6.0), 5.50 (1 H, finely split t, J = 7.5), 5.08 (1 H, finely split t, J = 7.5), 4.58 (1 H, m), 4.30 (1 H, m), 2.78 (2 H, t, J = 7.5), and 2.25–1.50 (13 H, complex absorptions with strong, finely split peaks at 1.75–1.65 for approximately 9 H).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.88; H, 10.15.

Thermolysis of Tetraene 35 to Triene 36. Tetraene **35** (19.15 g; 87.80 mmol) under an argon atmosphere was heated in a sealed tube for 2.5 hr at 190°. Fractional distillation gave 12.80 g (67%) of triene **36** as a pale yellow liquid: bp 96–100° (0.03 mm); 99% pure by vpc;[28c,46] nmr (CCl_4) δ 9.65 (1 H, d, J = 1.5), 5.85–4.85 (4 H, m), 3.0 (1 H, broad s), 2.68 (2 H, t, J = 7.5), and 2.4–1.5 (14 H, m with two finely split singlets at 1.68 and 1.60 in the ratio 1:2 for a total of 9 H).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.51; H, 10.19.

Acknowledgment. This work was generously supported by the National Institutes of Health and by the Hoffmann-La Roche Anniversary Foundation.

(46) A mixture of three stereoisomers in a ratio of 17:72:11.

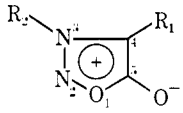
Stable Carbonium Ions. XCVII.[1a] Protonation of 3-Phenylsydnone, Its Derivatives, and Related Model Compounds

George A. Olah, David P. Kelly,[1b] and Nausicaa Suciu[1c]

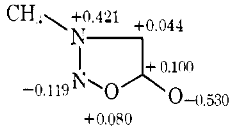
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received October 2, 1969*

Abstract: Protonation of the mesoionic 3-phenylsydnone and 1,1-disydnonylethylene in FSO_3H-SbF_5 solution is shown to occur on the carbonyl oxygen atom, by analogy with protonation of regular carbonyl groups. Unlike diphenylmethyl- and triphenylcarbinols, 4,4′-bis(3-phenylsydnonyl)methyl- and phenylcarbinols do not form tertiary carbonium ions in FSO_3H-SbF_5 solution, indicating poor stabilizing ability by the adjacent positively charged sydnonyl rings. 4,4′-Bis(3-phenylsydnonyl) ketone and the corresponding α-diketone protonate on the exocyclic carbonyl oxygen atoms in preference to the sydnone carbonyl oxygens.

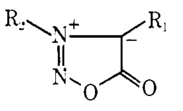
Due to their unique mesoionic character, sydnones have been the subject of continued study since their discovery in 1935.[2] The aromatic 6π-electron system obtained by removal of one π electron onto the exocyclic oxygen atom[3] (I) is unequally distributed around the ring as shown by the relatively high-field nmr absorption of the 4 proton,[4] molecular orbital calculations (II),[5,6] and their behavior as 1,3 dipoles.[7] Both the proton shift and dipolar reactivity can be rationalized in terms of the localized azomethine–imine system III. Recently Roche and Kier used ω-HMO calculations to study the chemical reactions of sydnones.[6] By a comparison between the π-electron energies of the protonated and nonprotonated heteroatomic system, they concluded that protonation of 3-methylsydnone (I, R_1 = H, R_2 = CH_3) should occur preferentially on the number two nitrogen atom. This conclusion is surprising (even when supported by the observations of a weak N–H stretch in the infrared) in view of previous electron density calculations,[5] which showed a greater negative charge on the exocyclic oxygen atom (II).[8]



I



II



III

We have examined the nmr spectra of 3-phenylsydnone (I, R_1 = H, R_2 = C_6H_5) and some of its derivatives[9] in super acid solutions in order to clarify the site of protonation and also to study the effect of sydnonyl groups as neighboring substituents in carbonium ions.

