

237° (lit.¹⁰ mp 234–236°) in 95% yield, identical with authentic material. The overall yield in the entire sequence is 30% starting from cortisolone (1).

The conversion of 9 to cortisone acetate in 42% yield is already known,¹¹ and 9 can also be converted to prednisolone acetate.¹² Thus, our procedure accomplishes new syntheses of both of these compounds. Although the conversion of 1 to cortisone acetate involves a number of steps and proceeds in an overall yield of only 12.5%, this is largely because of the arbitrary choice of starting material. The remote functionalization reaction itself, by which the ring C functionality is introduced, proceeds in good yield and with excellent selectivity. In appropriate sequences it should furnish an attractive alternative to the microbiological functionalization methods currently in use.

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(11) R. M. Evans, J. C. Hamlet, J. S. Hunt, P. G. Jones, A. G. Long, J. F. Oughton, L. Stephenson, T. Walker, and B. M. Wilson, *J. Chem. Soc.*, 4356 (1956).

(12) Ch. Meystre, H. Frey, W. Voser, and A. Wettstein, *Helv. Chim. Acta*, **39**, 734 (1956).

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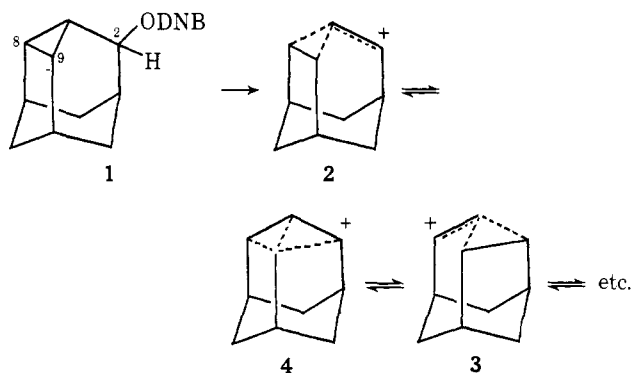
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Stable Carbocations. CLXXV.¹ 8,9-Dehydro-2-adamantyl Cations

Sir:

In an attempt to generate a cyclopropylcarbinyl cation that would be geometrically defined and of potential C_{3v} symmetry, Baldwin and Foglesong examined the solvolysis of 8,9-dehydro-2-adamantyl 3,5-dinitrobenzoate (1).² They found that solvolysis of 1



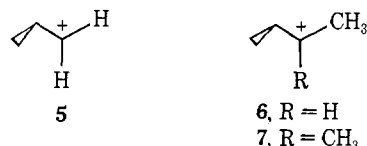
occurs with the marked rate acceleration characteristic of cyclopropylcarbinyl systems,³ and (*via* labeling studies) that the original 2, 8, and 9 positions of 1 achieve nearly complete equivalence during solvolysis.² Baldwin and Foglesong suggested the bridged, nonclassical representation 2 for the charge-delocalized 8,9-

(1) Part CLXXIV: G. A. Olah, H. C. Lin, and D. A. Forsyth, *J. Amer. Chem. Soc.*, in press.

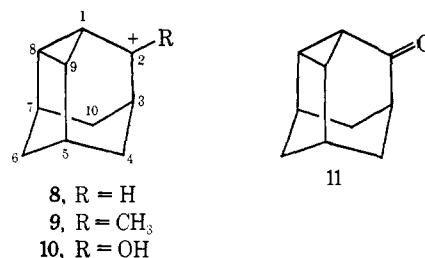
(2) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4303, 4311 (1968).

(3) For a review see K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 26.

dehydro-2-adamantyl cation and proposed that scrambling occurred *via* migration of the C₈–C₉ bond to give 3, etc. The ion-linking degenerate cyclopropylcarbinyl cations 2 and 3 were represented as bicyclobutonium ion 4.² Recently, we have studied by nmr the structures of cyclopropylcarbinyl cations 5–7 under stable ion



conditions.⁴ It is apparent from these studies that although the primary cyclopropylcarbinyl cation 5 is a rapidly equilibrating *nonclassical* ion, both the secondary (6) and tertiary (7) ions are *classical* ions with varying degrees of charge delocalization into the cyclopropane ring.⁴ In view of these studies, we now wish to report the direct observation of the 8,9-dehydro-2-adamantyl (8) and 2-methyl-8,9-dehydro-2-adamantyl (9) cations under stable ion conditions.



