alumina. Petroleum ether eluted 1.2 g of olefin V, mp 58–59° after recrystallization from methanol. The infrared spectrum was free of carbonyl absorption and the nmr spectrum consistent with structure V, showing the nonequivalent vinyl protons at 313 and 337 cps ($J \sim 2.5$ cps) and the C_{12}-methylene protons centered at *ca.* 260 cps (above the coalescence temperature).

Anal. Calcd for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.07; H, 5.78.

7-Isopropylidene-7,12-dihydropleiadene (VI). Following the above procedure for preparation of V, excess isopropyllithium was treated with 7(12H)-pleiadenone in ether–tetrahydrofuran. The crude product still contained some unidentified ketone (possibly from conjugate addition) but chromatography on alumina successfully separated the hydrocarbon VI from more polar materials by elution with petroleum ether. Recrystallization from methanol gave the analytical sample, mp 103–104°.

Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.21; H, 6.82.

The nmr spectrum showed two methyl singlets at 103 and 113 cps and the nonequivalent C_{12} protons as an AB spectrum centered at 266 cps with $\delta_{AB} = 74$ cps and $J_{AB} \sim 14$ cps.

7,12-Dihydro-8,11-dimethylpleiadene (IV). The same sequence of steps were used as in the preparation of I from 8-benzoyl-1-naphthoic acid.

8-(2,5-Dimethylbenzoyl)-1-naphthoic acid[33] was subjected to Huang–Minlon reduction, as above, giving only *ca.* 5% of the reduced acid (confirmed by infrared spectra). The latter was not characterized further but cyclized directly in hot polyphosphoric acid to 8,11-dimethyl-7(12H)-pleiadenone, $\nu_{\max}^{>=O}$ 1670 cm⁻¹. The ketone was subjected to mixed hydride reduction (as in preparation of I and II), giving IV as white needles (from methanol–benzene), mp 190–191°.

Anal. Calcd for $C_{10}H_{18}$: C, 93.0; H, 7.03. Found: C, 93.05; H, 6.90.

The nmr spectrum at 30° showed the methyl signal at 143 cps and the C_7 and C_{12} methylene protons as a broad hump centered at 265 cps, which sharpened into an AB quartet, $\delta_{AB} \sim 41$ cps and $J_{AB} \sim 15$ cps, on cooling to −20°.

7,12-Dihydro-8-methylpleiadene-12,12-d_2 (III). As in the above-described preparations of Ia nd IV, 1-*o*-toluoyl-8-naphthoic acid was prepared by addition of *o*-tolylmagnesium bromide to 1,8-naphthalic anhydride in ether–toluene, in 70% yield, mp 195–197°. Huang–Minlon reduction of this keto acid proceeded in 41% yield to 8-(*o*-methyl)benzyl-1-naphthoic acid, mp 165–168°, whose infrared and nmr spectra were consistent with the proposed structure. Cyclization of the methylene acid with PPA produced 11-methyl-7(12H)-pleiadenone in 58% yield, mp 143–148°; mixed hydride reduction of the ketone with lithium aluminum hydride (or deuteride) and aluminum chloride in ether afforded III or the undeuterated analog in 75% yield, mp 140–141° (from methanol).

Anal. Calcd for $C_{19}H_{14}D_2$: C, 92.64; H, 7.36. Found: C, 92.62; H, 7.12.

Nuclear Magnetic Resonance Experiments. Variable-temperature nmr measurements were performed on an A-60 spectrometer equipped with a calibrated A-6040 temperature controller. Determinations of coalescence temperatures and maximum peak separations in the absence of exchange were done at least four times for each compound and usually by different operators (J. F. B. and M. K.) at widely separated times. Coalescence temperatures were determined to ±1° by numerous readings immediately above and below the apparent coalescence temperature.

Acknowledgment. We are grateful to the National Science Foundation for partial support of this research. P. T. L. wishes to thank the University of Illinois Chemistry Department for appointment to a Visiting Lectureship for the fall semester 1963–1964, during which a large portion of the variable-temperature nmr studies were performed. Special thanks are due Mr. Dick Johnson and his associates in the University of Illinois Spectroscopy Laboratory.

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(33) F. A. Mason, *J. Chem. Soc.*, **125**, 2119 (1924).

7,12-Dihydropleiadenes. II. Conformational Analysis of Some 7-Substituted 7,12-Dihydropleiadenes[1]

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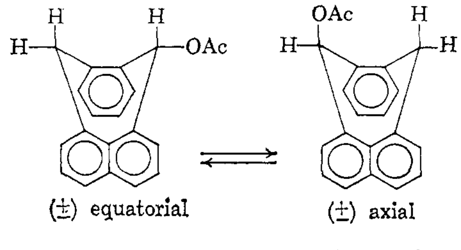
Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received October 25, 1965*

Abstract: The syntheses of 7-chloro-, 7-methoxy-, and 7-acetoxy-7,12-dihydropleiadenes have been accomplished and the conformational preferences of these groups, as well as a 7-phenyl group, established as axial. Evidence for these conclusions is obtained from nmr spectroscopy, using conformationally homogeneous model 7,12-dihydropleiadenes of known stereochemistry, and evaluation of long-range coupling between C_7 and C_{12} protons and aromatic protons. When ring inversion is slow, the diastereomeric C_{12}-methylene protons show AB quartets with $\Delta\nu_{AB}$ *ca.* 1–2 ppm, the equatorial protons appearing at higher field than the axial ones.

In the first paper of this series,[3] it was established that simple 7,12-dihydropleiadenes (DHP) undergo boat-to-boat ring inversion at rates too fast to permit isolation of atropisomers (unless 7-alkylidene groups were used to restrict inversion). Thus 7-substituted dihydropleiadenes will exist as a mobile equilibrium mixture containing two diastereomeric conformers, as illustrated for 7-acetoxy-7,12-dihydropleiadene. In this



paper we discuss the evaluation of the conformational equilibrium constants of four 7-substituted DHP's and

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(1) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

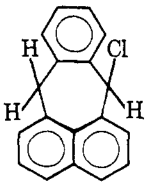
(2) (a) Alfred P. Sloan Foundation Fellow, 1963–1967; (b) National Science Foundation Predoctoral Fellow, 1962–1964.

