(70.0%) of colorless product, bp 64–67° (45 mm) (lit. bp 65° (45 mm),[10] 65.5–66° (50 mm[11])).[24] The ^{1}H nmr spectrum of the product (CCl_4) showed a quartet at 4.47 ppm ($J_{\mathrm{H,F}} = 8.3$ Hz); the ^{19}F spectrum showed a triplet at 12.88 ppm. The ir spectrum (cap film) showed strong absorptions at 1380 and 1180 cm^{-1} ($-SO_2-$).

Preparation of Tresylates. To an approximately 0.2 *M* solution of the alcohol in methylene chloride[25] solution containing a 15% molar excess of triethylamine at −15 to −25° (ice-salt or ice-methanol bath) was added a 10% excess of tresyl chloride over a period of 15–30 min.[26] Stirring for an additional 10–15 min completed the reaction. The reaction mixture was transferred to a separatory funnel, and washed with ice water, cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine. Drying the methylene chloride solution over magnesium sulfate followed by solvent removal gave the tresylate, usually as a colorless oil.[27] ^{1}H nmr spectra of tresylate esters show a quartet at about 3.9 ppm ($J_{\mathrm{H,F}} = 8.8$ Hz).

Acknowledgment. This research was supported in part by Grant AT(11-1)-1008 from the U. S. Atomic Energy Commission (Document No. COO-1008-14).

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[23] Excess chlorine, hydrogen chloride, cyanogen chloride, and most of the trifluoroacetic acid pass through the 0° trap. An efficient liquid nitrogen trap following the 0° trap is recommended. Do not distill to dryness; although we have had no difficulty, a possibility of peroxide formation during the chlorination exists.

[24] If too little water is present in the reaction mixture a considerable fraction, bp 45–50° (45 mm), is obtained. The ^{1}H nmr spectrum of this fraction (CCl_4) shows a quartet at 4.24 ppm ($J_{\mathrm{H,F}} = 9.5$ Hz). This material is believed to be the corresponding sulfinyl chloride and may be obtained in good yield if only 1 mole of water/mole of thiocyanate is used.

[25] Depending on the solubility of the alcohol and product, tresylate, pentane, or hexane may also be used as solvent.

[26] Triethylamine was distilled from phthalic anhydride, dried over potassium hydroxide pellets, and redistilled. Methylene chloride was taken from a freshly opened bottle. Anhydrous reaction conditions were maintained.

[27] The more reactive the product tresylate, the more slowly the tresyl chloride was added and the lower the temperature. For very reactive systems the glassware used in the work-up was prechilled and the temperature of the tresylate was never allowed to exceed 0°. Occasionally, it is necessary to omit the bicarbonate washes. In this case the product must be used at once as decomposition on storage is rapid

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Stable Carbocations. CXIX.[1] Carbon-13 Nuclear Magnetic Resonance Spectroscopy Study of the Structure of Allyl Cations

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Received November 30, 1970

Abstract: The structure of a series of substituted allyl cations was studied by ^{13}C nmr spectroscopy. The results indicate little 1,3-interaction in most allyl cations. However, the 4-chloro-1,2,3,4-tetramethylcyclobutenyl cation does show significant 1,3-interaction. A novel reaction, the generation of an allyl cation by hydride abstraction from an olefin, is also reported.

The structure of the allyl cation and its substituted derivatives has been the subject of extensive studies.[3] Theoretical calculations give conflicting answers as to whether structure **1** (little or no 1,3-interaction) or structure **2** (substantial 1,3-interaction) is to be preferred.[4,5] While proton magnetic resonance (pmr) and uv data have been interpreted in terms of structure **2**,[6] chemical evidence has been inconclusive. For example, a recent study of the solvolysis of secondary allylic chlorides indicates that the transition state in the solvolysis resembles **1** rather than **2**,[7] while a solvolysis study in the cyclobutyl ring system (where, as Katz[6a] has pointed out, steric constants should lead to abnormally large 1,3-interaction) indicates that the transition state resembles **2**.[8] In view of the disparate results and the known sensitivity of ^{13}C nmr chemical shifts to charge density, we felt that a ^{13}C magnetic resonance (cmr) study would help elucidate the structure of the allyl cations. In the course of this work we have also found a new method for the generation of allyl cations, *i.e.*, hydride abstraction from an olefin.


