzene at room temperature gave a very unstable non-



1, R = H
3, R = NHCOCH$_3$

2, R = H
4, R = NHCOCH$_3$

carbonyl containing organometallic compound. No amine was isolated from these reactions. However, treatment of **1** with $Fe_3(CO)_{12}$ in benzene containing a small amount of methanol (conditions under which the hydridoundecacarbonyltriferrate anion is generated)[5] did result in the formation of the deoxygenated product **2** in 42% yield. Similarly, 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxyl (**3**) gave the amine **4** in 55% yield and **6** was obtained from **5** in 41% yield. There-



5 **6**

fore, $Fe_3(CO)_{12}$ is a useful reagent for reducing nitroxyl radicals to amines.[10] No bipiperidyl or bipyrrolidyl derivatives were produced in these reactions,[11] although small amounts of *N*-formyl amines[4,6,12] were apparently formed.

(1) H. Alper and E. C. H. Keung, *Tetrahedron Lett.*, 53 (1970).
(2) H. Alper and J. T. Edward, *Can. J. Chem.*, **48**, 1543 (1970).
(3) A. S. Filatov and M. A. Englin, *Zh. Obshch. Khim.*, **39**, 783 (1969); *J. Gen. Chem. USSR*, **39**, 743 (1969).
(4) H. Alper, *Inorg. Chem.*, **11**, 976 (1972).
(5) J. M. Landsberg, L. Katz, and C. Olsen, *J. Org. Chem.*, **37**, 930 (1972).
(6) H. Alper, *Organometal. Chem. Syn.*, **1**, 69 (1970).
(7) Y. Becker, A. Eisenstadt, and Y. Shvo, *Tetrahedron Lett.*, 3183 (1972).
(8) E. G. Rozantsev, "Free Nitroxyl Radicals," Plenum Press, New York, N. Y., 1970.
(9) O. H. Griffith and A. S. Waggoner, *Accounts Chem. Res.*, **2**, 17 (1969).
(10) For other reductive methods, see N. Kornblum and H. W. Pinnick, *J. Org. Chem.*, **37**, 2050 (1972), and references cited therein.
(11) D. Mackay and W. A. Waters, *J. Chem. Soc. C*, 813 (1966), unsuccessfully attempted to prepare bi(2,2,6,6-tetramethyl)piperidyl from *N*-nitroso-2,2,6,6-tetramethylpiperidine.
(12) W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *J. Amer. Chem. Soc.*, **87**, 3080 (1965).