Results and Discussion

3-Phenylsydnone. In trifluoroacetic acid solution at −10 to +10°, fine structure appears for the phenyl group absorption, and the sydnone ring methine proton (H_4) is shifted downfield by 0.71 ppm from that in $CDCl_3$ solution (Table I). No separate OH or NH signal was observed due to exchange with the solvent. However, in $HSO_3F-SbF_5-SO_2$ solution at −60–90°, a one-proton, temperature-dependent signal is observed at δ 10.24, the phenyl protons are slightly shifted, and the sydnone 4-H signal is downfield of the phenyl protons at δ 8.33 (Figure 1). The temperature-dependent signal at δ 10.24 is not an N–H proton since protonation of nitrogen lone pairs in sp^2 orbitals gives rise to signals at around δ 14, which, even at −90°, are generally broad.[10] Both the chemical shift and the temperature dependence of the observed proton indicate that it is of intermediate character between

---

(1) (a) Part XCVI: J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, in press; (b) Postdoctoral Research Associate, 1969; (c) Institute of Inframicrobiology; Acad. R.S.R., Bucharest 1, Rumania.

(2) J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, 899 (1935). For review articles see: (a) W. Baker and W. D. Ollis, *Quart. Rev.* (London), 11, 15 (1957); (b) F. H. C. Stewart, *Chem. Rev.*, 64, 129 (1964); (c) N. Suciu, *Stud. Cercet. Chim.*, 16, 117 (1968).

(3) W. Baker and W. D. Ollis, *Chem. Ind.* (London), 910 (1955).

(4) F. H. C. Stewart and N. Danieli, *ibid.*, 1926 (1963).

(5) (a) C. B. Kier and E. B. Roch, *J. Pharm. Sci.*, **55**, 807 (1966); (b) K. Sundaram and W. P. Purcell, *Int. J. Quantum Chem.*, **2**, 145 (1968); (c) J. A. Singer and W. P. Purcell, *J. Med. Chem.*, 10, 754 (1967).

(6) E. B. Roche and L. B. Kier, *Tetrahedron*, **24**, 1673 (1968).

(7) R. Huisgen, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 51.

(8) A more recent calculation,[5b] indicates less difference between the N-2 and the O-6 atoms.

(9) (a) N. Suciu, Gh. Mihai, M. Elian, and E. Stroescu, *Tetrahedron*, 21, 1369 (1965); (b) N. Suciu and Gh. Mihai, *ibid.*, **24**, 33 (1968); (c) *ibid.*, **24**, 37 (1968).

(10) (a) G. A. Olah and D. P. Kelly, *J. Amer. Chem. Soc.*, in press; (b) G. A. Olah and G. D. Mateescu, *ibid.*, **92**, 1430 (1970).

Table I. Pmr Chemical Shifts[a] of 3-Phenylsydnone Derivatives

Compd	Solvent	$\delta_{C_6H_5}$	δ_R	δ_{OH}	T, °C
I, $R_1 = H$	$CDCl_3$	7.70 (s)[c]	R_1, 6.83 (s)		37
$R_2 = C_6H_5$	CF_3COOH	7.80 (m)	7.51 (s)		−8
	$HSO_3F-SbF_5-SO_2$	8.1 (m)	8.33 (s)	10.24	−95
V, $R = CH_3$	$CDCl_3$-DMSO-d_6	7.3–7.7 (m)	R_3, 1.88 (s)	5.85 (br)	37
	H_2SO_4	[7.3–8.3 (m)	6.73 (s)][b]		7
	CF_3COOH	[7.80 (s, br)	6.28 (s, br)][b]		−8
	$HSO_3F-SbF_5-SO_2$	8.05 (s)	2.17 (s)		−60
V, $R_3 = C_6H_5$	$CDCl_3$-DMSO-d_6	7.2–7.6 (m)			37
	CF_3COOH	7.48 (s), 7.22 (sh)			−8
	$HSO_3F-SbF_5-SO_2$	7.6 (s), 7.3 (s) (integ ∼5:1)			−80
VI, $R_4 = CH_2$	$CDCl_3$-DMSO-d_6	7.55–7.85 (m)	R_4, 5.84 (s)		37
	H_2SO_4	7.3–8.3 (m)	6.73 (s)		7
	CF_3COOH	7.70 (s, br)	6.28 (s, br)		−8
	$HSO_3F-SbF_5-SO_2$	7.8–8.2 (m)	6.77 (s)	11.1 (s, 2 H)	−70
VI, $R_4 = O$	$CDCl_3$-DMSO-d_6	7.86 (s)			37
	$HSO_3F-SbF_5-SO_2$	7.83 (s, br)		12.1 (s, <1 H)	−60
VII, $R_5 = H_2$	$CDCl_3$-DMSO-d_6	8.0 (s)	R_5, 8.12 (s)		37
$R_6 = O$	$HSO_3F-SbF_5-SO_2$	8.19 (s)	8.19		−70
VII, $R_5 = R_6 = O$	$CDCl_3$-DMSO-d_6	8.09 (s)			37
	$HSO_3F-SbF_5-SO_2$	7.8–8.2 (m)		13.1 (s, 2 H)	−80