1


2

Results

Generation of Allyl Cations and Their Nmr Studies. The allyl cations studied were generally prepared from the appropriate cyclopropyl alcohols *via* ionization in SbF_5–SO_2 or SO_2ClF solution or by ionization of allylic halides or alcohols. All had pmr spectra identical with those previously reported.[6a,9,10]

Addition of 1,2,5-trimethylcyclopentan-2-ol (**4**) to a solution of SbF_5 in SO_2 at −78° yielded ion **3g** with pmr

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[1] Part CXVIII: G. A. Olah, *J. Amer. Chem. Soc.*, in press. Note change in title of series of publication to "Stable Carbocations," instead of previously used "Stable Carbonium Ions." Carbonium ions, as outlined in part CXVIII, are pentacoordinated ions as contrasted with trivalent carbenium ions; the generic naming of carbocations (in accordance with the naming of carbanions) seems to be appropriate.

[2] (a) National Institutes of Health Postdoctoral Research Fellow; (b) Postdoctoral Research Associates.

[3] For a review, see N. C. Deno in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. II, Interscience, New York, N. Y., 1967, pp 783–785.

[4] I. M. Simonetta and E. Heilbronner, *Theor. Chim. Acta*, **2**, 228 (1967).

[5] D. T. Clark and D. R. Armstrong, *ibid.*, **13**, 365 (1969).

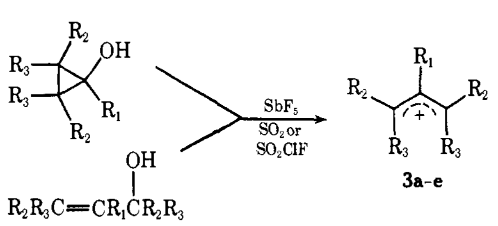
[6] (a) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964); (b) G. A. Olah and M. B. Comisarow, *ibid.*, **86**, 5682 (1964).

[7] R. H. Griffin and J. G. Jewett, *ibid.*, **92**, 1104 (1970).

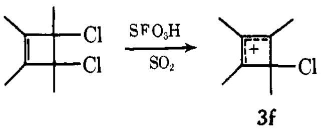
[8] E. F. Kiefer and J. D. Roberts, *ibid.*, **84**, 784 (1962).

[9] (a) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, **85**, 2995 (1965); (b) G. A. Olah and M. Calin, *ibid.*, **90**, 4672 (1968).

[10] G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 6082 (1968).



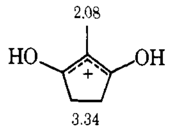
3a-e



3f

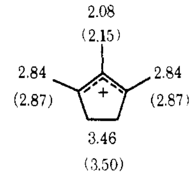
a, $R_1 = R_2 = R_3 = CH_3$
b, $R_1 = H; R_2 = R_3 = CH_3$
c, $R_1 = R_2 = CH_3; R_3 = H$
d, $R_1 = R_2 = H; R_3 = CH_3$
e, $R_1 = C_6H_5; R_2 = CH_3; R_3 = H$

absorptions at δ 3.46 (4 H), 2.84 (6 H), and 2.08 (3 H). The multiplets at 3.46 and at 2.84 are broadened and coupled as determined by decoupling experiments; the ion was stable to −30°. A similar spectrum was obtained with SbF_5–SO_2ClF with absorptions at 3.50, 2.87, and 2.12. Comparison of ion **3g** with published allylic ions such as **5** and **6** indicates that **3g** is the 1,2,3-trimethylcyclopentenyl cation.[9] Comparison of the ^{13}C chemical shifts for ion **3g** with those of other ions examined (Table I) also supports this structure. The same ion **3g** was also obtained from 1,2,3-trimethylcyclopent-1-ene (**7**) in SbF_5–SO_2ClF at −100°.



