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NUCLEAR MAGNETIC RESONANCE SPECTRA OF CYCLOPROPYL IONS

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Some of the results we obtained in our studies of positive cyclopropyl ions differ from the observations reported by Pittman and Olah (1).

The Tables I, II and III collect our data on the NMR spectra of twentyfour cyclopropyl ions. Three of the ions are also described by Pittman and Olah: the data on one of these three are in close agreement with our values, the data and spectra of the other ions are essentially different, however.

The spectrum of the cyclopropyl-p-tolyl-carbinol, in HSO_3F-SbF_5-SO_2, recorded at -79°C (Fig. 4) is comparatively simple and can be used as a key to the interpretation of the more complicated spectra. The absorption lines can easily be attributed to the different (groups of) protons in the molecule. The signal of the exocyclic proton is found as a doublet at approximately 9.00 ppm downfield from TMS with J=13 cps; the signals from the α - and β -hydrogens on the cyclopropylring are shifted 2-3 ppm downfield which is about the same value Pittman and Olah report. The phenyl absorptions are noteworthy as they show positively that the hydrogens at the ortho positions are non-equivalent; the non-equivalency of the meta protons is as expected, less pronounced. Here, as in the comparable spectra of the other cyclopropyl aryl ions, the difference of the chemical shift of the ortho protons is about 0.5 ppm. Moreover in all these compounds the doublets

Table 1 *)

Chemical Shifts of Cyclopropyl Aryl Carbonium Ions

Starting carbinol	T(°C)	Chemical shifts in ppm from TMS				
		Phenyl protons	H exoc.	Cyclopropyl protons α	Cyclopropyl protons β	Subst.
Cyclopropyl phenyl	-70	8.02; 8.17; 8.35; 8.47; 8.77; 8.90	9.23	4.09	3.42; 3.60	-
Cyclopropyl p-tolyl	-60	7.70; 7.82; 8.02; 8.16; 8.57; 8.70	8.94	3.87	sign. from 2.92 to 3.37	CH_3:2.67
Cyclopropyl p-anisyl	-70	7.33; 7.43; 8.12; 8.27; 8.63; 8.78	8.41	3.27	sign. from 2.12 to 2.80	OCH_3:4.25
Cyclopropyl p-ethylphenyl	-70	7.75; 7.87; 8.10; 8.12; 8.64; 8.77	9.00	3.89	2.97	CH_2: 2.97 CH_3: 1.3
Cyclopropyl p-*iso*-propylphenyl	-70	7.85; 7.95; 8.14; 8.27; 8.69; 8.83	8.97	3.84	3.07 to 3.28	CH:obsc. CH_3: 1.3
Cyclopropyl 3,4-dimethylphenyl	-70	7.67; 7.82; 7.93; 8.07; 8.50; 8.62	8.89	3.77	2.87 to 3.34	CH_3:2.58 CH_3:2.48 (doublet)
Cyclopropyl p-fluorophenyl**)	-75	multiplets at 8.88; 8.37 and 7.66	9.08	3.96	sign. from 3.29 to 3.52	-
Cyclopropyl p-chlorophenyl**)	-75	7.87; 8.00; 8.13; 8.30; 8.67; 8.80	9.18	4.07	sign. from 3.42 to 3.65	-
Cyclopropyl p-bromophenyl**)	-80	8.10; 8.10; 8.19; 8.54; 8.69	9.20	4.10	sign. from 3.50 to 3.67	-