[a] In parts per million from external TMS for acid solutions and internal TMS for neutral solutions. [b] Dehydration occurs to VI, $R_4 = CH_2$; see text. [c] Singlet, s; multiplet, m; broad, br.

that attached to a carbonyl oxygen ($C{=}O^+{-}H$) and that attached to the oxygen of a more highly polarized bond ($X^+{-}O^-$).

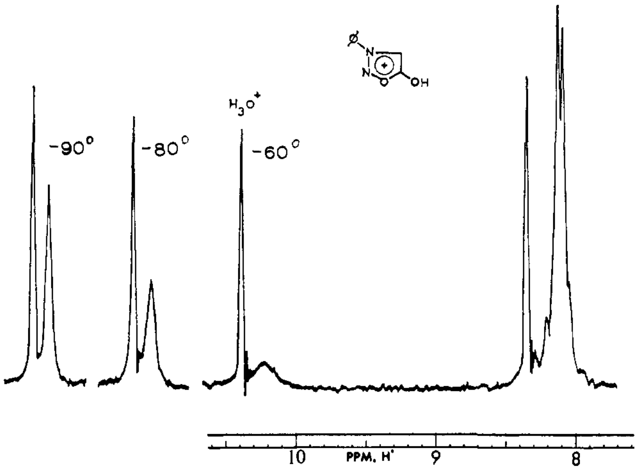


Figure 1.

In order to be able to further elucidate the structure of protonated 3-phenylsydnone, it seemed desirable to study related model compounds. δ-Butyrolactone protonates under similar conditions on the carbonyl oxygen atom, without cleavage,[11] to give two sharp singlets (integrating for one proton) at 12.35 and 12.12 ppm (1:3) (Figure 2), shifts similar to that observed for protonated esters.[12a] As the temperature is raised the downfield signal moves upfield until at −50° the two signals are coincident, and also broadened by exchange. This observation of separate $C{=}O^+{-}H$ signals is consistent with two geometric isomers, the configuration with the more shielded proton (IX) being preferred. The shift of only the downfield signal with temperature indicates that only δ_{OH} for X is temperature sensitive, since an equilibration IX ⇌ X would result in a chemical shift between that of the separate isomers. As in protonated esters, allylic coupling of the OH proton to the δ protons is not observed,[12a,c] the perturbation of the methylene proton triplet at δ 3.62 being due to second-order splitting rather than to allylic coupling.[12b]

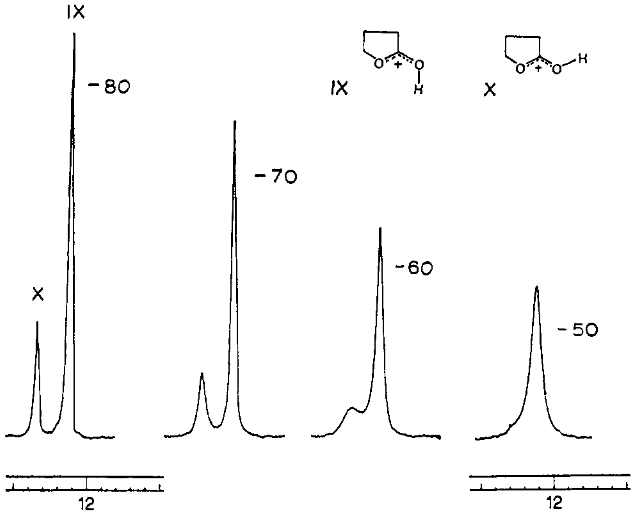


Figure 2.

