gnards,[9] based on the nonequivalence of methyl groups somewhat distant from the carbon atom bearing the magnesium atom. From the width of the lines we can estimate that the *exo–endo* isomerization reaction half-life time is greater than 0.5 sec.

Acknowledgment. We are grateful for support of this research by a Frederick Gardner Cottrell Grant from the Research Corporation.

(9) G. M. Whitesides and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4878 (1965).

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Characterization of Functional Groups by Nuclear Magnetic Resonance. I. Classification of Alcohols from the Fluorine-19 Spectra of Trifluoroacetates[1]

Sir:

We wish to describe an nmr scheme for classification of hydroxyl compounds which in our hands has generally proved to be more reliable and informative than other recently described nmr techniques.[2]

Because a number of functional groups can be acetylated, we initially considered that the acetate group might be a useful nmr probe for classification purposes. Unfortunately, the differences in chemical shift between acetate groups of isomeric alcohols are only a few cycles/second and provide no dependable scheme for classification. The fact that ^{19}F chemical shifts are in general about an order of magnitude larger than ^{1}H chemical shifts for a given structural perturbation suggested to us that ^{19}F nmr chemical shifts of the trifluoroacetyl derivatives of alcohols and perhaps amino, mercapto, and phenolic functional groups might provide reliable classification schemes.

Study of the ^{19}F nmr spectra of the trifluoroacetate (TFA) esters of a large number of alcohols revealed that the TFA groups give sharp ^{19}F signals and that the order of shielding is always primary < secondary < tertiary. Figure 1a illustrates this for a mixture of these three classes of alcohols.[3,5] Figures 1b, c, and d show results for mixtures of alcohols, illustrating the general nature of substituent effects on the chemical shift of the TFA group.[6] Figure 1d illustrates a rather