(3) P. T. Lansbury, J. F. Bieron, and M. Klein, *J. Am. Chem. Soc.*, **88**, 1477 (1966).

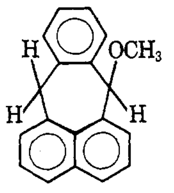
compare the relative steric bulks of the groups in DHP's with their conformational preferences in other mobile alicyclic systems, *e.g.*, cyclohexane, or their ability (presumably based on steric bulk) to influence conformational changes such as racemization of optically active biphenyls. In addition, we attempt to estimate the relative importance of conformer populations *vs.* "intrinsic asymmetry" on the remarkably large magnetic nonequivalence[4] ($\Delta\nu$ = 1–2 ppm) of the C_{12}-methylene protons in 7-substituted 7,12-dihydropleiadenes.

Results and Discussion

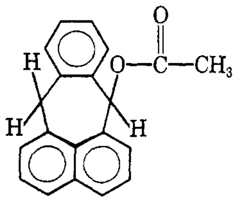
By allowing 7-hydroxy-7,12-dihydropleiadene to react separately with hydrogen chloride, acidified methanol, and sulfuric acid–acetic acid, the corresponding 7-chloro- (I), 7-methoxy- (II), and 7-acetoxy-7,12-dihydropleiadenes (III) were obtained. 7-Phenyl-7,12-dihydropleiadene (IV) was available from a previous study[5] and its conformational analysis will be discussed first, since a somewhat different line of reasoning from that employed with compounds I–III was used.



I

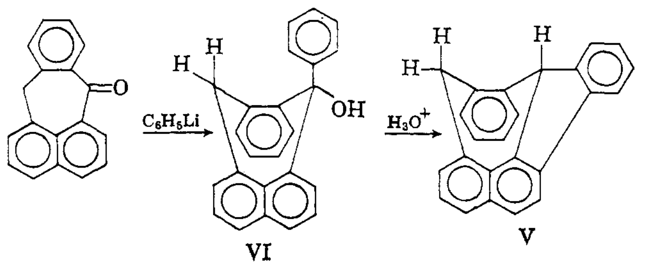


II

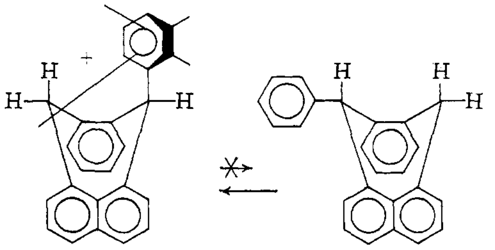


III

The nmr spectrum of IV was temperature invariant from +40 to −60°, showing the nonequivalent C_{12} protons as a pair of doublets ($J \sim 15$ cps) centered at 237 cps[6] and separated by 53 cps. The center of the C_{12} AB spectrum is thus *ca.* 0.4 ppm *upfield* from the methylene spectrum of DHP, which is centered at 260 cps at −30° when ring inversion is hindered. Furthermore, we have prepared and examined the spectrum of 1,12-*o*-phenylene-7,12-dihydropleiadene (V), a rigid analog of the dihydropleiadene system, in which the C_7-aryl substituent is restricted to an "equatorial-like" position. The alcohol VI resulting from phenyllithium addition to 7-pleiadenone displayed a pair of doublets due to the C_{12} protons at 228 cps (similar to IV), but in V the C_{12}-methylene spectrum appeared at 272 cps ($\Delta\nu_{AB}$ = 59 cps, $J_{AB} \sim 15$ cps). We take these results to mean that in IV (and in VI as well) the phenyl group occupies the axial position and that the upfield shift of the C_{12} protons is a consequence of the diamagnetic anisotropy of the benzene ring, which assumes a low-energy conformation suitable for diamagnetic shielding of the C_{12} protons.



VI V



IVa IVb

The shielding of methylene protons which lie over the benzene π cloud has been amply demonstrated in paracyclophanes[7] and 1,2-diarylcycloalkanes.[8] Conversely, in V the C_{12} protons lie more remote from and coplanar with the C_7-aryl group and experience only a small deshielding effect[9] as expected. The assignment of conformation IVa for 7-phenyl DHP is further strengthened by long-range spin–spin coupling studies, which are discussed below, as well as the similar axial preferences deduced for I–III by unambiguous and independent means.

For evaluating the conformational preferences of the methoxy and acetoxy groups in the dihydropleiadene ring system, we chose to compare the methyl chemical shifts in II and III with those of appropriate conformationally homogeneous DHP's in which the methoxy and acetoxy groups would be constrained essentially to one or the other configuration. Similarly, *cis*- and *trans*-4-*t*-butylcyclohexyl-X derivatives have been used to determine the conformer populations in cyclohexyl-X.[10] However, rather than calculate equilibrium constants from the chemical shifts of II (or III) and the two appropriate model compounds,[11] the latter were used only to verify peak assignments and K_{eq} was determined by direct integration of the peak areas due to the two individual conformers in the absence of fast ring inversion.[12] The prospects for such an approach were considered excellent since *trans*-7,12-dimethoxy DHP (A) and *trans*-7,12-diacetoxy DHP (B) showed well-separated methyl signals in the absence of interconversion.[3] It can be shown that the high-field signal in each of the above low-temperature spectra is due to the axial substituent by considering the conformationally biased model compounds shown.[13] Clearly, the methoxy signals in VII and IX correspond well to the chemical shifts in "frozen" *trans*-7,12-dimethoxy DHP and the acetates also agree

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(4) For pertinent references, see (a) W. L. Meyer, *et al.*, *ibid.*, **87**, 1573 (1965); (b) G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964); (c) J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961); (d) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).

(5) P. T. Lansbury, *J. Am. Chem. Soc.*, **81**, 4325 (1959).

(6) All chemical shifts are given in cps downfield from internal TMS at 60 Mc operating frequency. Spectra discussed in this paper are reproduced in the Ph.D. thesis of J. F. Bieron, State University of New York at Buffalo, 1965, or available from P. T. Lansbury on request.