The parent secondary ion 8 and the tertiary ion 9 were prepared from the corresponding alcohols^{5,6} in $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}(\text{SO}_2)$ solutions at -120 and -78° , respectively. The pmr spectrum of ion 8 (Figure 1a) shows a deshielded doublet of doublets at δ 7.96 (three protons), a quartet at 4.92 (one proton), and two broad peaks at 3.20 and 2.60 (three and six protons, respectively). In contrast, the bridgehead proton H_1 in ion 9 (Figure 1b) is a triplet, since it is coupled with two equivalent protons (H_8 and H_9). The latter appear as a broad multiplet at δ 5.69. Moreover, the two H_6 methylene protons in 9 are nonequivalent and display an AB quartet centered at δ 2.60 ($J = 11.2$ Hz). Similarly, the two H_6 methylene protons in protonated 8,9-dehydro-2-adamantanone (10) (prepared from ketone 11⁵ in $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$ solution) appear as an AB quartet centered at δ 2.45 ($J = 11.0$ Hz).⁷

In order to further define the structures of the 8,9-dehydro-2-adamantyl cations, we have obtained their Fourier transform (FT) ^{13}C nmr spectra. The complete cmr parameters with resonance assignments for ions 8–10 are summarized in Table I. As is apparent, the cmr spectra of ions 8 and 9 are strikingly different. Consistent with a rapidly equilibrating system, the ^{13}C nmr spectrum of 8 shows only four carbon resonances. In contrast, tertiary ion 9 displays the behavior char-

(4) G. A. Olah, C. I. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **94**, 146 (1972).

(5) R. K. Murray, Jr., and K. A. Babiak, *Tetrahedron Lett.*, 319 (1974).

(6) R. K. Murray, Jr., and K. A. Babiak, *Tetrahedron Lett.*, 311 (1974).

(7) The hydroxy proton absorption at δ 12.84 in ion 10 is a sharp singlet at -80° , which gradually becomes broadened as the temperature rises and collapses with the acid peak at -30° . Upon cooling to -80° , the original singlet is reformed.

Table I. Proton and Carbon-13 Nmr Parameters of 8,9-Dehydro-2-adamantyl Cations^a

Skeletal position	R = H			R = CH ₃			R = OH		
	$\delta^1\text{H}$	$\delta^{13}\text{C}$	$J^{13}\text{CH}$	$\delta^1\text{H}$	$\delta^{13}\text{C}$	$J^{13}\text{CH}$	$\delta^1\text{H}$	$\delta^{13}\text{C}$	$J^{13}\text{CH}$
1	4.92, q ^b	85.1	186.2 (d)	4.25, t ^c	71.8	186.9 (d)	3.10, b	42.0	175.4 (d)
2	7.96, d-d ^b	157.0	177.7 (d)		274.4			240.9	
3	3.20, m	38.2	143.2 (d)	3.43, m	47.3	142.4 (d)	3.10, b	40.9	143.5 (d)
4, 10	2.60, m	49.3	134.2 (t)	2.58, m	47.3	134.3 (t)	2.68, m	42.8	137.9 (t)
5, 7	3.20, m	38.2	143.2 (d)	2.94, m	34.5	144.1 (d)	3.10, b	32.9	141.0 (d)
6	2.60, m	49.3	134.2 (t)	2.60, q ^d	47.3	134.3 (t)	2.45, q ^d	48.5	129.4 (t)
8, 9	7.96, d-d	157.0	177.7 (d)	5.69, m	100.7	181.5 (d)	4.42, m	67.8	173.9 (d)
OH							12.84, s		
CH ₃				3.35, s	33.5	127.7 (q)			

^a Proton and carbon-13 chemical shifts are in parts per million from external TMS (capillary); J values are in hertz; multiplicities: b = broad singlet, d-d = doublet of doublets, d = doublet, q = quartet, s = singlet, t = triplet. ^b $J_{1,2} = 7.0$ Hz, $J_{2,3} = 6.5$ Hz. ^c $J_{1,8} = 58$ Hz. ^d $J = 11.0$ Hz.