As a further model for a polarized X–O bond we examined the behavior of some pyridine N-oxides in the super acid solution. Pyridine N-oxide O protonates (δ 9.86) to give a temperature-dependent signal observable only at temperatures lower than −70° (Table II). Modification of the polarity of the N–O bond by a 4-nitro or 4-cyano substituent results in a more "carbonyl-like" behavior with the OH proton observable at δ 11.0 (Table II). As the basicity of the oxygen atom is

[11] In contrast, α,α-dimethyl-β-propiolactone in HF–BF_3 at −80° gives only the spectrum of the acyl-oxygen cleaved product, protonated hydroxymethyldimethylacetyl cation; H. Hogeveen, *Rec. Trav. Chim. Pays-Bas*, 87, 1303 (1968).

[12] (a) G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, 89, 5694 (1967); (b) the spectra of protonated lactones will be discussed in a future paper; (c) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, 91, 2943 (1969).

Table II. Pmr Chemical Shifts[a] and Coupling Constants[b] of Some Model Compounds

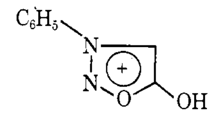
Compd	Solvent	Parameters	T, °C
γ-Butyrolactone	$HSO_3F–SbF_5–SO_2$	5.52 (t, J = 7.5, 2 H_γ),[c] 2.62 (t, J = 7.5, 2 H_α), 2.81 (m, 2 H_β), 12.12 (s, 0.75 H), 12.35 (s, 0.25 H)	−80
	CCl_4	4.27 (m, 2 H_γ, 2.5–2.0 (m, 4 $H_{\alpha,\beta}$)	37
Pyridine-N-oxide	$HSO_3F–SbF_5–SO_2$[d]	9.2–8.0 (m, 5 H) 9.86 (s, 1 H)	−90
	$CDCl_3$	8.28 (m, 2 H), 7.37 (m, 3 H)	37
4-Nitropyridine-N-oxide	$HSO_3F–SbF_5–SO_2$	9.31 (q, $J_{AB} + J_{AB'}$ = 7, 4 H), 10.94 (s, 1 H) [9.03 (d, $J \sim 7.5$, 2 H), 9.27 (d, $J \sim 7.5$, 2 H), 10.76, (s, 1 H)][e]	70
	$CDCl_3–DMSO-d_6$	8.66 (q)	37
4-Methoxypyridine-N-oxide	$HSO_3F–SbF_5–SO_2$	8.78 (d, J = 7.5, 2 H), 7.63 (d, 2 H, J = 7.5), 4.35 (s, 3 H)	−80
	$CDCl_3–DMSO-d_6$	8.58 (d, $J \sim 8$, 2 H), 7.32 (d, $J \sim 8$, 2 H), 4.04 (s, 3 H)	37
Benzophenone	$HSO_3F–SbF_5–SO_2$	8.42–7.75 (m, 10 H), 12.4 (s, 2 H)	−90
	$CDCl_3–CCl_4$	9.0 (m, 4 H), 7.75 (m, 6 H)	37
Benzil	$HSO_3F–SbF_5–SO_2$	9.0 (m, 4 H), 8.3 (m, 6 H), 14.4 (s, br, 2 H)	−90
	$CDCl_3–CCl_4$	8.33 (m, 4 H), 7.92 (m, 6 H)	37
Desoxybenzoin	$HSO_3F–SbF_5–SO_2$	8.8–7.7 (m, 5 H), 7.6 (s, 5 H), 5.31 (s, 2 H), 12.25 (s, 1 H)	−80
	CCl_4	9.0–8.75 (m, 2 H), 8.4–8.1 (m, 3 H), 8.16 (s, 5 H), 4.10 (s, 2 H)	

[a] In parts per million from external (capillary) TMS for acid solutions, internal TMS for neutral solutions. [b] In hertz. [c] t = triplet; m = multiplet; s = singlet; q = quartet; br = broad. [d] $HSO_3F–SbF_5$, 3:1. [e] From 100-MHz spectra.