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**) in HSO_3F-SO_2

FIG.1

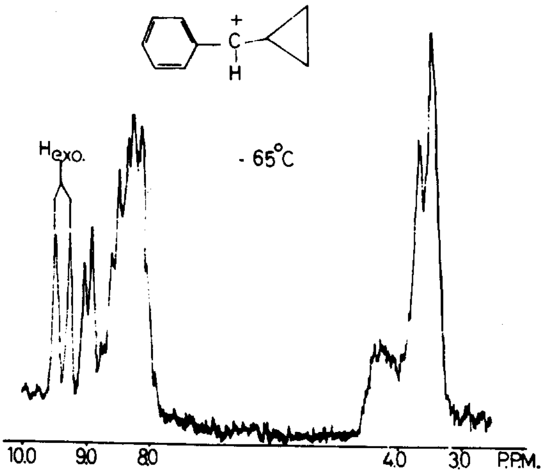


FIG. 2

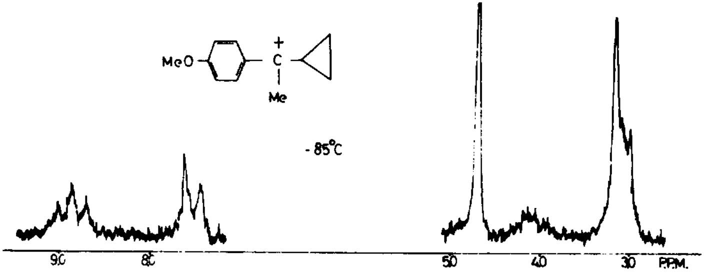


FIG.3

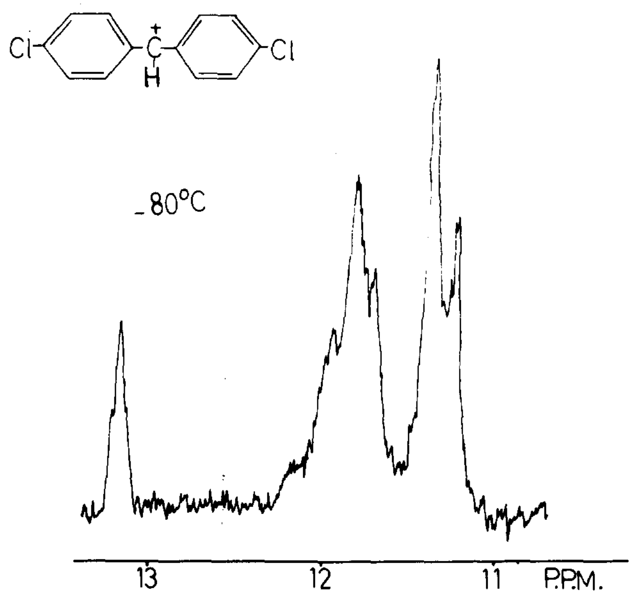
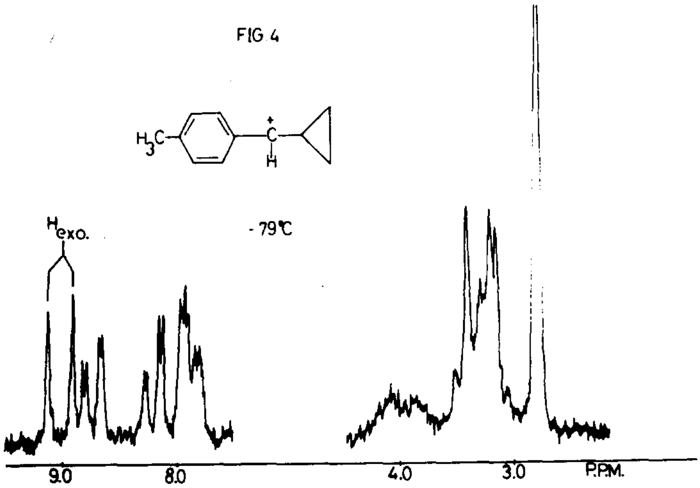


FIG 4



of the ortho protons show additional splittings (1-2 cps) because of the different meta couplings. The spectrum of the cyclopropyl phenyl ion is shown in Fig. 1. The absorption lines due to the exocyclic proton and to the ortho phenyl hydrogens can be distinguished. Data on the cyclopropyl aryl ions are collected in Table 1.

The spectra recorded at -60°C are identical with those recorded at lower temperatures, however, as it is our experience that the ions decompose extremely rapidly at this temperature, we think that the different results of Pittman and Olah find their origin in the fact that all their spectra were recorded at -60°C. At -75°C decomposition, though less rapid, is still observed. Therefore no temperature dependence of these spectra can be shown, in contrast of those of the cyclopropyl aryl methyl ions.

Fig. 2 shows the spectrum of the cyclopropyl-p-anisyl methyl carbonium ion recorded at -85°C. The low field signals due to the ortho protons especially are broadened. The phenyl signals narrow again when the temperature is raised. The spectra of the other cyclopropyl aryl methyl ions investigated show the same picture. The difference between our spectrum of the cyclopropyl-p-tolyl methyl ion and that recorded by Pittman and Olah is probably due again to the fact that their spectrum is recorded at a considerably higher temperature. Here the rigidity of the molecule plays the most important role, rather than decomposition.
Table II lists chemical shifts in cyclopropyl aryl methyl ions.