(7) D. J. Cram and M. Goldstein, *J. Am. Chem. Soc.*, **85**, 1063 (1963); (b) J. S. Waugh and R. W. Fessenden, *ibid.*, **79**, 846 (1957).

(8) L. M. Jackman, "Applications of N.m.r. Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 125.

(9) Actually the downfield shift may be a result of the somewhat different geometry in V as compared with the flexible DHP system.

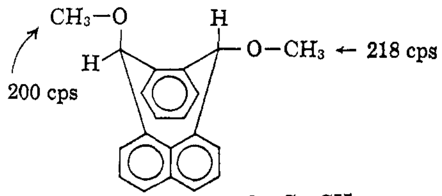
(10) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, pp 152, 435, and references cited therein.

(11) Ring deformation effects in the model compounds, which are not present in the equilibrating compound, may make the calculation $K = (\delta_A - \delta)/(\delta - \delta_E)$ quantitatively invalid (see ref 10, p 77).

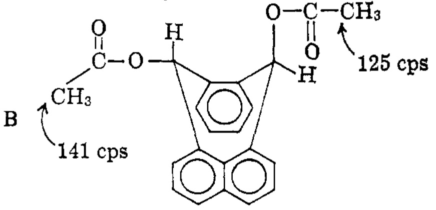
(12) The conformational preferences of the cyclohexyl halides were determined by this low-temperature method: A. J. Berlin and F. R. Jensen, *Chem. Ind.* (London), 998 (1960).

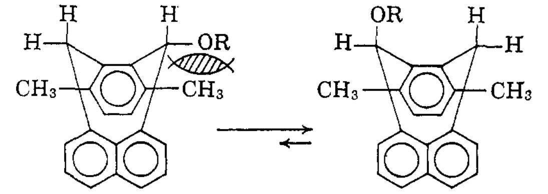
(13) The structures shown on the left of each equation have two *large* groups quite close to each other and hence are of high-energy content, such as 1,3-diaxially substituted cyclohexanes.

A

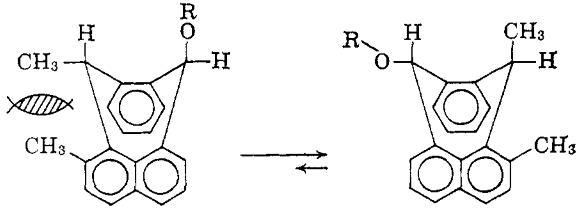


B





R δ_{CH_3}40°
VII, CH3 201 cps
VIII, Ac 123 cps



R δ_{CH_3}40°
IX, CH3 217 cps
X, Ac 143 cps

satisfactorily.[14a] Due to difficulties in synthesizing 1,12-dimethyl-7-acetoxy-7,12-dihydropleiadene, the actual model compound for equatorial acetate was 7-methyl-12-acetoxy-7,12-dihydropleiadene (X) which was considered likely to have mainly the desired equatorial acetate conformation.[14b] The acetate methyl signal in X did in fact agree well with the equatorial acetate signal in "frozen" III (see below).

Knowing the expected positions of axial and equatorial methoxy groups, we examined the nmr spectrum of II at several temperatures and found that the original methoxy signal at 203 cps separated into two signals at 200 and 218 cps in the low-temperature spectrum, the former being most intense, as shown in Figure 1. Integration of the two methine signals at −20° gave K_e = [axial OCH$_3$]/[equatorial OCH$_3$] = 2.2 and, at −42°, K_e = 2.5 corresponding to $\Delta F° = -0.41 \pm 0.1$.

The axial preference of a C_7-methoxy group becomes greater when a substituent is present at C_1, apparently because the C_{12} hydrogens are now distorted in such a way as to relieve "bow–stern" compression.[15]

Having available chemical shift data for VIII, X, and *trans*-7,12-diacetoxy DHP, we proceeded to analyze the low-temperature spectrum (−10 to −40°) of III, noting that the axial acetate signal, δ_{CH_3} = 122 cps, was *ca.* 3.0 to 3.3 times more intense than the equatorial signal at 148 cps, corresponding to $\Delta F° = -0.55 \pm 0.1$ kcal/mole for the free-energy difference between equatorial and the more stable axial 7-acetoxy DHP.

Several additional interesting features were evident in the low-temperature spectra of II and III. First, in II, as well as XI, it is quite clear that of the two C_7-methine proton signals, the *high*-field one is of greater area and therefore must be equatorial, since the corresponding axial methoxy signal was also the major one. This conclusion is also reached by careful examination of line widths (at half-height) of the C_{12}-methylene AB spectrum. Clearly the low-field doublet has greater line widths than does either the high-field doublet or the high-field (equatorial) methine signal (see Figure 1). Again, we assign the broad doublet to the *axial* C_{12} proton, concluding that long-range coupling of this proton with aromatic protons in *ortho* and *para* positions causes the broadening. Extensive studies of such coupling by Sternhell and others[16] have shown that the greatest effect results when the benzylic C–H bond lies perpendicular to the aromatic ring, thus allowing efficient σ–π overlap. In fact, I–IV (and numerous other DHP's) all show line broadening of the low-field doublet in the AB quartet (in the low-temperature spectra). Furthermore, the methine signal (or the major one of two, when two conformers are present) generally has a narrower width, comparable to the high-field *equatorial* C_{12} proton. The only exception to the latter situation was with IV but this is readily rationalized when we reconsider the conformation IVa (above) deduced to account for the diamagnetic shielding of the C_{12} protons. Clearly the *phenyl* ring protons can couple with the C_7 proton, although the naphthalene and *o*-phenylene groups cannot. The above reasoning required experimental verification and this was obtained from spin decoupling by means of double- and triple-resonance experiments. For example, 7-chloro-7,12-dihydropleiadene (I) shows a temperature-invariant spectrum in the range +40 to −60°, indicative of a single, stable conformer, as in the case of IV. Observation of the AB quartet (centered at 293 cps, with $\Delta\nu_{AB}$ = 108 cps) with simultaneous irradiation of the aryl proton region sharpened the axial C_{12} doublet line width from 2.8 to 1.9 cps, and then with simultaneous irradiation of the aryl and equatorial C_{12} signals (to remove geminal coupling also) a single signal with half-height width 1.9 cps, as is the *equatorial* C_7 proton, resulted. Thus the conformation of I is established as chlorine axial. Similar double resonance experiments with II, III, V, and VII served to confirm the axial proton assignments discussed above.[17] In Table I half-height widths for the aliphatic protons in pertinent compounds are given.