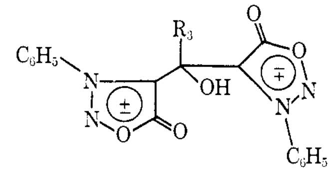
reduced (with concomitant deshielding of the attached proton) exchange of the attached proton would be expected to be more facile. However, the OH signal of 4-nitropyridine N-oxide is much sharper than that of pyridine N-oxide, presumably because in the former case the aromatic ring is deactivated toward a second protonation (which could lead to exchange of the proton on oxygen). Although the N-oxide oxygen of 4-methoxypyridine N-oxide is more basic than those of the above compounds, the N–O proton is not observed, because the presence of a second basic site (OCH_3) allows diprotonation and thus exchange to occur.[13]

The behavior of the proton on the exocyclic oxygen atom of 3-phenylsydnone, intermediate between that on a normal carbonyl group and that on a highly polarized N–O group, is also exhibited in O-protonated lactams, for example, 2-pyrrolidinone (δ 10.0).[14]

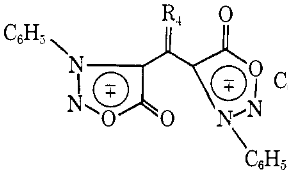
Our results clearly show that 3-phenylsydnone is protonated on the exocyclic oxygen atom, rather than the nitrogen-2 atom as previously suggested, giving a species which can be properly represented as IV.



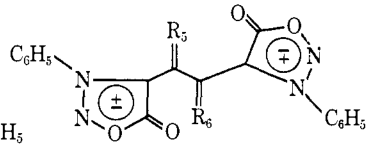
IV



V



VI



VII

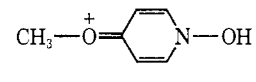
The substantial downfield shift of the sydnone-ring methine (4) proton indicates an increase in the heteroatomic ring current brought about by a more even distribution of the π-electron density. The shift is similar to that observed in protonated vinylene carbonate (δ 8.2),[15] but is well upfield of the α protons in protonated pyridazine (δ 10.11),[10] presumably due in part to this unequal distribution and in part to inductive shielding by the oxygen atoms.

1,1-Disydnonylethylene and 4,4′-Bis(3-phenylsydnonyl)methylcarbinol.[9c] Although the exocyclic oxygen atoms are protonated, the olefinic double bond in 1,1-disydnonylethylene (VI, R_4 = CH_2) remains unprotonated in the super acid solution (Table I) whereas the analogous diphenylethylene gives the diphenylmethylcarbonium ion.[16] Thus the protonated 3-phenylsydnonyl rings donors are insufficient to stabilize the carbonium ion form. The hydroxyl group of bis(3-phenylsydnonyl)methylcarbinol (V, R_3 = CH_3) merely protonates under the same conditions (rapid exchange prevents observation of the O^+H_2 protons), but on decreasing the acid strength (by either using H_2SO_4 or CF_3COOH as solvent, or by quenching) rapid elimination occurs to the olefin (VI, R_4 = CH_2). Whereas diphenylmethylcarbinol and 1,1-diphenylethylene give the same visible spectra (Table III) in H_2SO_4 because they both form the diphenylmethylcarbonium ion,[16] the two sydnone derivatives V (R_3 = CH_3) and VI (R_4 = CH_2), give the same spectrum (Table III) because the corresponding ion is unstable and the methyl carbinol rapidly dehydrates (Scheme I).

