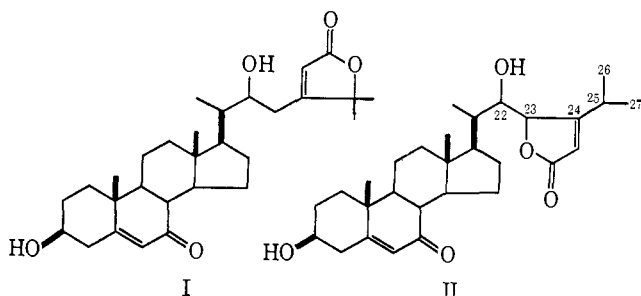
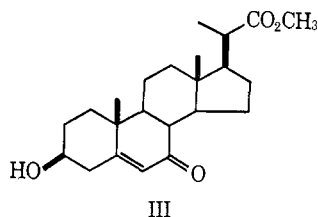


extended conjugation of the α,β -unsaturated ketone on dehydration to a $\Delta^{3,5-7}$ -one.

At that point structures I and II appeared to be the most plausible ones which accommodate all the facts discussed above (the methyl group positions and the stereochemistry being based on biogenetic analogies). The facile rearrangement leading to the formation of fragment a would be sterically possible in the case of structure II since it could take place after opening of the lactone ring. The abundant $C_7H_{11}O_2$ ion (m/e 127) in the tetrahydro derivative favored II because in this



case cleavage of the C-22,C-23 bond produces a positive charge next to oxygen rather than an unstabilized primary carbonium ion.



As a mass spectrometric model the ester III was prepared,⁵ and the spectrum was found to correspond surprisingly close to that of antheridiol in the region below m/e 400, in terms of both abundance and elemental composition of the ions. The region between mass 300 and 400 reflected the presence of an additional CH_2O ($COOCH_3$ vs. CHO) in III as compared with fragment a. The few abundant low-mass ions present in the spectrum of antheridiol and absent in III are due to fragments (b and b - CH_3) derived from the side chain, i.e., m/e 126 ($C_7H_{10}O_2$) and 111 ($C_6H_7O_2$). The close similarity of the mass spectrum of antheridiol and compound III confirms the identity of the kind and position of substituents in the steroid nucleus of both compounds.

The nmr spectrum of antheridiol, determined (4 mg in $CDCl_3$ - CD_3OD , 4:1) when more and purer material had become available, confirmed the choice of II for the structure of this compound. This spectrum shows two olefinic protons (at 5.69 and 5.77 ppm), the C-18 and C-19 methyl groups at 0.70 and 1.20 ppm, and C-26 and C-27 methyl groups (or *vice versa*) as doublets centered at 1.17 and 1.22 (spacing of 7 Hz). The C-21 methyl group is hidden under the complex multiplet caused by the C-19, C-26, and C-27 methyl groups. In addition the single proton on C-22 is a broad doublet at 3.60 ppm (spacing of 8 Hz) coupled with the single proton on C-23 at 4.94 ppm (confirmed by spin-decoupling experiments).

(5) Prepared by CrO_3 -HOAc oxidation at 60° of the methyl ester of 3 β -acetoxybisanor-5-cholenic acid, followed by $EtOH$ - K_2CO_3 hydrolysis; mp 184-186°, λ_{max} 237 m μ (ϵ 1.33×10^4), and ν_{max} 3570, 1724, and 1672 cm^{-1} .

In recent years, the isolation of a small number of hormones controlling sexual reproduction in fungi has been reported⁶ and the characterization of one, sirenin, has just been accomplished.⁷ Antheridiol is of particular interest since, if the proposed structure is correct, it is the first steroidal sex hormone to be recognized in the plant kingdom. It differs from mammalian sex hormones particularly in that it has a much longer side chain attached at C-17.

The proposed structure II for antheridiol must be considered as tentative until availability of this compound permits accumulation of further experimental evidence. The synthesis of structure II would be the most direct way to prove the structure of antheridiol since the isolation of this hormone in any quantity is difficult to achieve.

Acknowledgment. This investigation was supported by the National Institutes of Health, Grants GM 12150 and HD 00850 (at New York Botanical Garden) and GM 09352 (at Massachusetts Institute of Technology).