There is a resemblance of these spectra with those of the carbonium ions derived from e.g. 4,4'-dibromo- and 4,4'-dichlorobenzohydrol and recorded at lower temperatures (Fig.3). At -40°C the ion derived from 4,4'-dichlorobenzohydrol shows the expected quartet due to the phenyl hydrogens; at -70°C the low field doublet of this quartet, due to the ortho protons, is broadened to a singlet and at -80°C the ortho protons show a broadened multiplet.

In an earlier stage of our investigations cyclopropyl aryl ketones were investigated. We could show a temperature dependence of the spectra of the cyclopropyl-4-fluoro-,cyclopropyl-4-chloro- and cyclopropyl-4-bromophenyl hydroxonium ions, where the low field phenyl doublet is broadened and the hydroxonium hydrogen signal

Table II [*)]

Chemical Shifts of Cyclopropyl Aryl Methyl Carbonium Ions

Starting carbinol	T(°C)	Chemical shifts in ppm from TMS				
		Phenyl protons	CH_3 exoc.	Cyclopropyl protons		Subst.
				α	β	
Cyclopropyl *p*-tolyl methyl	-80	7.72; 7.84 8.58(br.doublet)	2.88	4.03	3.05	CH_3:2.67
Cyclopropyl *p*-anisyl methyl	-85	7.32; 7.47 8.59;8.76;8.90	2.69	3.62	2.51 2.60	OCH_3:4.22
Cyclopropyl *p*-ethylphenyl methyl	-85	7.81; 7.91; 8.68(br.sing.)	2.91	4.03	3.06	CH_2:obsc. CH_3:1.35
Cyclopropyl *p*-*iso*-propylphenyl methyl	-80	7.80; 7.94; 8.66(br.sing.)	2.88	4.06	3.07	CH:obsc. CH_3:1.38
Cyclopropyl *p*-*tert*. butylphenyl methyl	-80	7.94; 8.10; 8.62(br.sing.)	2.89	4.03	3.15	CH_3:1.45
Cyclopropyl *p*-chlorophenyl methyl	-70	7.77; 7.92; 8.45; 8.58	2.92	4.06	3.37	-

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[*)] Spectra were recorded at 60 Mc.
The $(CH_3)_4N^+$ ion was used as an internal reference. The difference in chemical shift between the reference and TMS (external) was estimated as -3.20 ppm.
For multiplets centered positions are given.
The compounds were dissolved in mixtures of HSO_3F and SO_2 containing less than 20% SbF_5(b.w.).

Table III*)

Chemical Shifts of Protonated Cyclopropyl Aryl Ketones

Starting ketone	T(°C)	Chemical shifts in ppm from TMS				
		$=\overset{+}{C}H$	Phenyl protons	Cyclopropyl protons α	β	Subst.
Cyclopropyl phenyl	-80	12.07	signals from 7.97 to 8.50	3.37	2.60	-
Cyclopropyl *p*-tolyl	-70	11.73	7.64; 7.77; 8.23; 8.37	3.37	2.47	CH_3:2.55
Cyclopropyl *p*-anisyl	-80	11.23	7.25; 7.40; 8.37; 8.50	3.22	2.17; 2.27	OCH_3:4.08
Cyclopropyl *p*-ethylphenyl	-85	11.67	7.70; 7.85; 8.30; 8.44	3.33	2.45	CH_2:2.93 CH_3:1.34
Cyclopropyl *p*-*iso*-propylphenyl	-85	11.67	7.77; 7.88; 8.33; 8.45	3.34	2.47	CH:hidden CH_3:1.35
Cyclopropyl *p*-*t*-butylphenyl	-80	11.80	8.00; 8.10; 8.40; 8.50	3.40	2.47	CH_3:1.42
Cyclopropyl *p*-fluorophenyl	-75	11.87	7.45;7.60;7.74; 8.50(br.singlet)	3.30	2.45; 2.57	-
Cyclopropyl *p*-chlorophenyl	-80	11.99	7.83; 7.97; 8.34; 8.47	3.35	2.60	-
Cyclopropyl *p*-bromophenyl	-85	12.17	7.97; 8.10; 8.23(br.sing.)	3.34	2.60	-

tends to a broadened multiplet.

Data on the ketones are listed in Table III.

Further analysis of the spectra will be published in a forthcoming publication.

REFERENCE

(1) C.U. Pittman Jr., G.A. Olah, J.Am.Chem.Soc., **87**, 5123 (1965)