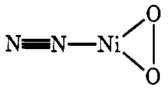
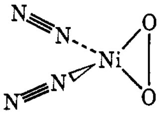
cm^{-1}) and *three* absorptions in the $^{15}N_2$ region (2207, 2195, and 2184 cm^{-1}). These data prove that the species giving rise to the N–N stretching modes at 2283 and 2260 cm^{-1} contains *two* dinitrogen ligands, most probably in a cis configuration.

The O–O stretching mode originally at 972 cm^{-1} in $^{16}O_2/^{14}N_2/Ar$ mixtures produces a *doublet* pattern at 972 and 921 cm^{-1} in $^{16}O_2/^{18}O_2/^{14}N_2/Ar$ mixtures. These data prove that the species giving rise to the O–O stretching mode at 972 cm^{-1} contains a single dioxygen ligand. The diffusion characteristics of the absorptions at 2283, 2260, and 972 cm^{-1} parallel each other during warm-up experiments and can be assigned to a single chemical species containing *two* dinitrogen and *one* dioxygen ligand coordinated to a single nickel atom, that is, bis(dinitrogen)monodioxygennickel, $(N_2)_2Ni(O_2)$ (IV).

The preliminary experiments have shown that binary mixed dinitrogen–dioxygen complexes of nickel are capable of existence under conditions of matrix isolation. From the number and frequencies of the N–N and O–O stretching modes (compared to their parent molecules $Ni(N_2)_n$ and $Ni(O_2)_m$ where n = 1–4 and m = 1–2), their diffusion behavior and $^{14}N_2/^{14}N^{15}N/^{15}N_2/^{16}O_2/Ar$ and $^{16}O_2/^{16}O^{18}O/^{18}O_2/^{14}N_2/Ar$ isotope multiplet patterns, we conclude that the new complexes are $(N_2)Ni(O_2)$ and $(N_2)_2Ni(O_2)$, containing "side-on" bonded dioxygen and "end-on" bonded dinitrogen in both complexes. Further experiments are presently in progress, and we are also extending these reactions to include Pd and Pt.


III


IV

The discovery and characterization of mixed dinitrogen dioxygen transition metal complexes should prove to be of considerable importance in assessing the bonding characteristics of O_2 and N_2 ligands when coordinated to the same metal atom and when competing with each other for bonding electrons.

Of greater importance, however, is the realization that mixed dinitrogen dioxygen complexes could conceivably have a transient existence in those biological systems, which have the property of fixing dinitrogen or carrying dioxygen in an atmosphere composed of the mixed ligands themselves. In this context we note that purified nitrogenase from Azobacter and Clostridia is rapidly inactivated by O_2; the Mo-Fe protein and the Fe protein are both O_2 sensitive.[5]

Acknowledgments. We wish to thank the Deutscher Akademischer Austauschdienst for a scholarship (W. E. K.) and the National Research Council of Canada and the Research Corporation for financial assistance.

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Stable Carbocations. CXLVIII.[1] 3-Nortricyclyl Cations. The Continuity of the Mode of Charge Delocalization in Carbocations with or without Significant Bridging

Sir:

We have discussed extensively in our preceding work the question of σ-bond delocalization (bridging) in carbocations *via* two-electron, three-center bond formation (carbonium ion formation).[2] A mechanism concerning the ability of strained σ bonds in stabilizing neighboring cationic centers without significant movement of the involved nuclei has recently been suggested ("vertical stabilization") by Traylor.[3] Accordingly strained (or polarizable) σ bonds may stabilize neighboring cationic centers by electronic interaction without concurrent nuclear movement, *i.e.*, *without* altering the length or angles around such bonds as the transition state is approached. Qualitative theoretical treatments of carbenium ion systems which are stabilized through hyperconjugation (σ–p delocalization) are available.[4,5] As interesting as Traylor's suggestion is,[3] according to theoretical considerations the electronic hyperconjugative interaction will *always* be accompanied by some geometrical readjustment (in the Frank–Condon sense, *i.e.*, electronic movement is always accompanied by nuclear movement). The extent of such deformation, however, can vary greatly in different systems. Hoffmann, *et al.*,[6a] recently emphasized that there is *no* dichotomy between participation with or without bridging based on theoretical grounds. Hehre and Hiberty[6b] further cautioned about the importance of vertical stabilization in theoretical studies.

In order to gain more insight into the problem of carbenium ion stabilization by hyperconjugation with or without bridging, we have now chosen a system wherein the strained C–C σ bonds are locked in a rigid framework which prohibits bridging due to the geometrical rigidity, *i.e.*, the 3-nortricyclyl cations.[7]

Among the neighboring groups which are able to stabilize cationic centers whether through hyperconjugation or bridging, the effect of the cyclopropyl group

(1) Part CXLVII: G. A. Olah, G. Liang, and P. W. Westerman, *J. Amer. Chem. Soc.*, submitted for publication.