(6) L. Machlis in "The Fungi," Vol. II, G. C. Ainsworth and A. S. Sussman, Ed., Academic Press, New York, N. Y., 1966, p 415.

(7) L. Machlis, W. H. Nutting, and H. Rapoport, *J. Am. Chem. Soc.*, **90**, 1674 (1968).

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Gas-Phase Acidities of Carbon Acids

Sir:

Extensive studies of acidities of carbon acids have been reported for a number of solvent systems.¹ The problem of solvent medium effects makes interpretation difficult in some cases, so that it is desirable to undertake gas-phase studies not only to obtain intrinsic acidities but also to analyze solvent and counterion phenomena.² We wish to report some preliminary studies of gas-phase proton-transfer reactions of carbon acids and carbanionic bases, work which allows us to obtain relative gas-phase acidities. Making use of ion cyclotron resonance (ICR) spectroscopy, we have found the acidities: acetylacetone > acetyl cyanide > hydrogen cyanide. This work constitutes the first direct measurement of relative acidities of neutral compounds in the gas phase, and the technique is clearly applicable to studying a wide range of compounds.

The utility of ICR for studying ion-molecule reactions has been shown previously.³ The detection of

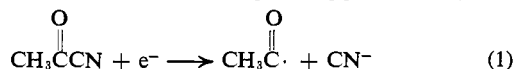
(1) (a) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **90**, 2821 (1968), and references cited therein; (b) A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *ibid.*, **89**, 59 (1967); A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *ibid.*, **89**, 63 (1967); (c) E. C. Steiner and J. M. Gilbert, *ibid.*, **85**, 3054 (1963); **87**, 382 (1965); E. C. Steiner and J. D. Starkey, *ibid.*, **89**, 2751 (1967); (d) K. Bowden and A. F. Cockerill, *Chem. Commun.*, 989 (1967).

(2) See ref 1a for relevant comments on this point.

(3) (a) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966); (b) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **89**, 4569 (1967); (c) J. D. Baldeschwieler, *Science*, **159**, 263 (1968); (d) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968); (e) J. M. Henis, *J. Am. Chem. Soc.*, **90**, 844 (1968); (f) G. A. Gray, *ibid.*, **90**, 2177 (1968).

ions is based on the resonance principle that an ion orbiting in a magnetic field at a frequency characteristic of its mass:charge ratio can absorb energy from an alternating electric field $E_1(t)$ if the frequency of $E_1(t)$ equals the cyclotron frequency of the ion. By operating at a fixed observing frequency for $E_1(t)$, a mass spectrum is obtained by sweeping the magnetic field. A highly specific double-resonance technique provides a means of determining whether two ions of different mass, even in a complex mixture of ions and neutrals, are coupled chemically. Experimentally this is achieved by observing changes in the signal intensity of a product ion upon irradiation of a reactant ion with a second radiofrequency electric field, $E_2(t)$, applied at the cyclotron frequency of the reactant ion. The resulting increase in kinetic energy of the reactant ion, in turn, changes the rate constants for reactions which it is undergoing, thus accounting for changes in product ion intensity.

The single-resonance negative ion spectrum^{4a} of acetyl cyanide obtained with an ionizing electron energy of 2.2 eV (uncor) and at a low pressure ($<10^{-6}$ torr), where essentially no ion-neutral collisions occur, contains only one peak at m/e 26 (CN^-). For this low electron energy, the production of CN^- is probably the dissociative resonance capture process,⁵ eq 1. As the pressure is increased, an $M - 1$ peak appears at m/e 68



($-\text{CH}_2\text{COCN}$) and increases relative to the m/e 26 peak until its intensity is greater than that of the m/e 26 peak. When a pulsed double-resonance⁶ experiment is carried out at a pressure where the signal intensities of the m/e 26 and 68 peaks are comparable, irradiation of the m/e 26 peak (radiofrequency amplitude 0.044 V)^{4b} results in a decrease in the m/e 68 ion intensity. This decrease is consistent with an exothermic ion-molecule reaction whose specific rate constant decreases with increasing reactant kinetic energy, typical of exothermic ion-molecule reactions observed thus far.⁷ The relative intensity behavior of the m/e 26 and 68 peaks with changes in pressure and the double-resonance result give direct evidence for the proton-transfer reaction, eq 2.