In contrast to 3-phenylsydnone itself, the methyl carbinol V (R_3 = CH_3) has a complex phenyl proton nmr pattern which collapses to a singlet in $HSO_3F–SbF_5$ solution whereas the phenyl pattern for the olefin VI is little changed from that in neutral solution. The protons on the sydnone exocyclic oxygens are ~1 ppm downfield from that of the parent 3-phenylsydnone, which indicates that delocalization of electron density onto the ethylene group is occurring, resulting in a less polarized C=O bond. Quenching of the solution at low temperature in methanol–Na_2CO_3 yields the olefin

---

(13) The shift of δ 4.32 for the methyl group indicates a significant contribution from the form



(14) G. A. Olah, D. L. Brydon, and R. D. Porter, *J. Org. Chem.*, **35**, 313 (1970).

(15) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **90**, 1884 (1968).

(16) (a) N. C. Deno, P. T. Groves, and G. Saines, *ibid.*, **81**, 5790 (1959); (b) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952); (c) G. A. Olah and M. W. Meyer, "Friedel-Crafts and Related Reactions," Vol. 1., G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1963, p 659.

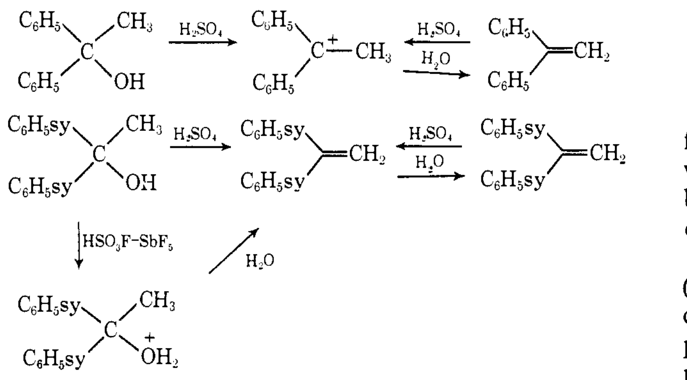
Table III. Visible Spectra of 3-Phenylsydnone Derivatives of H_2SO_4 Solution

Compd	λ_{max}, mμ	Duration of observation, min	Color	Remarks
V, $R_3 = CH_3$	450	20	Red → orange	*Cf.* $(C_6H_5)_2C(CH_3)OH$, 430 mμ[a]
VI, $R_4 = CH_2$	450	20	Orange	*Cf.* $(C_6H_5)_2C{=}CH_2$, 430 mμ[a]
V, $R_3 = C_6H_5$	468	30	Red	*Cf.* $(C_6H_5)_3COH$, 428,[a] 431 mμ[b]
VI, $R_4 = O$	329, 240	30	Yellow	
VII, $R_5 = H_2$ $R_6 = O$	615	30	Deep blue	
VII, $R_5 = R_6 = O$	620	30	Deep blue	

[a] Reference 15. [b] R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, 37, 1402 (1959).

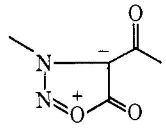
VI ($R_4 = CH_2$) identical with that obtained from the quenching of the H_2SO_4 and CF_3COOH solutions.

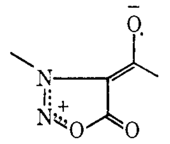
Scheme I



4,4′-Bis(3-phenylsydnonyl)phenylcarbinol[9c] (V,R_3 = C_6H_5), in H_2SO_4, CF_3COOH, and $HSO_3F{-}SbF_5$ solutions, gives intense, red solutions. As in the nmr spectra of the methylcarbinol, the complex phenyl proton pattern of the neutral solution collapses to two broad singlets in $HSO_3F{-}SbF_5{-}SO_2$ solution, which integrate *ca.* 5:1 (Table I). Although the central phenyl group does not give a separate signal which would confirm the absence of the carbonium ion as above, that this is the case is confirmed by the fact that quenching of these acid solutions (H_2SO_4,CF_3COOH, or $HSO_3F{-}SbF_5$) in methanol yields the starting carbinol, unlike the somewhat analogous triphenylcarbinol, which after dissolution in acid, yields the methyl ether when quenched in methanol.[17]