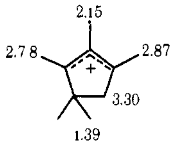
5

SbF_5-SO_2



3g

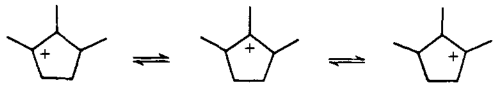
SbF_5-SO_2 (SbF_5-SO_2ClF)



6

96% H_2SO_4

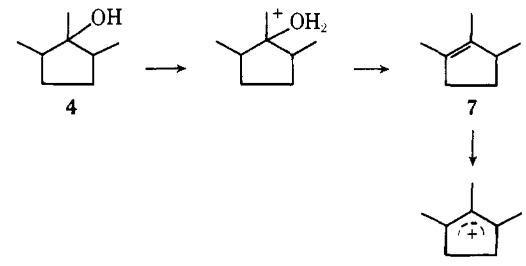
Competitive protonation of the olefin occurs to a small extent in SbF_5–SO_2ClF, and to a greater extent in FSO_3H–SO_2ClF, to yield the rapidly equilibrating 1,2,3-trimethylcyclopentyl cation (**8**). This ion was also obtained from 1,2,3-trimethylcyclopentane in SbF_5–SO_2ClF and has pmr absorptions of δ 3.8 (>CH), 2.9 ($-CH_2$), 2.61 ($C_{1,3}$–CH_3), and 2.38 (C_2–CH_3) at −80°.



8

We wish to propose that the mechanism for the formation of ion **3g** from 1,2,5-trimethylcyclopentan-2-ol (**4**) involves initial protonation of the hydroxyl group followed by dehydration to the olefin **7** and hydride abstraction to ion **3g** as shown in Scheme I. This mechanism is supported by the fact that olefin **7** does yield only ion **3g** on treatment with either SbF_5–SO_2ClF[11] or FSO_3H–SO_2ClF. This is the first reported case of hydride abstraction from an olefin to yield an allylic cation.[12]

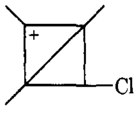
Scheme I



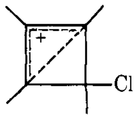
The ^{13}C chemical shifts of the allyl cations studied and some related reference olefins are shown in Table I.[13] The cmr spectra were obtained by the indor method. The room temperature cmr shifts of the related olefins previously reported[14] differ from our shifts measured in SO_2ClF at −70° by not more than 0.6 ppm. Friedel and Retcofsky have found that alkyl substituents have a predictable influence on the ^{13}C chemical shifts of olefins. Where ambiguities existed, assignments of cmr shifts in the reference olefins were made on the basis of their correlations.

Discussion

Column 7 of Table I shows the differences ($\Delta\delta C_2$) between the ^{13}C chemical shifts of C_2 in the allyl cations and the corresponding carbon ($\delta^{13}C$) in the appropriate reference olefin. For ions **3a–e** and **3g** these differences are between 9 and 24 ppm while for ion **3f** the difference is 34.2 ppm. Typically, a positively charged carbon will cause inductively a deshielding of between 5 and 15 ppm in a neighboring carbon atom.[15] Deshielding may be as large as 26 ppm as in the adamantyl cation.[16] Thus the deshielding of C_2 in the allyl cations **3a–e** and **3g** may readily be explained as due to the inductive effect of the neighboring carbon atoms without having to postulate significant 1,3-interaction. On the other hand, the deshielding at C_2 in ion **3f** indicates that structure **9** is a significant resonance contributor to ion **3f**. Thus ion **3f** is best represented by structure **10**.



9



10

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(11) The question can be raised: is the hydride abstraction affected by SbF_5 itself, or by the strong protic superacid which is always present to some extent in "neat" SbF_5, due to unavoidable impurities? It has been known for some time in our laboratories that SbF_5 (neat or diluted with SO_2ClF) is a very suitable solvent medium to form stable carbonium ions from hydrocarbons. These reactions are, however, always accompanied by formation of some H_2 and/or proteolytic C–C bond cleavage reactions. H_2 formed can reduce antimony pentafluoride to antimony trifluoride and hydrogen fluoride. Thus hydride abstraction by SbF_5 is not necessarily considered to take place by the Lewis acid itself, but as a protolytic process by SbF_5 and ubiquitous proton acid impurities with increasing amounts of HF formed *via* reduction of SbF_5 as the reaction proceeds.

