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 $\sigma$ 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 $\sigma$-delocalized nonclassical 2-norbornyl cation **7**, the partially $\sigma$-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 $\sigma$ 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. $\sigma$ 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 ($\sigma$–$\pi$ 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 ($\sigma$-bond delocalization or bridging *vs.* hyperconjugation or "vertical stabilization").

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

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## 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 SN1 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

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

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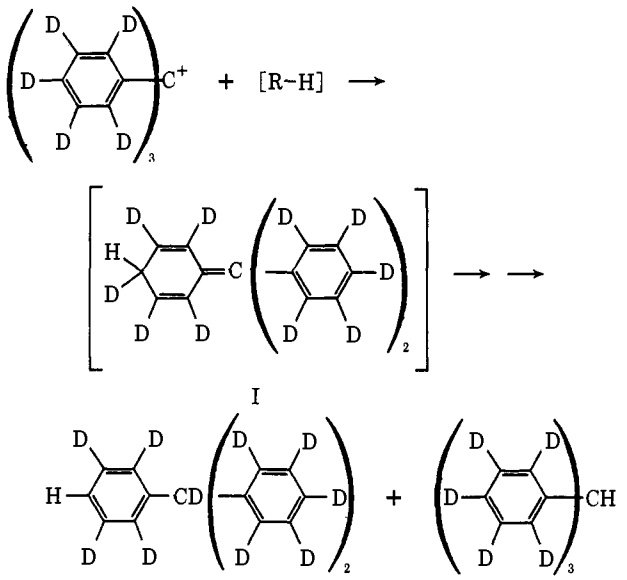
the triphenylcarbenium ion in its reactions with hydrogen donors, we studied the reactions of the perdeuteriotriphenylcarbenium ion (as the hexafluorophosphate salt prepared by the reaction of HF and $PF_5$ with perdeuteriotriphenylmethyl chloride, which in turn was prepared by the $AlCl_3$-catalyzed reaction of hexadeuteriobenzene with carbon tetrachloride)[5] with hydrogen (*i.e.*, protium) donors, such as lithium aluminum hydride, sodium borohydride, and cycloheptatriene (Table I). The reactions are conveniently followed by

**Table I.** Product Distribution in Hydrogen Transfer Reactions with Perdeuteriotriphenylcarbenium Ion

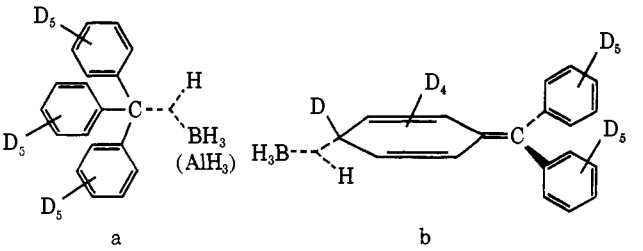
| R–H | Solvent | Rxn temp, °C | % $(C_6D_5)_3CH$ | % $(C_6D_5)_2(C_6D_4H)$-CD |
|---|---|---|---|---|
| $LiAlH_4$ | Ether | 25 | 90 | 10 |
| $NaBH_4$ | THF | 25 | 89 | 11 |
| Cycloheptatriene | $SO_2$ | −20 | 94 | 6 |
| Cycloheptatriene | $AsF_3$–$CH_2Cl_2$, 2:1 | 25 | 87 | 13 |

pmr spectrometry. If hydrogen abstraction occurs involving secondary ring carbenium ion sites, cyclohexadienylidenediphenylmethane (I) is formed, rearrangement of which gives triphenylmethane with at least partial protium content in the rings. The amount of abstracted protium remaining on the ring and the amount migrating to the aliphatic carbon depends on the relative migratory aptitude of protium *vs.* deuterium, *i.e.*, on the kinetic hydrogen isotope effect of the migration.



I

We have recently demonstrated that $AlH_4^-$ and $BH_4^-$ act as $\sigma$ donors in protolytic reactions.[6] The Al–H and B–H bonds are protonated, giving $AlH_5$ and $BH_5$ intermediates. If similar reactions of $AlH_4^-$ and $BH_4^-$ with trivalent carbenium ions are considered, the intermediates for the reactions will be triangular, two-electron, three-center bonded carbonium ions. The ambident triphenylcarbenium ion could thus give at least two such intermediates, a and b. The data summarized in Table I show 6–13% hydrogen incorporated into the rings, corresponding to 12–26% reaction at ring sites. This assumes no isotope effect (*i.e.*, equal migratory aptitude of H and D). If, however, a kinetic hydrogen isotope effect in the range of $k_H/k_D = 3$–4 is assumed (the work of McDonough and Dauben[7] showed that hydrogen abstractions by triphenylcarbenium ion generally show sizable hydrogen isotope effects), the reaction at ring sites becomes 36–48% to 48–100%.