Table II. Carbon-13 Chemical Shifts for Cyclopropane and Carbenium Carbons in 8,9-Dehydro-2-adamantyl, Cyclopropylcarbinyl,^a 3-Nortricyclyl, and 2-Adamantyl^b Cations

R	Cyclopropylcarbinyl			3-Nortricyclyl			2-Adamantyl					
	C ₁	C ₂	C ⁺	C ₁	C ₂	C ⁺	C ₂	C ₁	C ⁺	C ₁	C ₉	C ⁺
H	85.1	157.0	157.0	66.6	59.1	250.8	86.3	111.6	258.5			
CH ₃	71.8	100.7	274.4	56.8	53.5	281.9	67.5	83.7	293.2	66.3	52.6	323.0
OH	42.0	67.8	240.9	21.2	11.4	208.8	41.3	38.2	223.8	47.5	44.2	267.1

^a The carbon shifts for the cyclopropylcarbinyl cations were originally obtained using the INDOR method.⁴ We have obtained slightly modified shifts for these ions by using the FT method and the present assignments are considered correct.^{9b} ^b For 2-adamantyl cations see G. A. Olah, G. Liang, and Gh. D. Mateescu, *J. Org. Chem.*, in press.

acteristic of a static tertiary carbenium ion. Thus, replacement of the hydrogen at the carbenium center in **8** by a methyl group apparently stops rapid equilibration in this system. Moreover, it should be noted that although ion **8** exists in a degenerate, rapidly equilibrating form, the $J^{13}\text{CH}$ coupling constants for the cyclopropane carbons in **8** and the static ion **9** are almost identical. Previously, we have found for nonclassical ions in other systems that the magnitude of $J^{13}\text{CH}$ is substantially different from that in classical ions.⁸ Consequently, nonclassical carbonium ion structures such as **4** can be excluded as the sole representation for the 8,9-dehydro-2-adamantyl cation. Furthermore, in Table II the cmr chemical shifts for the cyclopropane and carbenium carbons in ions **8–10** are compared with corresponding cyclopropylcarbinyl and 3-nortricyclyl cations. The striking similarities present in these sets of ions are apparent.

Thus, based on both ^1H and ^{13}C nmr data, we conclude that both secondary and tertiary 8,9-dehydro-2-adamantyl cations are of carbenium ion nature with the usual charge delocalization into the cyclopropane ring. Secondary ion **8** is represented as a partially delocalized, equilibrating classical ion and tertiary ion **9** is a static classical ion. Of course, equilibrating classical cyclopropylcarbinyl cations of **8** would result in the averaging of the C₈ and C₉ chemical shifts with that of the carbenium ion center. From the cmr data of static tertiary ion **9**, and the previously studied 3-nortricyclyl cations,⁹ the ^{13}C shift of a related static secondary

(8) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **96**, 189, 195 (1974); G. A. Olah, G. Liang, Gh. D. Mateescu, and J. L. Riemschneider, *ibid.*, **95**, 8698 (1973), and references cited therein.

(9) (a) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **95**, 3792 (1973); (b) G. A. Olah and G. Liang, *ibid.*, **96**, in press.