(12) Deno[3] has referred to unpublished results in which cyclic olefins were oxidized to allyl cations by 20% SO_3, 80% H_2SO_4. However, no experimental details were presented.

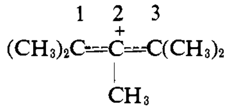
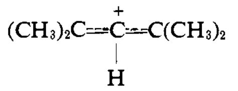
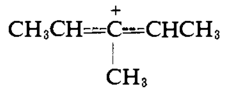
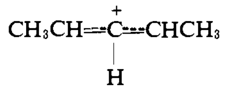
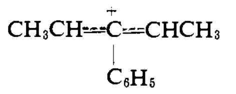
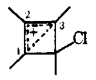
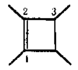
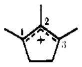
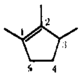
(13) We have previously reported the observation of the pmr spectra of the allyl and 2-methylallyl cations from ionization of the corresponding fluorides in SbF_5–SO_2 solution.[6b] However, we have been unable to generate these ions in sufficient concentration to obtain their cmr spectra. Attempts to generate sufficiently concentrated solutions of these ions from the corresponding allylic alcohols, cyclopropanols, allyl chloroformates, cyclopropyl acetates and tosylates, and cyclopropyloxocarbonium ions were also unsuccessful.

(14) R. A. Friedel and H. L. Retcofsky, *J. Amer. Chem. Soc.*, **85**, 1300 (1963).

(15) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

(16) G. A. Olah and Gh. D. Mateescu, to be published.

Table I. Cmr Chemical Shifts of Allyl Cations and Related Reference Olefins in SO_2ClF at −70°

Ion		$^{13}C^a$		Reference olefin	$\delta^{13}C_R{}^b$	$\Delta\delta C_2{}^c$
		C_1,C_3	C_2			
 $\overset{1}{(CH_3)_2C}{=}\overset{\overset{2}{+}}{\underset{CH_3}{C}}{=}\overset{3}{C}(CH_3)_2$	**3a**	−31.3	+41.3	$\overset{1}{(CH_3)_2C}{=}\overset{2}{C}(CH_3)\overset{3}{C}HCH_3)_2$	+54.4	−13.1
 $(CH_3)_2C{=}\overset{+}{\underset{H}{C}}{=}C(CH_3)_2$	**3b**	−41.0	+51.6	$(CH_3)_3C{=}CHCH(CH_3)_2$	+61.4	−9.8
 $CH_3CH{=}\overset{+}{\underset{CH_3}{C}}{=}CHCH_3$	**3c**	−36.0	+33.2	$CH_3CH{=}C(CH_3)CH_2CH_3$	$+56.8^{d,e}$	23.6
 $CH_3CH{=}\overset{+}{\underset{H}{C}}{=}CHCH_3$	**3d**	−46.6	+41.9	$CH_3CH{=}CHCH_2CH_3$	-59.5^e	−17.6
 $CH_3CH{=}\overset{+}{\underset{C_6H_5}{C}}{=}CHCH_3$	**3e**	−42.7	+31.8	$CH_3CH{=}C(C_6H_5)CH_2CH_3$	+48.5	−16.7
	**3f**	−1.6	+16.9		+51.1	−34.2
	**3g**	−54.3	+37.4		+53.0	−15.6

^{a} In parts per millions from CS_2. ^{b} $\delta^{13}C_R$ is the chemical shifts of C_2 in the substituted pentenes and C_2 in both 1,2,5-trimethylcyclopentene and 1,2,3,4-tetramethylcyclobutene in parts per millions from CS_2. ^{c} $\Delta\delta$ is the difference between the cmr chemical shift of C_2 in the allyl cations and $\delta^{13}C_R$. ^{d} Average of +56.4 ppm and 57.1 ppm for the cis and trans isomers. ^{e} Reference 12.

