A quite similar situation exists for the alcohols. The OH proton appears at 3.1 ppm for the *cis* and at 5.2 ppm for the *trans* isomer; the proton geminal to the OH is centered at 4.1 ppm for the *cis* and 4.3 ppm for the *trans* isomer. Ring methylene protons are centered at 2.4 and 1.4 ppm for the *cis* and at 2.1 ppm for the *trans* isomer. In the alcohols, as determined by relative integrated peak areas,[12] remaining tertiary protons of the isopropyl group and C_3 appear overlapped by the high-field methylene resonances. The same situation was observed in the amines.

If our conformational picture of cyclobutane is a reasonable one, analogies with nmr effects in cyclohexane should be valid. The large variance between the *cis* and *trans* ring methylene signals is strongly reminiscent of the "axial effect" observed in the cyclohexanes.[13-17] It has been observed in several instances that axial substituents cause a narrowing and intensification of the resonance due to equatorial and axial ring protons. Such cases as OH in the decalins[16] and steroids[18] and alkyl groups in cyclohexanes[19] are illustrative.

Equatorial protons ordinarily absorb at lower field than axial protons in cyclohexane. This distinction is actually seen only in temperature-frozen or conformationally homogeneous (*i.e.*, *t*-butylcyclohexane[20]) systems, since ring equilibration causes averaging. If, in a homogeneous disubstituted system, the shielding effects of substituents on axial *vs.* equatorial protons were disparate but unopposed, one would expect broadening of overlapping resonances or even separation, whereas opposition would result in narrowing of the signal. Equatorial alkyl groups have been shown to shield *cis* (axial) adjacent protons more strongly than *trans* (equatorial),[19] while axial substituents (including OH and alkyl) shield *cis* (equatorial) adjacent protons and deshield *trans* (axial) adjacent protons.[18,19] Thus, in the *trans* 3-isopropylcyclobutane isomers, with predominantly equatorial isopropyl and axial OH or NH_2 expected, effects are opposed, resulting in resonance narrowing and overlapping for the ring methylene signals. In line with previous reasoning, in the *cis* isomers equatorial OH or NH_2 groups, which are strongly electronegative, must deshield *trans* (equatorial) more than *cis* (axial) ring protons, so that the equatorial protons more strongly deshielded by equatorial OH or NH_2 appear further downfield than the axial protons more strongly shielded by the equatorial isopropyl group. A similar effect may be noted in *trans*-4-*t*-butyl- and *cis*-3-*t*-butylcyclohexylamine, which possess equatorial NH_2 groups and two separate ring methylene signals, whereas their isomers have single more intense bands at intermediate field.[15] We have likewise observed an analogous but much less pronounced effect in the 3-isopropylcyclobutanecarboxylate esters.[21]

The present results are therefore intelligible only in terms of a relatively homogeneous nonplanar system containing predominantly or exclusively equatorial isopropyl and axial or equatorial OH or NH_2. The equilibrium depicted in Figure 1 must lie substantially to the left for both sets of isomers. We believe this to be the first instance of the successful use of a holding group in cyclobutane. A sound basis is thus at hand for further investigations of conformational distinctions in this system.

Acknowledgment. The authors are indebted to the Directorate of Chemical Sciences, Air Force Office of Scientific Research, for Grant No. AFOSR-123-63 which provided financial support for this work. We are grateful to Varian Associates for their kindness in running nmr spectra of the amines.

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[12] Relative areas going upfield: *cis* OH, 1:1:2:4:6; *trans* OH, 1:1:6:6; *cis* NH_2, 1:2:6:6, *trans* NH_2, 1:8:6.

[13] J. I. Musher, *Spectrochim. Acta*, **16**, 835 (1960).

[14] N. Muller and W. C. Tosch, *J. Chem. Phys.*, **37**, 1167 (1962).

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[19] H. Booth, *Tetrahedron*, **22**, 615 (1966).

[20] E. Eliel and M. H. Gianni, *Tetrahedron Letters*, 97 (1962).

[21] I. Lillien and R. A. Doughty, unpublished work.

[22] Based in part on the dissertation submitted by R. A. Doughty to the Graduate School of the University of Miami in partial fulfillment of the requirements for the Ph.D. Degree in chemistry.

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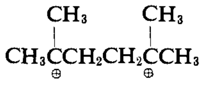
Stable Carbonium Ions. XXXII.[1] Alkyldicarbonium Ions

Sir:

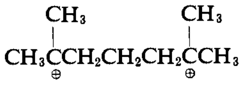
Recently we reported the direct observation of alkylenedioxodicarbonium ions (acyl dications).[2] No observation of alkyldicarbonium ions has yet been reported.

We now wish to report the direct observation of the first stable alkyldicarbonium ions. When 2,5-dichloro-2,5-dimethylhexane[3] and 2,6-dichloro-2,6-dimethylheptane[4] were dissolved in SO_2–SbF_5 solution at low temperature, clean, slightly colored solutions resulted which gave the spectra shown in Figures 1 and 2. These spectra are those of the dicarbonium ions I and II, respectively, in the form of the di-SbF_5Cl^- salts.



$$CH_3\underset{\oplus}{\overset{CH_3}{C}}CH_2CH_2\underset{\oplus}{\overset{CH_3}{C}}CH_3$$

I



$$CH_3\underset{\oplus}{\overset{CH_3}{C}}CH_2CH_2CH_2\underset{\oplus}{\overset{CH_3}{C}}CH_3$$

II

The dication nature of these ions was deduced from three observations: (1) the nmr spectra, indicative of the ions, in particular the downfield shifts of the methyl and methylene groups adjacent to the positively charged carbon atoms;[5] (2) the long-range coupling of the methyl groups with the adjacent methylene groups through the sp^2 center;[5,6] and (3) the isolation of dimethyl ethers on quenching solutions of the dications in methanol at −78°.[7]

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[1] Part XXXI: G. A. Olah, M. B. Comisarow, and E. Namanworth, *J. Am. Chem. Soc.*, in press.