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[14] (a) Apparently any long-range shielding by the added methyl groups in VII–X, which were present to ensure the desired conformations of the functional groups, is sufficiently small to be of no trouble. This is further borne out in the high-temperature spectrum of 1-methyl DHP, also 8-methyl DHP, in which *both* methylene groups absorb as a single peak at 265 cps. (b) Regardless of whether X is *cis* or *trans*, the acetoxy group is most certainly equatorial, wholly or in part. This is because *cis*-X is entirely diequatorial (see models), whereas one of the two *trans* conformations of X has equatorial OAc. Further verification that equatorial OAc has $\delta_{CH_3} \sim 143$ cps comes from the nmr spectrum of conformationally biased 1-methyl-*trans*-7,12-diacetoxy DHP, which shows axial OAc at 127 cps and equatorial OAc at 144 cps: A. J. Lacher, unpublished results.

[15] In 1-chloro- and 1-methyl-7-methoxy DHP's, $\Delta F°$ is 0.45–0.50 kcal/mole at *ca.* −20° and the C_{12} protons show less magnetic nonequivalence compared with II: A. J. Lacher and F. D. Saeva, unpublished results.

[16] (a) S. Sternhell, *Pure Appl. Chem.*, **14**, 15 (1964); (b) H. Rottendorf and S. Sternhell, *Tetrahedron Letters*, 1289 (1963).

[17] It can be seen that the conformational preference of any C

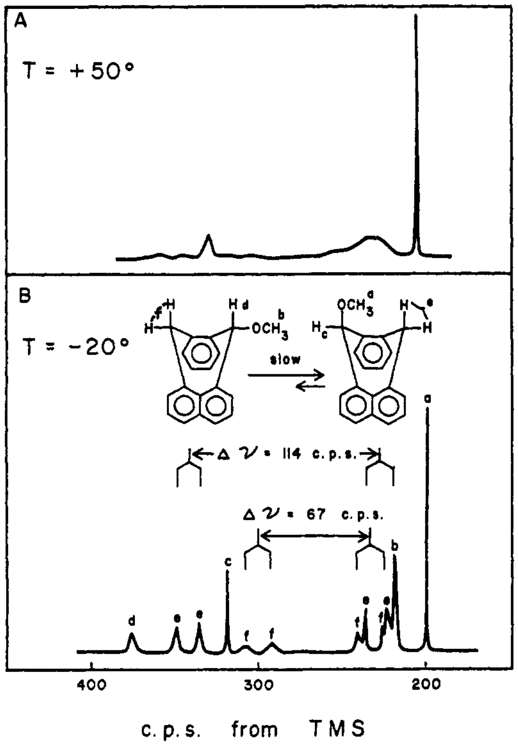


Figure 1. Partial 60-Mc nmr spectra of 7-methoxy-7,12-dihydropleiadene in $CDCl_3$ at +50° (A) and −20° (B).

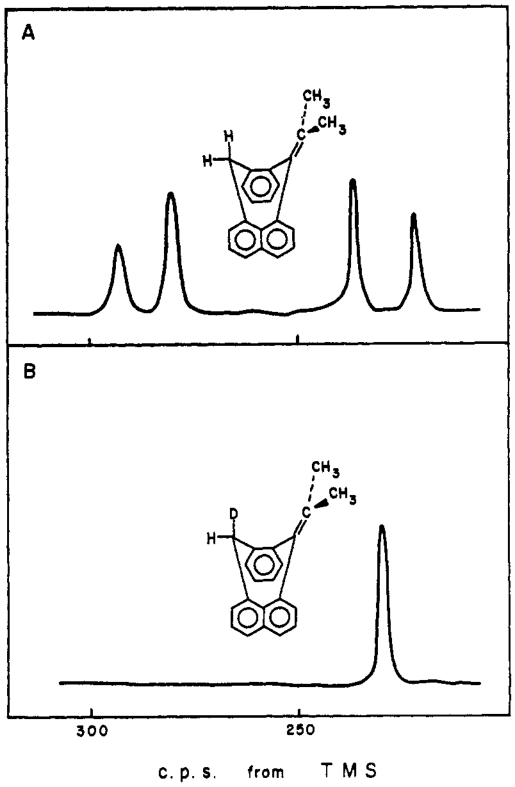


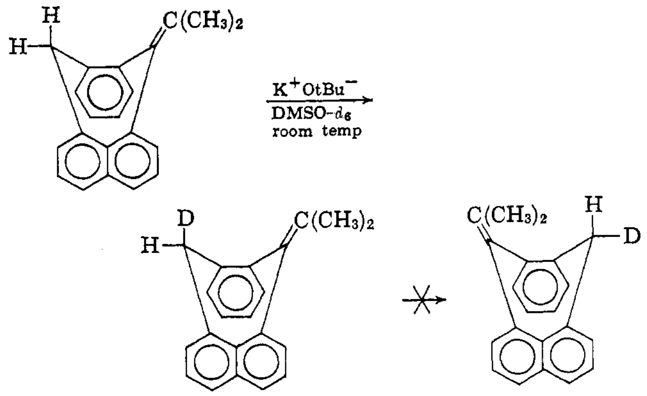
Figure 2. Partial 60-Mc nmr spectra of 7-isopropylidene-7,12-dihydropleiadene in dimethyl sulfoxide-d_6: (A) the C_{12}-methylene protons before exchange; (B) the C_{12}-methylene protons 5 min after addition of potassium *t*-butoxide.

Table I. Peak Widths of Aliphatic Proton Signals in 7-Substituted 7,12-Dihydropleiadenes[a]

Compd	H_A,[b] cps	H_B, cps	H_C, cps
I	2.8 (1.9)	1.9	1.9
VII	3.1 (1.8)	1.5	1.5
IVa	2.9 (1.2-1.6)	1.7	2.9
V	3.3 (2.0)	2.0	3.0

[a] The peak widths at half-height are estimated to be accurate to ±0.2 cps. [b] Values in parentheses indicate sharpened peak resulting from simultaneous irradiation of the aromatic proton region.