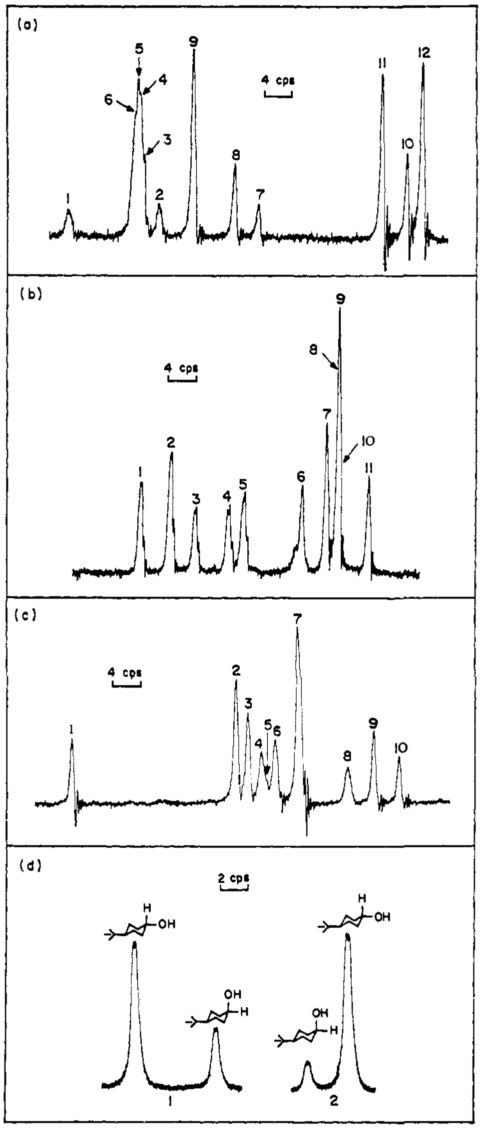

Figure 1. ^{19}F nmr spectra of the trifluoroacetates of some hydroxyl compounds; chemical shifts in parts per million (±0.01) from 10% internal $CFCl_3$ given in parentheses; chemical shifts of overlapping signals determined from more highly resolved spectra of ester mixtures with fewer components. Increasing field to right: (a) 1, CH_3OH (74.21); 2, CH_3CH_2OH (74.43); 3, $CH_3CH_2CH_2OH$ (74.40); 4, $CH_3CH_2CH_2CH_2OH$ (74.39); 5, $(CH_3)_2CHCH_2OH$ (74.38); 6, $(CH_3)_3CCH_2OH$ (74.37); 7, $CH_3CHOHCH_3$ (74.68); 8, $CH_3CHOHCH_2CH_3$ (74.62); 9, $CH_3CH_2CHOHCH_2CH_3$ (74.52); 10, $(CH_3)_3COH$ (75.05); 11, $(CH_3)_2(CH_3CH_2)COH$ (74.99); 12, CF_3CO_2H (75.08) (20% ester mixture in dimethyl sulfoxide). (b) 1, $CH{\equiv}CCH_2OH$ (74.95); 2, $C_6H_5CH_2OH$ (75.02); 3, $CH_2{=}CHCH_2OH$ (75.08); 4, $(CH_3)_3CCH_2OH$ (75.17); 5, $CH_3CH_2CH_2OH$ (75.20); 6, lanosterol (75.35); 7, cholesterol (75.41); 8, cyclopentanol (75.43); 9, cyclohexanol (75.44); 10, cycloheptanol (75.45); 11, $CH_3CHOHCH_3$ (75.52) (15% ester mixture in methylene chloride). (c) 1, C_6H_5OH (73.85); 2, CH_2OHCH_2OH (74.27); 3, $CH_2OHCH_2CH_2OH$ (74.30); 4, $CH_3CHOHCH_2\mathit{OH}$ (74.33); 5, CHF_2CH_2OH (74.34); 6, CF_3CH_2OH (74.37); 7, CH_3CH_2OH (74.43); 8, $CH_3CH\mathit{OH}CH_2OH$ (74.55); 9, $CH_3CHOHCH_2CH_3$ (74.62); 10, $CH_3CHOHCH_3$ (74.68) (20% ester mixture in dimethyl sulfoxide). (d) From two different mixtures of 4-*t*-butylcyclohexanols: 1, *trans* isomer (74.99), *cis* isomer (75.09) (5% in dimethyl sulfoxide); 2, *cis* isomer (76.28), *trans* isomer (76.32) (5% in pentane).

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(1) This paper presents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.

(2) See, for example: (a) O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964); (b) A. Mathias, *Anal. Chim. Acta*, **31**, 598 (1964); (c) V. W. Goodlett, *Anal. Chem.*, 37, 431 (1965).

(3) All ^{19}F spectra shown here were taken at 56.4 Mc with a Varian HR instrument equipped with the field-frequency lock system described previously.[4] The lock signal was derived from 5 to 10% added 1,1,2,2,-tetrafluoro-1,2-dibromoethane. Other spectra were recorded with a Varian A-56/60.

(4) D. D. Elleman, S. L. Manatt, and C. D. Pearce, *J. Chem. Phys.*, **42**, 650 (1965).

(5) The TFA's were prepared by direct addition of trifluoroacetic anhydride to the alcohols or to the alcohols in an inert solvent followed by removal of excess anhydride and the acid formed either by vacuum or by extraction with dilute aqueous bicarbonate followed by drying. Reaction of primary and secondary alcohols is complete in several minutes. Tertiary and some polyhydroxyl compounds require longer and perhaps more than one treatment with anhydride to achieve complete reaction.

(6) A single electronegative substituent β to the hydroxyl group causes a downfield shift as might be expected on purely inductive grounds (see Figure 1c); the fact that the TFA of 1,1-difluoroethanol is at lower field than that of 1,1,1-trifluoroethanol indicates that simple inductive arguments are invalid here.

interesting solvent shift for two mixtures of the TFA esters of *cis*- and *trans*-4-*t*-butylcyclohexanol.[7]

For a single unknown alcohol or a mixture of alcohols our operational procedure consists of TFA preparation, dissolution in a solvent if necessary, addition of a small amount of ethyl trifluoroacetate as an internal reference, and recording of the spectrum. Ethyl trifluoroacetate is a reliable internal standard because at 56.4 Mc all other primary TFA's are downfield (2–17 cps), all phenol TFA's downfield (30 cps or more), all secondary TFA's upfield (3–15 cps), and all tertiary TFA's upfield (30–36 cps).

We do not wish to claim that the trifluoroacetylation–^{19}F nmr technique is in every case the simplest and best means of characterizing hydroxyl groups. There will certainly be instances where other techniques are adequate. However, the method described here does have certain obvious advantages. First, with this method, one is looking at the signal from three ^{19}F nuclei *vs.* one ^1H nucleus (as in the case of several other recently described nmr techniques) which can be a multiplet.[8] Thus, at worst, a signal to noise increase of around 2.5 should be realizable. In addition, because one observes the ^{19}F spectrum, signals from the other protons in the molecules of interest are far removed and the restrictions on the choice of solvent are essentially removed.

[7] Although chemical shift concentration and solvent effects have been observed, so far for mixtures of TFA's chemical shifts are always in the order of shielding primary < secondary < tertiary. Comparison of the data in Figure 1 for the chemical shifts in parts per million for the TFA's of *cis*-4-*t*-butylcyclohexanol (A) (75.09) and *trans*-4-*t*-butylcyclohexanol (B) (74.99) with those of 2-methyl-2-butanol (C) (74.99) and *t*-butyl alcohol (D) (75.05) would seem to refute this statement. However, this is an example of the concentration effects. In one case (Figure 1d) the solution was 5% in ester and in the other case (Figure 1a) 20% in ester. In a 20% ester mixture of DMSO (7% CCl_3F) A, B, C, and D show chemical shifts of 74.57, 74.69, 75.00, and 75.06 ppm, respectively.