These conclusions are borne out by calculations of the charge density at C_2. Previously a pmr deshielding of 0.3 ppm of the methyl group at C_2 in the pentamethylallyl cation (**3a**) relative to an assumed value of 1.7 ppm for the chemical shift of a methyl group attached to an sp^2 center has been interpreted to mean that there is significant 1,3-interaction in allyl cations and has led to a calculated charge density of 0.13 at C_2 in **3a**.[4] Similar calculations for the hexamethylcyclopentenyl and the pentamethylcyclobutenyl cations based on deshieldings of the methyl group at C_2 of 0.69 and 0.91 ppm, respectively, give charge densities at C_2 of 0.20 and 0.28 unit of positive charge, respectively.[6a] However, assuming an average ^{13}C chemical shift of +100 in the reference olefins for the carbons corresponding to C_1 and C_3 in the allyl cations[17] leads to a calculated charge density of 0.048 unit of positive charge at C_2 for both the pentamethylallyl cation (**3a**) and the 1,2,3-trimethylcyclopentenyl cation (**3g**). These calculated charge densities indicate little, if any, 1,3-interaction. By contrast, ion **3f** has a charge density of 0.144 unit of positive charge at C_2. Furthermore, deshieldings of 0.3–1.0 for methyl groups attached to C_2 in unsubstituted allyl cations can easily be explained on the basis of an inductive effect due to charge accumulation at C_1 and C_3 (*e.g.*, the protonation of ethanol causes a deshielding of 1.0 ppm for the methyl group). The fact that the methyl group at C_2 in ion **3f** is deshielded by only 0.65 ppm as well as the differences between the charge densities calculated from pmr and cmr data are indications that proton magnetic resonance is a poor method for determining charge distributions in these ions.

It is interesting to note that, with the exception of ion **3f**, the substituent correlations that Friedel and Retcofsky[14] established for olefins may be used without modification in estimating the cmr shift of C_2 in allylic cations while estimates of the C_1 and C_3 ^{13}C chemical shifts requires use of correction factors significantly larger than those used for alkenes. This fact indicates also that there is little charge density at C_2 in ions **3e–e** and that ion **3f** is substantially different from the other ions studied.

Thus, in contrast to previously reported spectroscopic data,[6] cmr spectroscopy demonstrates that structure **1** is generally the best representation for allyl cations. Where steric constraints make overlap between p orbitals on C_1 and C_3 more favorable, as in the cyclobutenyl system of Katz,[6a] structure **2** becomes the better representation. Because of this overlap, ion **3f** must be considered, as pointed out by Winstein, a homocyclopropenyl cation, *i.e.*, a monohomoaromatic ion.[18]

Experimental Section

Nmr Spectra. Solutions of the ions were prepared as described previously.[19,20] The proton spectra were obtained at 100 MHz using a Varian Associates Model HA-100 nmr spectrometer. ^{13}C indor spectra were obtained as described previously.[21]

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[17] In general sp^2 carbons have ^{13}C chemical shifts between +50 and +85 ppm and sp^3 carbons allylic to double bonds have ^{13}C chemical shifts between +150 and +180.[13] Assuming an average ^{13}C chemical shift greater than +100 ppm leads to lower charge densities at C_2.

[18] S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

[19] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967).

[20] G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968).

[21] G. A. Olah and A. M. White, *ibid.*, **91**, 2943 (1969).

1,2,5-Trimethylcyclopentanol was prepared from 2,5-dimethylcyclopentanone and CH$_3$MgI. 2,5-Dimethylcyclopentanone (12.6 g) gave 7.0 g (48%) of 1,2,5-trimethylcyclopentanol, bp 45° (4.5 mm) [lit.[22] bp 176.6° (749 mm)].

1,2,3-Trimethylcyclopentene. 1,2,5-Trimethylcyclopentanol (2 g) was added to ZnCl$_2$ (2 g) and the mixture was heated to 160°. The olefin (bp 121°)[23] was distilled from the reaction mixture as it formed giving 1.5 g (87.2%).

Acknowledgment. Support of this work by grants from the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

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(22) A. V. Koperina and B. A. Kazanskii, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 302 (1968).