A 1:1 mixture of acetyl cyanide and hydrogen cyanide under similar conditions gives identical results. In addition, no proton transfer can be observed from HCN to

(4) (a) Spectra were obtained using a Varian V-5900 ICR spectrometer which has been described along with modifications for double resonance. See ref 3b-d. (b) Peak-to-peak voltage was measured externally at the input to the reaction cell.

(5) C. E. Melton in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 163.

(6) See ref 3b-d.

(7) For general information on ion-molecule reaction rate energy dependence see: (a) "Ion-Molecule Reactions in the Gas Phase," *Advances in Chemistry Series*, No. 58, American Chemical Society, Washington, D. C., 1966; (b) V. L. Tal'rose and G. V. Karachevtsev, *Advan. Mass Spectry.*, 3, 211 (1966); (c) D. P. Stevenson in "Mass Spectrometry," C. A. McDowell, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p 589; (d) C. E. Melton in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 65; (e) F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. Reaction Kinetics*, 1, 69 (1961); (f) K. R. Ryan and J. H. Futrell, *J. Chem. Phys.*, 43, 3009 (1965); (g) J. L. Beauchamp, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1967.

$-\text{CH}_2\text{COCN}$, which suggests that this reverse reaction is endothermic.⁸ Thus, CN^- has a greater proton affinity than $-\text{CH}_2\text{COCN}$; *i.e.*, acetyl cyanide is a stronger acid than HCN in the gas phase.

The single-resonance spectrum of a 1:1 mixture of acetyl cyanide and acetylacetone (2.2 eV, uncor) contains only the peak for CN^- at low pressure. At higher pressures, an $M - 1$ peak for acetylacetone (Ac_2CH^-) at m/e 99 appears, as well as $-\text{CH}_2\text{COCN}$ at m/e 68. Irradiation of $-\text{CN}$ and $-\text{CH}_2\text{COCN}$ results in a decrease in the intensity of Ac_2CH^- , but irradiation of Ac_2CH^- produces no change in the intensity of $-\text{CH}_2\text{COCN}$. From these results the order of gas-phase acidity, $\text{Ac}_2\text{CH}_2 > \text{AcCN} > \text{HCN}$, is obtained.

The proton transfer observed from acetylacetone probably involves the enol, since in the gas phase $>90\%$ acetylacetone exists in this form.⁹ Since the enol is thermodynamically more stable, it must be less acidic than the ketone; thus the order of the carbon acidities is maintained irrespective of whether the enol or keto tautomer of acetylacetone is transferring a proton.

The $\text{p}K_a$ of acetylacetone¹⁰ is 9.0 and that of hydrogen cyanide¹¹ is 9.2 in aqueous medium. Thus, the gas-phase and solution acidities of Ac_2CH_2 and HCN fall in the same order, although *a priori* one could not have predicted this result.

Similar experiments show that toluene is a stronger acid than water and that both of these are weaker than HCN. Thus, we should eventually be able to generate a scale of relative gas-phase acidities. These studies are now in progress.

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(8) See ref 7b,c,e,g.

(9) (a) J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.*, 73, 4353 (1951); (b) E. Funck and R. Mecke in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, Inc., New York, N. Y., 1959, p 433; (c) J. B. Conant and A. F. Thompson, Jr., *J. Am. Chem. Soc.*, 54, 4039 (1932).

(10) (a) R. G. Pearson and R. L. Dillon, *ibid.*, 75, 2439 (1953); (b) F. Hashimoto, J. Tanaka, and S. Nagakura, *J. Mol. Spectry.*, 10, 401 (1963).

(11) (a) R. M. Izatt, J. J. Christensen, R. T. Pack, and R. Bench, *Inorg. Chem.*, 1, 828 (1962); (b) K. P. Ang, *J. Chem. Soc.*, 3822 (1959).

(12) National Science Foundation Predoctoral Fellow, 1966-present.

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Backside Attack on "Bent" σ Bonds

Sir:

Recently, we conclusively demonstrated that the addition of electron-deficient olefins and acetylenes to bicyclo[2.1.0]pentane occurred *via* the formation of a diradical intermediate.¹ It was suggested that this

(1) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Am. Chem. Soc.*, 90, 4746 (1968); see also W. R. Roth and M. Martin, *Tetrahedron Letters*, 4695 (1967).