[8] As can be seen in the spectra shown above and more readily in spectra recorded at slightly slower sweep rates, there exist small splittings (0.15–0.30 cps) of the CF_3 groups with the proton(s) five bonds removed.

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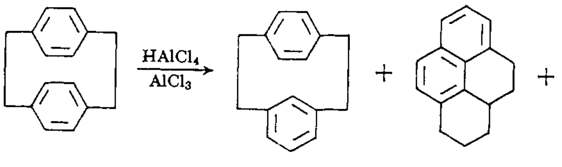
[2.2]Metaparacyclophane, a Highly Strained Ring System[1]

Sir:

Treatment of powdered [2.2]paracyclophane[2] (I) with a solution of dry methylene chloride saturated with hydrogen chloride and aluminum chloride at 0° for 30 min produced [2.2]metaparacyclophane[3] (II) in 44% yield, 1,2,2a,3,4,5-hexahydropyrene[3] (III) in 10% yield, bibenzyl (IV) in trace amounts, and a 7% yield of starting material. These products were isolated by preparative vpc on a 20% Epon 1001 on Firebrick column at 165° under 15 psi of helium, and they exhibited the following retention times: I, 63 min, mp 285–287°, undepressed by admixture with authentic material; II, 48 min, mp 81–81.5°; III, 128 min, mp 102.5–103.3° (lit.[4] 103–105°); IV, 15 min, mp 49–50°, undepressed upon admixture with an authentic sample.



I II III

$(C_6H_5)_2CH_2$
IV

The structure of [2.2]metaparacyclophane was assigned on the basis of its combustion analysis,[3] degradation products, and nmr (in carbon tetrachloride) and ultraviolet absorption spectra (in 95% ethanol). Reduction of II with potassium metal in dimethoxyethane produced *m,p'*-dimethylbibenzyl (V), an oil,[3] which when oxidized with potassium permanganate gave a mixture of isophthalic and terephthalic acids, identified by the retention times of their dimethyl esters on vpc.[5] The ultraviolet (Figure 1) and nmr spectra of V support the assigned structure. The former exhibits bands expected from a mixture of *m*- and *p*-xylenes. The latter gave the following bands: eight protons centered at τ 3.05 (four protons as a singlet at τ 3.03 assigned to the *para*-disubstituted benzene ring and four protons at τ 3.06 (partially masked by the above peak and possessing a typical *meta* splitting pattern assigned to the *meta*-disubstituted benzene ring); four protons as a singlet at τ 7.22 (methylene protons); six protons as a singlet at τ 7.74 (methyl protons). Direct oxidation of [2.2]metaparacyclophane with potassium permanganate gave the expected isophthalic and terephthalic acids.[5]

The nmr spectrum of [2.2]metaparacyclophane (II) strongly supports the assigned structure. Although protons a and b are shielded by the ring currents of the transannular aromatic nuclei, the effect is considerably less than that observed for the two protons that correspond to a in [2.2]metacyclophane[6] (τ 5.73). The ultraviolet spectrum of II (Figure 1) is strikingly different from that of the open chain model (V). The cycle exhibits a new and intense band at ~240 mμ which is not far from the 244 mμ band of [2.2]paracyclophane which was attributed to mixing of transannular charge transfer with normal excited states.[7] The remnants of the fine structure in the spectrum of the open-chain model are visible in that of the cycle (II) in the 260–280 mμ region. The bands at 283 and 291 mμ in the spectrum of the cycle are absent in that of the open-chain compound and are probably associated mainly with a serious deformation of the *para*-substituted benzene ring from its normally planar configuration. Molecular models suggest that this deformation is much greater than that in [2.2]paracyclophane, whose side-chain substituted aromatic carbon atoms are bent out of the plane of the other four aromatic carbon atoms by 13°. That such bending causes bathochromic

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[1] The authors wish to thank the National Science Foundation for a grant used in support of this research.

[2] D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951).

[3] Combustion analysis gave carbon and hydrogen values less than 0.2% from theory.

[4] W. Baker, J. F. W. McOmie, and J. M. Norman, *J. Chem. Soc.*, 1114 (1951).

[5] D. J. Cram and H. P. Fischer, *J. Org. Chem.*, **30**, 1815 (1965).

[6] N. L. Allinger, M. A. Da Rooge, and R. B. Hermann, *J. Am. Chem. Soc.*, **83**, 1974 (1961).

[7] R. C. Helgeson and D. J. Cram, *ibid.*, in press.