(23) W. A. Noyes and C. E. Burke, *J. Amer. Chem. Soc.*, **34**, 174 (1912).

The Preparation and Reactions of Cyclopropylallyl Cations

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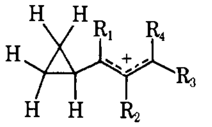
Contribution from the Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada. *Received November 16, 1970*

Abstract: Cyclopropylallyl cations rearrange at measurable rates to give a variety of cyclohexenyl and cyclopentenyl cations. The reaction was studied in three different acid solvents, H$_2$SO$_4$, FSO$_3$H, and FSO$_3$H–SbF$_5$, the "acidity" increasing greatly in the order given. The exact products are quite different in each solvent and a mechanism is proposed to account for the product cations actually observed.

The 3-cyclopropylallyl cations (Ia–c) can all be directly observed at moderately low temperatures (*e.g.*, −50°). However, at higher temperatures each disappears by a clean first-order kinetic process.

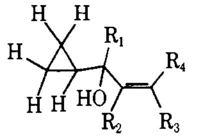


Ia, R$_1$ = R$_3$ = R$_4$ = CH$_3$; R$_2$ = H
b, R$_1$ = R$_2$ = R$_3$ = CH$_3$; R$_4$ = H
c, R$_1$ = R$_2$ = R$_3$ = R$_4$ = CH$_3$

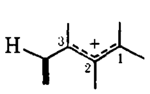
In this paper, we present a detailed study of this system, including the characterization of the cyclopropylallyl cations, rate measurements in three different acid solvents, the measurement of activation parameters, and a complete product characterization study.

Ions of type I have been reported only in cases where the allylic system is part of a five- or six-membered ring, *i.e.*, cyclopropyl-substituted cyclopentenyl or cyclohexenyl cations.[1] These ions, in marked contrast to those studied in this work, are "stable" at room temperature in concentrated acid solvents.[2]

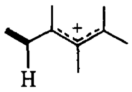
The Cyclopropylallyl Cations. Each cyclopropylallyl cation was prepared from the corresponding alcohol (IIa, b, c) and a strong acid solvent in the usual way. Three different strong acid solvents, FSO$_3$H, H$_2$SO$_4$, and FSO$_3$H–SbF$_5$ (1:1 or 4:1), these covering a wide range of "acid strength," were used. All reactions have been carried out *in situ*, in most cases employing 10% w/v[3] solutions. Table I lists the nmr assignments for the three ions Ia–c. The cyclopropyl ring protons appear as broad peaks partially obscured by the methyl resonances and no attempt has been made to analyze these. Only in Ib is it possible to easily assign the protons of the allyl portion. In Ia, the assignment is based partly on a comparison of the spectrum with that from Ib and partly on an analysis of the reversible temperature dependence of the chemical shifts of the protons, tabulated in Table II. Relative to three separate reference signals, one methyl resonance shifts to higher fields as the temperature increases, one shifts to lower fields, and one remains constant. In addition, the C2 proton shifts strongly to higher fields. To interpret this temperature effect one must consider the possible conformations of the ion. With a cyclopropyl ring in a bisected conformation, there are four possibilities, arbitrarily labeled A, B, C, and D.[4] One



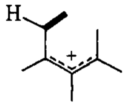
IIa, R$_1$ = R$_3$ = R$_4$ = CH$_3$; R$_2$ = H
b, R$_1$ = R$_2$ = R$_3$ = CH$_3$; R$_4$ = H
c, R$_1$ = R$_2$ = R$_3$ = R$_4$ = CH$_3$



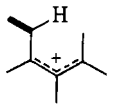
A



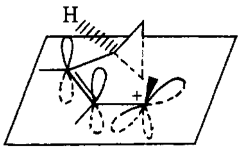
B



C



D



E

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(1) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965).

(2) The term "stable," as used in this paper, means that the ions have an extended existence at 25° in the order of days or weeks.

(3) Weight of alcohol in grams per volume of acid in milliliters.

(4) It is questionable whether any of the conformations of Ia or Ic are completely planar because of the steric repulsion of the two "upright" substituents.