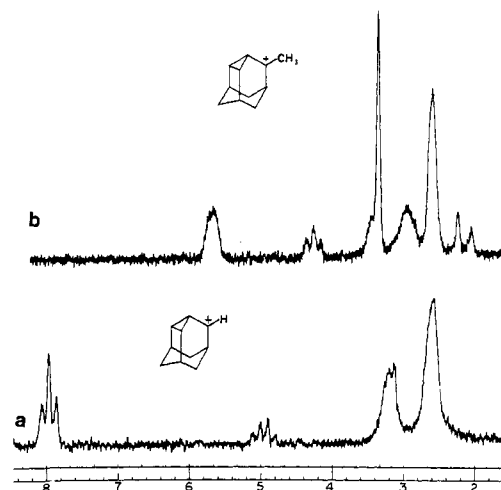
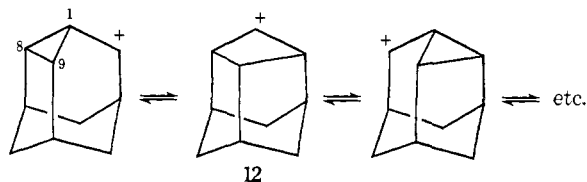


Figure 1. The 60-MHz pmr spectra of the (a) 8,9-dehydro-2-adamantyl and (b) 2-methyl-8,9-dehydro-2-adamantyl cations in $\text{FSO}_3\text{H-SO}_2\text{ClF}$ (SO_2) solution at -120 and -78° , respectively.

carbenium center can be estimated as ca. 235 ppm. Using this value and the estimated ^{13}C shift (125 ppm) of cyclopropane carbons C₈ and C₉, one obtains a calculated value of 162 ppm for C₁, C₈, and C₉ in **8**. The observed experimental value is 157.0 ppm.

Finally, examination of models of the 8,9-dehydro-2-adamantyl cation suggests that the C₈–C₉ bond in this ion is situated in an unfavorable alignment for a Wagner–Meerwein type migration (as suggested by Baldwin and Fogleson²). The degeneracy of the intermediate ion(s) observed in the solvolysis of 8,9-dehydro-2-adamantyl derivatives then would indicate that the intermediate ion formed is bridged. There is, however,

no certainty that any single formula can be utilized to represent in full the ion(s). Alternatively, the degenerate equilibration of the parent 8,9-dehydro-2-adamantyl cation may also be accounted for by an initial C₁-C₉ bond shift to give the 2,5-dehydro-4-protoadamantyl cation (**12**), followed by migration of



the C₈-C₉ bond,¹⁰ a situation very similar to the adamantyl-protoadamantyl rearrangement.¹¹

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(10) For a detailed discussion of the cyclopropylcarbinyl to cyclobutyl rearrangement see K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970).

(11) D. Lenoir, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **96**, 2138 (1974), and references cited therein.

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An "Alkylcarbene" Complex of Tantalum by Intramolecular α -Hydrogen Abstraction

Sir:

In the vast majority of transition metal carbene complexes the carbene carbon bears a heteroatom substituent.¹ Only rarely does it bear a proton.² No example of an alkylcarbene (or alkylidene) complex, which contrasts sharply with these trends, has been reported. A thermally stable neopentylidene complex of tantalum has now been isolated and is described here along with the results of some preliminary studies concerning the mechanism of its formation.

The reaction of 2 mol of neopentyl lithium with Ta[CH₂C(CH₃)₃]₃Cl₂³ in pentane at room temperature over a period of approximately 1 hr yields 2 mol of lithium chloride (isolated and analyzed), 1 mol of neopentane (measured and identified by gc-mass spectral methods), and a highly soluble, orange, crystalline

(1) (a) F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, **16**, 487 (1972); (b) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); (c) D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, **2**, 99 (1973); (d) C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, **95**, 5833 (1973); (e) A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *J. Amer. Chem. Soc.*, **95**, 5430 (1973).

(2) B. Cetinkaya, M. F. Lappert, and K. Turner, *J. Chem. Soc., Chem. Commun.*, 851 (1972).