An additional experiment which served to confirm the above assignments of C_{12} diastereomeric proton signals was the highly specific hydrogen–deuterium exchange of 7-isopropylidene-7,12-dihydropleiadene in dimethyl sulfoxide-d_6 with potassium *t*-butoxide. Since ring inversion does not occur at room temperature in this compound,[3,18] equilibration of the two diastereomeric sites is not possible and the course of exchange can be followed by nmr. As seen in Figure 2, the low-field doublet of the C_{12}-methylene AB spectrum has disappeared within 5 min at room temperature and the upfield doublet has changed to a broad singlet. No further changes appeared in the nmr spectrum after 15 additional min. These changes are clearly consistent with specific deuteration at the axial position, which is favored on steric and stereoelectronic grounds.[19]



In certain 7-substituted 7,12-dihydropleiadenes known to contain comparable amounts of both conformers when ring inversion is prevented, only one AB quartet was observed for the C_{12} diastereomeric protons in low-temperature spectra.[20] However, in II and III two

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substituent is derivable from inspection of the line width of the C_7-methine proton and comparison with the C_{12} protons. Whenever the C_7–H signal has a line width comparable to the *narrower* C_{12} doublet, the C_7–X group must of necessity be axial.

(18) However, at elevated temperatures (*ca.* 120°), inversion proceeds at a convenient rate and "racemization" of the axial monodeuterio compound is being studied kinetically: M. Klein, unpublished results.

(19) For example, triphenylmethane-α-*t* undergoes proton exchange with lithium cyclohexylamide in cyclohexylamine 5 × 10^5 more rapidly than triptycene-1-*t*, mainly due to resonance stabilization in the triphenylmethide ion: A. Streitwieser, Jr., R. A. Caldwell, and M. R. Granger, *J. Am. Chem. Soc.*, **86**, 3578 (1964).

(20) For example, the nmr spectrum of 7-ethyl-α,α-d_2-7,12-dihydropleiadene at −30 to −50° shows a pair of methyl signals of *ca.* 6:4 relative intensity and two C_7-methine signals but only one quartet, centered at 260 cps with $\Delta\nu_{AB} \sim 79$ cps. The presence of two conformers are indicated and apparently the C_{12} proton signals are relatively unaffected. It should be mentioned, however, that at 100 Mc one can distinguish two distinct but nearly overlapping AB spectra: P. T. Lansbury and A. J. Lacher, unpublished results. Studies of the conformational preferences of 7-ethyl and 7-methyl DHP will be published shortly.

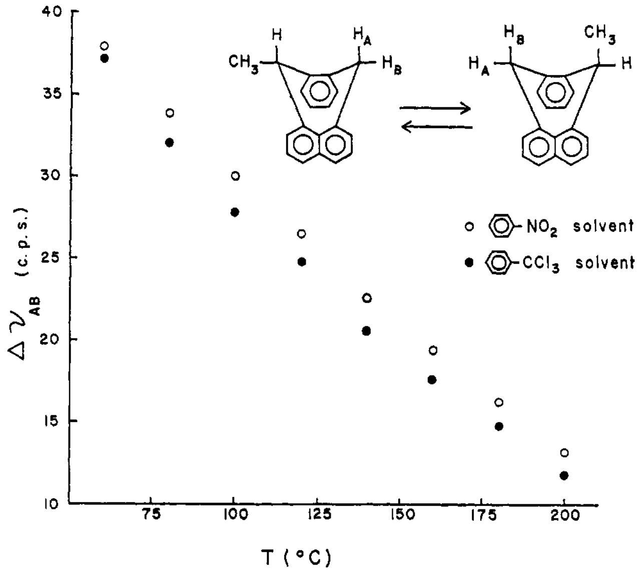
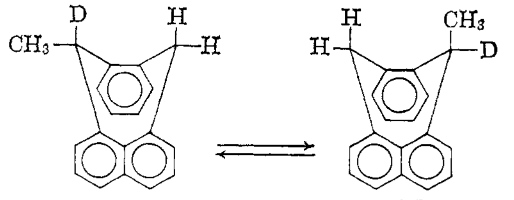


Figure 3. Temperature dependence of $\Delta\nu_{AB}$ for the diasteromeric C_{12} protons of 7-methyl-7,12-dihydropleiadene.

distinct AB quartets were easily discernible in the low-temperature spectra. At −20°, the spectrum of II (Figure 1) shows a weak intensity quartet (due to the equatorial methoxy conformer) centered at 265 cps, with $\Delta\nu_{AB}$ = 67 cps, and a high-intensity quartet (arising from the predominating conformer with axial OCH_3) centered at 286 cps, with $\Delta\nu_{AB}$ = 114 cps. It is apparent from examination of the spectrum that the *equatorial* C_{12} protons in both conformers have nearly identical chemical shifts but that the axial C_{12} proton in the axial OCH_3 conformer is at lower field than when OCH_3 is equatorial. This assignment is consistent with the paramagnetic deshielding effect (arising from bond anisotropy, dipole and inductive effects, and van der Waals repulsion) expected of an axial methoxy group upon its neighboring transannular proton. The situation with III is entirely analogous, the two equatorial C_{12} protons showing similar chemical shifts and the two axial C_{12} protons having substantially different ones. It should also be noted that axial C_{12} proton peaks in II and III were broadened relative to the equatorial C_{12} peaks, as expected from long-range coupling (see above).

