

Dan Fărcașiu\* and Mark Kizirian [1]

Department of Chemistry, Clarkson University,  
Potsdam, NY 13676Department of Chemical and Petroleum Engineering, University of Pittsburgh,  
1249 Benedum Hall, Pittsburgh, PA 15261.

Received April 17, 1990

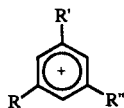
The previously unknown 2,4,6-trisubstituted pyrylium salts **1-4**, carrying cyclopropyl and methyl or phenyl substituents in the same molecule, and **5-8**, substituted with isopropyl groups instead of cyclopropyl, were synthesized as perchlorates. The electronic spectra and the C-13 nmr spectra of the two groups of compounds were compared. A cyclopropyl group has a bathochromic effect on the electronic spectrum roughly half that exerted by a phenyl; replacement of an alkyl by a cyclopropyl shifts the highest wavelength absorption band by about 20 nm. Presence of phenyl substituents reduces the bathochromic effects of cyclopropyl substituents. The effects of both cyclopropyl and phenyl substituents on the electronic spectra are smaller for pyrylium than for tropylium. The nmr signals for all the ring carbons are shifted upfield upon replacement of isopropyl by cyclopropyl; in particular, the effect of substituents in position 2 upon the chemical shift of C(4) indicates that the electron-releasing effect varies in the series alkyl < phenyl < cyclopropyl, in agreement with the findings for 2,6-disubstituted pyrylium salts. The difference between the chemical shifts for the methine and methylene carbons of the three-membered ring is a function of the electron demand of the cationic heterocycle.

*J. Heterocyclic Chem.*, **27**, 2041 (1990).

## Introduction.

The special electronic properties of the three-membered carbon rings, particularly their ability to supply electrons to carbocationic centers has been a long standing subject of investigation [2]. An interesting application of the cyclopropyl as substituent has been the synthesis of aromatic cations of exceptional stability, such as tri- and tetracyclopropylcycloheptatrienyl [3] and tricyclopropylcyclopropenyl [4].

We wanted to prepare cationic compounds with various groups present in the same molecule, so that the properties of alkyl, phenyl and cyclopropyl as substituents can be compared better. The pyrylium system seemed ideally suited for this purpose, because the ring can be assembled in a wide variety of ways from acyclic fragments [5], but the only pyrylium salts with three-membered ring substituents which we found in literature are the 2,6-dicyclopropyl- and 2,6-bis(1-methylcyclopropyl)pyrylium perchlorates [6]. We have prepared now the cyclopropyl-containing cations **1-4**, also as perchlorates. We have prepared the isopropyl-substituted analogs **5-8** as well, of which **8**, is also new. As a measure of the electron donating ability of substituents toward the positively charged ring in the ground and excited states, the C-13 nmr and the uv-visible spectra of the new compounds were recorded, and compared with the spectra of previously investigated salts of **5**, **9**, and **10**.



- 1 R = R'' = *c*-Pr, R' = Me
- 2 R = *c*-Pr, R' = R'' = Me
- 3 R = R'' = *c*-Pr, R' = Ph
- 4 R = *c*-Pr, R' = R'' = Ph
- 5 R = R'' = *i*-Pr, R' = Me
- 6 R = *i*-Pr, R' = R'' = Me
- 7 R = R'' = *i*-Pr, R' = Ph
- 8 R = *i*-Pr, R' = R'' = Ph
- 9 R = R' = R'' = Me
- 10 R = R' = R'' = Ph

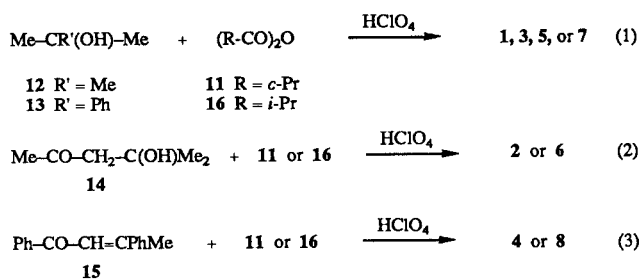
## Synthesis.