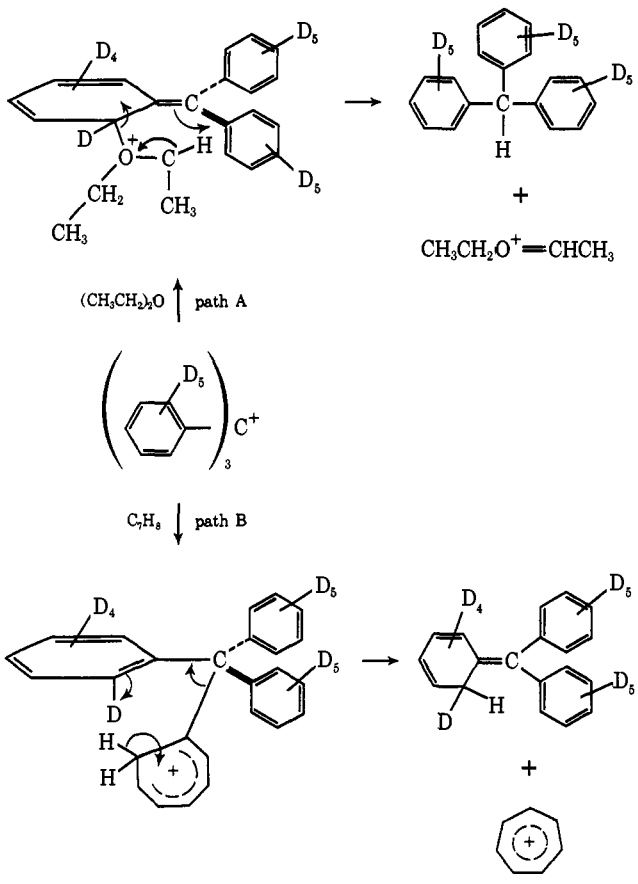
a b

There is no hydrogen transfer to the triphenylcarbenium ion from isoalkanes. We have also not observed hydrogen transfer between triphenylcarbenium ion and triphenylmethane. In contrast, trialkylsilanes are excellent hydrogen donors. The transferred hydrogen was found exclusively at the aliphatic carbon. The differing behavior may be due to the larger size of silicon and the weaker and longer Si–H bond, both contributing to exposing the Si–H bond more to attack by the tertiary carbenium center. Silicon can also be more easily distorted in the transition state.

The reaction mechanism of hydrogen abstraction from cycloheptatriene and other hydrogen donors containing $\pi$- or n-electron pairs must involve initial interaction of the much more nucleophilic $\pi$- or n-electron pairs with the triphenylcarbenium ion at one of its electron-deficient sites. This interaction may not lead to stable tritylated olefins or onium ion compounds, but it brings the hydrogen donor C–H bond into bonding distance from the ambident substrate. Subsequent reaction results in hydrogen migration to the triphenylcarbenium ion. Depending on the site of initial interaction, the hydrogen transfer can take place either at one of the ortho or para ring positions (path A) or at the central carbenium center (path B). Simple olefins such as 1-butene and 3-methyl-1-butene fail to react with the triphenylcarbenium ion. Olefin and triphenylcarbenium ion can be recovered from the reaction mixture. Many ethers, aldehydes, amines, and formic acid transfer hydrogen to the triphenylcarbenium ion. All n-electron containing hydrogen donors show hydrogen transfer exclusively to the aliphatic carbon. In these systems the primary interaction is considered to be that of n-donor, nonbonded electron pairs with the ring carbenium sites (path A).

The results are in accord with the general concept of carbocation reactivity[8] with C–H or B–H (Al–H) bonds acting as electron donors in the hydrogen transfer step. It also answers the question of how hydrogen transfer can take place between these bonds and the rather crowded tertiary triphenylcarbenium ion.

(5) C. R. Hauser and B. E. Hudson, Jr., "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 842.
(6) G. A. Olah, P. W. Westerman, Y. K. Mo, and G. Klopman, *J. Amer. Chem. Soc.*, **94**, 7859 (1972).
(7) L. M. McDonough, Ph.D. Thesis, University of Washington, 1960, advisor H. I. Dauben, Jr.
(8) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).



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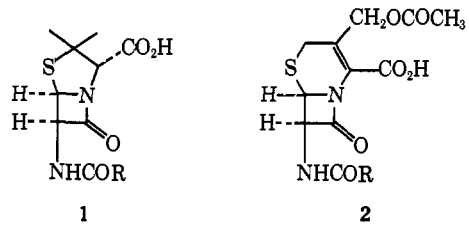
## Use of Chiral Isopropyl Groups in Biosynthesis. Synthesis of (2*RS*,3*S*)-[4-$^{13}$C]Valine

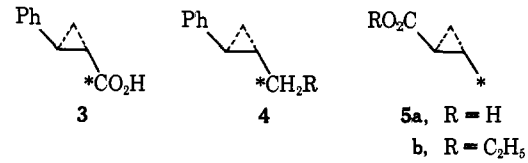
*Sir:*

In spite of extensive efforts over the past two decades, the detailed biosynthetic pathway to the β-lactam antibiotics, penicillin and cephalosporin, is still unknown.[1] The evident relationship of the penam (**1**) and 3-cephem



(**2**) derivatives to the amino acids L-valine and L-cysteine has been established by appropriate incorporation experiments.[2] Since L-valine has been successfully incorporated into both systems, **1** and **2**,[2] we decided to use a valine with a chiral isotopic label ($^{13}$C) at the 4 position as a probe for the stereochemical fate of this isopropyl group, during conversion to the β-lactam products.