4,4′-Bis(3-phenylsydnonyl) ketone[9c] (VI, R_4 = O) in $HSO_3F{-}SbF_5{-}SO_2$ gives a yellow solution, the pmr spectrum of which shows only the unchanged phenyl signal and a one-proton, low-field singlet at 12.1 ppm, which was relatively[18] temperature insensitive. We assign this proton[19] to the protonated exocyclic carbonyl group (VI, R_4 = O^+H) in view of the fact that α,β-unsaturated ketones,[20] and in particular benzophenone,[21] give temperature-insensitive signals at 12.4 ppm (Table II). No separate signals for the protons on the sydnone carbonyl oxygens were observed. This preference for the protonation of the exocyclic carbonyl group may be explained by consideration of the extreme form of the sydnone ring, in which the exocyclic carbonyl has greater polar character than that in the ring. Protonation of this carbonyl group then precludes the

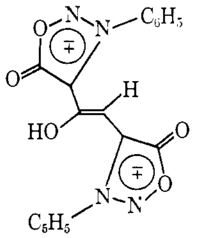




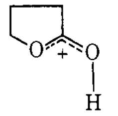
formation of another positive center at the carbonyl within the ring. This interpretation is also supported by the fact that in alkaline medium, nucleophilic attack occurs preferentially at the exocyclic carbonyl group.[9b]

4-Phenylsydnonylmethyl 4′-Phenylsydnonyl Ketone[9c] (VII, R_5 = H_2, R_6 = O). The nmr spectrum of this compound in neutral solution reveals the methylene protons at 8.12 ppm, considerably deshielded in comparison with normal deshielded methylene groups[22] (Table I). Models indicate, apart from much steric hindrance, that these methylene protons may be in the deshielding regions of three carbonyl groups (the normal α-H position to the exocyclic C=O, and the in-plane, adjacent-to-oxygen[23] position to the cyclic C=O groups) and one phenyl group. This together with the possibility of increased sp^2 character of the methylene carbon may account for this unique chemical shift.

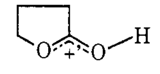
When this compound is dissolved in $HSO_3F{-}SbF_5{-}SO_2$ the phenyl protons are shifted downfield by 0.2 ppm and overlap the presumably unaltered methylene protons, since only a single absorption is observed (Table I). The protons both on the exocyclic and the cyclic carbonyl oxygens are not observable, even at −90°, presumably because of exchange through a diprotonated form of the enol VIII. Neither this nor



VIII



IX



X

any of the other sydnone derivatives showed any sulfination of the phenyl nucleus, either in H_2SO_4 or

---

(17) H. A. Smith and R. J. Smith, *J. Amer. Chem. Soc.*, 70, 2400 (1948).

(18) As compared with that of 3-phenylsydnone.

(19) The signal always integrated to less than one proton (0.5–0.8).

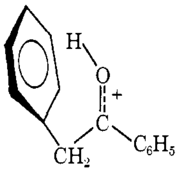
(20) G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, 90, 938 (1968).

(21) Compare δ 12.23, M. Brookhart, G. C. Levy, and S. Winstein, *ibid.*, **89**, 1735 (1967).

(22) For example, desoxybenzoin δ CH_2 = 4.10 (Table II) and homotropylium cation, δ CH_b = 5.2; J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *ibid.*, 84, 2842 (1962); C. E. Keller and R. Pettit, *ibid.*, **88**, 606 (1966).

(23) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, II," Pergamon Press, London, 1968.

"magic acid" solution. The sydnone rings are apparently sufficiently deactivating to protect the phenyl rings from electrophilic attack. In contrast to this, protonation of desoxybenzoin results in a downfield shift (~1 ppm) of the methylene group and rapid sulfination of the phenyl ring adjacent to the methylene group, as evidenced by the changes in the phenyl and methylene absorptions, and the appearance of two singlets at δ 9.8, which we assign to protonated sulfinic acid groups.[24] As the C═O⁺—H protons in the series $C_6H_5COC_6H_5$, $C_6H_5COCH_3$, and CH_3COCH_3 are at δ 12.4, 13.0, and 14.2, respectively, consistent with decreasing ability to donate electron density to the positive center,[21] the observation of the C═O⁺—H proton at δ 12.2 in desoxybenzoin (Table II) may at first seem unusual. However, it has been shown that in some protonated β-phenyl ketones, the anisotropy of the benzene ring can result in the observation of two signals, the upfield one being assigned to the configuration with the C═O⁺—H proton *syn* to the phenyl nucleus and the downfield signal to the *anti* configuration.[25] We, therefore, tentatively assign the one-proton signal at δ 12.2 to the *syn* configuration of desoxybenzoin, XI.