(2) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(3) (a) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971); (b) T. G. Traylor, R. S. Brown, and N. A. Clinton, *ibid.*, **92**, 5228 (1970); (c) T. G. Traylor, H. J. Berwin, and W. Hanstein, *ibid.*, **92**, 829 (1970); (d) T. G. Traylor and J. C. Ware, *ibid.*, **89**, 2304 (1967).

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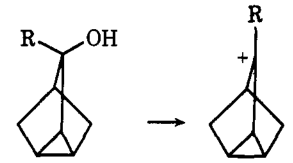
(6) (a) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972); (b) W. J. Hehre and P. C. Hiberty, *ibid.*, **94**, 5917 (1972).

(7) (a) C. C. Lee and B. S. Hahn, *J. Amer. Chem. Soc.*, **92**, 2583 (1970); (b) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965; (c) M. Simonett and S. Winstein, *J. Amer. Chem. Soc.*, **76**, 18 (1954); (d) J. Paasivirta, *Justus Liebigs Ann. Chem.*, **686**, 1 (1965); (e) R. K. Lustgarten, *J. Amer. Chem. Soc.*, **94**, 7602 (1972); (f) M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); (g) S. Winstein, *Quart. Rev., Chem. Soc.*, 141 (1969); (h) P. R. Story and B. C Clark, Jr., "Carbonium Ions," Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., in press, Chapter 23.

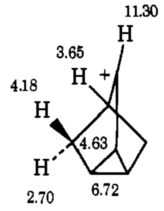
is well documented.[6b,7e,8] Bisected geometry has been shown to be the most favorable for the cyclopropane ring to participate in cyclopropyl carbinyl cations. We succeeded to observe cyclopropylcarbinyl cations under stable ion conditions and[8d,9] further confirmed that the bisected conformation of the cation is the most favorable for stabilizing the ions. 3-Nortricyclyl cations (**1**) have exactly the favorable conformation for maximum charge delocalization in which the cyclopropane ring is situated in the favored bisected geometry in relation to the carbenium center. However, due to the rigidity of the tricyclic system such delocalization would be followed by only minimal nuclear movement. We therefore prepared and directly observed a series of these carbenium ions in superacid media in order to study (by ^1H and ^{13}C nmr spectroscopy) the degree of charge delocalization in these rigid systems and to compare them with more flexible cyclopropylcarbinyl ions.



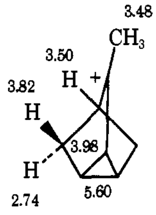
2 **1**

$R = H, CH_3, CH_2CH_3$

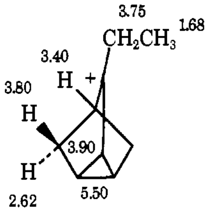
The 3-nortricyclyl cations **1** were obtained in SbF_5–SO_2ClF solution at −78° from the corresponding alcohols **2**.[10a] The pmr shifts (in δ from capillary tetramethylsilane) for secondary ion **1**-H and tertiary ions **1**-CH_3 and **1**-CH_2CH_3 are shown on the formulas. Protonated 3-nortricyclanone **1**-OH was also obtained in FSO_3H-SbF_5 solution at −78°. Two isomeric protonated forms were observed in the ratio of 75:25.[10b]



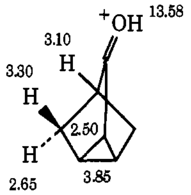
1-H



1-CH_3

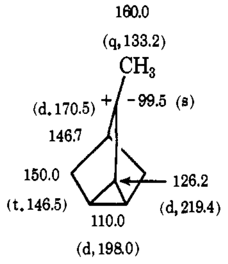


1-CH_2CH_3

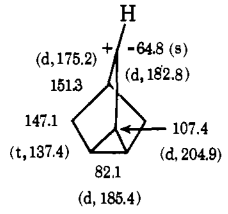


1-OH

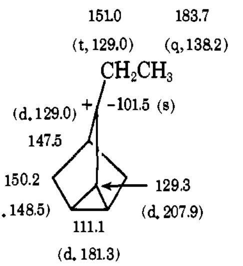
The corresponding ^{13}C nmr parameters of the 3-nortricyclyl cations were also obtained by use of the Fourier-transform ^{13}C nmr technique (all cmr shifts are in $\delta_{^{13}C}$ from capillary CS_2).