(3) (a) This species was prepared from TaCl₅ and 1.5 mol of Zn[CH₂C(CH₃)₃]₂ in pentane. It has also been prepared by Mowat and Wilkinson from (CH₃)₃CCH₂MgCl and TaCl₅ in diethyl ether.^{2b} (b) W. Mowat and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1120 (1973).

compound with the formula Ta[CH₂C(CH₃)₃]₃[CHC(CH₃)₃] (**1**) in quantitative yield: ¹H nmr (τ) in C₆D₆, 8.09 (s, 1), 8.57 (s, 9), 8.85 (s, 27), 9.16 (s, 6); mass spectrum, parent ion at 464.2857 (calcd 464.2821); cryoscopic molecular weight in benzene, 472; mp (sealed capillary), 71°. *Anal.* Calcd for TaC₂₀H₄₈: C, 51.72; H, 9.33; Ta, 38.95. Found: C, 51.39; H, 9.31; Ta, 41.22. The reaction of 5 mol of (CH₃)₃CCH₂MgCl with TaCl₅ in diethyl ether also produces **1** which may be sublimed (essentially distilled) from the crude reaction mixture in ca. 50% isolated yield at 75° and <1 μ . The neopentylidene complex reacts violently with oxygen and moisture but may be stored indefinitely at room temperature in an inert atmosphere. Its reaction with 5 mol of DCl in hexane gave 3.7 mol of neopentane which was found by mass spectrometry to be a mixture of three parts of neopentane-*d*₁ and one part of neopentane-*d*₂.

Further proof of the essential structural features of **1** is provided by ¹³C nmr. In C₆D₆ the neopentylidene α -carbon is found at 250.1 ppm downfield from TMS, a shift which is at the high field end of the range of chemical shifts for α -carbon atoms in other carbenoid ligands.⁴ In the uncoupled spectrum this resonance is a doublet due to coupling to the single α -hydrogen ($J = 90$ Hz). Other resonances were similarly identified at 113.7 (neopentyl α -carbons, triplet, $J = 107$ Hz), 35.2 (neopentyl γ -carbons, quartet, $J = 124$ Hz), 34.9 (neopentylidene γ -carbons, quartet, $J = 124$ Hz), 35.3 (neopentyl β -carbons), and 47.0 ppm (neopentylidene β -carbon) downfield from TMS. It is unknown at this time whether the apparent equivalence of the neopentyl ligands in pseudo-tetrahedral **1** is due to insufficient stereochemical influence of a nonrotating neopentylidene moiety or to rotation about the metal-neopentylidene carbon bond.

The mechanism of formation of **1** was studied by deuterium labeling techniques. The reaction of Ta[CD₂C(CH₃)₃]₃Cl₂ with 2 mol of LiCH₂C(CH₃)₃ produced 1 mol of neopentane with an isotopic distribution shown in Table I (run A).⁵ The organometallic product was labeled at the carbenoid carbon to the extent of 38%.⁶ When a deficiency of lithium reagent was used (run B) only 0.5 mol of essentially identically labeled neopentane was formed and 0.5 mol of pure Ta[CD₂C(CH₃)₃]₃Cl₂ recovered.⁷ A large excess of lithium reagent (run C) produced neopentane with a slightly higher proton content. This result is believed to be outside experimental error and may indicate an exchange of as much as 0.5 mol of -CH₂C(CH₃)₃ for -CD₂C(CH₃)₃ during the course

(4) (a) C. G. Kreiter and V. Formáček, *Angew. Chem., Int. Ed. Engl.*, **11**, 141 (1972); (b) J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 2419 (1972); (c) D. J. Ciappinelli, F. A. Cotton, and L. Kruczyński, *J. Organometal. Chem.*, **50**, 171 (1973); (d) G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, **12**, 1071 (1973); (e) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Amer. Chem. Soc.*, **95**, 8574 (1973).

(5) Isotopic distributions were estimated from the intensities of the peaks resulting from loss of one methyl group from neopentane. The fragmentation patterns of pure (CH₃)₃CCH₂D, (CH₃)₃CCHD₂, and (CH₃)₃CCD₃ were checked and found to be straightforward. Due to limitations of the instrument and the method of calculation, the maximum absolute error in these figures is estimated to be $\pm 3\%$.

(6) The method of determination is one of numerous and varied reactions which will be disclosed in future publications.

(7) Exchange of one alkyl to the extent of 10% could have been observed by ¹H nmr.