The virtual coincidence of the two AB spectra in 7-methyl- and 7-ethyl-7,12-dihydropleiadenes[20] suggests that here the magnetic nonequivalence between axial and equatorial protons is not substantially affected by the configuration at C_7. Thus, when ring inversion is not occurring, each diastereomeric conformer has one "pure" axial and one "pure" equatorial C_{12} proton. When 7-methyl-7,12-dihydropleiadene, for example, is heated to the point where ring inversion is fast compared with $\Delta\nu_\omega$, a time-average AB quartet with decreased chemical shift is expected since the C_{12} protons spend some time in each position. Clearly, increased heating should result in $\Delta\nu_{AB}$ approaching 0 as the conformer populations become more nearly equal. 7-Methyl DHP-7-*d* (XII) was considered to be appropriate for such a temperature study, the deuterium being present to remove the bothersome methine resonance, which overlaps that of the C_{12} protons. The methylene protons of XII appear as an AB quartet (actually the two superimposable quartets XIIa and XIIb) with $\Delta\nu_{AB}$ = 73 cps at −50° (in $CDCl_3$). At +30°, the AB quartet is washed out but a new time-averaged quartet, $\Delta\nu_{AB}$ = 39 cps, appears at +55°. We have examined $\Delta\nu_{AB}$ in XII up to 200° (in nitrobenzene and benzotrichloride) and find that the chemical shift decreases almost linearly with temperature, as shown in Figure 3. It appears that $\Delta\nu_{AB}$ will approach 0 at $\gtrsim$300°, where the conformer populations are presumably nearly equal. Although we cannot rule out some contributions of "intrinsic asymmetry" [4c,d] to the observed large chemical-shift difference between diastereomeric C_{12} protons in XII, it is clear that the conformer population effect[4a,b] is the most important contribution. In compounds I and IV where only a single conformer was detected over the range −60 to +40°, $\Delta F°$ is apparently sufficiently large to ensure that $\Delta\nu_{AB}$ remains unchanged. In Table II, we present chemical shift data on the diastereomeric C_{12} protons in the dihydropleiadenes discussed in this paper.



XIIa XIIb

Table II. Chemical Shifts of Diastereomeric C_{12} Protons

Substituent on 7,12-dihydropleiadene	Temp, °C	J_{AB}, cps	$\Delta\nu_{AB}$, cps	Center of AB quartet,[b] cps
7-Chloro	~40	14.5	108	293
	−60	14	111	294
1-Methyl-7-methoxy	−20	14.5	69	286
7-Methoxy[a]	−20			
Axial		14.5	114	286
Equatorial		15	67	265
7-Methoxy-8,11-dimethyl (RT)		14.5	97	287
7-Acetoxy[a]	−40			
Axial		14.5	102	287
Equatorial		15	71.5	276
7-Acetoxy				
8,11-Dimethyl (RT)		14.5	79	292
7-Carbomethoxy (RT)		15	54	258
	−30	15	51	258
7-Phenyl-7-hydroxy (RT)		15	39	228
7-Phenyl	30	14.5	50	237
1,12-(*o*-Phenylene) (RT)		14.5	59	272
7-Hydroxy				
8,11-Dimethyl (RT)		14.5	94	287

[a] Two AB spectra were observed, one arising from each conformer (see Discussion). [b] In cps downfield from internal TMS.

The fact that axial acetoxy and methoxy groups have chemical shifts at higher field than their equatorial analogs can be explained in terms of the diamagnetic anisotropy of the aryl rings, since the axial groups (*i.e.*, in VII and VIII) appear to lie in the positive shielding region above the ring planes[7,8] whereas the equatorial groups, as in IX and X, lie in the ring plane, such that the ring current effect produces deshielding. This line of reasoning is clearly not applicable to axial and equatorial protons bonded *directly* at C_7 and C_{12}, where the relative chemical shifts are opposite to those above. Hopefully further studies will lead to a better understanding of these data. It is also interesting that the relative steric bulks of groups in the above-mentioned 7-substituted 7,12-dihydropleiadenes, particularly Cl > OCH_3, OAc, differ from the corresponding cyclohexyl derivatives[21] (*A* values: $OCH_3 \sim 0.7$, OAc ~ 0.7, Cl ~ 0.3–0.4), although Cl is known to exert a larger "buttressing" effect than OCH_3 in hindering the racemization of optically active biphenyls. It remains to determine if effects other than pure steric bulk, *e.g.*, van der Waals forces, affect the conformational preferences in 7-substituted DHP's, so further speculation will be postponed until a greater variety of these derivatives have been studied.[22] We are also examining the conformational preferences and relative stabilities of *cis*- and *trans*-7,12-disubstituted 7,12-dihydropleiadenes.

Experimental Section[23]

7-Hydroxy-7,12-dihydropleiadene. 7(12H)-Pleiadenone (0.5 g, 2.06 mmoles) was dissolved in 25 ml of methanol and 0.442 g (10.6 mmoles) of sodium borohydride was added. After 5 hr at room temperature, water was added to the methanol solution and the resultant precipitate was filtered off and dried. Recrystallization from benzene–ligroin gave 0.30 g of colorless needles, mp 133–134°, whose infrared spectrum was free of carbonyl absorption and showed OH stretching at ~3200 and C–O stretching at 1064 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}O$: C, 87.7; H, 5.74. Found: C, 87.98; H, 5.94.

7-Chloro-7,12-dihydropleiadene (I). One gram of 7-hydroxy DHP was dissolved in 35 ml of benzene and hydrogen chloride gas was bubbled through the refluxing solution for 2 hr. On cooling, carbon dioxide was bubbled through the solution to expel excess hydrogen chloride and a small amount of sodium carbonate was added. After standing overnight, filtration and evaporation of the solution gave crude I (65%) as an oil which crystallized on standing. Recrystallization from petroleum ether (bp 30–60°) gave the analytical sample, mp 119.5–121°. The infrared spectrum showed no O–H absorption.

Anal. Calcd for $C_{18}H_{13}Cl$: C, 81.66; H, 4.95. Found: C, 81.56; H, 4.86.

7-Methoxy-7,12-dihydropleiadene (II). To a solution of 0.30 g of 7-hydroxy DHP in 30 ml of methanol was added several drops of concentrated hydrochloric acid, followed by a 12-hr reflux period. The solution was then poured into ice water, extracted with ether, and worked up as usual. Chromatography over alumina with petroleum ether as eluent gave pure II, mp 70–71° (from petroleum ether), whose infrared spectrum showed no O–H stretching but strong C–O stretching at 1081 cm^{-1}.

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.20. Found: C, 87.53; H, 6.29.