[2] G. A. Olah and M. B. Comisarow, *ibid.*, **88**, 3313 (1966).

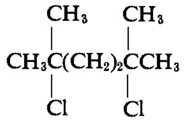
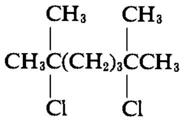
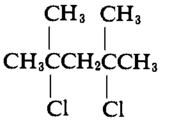
[3] H. A. Bruson, F. W. Grant, and E. Bobko, *ibid.*, **80**, 3633 (1958).

[4] H. Staudinger and W. Widmer, *Helv. Chim. Acta*, **9**, 546 (1926); we substituted glutaryl dichloride for the diester.

[5] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964), and other papers in this series.

[6] G. A. Olah and C. U. Pittman, Jr., *Advan. Phys. Org. Chem.*, **4**, 303 (1966).

Table I. Nmr Shifts and Couplings of Alkyldicarbonium Ions, Their Precursors, and Quenching Products[a]

	Starting material[b]	Ion in SbF_5–SO_2[c]	MeOH-quenched product[b]
 $\mathrm{CH_3\underset{Cl}{\overset{CH_3}{C}}(CH_2)_2\underset{Cl}{\overset{CH_3}{C}}CH_3}$	1.63 (s) 1.93 (s)	I, 4.24 (t), CH_3 5.04 (m), CH_2 $J \cong 3.0$ cps	1.08 (s), CH_3 1.39 (s), CH_2 3.08 (s), OCH_3
 $\mathrm{CH_3\underset{Cl}{\overset{CH_3}{C}}(CH_2)_3\underset{Cl}{\overset{CH_3}{C}}CH_3}$	1.55 (s) 1.70 (broad s)	II, 4.06 (t), CH_3 2.90 (q), CH_2 ~4.4 (m), CH_2 $J \cong 4.0$ cps	1.08 (s), CH_3 3.08 (s), OCH_3 ~1.30 (m), CH_2
 $\mathrm{CH_3\underset{Cl}{\overset{CH_3}{C}}CH_2\underset{Cl}{\overset{CH_3}{C}}CH_3}$	1.71 (s) 1.88 (s)	III, 3.17 (s), CH_3 8.08 (s), CH	Complex

[a] s = singlet, t = triplet, q = quadruplet, m = multiplet. [b] In CCl_4, internal TMS reference. [c] External TMS in $DCCl_3$ as reference.

We also attempted to obtain dicarbonium ions from 2,3-dichloro-2,4-dimethylpentane and 2,3-dichloro-2,3-dimethylbutane, but these attempts were unsuccessful.

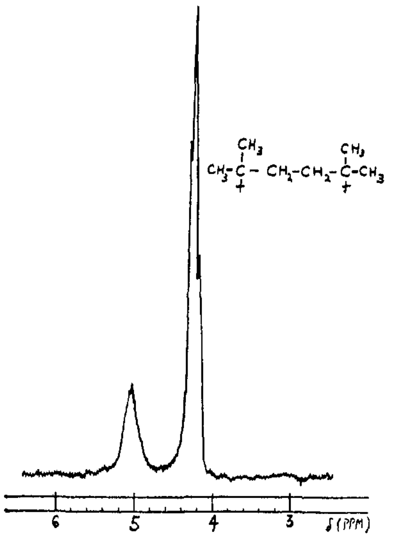
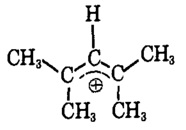


Figure 1.

When 2,4-dichloro-2,4-dimethylpentane[8] was added to an SbF_5–SO_2 solution, an nmr spectrum was obtained showing singlets at −3.21 and −8.14 ppm. The chemical shifts of the two lines are consistent with tetramethylallyl cation III, observed previously by Deno.[9] However, Deno reported a 1.2-cps separation of the nonequivalent methyl groups which we do not observe in our system and, furthermore, no coupling is observed from the allylic methyl groups to the methine proton.

The nmr data of the discussed alkyldicarbonium ions and their precursors are summarized in Table I. Integrated areas for all were in accord with the assigned structures. Although we made no other independent identification of the quenched products, their nmr spectra provide complete identification. Thus, from Table I it is readily apparent that the chemical shifts of the methyl groups on tertiary carbon to which is at-



III

tached a methoxyl group fall in the region of −1.08 to −1.36 ppm, and the shifts of the methoxyl groups are in the range of −3.08 to −3.20 ppm.

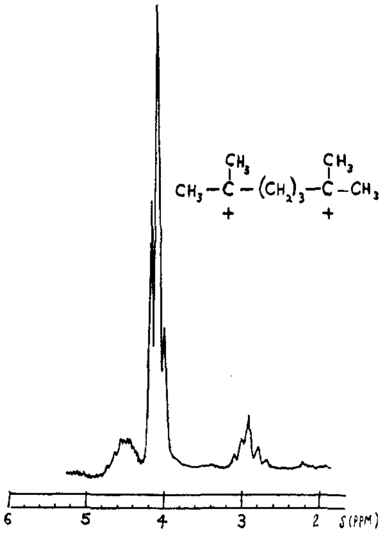


Figure 2.

Acknowledgment. The work was supported by grants of the National Science Foundation and the National Institutes of Health.

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(7) Quenching these solutions with MeOH at −78° in the presence of excess of K_2CO_3 gives high yields of nearly pure products.

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