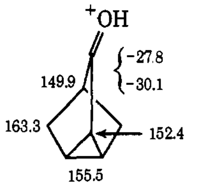
1-CH_3



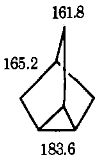
1-H



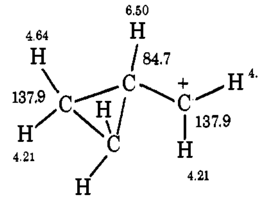
1-CH_2CH_3



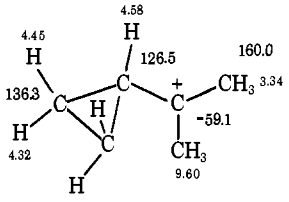
1-OH



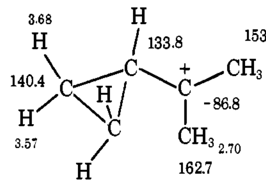
As the completely proton-decoupled cmr spectrum for the parent 3-nortricyclyl cation **1**-H shows only five resonances, the 3-nortricyclyl ion must be symmetrical. The carbenium carbon resonance was found at $\delta_{^{13}C}$ −64.8 ($\delta_{^{13}C}$ in ppm from external CS_2), which is only about 6 ppm more deshielded than that in ion **4** ($\delta_{^{13}C}$ −59.1); the cyclopropane ring carbons, however, are considerably more deshielded. Comparison of the cmr shifts of the carbenium carbon (sp^2) in ions **1**-H, **1**-CH_3, and **1**-C_2H_5 ($\delta_{^{13}C}$ −64.8, −99.5, and 101.5, respectively) with those of isopropyl (−125) and *tert*-butyl (−135) cations, respectively, indicate significant delocalization of positive charge by the cyclopropyl group. Models show that there is much more strain in the cyclopropane ring in cations **1** than in simple cyclopropylcarbinyl ions **3**–**6**. The pmr absorption for the secondary ^+CH proton in **1**-H (δ 11.3) is close to that of isopropyl cation (δ 13), yet the order of deshielding of the cyclopropyl hydrogens (and carbons the proton absorptions for the two different cyclopropyl positions (C_1, which is equal to C_6, and C_2)) in ion **1**-H is exactly reversed from those in the cyclo-



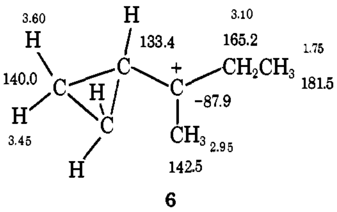
3



4



5



6

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[8] (a) V. Buss, R. Gleiter, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3927 (1971); (b) T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966); (c) Y. E. Rhodes and V. G. DiFate, *ibid.*, **94**, 7582 (1972); (d) C. U. Pittman and G. A. Olah, *ibid.*, **87**, 2998 (1965); (e) H. G. Richey, Jr., and J. M. Richey, *ibid.*, **88**, 4971 (1966); (f) V. W. Hückel, *J. Prakt. Chem.*, **28**, 27 (1965); (g) K. B. Wiberg, B. A. Andes, Jr., and A. J. Ashe, III, in ref 7h, Chapter 26; (h) D. Bethell and V. Gold, "Carbonium Ions, An Introduction," Academic Press, New York, N. Y., 1967.

[9] (a) G. A. Olah, P. D. Kelly, C. J. Jeuell, and R. D. Porter, *J. Amer. Chem. Soc.*, **92**, 2544 (1970); (b) G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968).

[10] (a) All alcohols were prepared from the ketone with appropriate Grignard reagents. They gave satisfactory microanalyses and had consistent nmr and infrared and mass spectra. (b) The two isomeric protonated forms of 3-nortricyclanone started to equilibrate at 0°. Detailed analysis of the pmr and cmr spectra will be reported in a forthcoming full paper.

propylcarbinyl cations. Both cmr and pmr parameters showed that the secondary cation **1**-H and the tertiary cations **1**-CH_3 and **1**-C_2H_5 are stabilized by charge delocalization the degree of which, as anticipated, is greater in the former.[10b] (The primary cyclopropylcarbinyl cation **3** has been observed exclusively as a bridged rapidly equilibrating nonclassical ion. In the secondary and tertiary analogs (**4–6**) bridging is far less advanced, and these ions are static carbenium ions. Bridging through σ delocalization is much further limited in the rigid 3-nortricyclyl system.) This is reflected by the more deshielded carbenium chemical shift in **1**. Steric factors and the rigidity of the system, therefore, are of great importance in dealing with the question of charge delocalization in carbocations.[6]

This point can be further emphasized considering the case of the completely σ-delocalized nonclassical 2-norbornyl cation **7**, the partially σ-delocalized 2-methyl-2-norbornyl cation **8**, and the classical 1-methylcyclopentyl cation **9**. The ^{13}C shifts for the carbenium centers for these ions were found at $+173$, -76, and -142 ppm, respectively.[11] The related carbenium cmr shifts for the *tert*-butyl cation **10** and the isopropyl cation **11** are $\delta_{^{13}C}$ -135 and -125, respectively.[12] The hyperconjugative stabilization believed to be involved in **10** and **11** is much smaller than the effects of σ delocalization.