7-Acetoxy-7,12-dihydropleiadene (III). A solution of 382 mg of 7-hydroxy DHP in 8 ml of carbon tetrachloride and 4 ml of chloroform was poured into 2.2 ml of concentrated sulfuric acid, yielding a deep red solution containing the carbonium ion. This was poured, with stirring, into 120 ml of glacial acetic acid (decolorization) and the resultant solution was immediately quenched with excess ice water. The mixture was rapidly extracted into ether and the latter washed with 10% sodium carbonate solution and water and dried over magnesium sulfate. Evaporation of solvent and chromatography of the residue over alumina, with benzene as eluent, afforded 76 mg of III, mp 111–113.5° (from ligroin), whose infrared spectrum (Nujol) showed acetate carbonyl at 1733 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.39; H, 5.69.

7-Hydroxy-7-phenyl-7,12-dihydropleiadene (VI). Treatment of 7(12H)-pleiadenone with excess phenyllithium in ether for 2 hr gave a purple solution. Hydrolysis with ammonium chloride solution, followed by conventional work-up gave the alcohol VI as colorless crystals, mp 189–192° (from methanol–water), in 75% yield. The infrared spectrum showed no carbonyl bands but did reveal O–H absorption at 3570 and 3450 and phenyl absorption at 697 cm^{-1}.

Anal. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.62. Found: C, 89.34; H, 5.51.

1,12-(*o*-Phenylene)-7,12-dihydropleiadene (V). When VI was dissolved hot acetic acid containing sulfuric acid catalyst (or in 98% formic acid), a bright, reddish purple color appeared. Within a few minutes on the steam bath the color had faded and the solution then was poured into ice water and extracted with ether. The ether extract was washed and dried, then concentrated to an oil which crystallized from ethanol–acetone. Recrystallization from ethanol–acetone gave colorless crystals of V, mp 200–201° (red melt), whose ultraviolet spectra show λ_{max}^{EtOH} at 266 mμ (ϵ 54,000) and 256 mμ (ϵ 34,000) as well as weaker maxima at 296, 308, and 322 mμ. The spectrum was very similar to that of 1,2-benzfluorene[24] and dissimilar to DHP's.

Anal. Calcd for $C_{24}H_{16}$: C, 94.6; H, 5.27. Found: C, 94.01; H, 5.91.

7-Methoxy-8,11-dimethyl-7,12-dihydropleiadene (VII). 8,11-Dimethyl-7(12H)-pleiadenone[3] was reduced by excess lithium aluminum hydride in ether. After the usual hydrolysis and work-up, the crude oily product was crystallized from chloroform–petroleum ether, mp 102–105°. The infrared spectrum showed O–H stretching at *ca.* 3330 cm^{-1} and no absorption in the carbonyl region.

Anal. Calcd for $C_{20}H_{18}O$: C, 87.55; H, 6.61. Found: C, 87.51; H, 6.80.

The above alcohol was refluxed for 12 hr in methanol containing a few drops of concentrated hydrochloric acid, as in the preparation of II, and worked up. Chromatography over alumina gave the methyl ether VII in 49% yield (starting from the ketone), mp 96–98°. The infrared spectrum of VII showed no O–H absorption but did show strong C–O stretching at ~1075 cm^{-1}.

Anal. Calcd for $C_{21}H_{20}O$: C, 87.40; H, 6.97. Found: C, 87.38; H, 7.12.

7-Methoxy-1,12-dimethyl-7,12-dihydropleiadene (IX). Anhydrous potassium *t*-butoxide (5.63 g, 0.051 mole) was dissolved in 100 ml of dimethyl sulfoxide, followed by addition of 10.3 g (0.04 mole) of 1-methyl-7(12H)-pleiadenone.[25] The latter addition resulted in an immediate purple coloration. After stirring for 30 min under N_2, 5 ml of methyl iodide (11.4 g, 0.081 mole) was added slowly (*via* hypodermic syringe) while cooling the reaction flask in ice. After 1 hr the colorless solution was poured into ice water and the crude solid product was filtered off, redissolved in benzene, and chromatographed over alumina. Elution with 4:1 petroleum ether–benzene gave pale yellow crystals of 1,12-dimethyl-7(12H)-pleiadenone in 49% yield (5.33 g), mp 121–123° (from ethanol). The carbonyl band in the infrared spectrum appeared at 1653 cm^{-1}, and the nmr spectrum showed methyl signals at 89 (doublet with $J \sim 8$ cps) and 157 cps.

Anal. Calcd for $C_{20}H_{16}O$: C, 88.2; H, 5.93. Found: C, 88.06; H, 5.96.

The above ketone was reduced overnight with lithium aluminum hydride in refluxing ether, then hydrolyzed with cold 10% hydrochloric acid and worked up. Infrared verified that the oily product was largely alcohol and contained only small amounts of unreacted ketone. This material was refluxed overnight with reagent grade methanol containing a drop of concentrated hydrochloric acid and then worked up as above. 7-Methoxy-1,12-dimethyl DHP (IX) was obtained by chromatography over alumina (petroleum ether as eluent) as an uncrystallizable oil, which did not give satisfactory elemental analysis. The structure was best confirmed by nmr (multiplicity and relative peak areas in parentheses): $\delta_{7\text{-}OCH_3}$ 217 (singlet, 3), $\delta_{7\text{-}H}$ 382 (singlet, 1), $\delta_{12\text{-}CH_3}$ 110 (doublet, $J \sim 7$ cps, 3), $\delta_{12\text{-}H}$ 282 cps (quartet, $J \sim 7$ cps, 1), and $\delta_{1\text{-}CH_3}$ 154 cps (singlet, 3).

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(21) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 163.

(22) Preliminary results indicate that 7-carbomethoxy DHP is essentially all axial and that 7-ethyl DHP has a slight equatorial preference: P. T. Lansbury and A. J. Lacher, unpublished results.

(23) Melting points are uncorrected. Infrared spectra were obtained on a Beckman IR-5A spectrometer, using Nujol mulls or neat films between sodium chloride plates. Ultraviolet spectra were measured on a Beckmann DK-2 spectrometer. Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60 spectrometer equipped with a variable-temperature probe and a Model A-6040 temperature controller. Carbon–hydrogen analyses were by Dr. Alfred Bernhardt, Mulheim, Germany.