XI

4,4′-Bis(3-phenylsydnonyl) α-diketone[9b,c] (VII, $R_5 = R_6 = O$) is diprotonated on the acyclic carbonyl oxygens as evidenced by the sharp, two-proton, temperature-insensitive singlet at δ 13.1 (Table I). This is in contrast to benzil and other diketones.[26] Benzil diprotonates to give a signal at δ 14.4 which is broad even at −90° (Table II). The presence of an adjacent carbonyl group withdraws electron density from the other carbonyl group, thus decreasing the basicity of the oxygen atoms and resulting in a lower field signal, broadened by exchange with the acid solvent.

As sydnonyl rings have been shown above to be poor electron donors compared to the phenyl nucleus, the C═O⁺—H protons on this α-diketone should be to lower field than those of benzil, an argument which also applies for the monoketone VI ($R_4 = O$). That the reverse is observed may be indicative of anisotropic shielding by the 3-phenyl rings, as is observed in some β-phenyl ketones.[26] Protonation of this diketone destroys the equivalence of the phenyl protons from a sharp singlet in neutral solution to a complex multiplet in $HSO_3F-SbF_5-SO_2$ solution as shown in Figure 6.[26]

The preference for protonation of the exocyclic carbonyl groups over the sydnone cyclic carbonyl groups has been discussed above. In both these ketones (VI, $R_4 = O$; VII, $R_5 = R_6 = O$) the ═O⁺—H proton signal is to higher field than in the corresponding phenyl analogs, indicating increased electronegativity of the oxygen atoms.

Experimental Section

Spectra. The nmr spectra were recorded on a Varian A56-60A instrument with a variable-temperature probe. The chemical shifts are in parts per million from external tetramethylsilane unless otherwise indicated. The visible spectra were recorded in H_2SO_4 at 20°. Both ultraviolet and infrared spectra of the sydnone derivatives have been previously described.[9c]

Compounds. The 3-phenylsydnone derivatives were prepared by Suciu.[9] All except 1,1-di(3-phenylsydnonyl)ethylene have been previously described. The latter was prepared[27] by suspending 1 g (27.4 mmol) of V, $R_3 = CH_3$,[9c] in 5–7 ml of concentrated H_2SO_4 at 0–5°. The intense red colored mixture is poured into 15 ml of MeOH and then water (150 ml) is added. The yellow precipitate (VI, $R_4 = CH_2$, 74% yield) had mp 172°.

Anal. Calcd for $C_{18}H_{12}N_4O_4$: C, 62.07; H, 3.47; N, 16.09. Found: C, 61.83; H, 3.55; N, 16.24.

Commercial samples of the model compounds were used as received. The protonated species were prepared by adding *ca.* 15 g of the compounds to a (~1.5 ml) solution of HSO_3-SbF_5 (1:1 *M*) in two parts (by volume) of SO_2 at −78° with rapid agitation. The acid solutions were quenched by adding them slowly, with vigorous agitation, into anhydrous methanol–Na_2CO_3, cooled in acetone–Dry Ice. Starting materials were recovered upon usual work-up proving that no skeletal changes took place upon protonation.

Acknowledgment. Support of this work by grants from the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

---

[24] M. Brookhart, F. A. L. Anet, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 5657 (1966).

[25] G. C. Levy and S. Winstein, *ibid.*, 90, 3574 (1968).

[26] G. A. Olah and M. Calin, *ibid.*, 90, 4672 (1968).

[27] (a) N. Suciu, Dr. Eng. Thesis, Polytechnical Institute Timisoara, Roumania, 1968; (b) V. Greco and M. Pesce, *J. Heterocycl. Chem.*, 6 (2), 259 (1969).