We have chosen the stereospecific, reductive opening of *trans*-2-methylcyclopropanecarboxylic ester (**5b**),[3] of known absolute configuration, as the method for generation of the chiral isopropyl group. Thus, carboxylation in THF of 2-phenylcyclopropylmagnesium bromide with [$^{13}$C]carbon dioxide[4] at −60° gave after esterification (diazomethane), equilibration to the trans isomer (potassium *tert*-butoxide in refluxing *tert*-butyl alcohol), and hydrolysis in methanolic potassium hydroxide at reflux, [$^{13}$C]carboxyl-labeled *trans*-2-phenylcyclopropanecarboxylic acid (85%), which after three recrystallizations as the quinine salt yielded (+)-*trans*-(1*S*,2*S*)-([1-$^{13}$C]carboxy)-2-phenylcyclopropane (**3**) of 100% optical purity, $[\alpha]^{22}D$ +314.0° (*c* 1.776, EtOH).[5] Reduction of the derived methyl ester (diazomethane)



with lithium aluminum hydride in ether at 0° gave the alcohol **4** (R = OH, 95%), $[\alpha]^{22}D$ +89.3° (*c* 3.72, EtOH),[6] which upon mesylation at −25° in methylene chloride and reduction (lithium aluminum hydride, ether, −40°) gave (+)-*trans*-(1*S*,2*S*)-([1-$^{13}$C]methyl)-2-phenylcyclopropane (69%) (**4**, R = H), bp 76° (20 mm), $[\alpha]^{25}D$ +96° (*c* 3.72, EtOH). Destructive ozonization of this hydrocarbon in carbon tetrachloride at room temperature gave after distillation (47%) (+)-*trans*-(1*S*,2*S*)-([1-$^{13}$C]methyl)-2-cyclopropanecarboxylic acid (**5a**), bp 98° (18 mm), $[\alpha]^{19}D$ +99.2° (*c* 3.09, EtOH). Following esterification (diazoethane) and distillation (+)-*trans*-(1*S*,2*S*)-([1-$^{13}$C]methyl)-2-cyclopropanecarboxylic acid ethyl ester (**5b**), bp 80° (70 mm), was obtained (64%): $^1$H nmr ($CDCl_3$)[7] δ 1.14 (dd, $J(^{13}C-^1H)$ = 128 and $J(^1H-^1H)$ = 5.5 Hz). Reductive cleavage of this substance with lithium in liquid ammonia (−78°) gave after preparative vpc pure (3*S*)-[4-$^{13}$C]-3-methylbutyric acid ethyl ester (**6**) in 18% yield;[8] $^1$H nmr ($CDCl_3$) δ 0.96 (m, $J(^{13}C-^1H)$

(1) P. A. Lemke and D. R. Brannon in "Cephalosporins and Penicillins," E. H. Flynn, Ed., Academic Press, New York, N. Y., 1972, p 370.

(2) (a) H. R. V. Arnstein and M. E. Clubb, *Biochem. J.*, **65**, 618 (1957); (b) H. R. V. Arnstein and P. T. Grant, *ibid.*, **57**, 353, 360 (1954); (c) S. C. Warren, G. G. F. Newton, and E. P. Abraham, *ibid.*, **103**, 902 (1967); (d) E. P. Abraham, G. G. F. Newton, and S. C. Warren, *I. A. M. Symp. Appl. Microbiol., Tokyo*, **6**, 79 (1964).

(3) The literature contains a number of examples of the stereospecific, reductive cleavage of acylcyclopropanes: *e.g.*, H. O. House and C. J. Blankley, *J. Org. Chem.*, **33**, 48 (1968); W. G. Dauben and E. J. Deving, *ibid.*, **31**, 3794 (1966).

(4) Obtained from Monsanto Research Corp., Miamisburg, Ohio, 92% isotopic purity.

(5) The optically pure acid (**3**) is reported to have $[\alpha]^{22}D$ +311.7° (*c* 1.78, EtOH) by Y. Inouye, T. Sugita, and H. M. Walborsky, *Tetrahedron*, **20**, 1695 (1964). These authors have correlated this substance with *trans*-1,2-dimethylcyclopropane, of known configuration; *cf.* W. von E. Doering and W. Kirmse, *Tetrahedron*, **11**, 272 (1960).

(6) This sequence is essentially that described by T. Sugita and Y. Inouye, *Bull. Chem. Soc., Jap.*, **39**, 1075 (1966).

(7) All spectra are 100 MHz; unless mentioned otherwise, only resonances resulting from direct interaction of $^{13}$C and $^1$H are reported in this communication.

(8) Examination of the reaction mixture by vpc indicated a yield of 40–50% of the desired product. All substances have been examined by vpc and shown to be homogeneous.