A further well documented case in which bridging occurs when feasible geometry is attainable is the 7-norbornenyl cation **12** and the 7-norbornadienyl cation **13**, which were observed directly by spectroscopic studies.[13] The geometrical and electronic structures of ions **7** and **13** have been discussed using MO theory,[13c] and the unsymmetrical structure for ion **13** has been uniformly suggested.[13e]

The highly shielded carbonium centers in ion **7** ($\delta_{^{13}C}$ $+173$), in ion **12** ($\delta_{^{13}C}$ $+159.8$) and in ion **13** ($\delta_{^{13}C}$ $+157.6$) are clearly pentacoordinated, formed by bridging through two-electron, three-center bond formation. The contrast with the trivalent electron deficient carbenium centers is striking.

In conclusion it is clear that hyperconjugative stabilization (electronic "vertical stabilization") must always be followed by nuclear movement and bond reorganization, the degree of which can, however, greatly vary. σ delocalization is further a more important factor in stabilizing carbenium ions than hyperconjugation, except in extremely rigid systems. In the rigid 3-nortricyclyl cations bridging interaction between the strained C–C bond of the cyclopropane ring and the empty p orbital (σ–π interaction) is extremely limited. Thus it can be considered a more or less limiting example of charge delocalization with minimal nuclear movement. Based on experimental data we thus agree with recent theoretical conclusions by Hoffmann, *et al.*,[6a] on the strong conformational consequences of hyperconjugation, and that no dichotomy exists between charge delocalization in carbocations with or without significant nuclear reorganization (σ-bond delocalization or bridging *vs.* hyperconjugation or "vertical stabilization").

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(11) (a) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970); (b) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *ibid.*, **91**, 3958 (1969).

(12) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(13) (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 6883 (1969); (b) see also ref 3 for further discussion; (c) R. Hoffmann, *J. Amer. Chem. Soc.*, **86**, 1259 (1964); (d) H. O. Onorodnyk and D. P. Santry, *ibid.*, **91**, 4711 (1969); (e) ref 8h, p 259, and references therein.

Electrophilic Reactions at Single Bonds. XV.[1] The Ambident Nature of the Triphenylcarbenium Ion in Some Hydrogen Transfer Reactions Involving Carbon–, Boron–, and Aluminum–Hydrogen Bonds

Sir:

The triphenylcarbenium ion finds widespread application in hydrogen abstraction reactions, such as the preparation of tropylium salts from cycloheptatriene.[2] In spite of the preparative and theoretical importance of hydrogen abstraction with triphenylmethyl cation salts, the mechanism of these reactions remained practically unexamined. Since products obtained are generally triarylmethyl derivatives, the reactions have usually been assumed to proceed by a simple S_N1 mechanism, where attack by the nucleophile occurs at the central carbenium atom. However, it is generally agreed that the triphenylcarbenium ion is propeller shaped with considerable positive charge delocalized onto the three rings, corresponding to its resonance forms.

In our preceding work[3] we provided evidence that hydrogen abstractions from C–H bonds by alkyl carbenium ions proceed *via* electron donation by the single bond through two-electron, three-center bonded carbonium ions. Due to the steric crowding around the tertiary carbenium center in the triphenylcarbenium ion, the formation of a two-electron, three-center bond at the carbenium center seems questionable. However, since the charge is also delocalized onto the three rings, it seems reasonable to assume that nucleophilic attack can also take place on the more available and less hindered para or ortho ring positions.

No indication that ring sites may be involved in any hydrogen transfer reactions with the triphenylcarbenium ion has so far been reported in the literature. However, Winstein[4] reported that the reaction of the triphenylcarbenium ion with dimethylketene dimethyl acetal yielded product by attack exclusively at the para ring positions.

We now wish to present experimental evidence indicating the ambident nature of the triphenylcarbenium ion in some hydrogen transfer reactions. This observation has substantial importance in elucidating the mechanism of these reactions.

In order to establish the reactive carbenium sites of

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[1] Part XIV: G. A. Olah, P. Schilling, J. S. Staral, and Y. Halpern, *J. Amer. Chem. Soc.*, submitted for publication.

[2] H. J. Dauben, Jr., *et al.*, *J. Amer. Chem. Soc.*, **79**, 4557 (1957); *J. Org. Chem.*, **25**, 1442 (1960).

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