(24) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

(25) L. F. Fieser and M. A. Peters, *J. Am. Chem. Soc.*, **54**, 3742 (1932).

1-Methyl-7-methoxy-7,12-dihydropleiadene. One-half gram of 1-methyl-7(12H)-pleiadenone[25] and 0.55 g of lithium aluminum hydride were dissolved in 25 ml of ether and stirred for 14 hr. Acid hydrolysis and conventional work-up produced the crude carbinol (infrared showed O–H stretching and no carbonyl absorption), which was dissolved in acidified methanol and refluxed overnight, as in the preparation of II. After chromatography over alumina, the methyl ether was obtained as crystals, mp 61.5–63° (from ethanol–water), in *ca.* 35–40% yield (0.218 g).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.59; H, 6.62.

7-Methyl-7,12-dihydropleiadene and 7-Methyl-7,12-dihydropleiadene-7-*d*. Methyl 8-benzyl-1-naphthoate was prepared from the reaction of 8-benzyl-1-naphthoic acid[3] with diazomethane in ether in quantitative yield. An ester group was confirmed by a carbonyl band in the infrared spectrum at 1730 cm^{-1}.

Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3. Found: C, 73.56; H, 5.16.

The ester was converted to 8-benzyl-1-acetylnaphthalene by inversion addition of ethereal methyllithium (slightly over 1 mole) to the ester in ether solvent. A conventional work-up gave the ketone as an uncrystallizable oil which was characterized by infrared spectroscopy, $\nu_{>=O}$ 1686 cm^{-1}.

The ketone from the preceding step was reduced by excess lithium aluminum hydride (or lithium aluminum deuteride) in ether to give 8-benzyl-1-(α-hydroxyethyl)naphthalene which again was characterized by infrared spectroscopy (no carbonyl absorption) as the correct reduction product.

The above oil was cyclized with acetic acid containing a drop of sulfuric acid on the steam bath for 2 hr. Dilution with ice water and ether extraction, followed by washing and drying, gave 7-methyl-7,12-dihydropleiadene, mp 104–105° (from ethanol).

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.27; H, 6.60.

7,12-Dihydro-7-acetoxy-12-methylpleiadene. To a suspension of 0.456 g (12 mmoles) of lithium aluminum hydride in 50 ml of anhydrous ether was added a solution of 1.796 g (6.85 mmoles) of 12-methyl-7(12H)-pleiadenone dissolved in 50 ml of dry tetrahydrofuran. The reaction mixture was stirred for 14 hr at room temperature and then hydrolyzed with water and 10% sodium hydroxide solution. The solid inorganic salts were filtered and washed with ether. The ether filtrates were combined, washed with water, dried over sodium sulfate, and concentrated to give a white solid. Recrystallization from ethanol–water gave 1.2 g of white, feathery crystals of the alcohol, mp 182–184°.

Anal. Calcd for $C_{19}H_{16}O$: C, 87.70; H, 6.18. Found: C, 87.51; H, 6.32.

The procedure used to prepare the acetate was the same as that used for the preparation of 7-acetoxy-7,12-dihydropleiadene. From 110 mg of 7-hydroxy-12-methyl-7,12-dihydropleiadene was obtained 35 mg of product, mp 141–143°, after two recrystallizations from petroleum ether (bp 60–110°). The infrared spectrum showed acetate carbonyl at 5.73 μ.

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.40; H, 6.00. Found: C, 83.85; H, 6.21.

Acknowledgment. We are grateful to the National Science Foundation for partial support of this work. Also, we are especially indebted to Professor D. J. Pasto of Notre Dame University for performing the spin decoupling nmr experiments and aiding in their interpretation.

The Electronic Spectra of Carbonium Ions in Strongly Acidic Solutions[1]

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Received December 10, 1965

Abstract: The ultraviolet and visible absorption spectra of a number of alkyl-, cycloalkyl-, aryl-, alkynylcarbonium ions, and of hydroxy- and oxocarbonium ions, the structures of which have been established by nmr spectroscopy, are reported in fluorosulfonic acid–antimony pentafluoride and concentrated sulfuric acid (oleum) solutions, generally at low temperatures. Alkylcarbonium ions are shown to exhibit *no* ultraviolet absorption above 210 mμ. Aryl-, cyclopropyl-, and alkynylcarbonium ions show characteristic ultraviolet absorption spectra. Alkyloxocarbonium ions show no ultraviolet absorption maxima above 210 mμ, whereas aryloxocarbonium ions absorb in the characteristic aryl-conjugated regions. The ultraviolet spectra of a number of protonated ketones (hydroxycarbonium ions) were also obtained and compared to the related carbonium ions.

The literature on the ultraviolet spectra of carbonium ions is extensive, but contains much uncertainty. This uncertainty has its origin in the lack of stability of carbonium ions in relatively weak acid solutions, and that the spectra were measured at room temperature. It is the purpose of this paper to report ultraviolet spectra of carbonium ions, all of which have been directly observed by nmr spectroscopy in the same acid–solvent systems and at the same temperatures at which the ultraviolet spectra were obtained. The development of extremely strong acid systems[2] has made it possible to prepare stable species and observe the spectra of carbonium ions of practically every structural class. Since low temperatures are necessary to retain the structural integrity of many of the carbonium ions, the spectra of these species were taken at −60°.

Results

A. Alkylcarbonium Ions. (a) Introduction. The ultraviolet spectra of many alkylcarbonium ions have been reported over the years, most notably by Symons and co-workers,[3–5] but these reports were questioned

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(1) Stable Carbonium Ions. XXI. Part XX: G. A. Olah, C. A. Cupas, and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 362 (1966).

(2) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **85**, 1328 (1963).

(3) J. A. Grace and M. C. R. Symons, *J. Chem. Soc.*, 958 (1959).

(4) J. Rosenbaum and M. C. R. Symons, *ibid.*, 1 (1961).

(5) J. Rosenbaum, M. Rosenbaum, and M. C. R. Symons, *Mol. Phys.*, **3**, 205 (1960).