Of the various methods available for building the pyrylium ring [5], diacylation of alkenes [7] was appropriate for the symmetrical ions **1** and **3**, while monoacylation of unsaturated ketones [8] was the method of choice for the unsymmetrical species **2** and **4**. Even though the reactions were conceptually straightforward, our efforts were hindered by the instability of the three-membered ring to strong acids, well documented for the cyclopropanecarboxylic acid [9]. Thus, reaction of *t*-butyl chloride with cyclopropanecarboxylic acid chloride in the presence of aluminum chloride or antimony pentachloride gave intractable tars. That some dicyclopropyl-methylpyrylium salt had been formed, was demonstrated, nonetheless, by treatment of the reaction mixture with ammonia [7,8d] and identification of a dicyclopropylmethylpyridine by gc-ms. Perchloric acid-catalyzed diacylation [7,10] by cyclopropanecarboxylic anhydride (**11**) yielded, however, the desired **1** and **3**, as perchlorates, from *t*-butyl alcohol (**12**) and 2-phenyl-2-propanol (**13**), respectively (equation 1). The yields were mediocre and the initial products were impure, but the purification of products was achieved, nonetheless, without undue difficulty, giving pyrylium salts pure enough for analysis and spectral determinations.

Monoacylation [10] of diacetonealcohol (**14**) with **11** and perchloric acid (equation 2) gave the 2-cyclopropyl-4,6-dimethyl pyrylium perchlorate (**2**). The 2-cyclopropyl-4,6-diphenylpyrylium perchlorate (**4**) was likewise obtained from 1,3-diphenyl-2-buten-1-one (**15**, equation 3). An attempt at acylating **15** with **11** and boron trifluoride etherate [11] led to 2,4,6-triphenylpyrylium fluoroborate [12], probably also on the account of the instability of **11** to

the Lewis acid.

Finally, the reactions of precursors **12-15** with isobutyric anhydride (**16**) gave the isopropyl-substituted pyrylium salts **5-8** (equations 1-3).



Along with the study of their properties, the cyclopropyl-substituted pyrylium cations have potential interest as starting materials for the synthesis of various other cyclic compounds, for example pyridines, phenols, naphthalenes, and azulenes [5b].

#### Spectroscopic Study.

The electronic spectra of pyrylium salts substituted with aryl [13] and alkyl groups [14] had been investigated by previous authors. Our results are presented in Table 1. The values for **9** and **10** are in agreement with those reported in the literature. A comparison of all the spectra obtained shows that the cyclopropyl substituent (in positions 2- and 6-) produces a bathochromic shift of the longest wavelength absorption, which is less than half the value observed for a phenyl substituent. Thus, the difference between **1** on one hand and **9**, or **5**, or **6** on the other, is about 45 nm, whereas replacement of the 2-, and 6-methyl substituents of **9** by phenyl groups brings about a shift of 107 nm [14] (*cf.* the line before the last in Table 1). A single

cyclopropyl group, as in **2**, shifts the same absorption band to longer wavelength by 25 nm relative to **9**; the shift induced by one phenyl group (2,4-dimethyl-6-phenylpyrylium compared to **9**) is 60 nm [14]. The mere increase in size of the substituents in the same positions from methyl to isopropyl had resulted in only insignificant shifts (3nm) [14]. The effect of cyclopropyl groups in positions 2 and 6 is smaller when position 4 is occupied by a phenyl group as in **3**, and it is essentially wiped out when one cyclopropyl and two phenyl groups exist in the molecule, as in **4**.

The changes which we observed for pyrylium parallel those reported for tropylium [15]. The response of the latter to substituent effects is greater, however. Thus, the longest wavelength absorption maximum for monosubstituted tropylium varied by 53 nm and by 93 nm upon replacement of isopropyl by cyclopropyl and by phenyl, respectively [15].

The proton [16] and carbon-13 nmr [17] spectra of a number of pyrylium cations are available in literature. We recorded the carbon spectra for compounds **1-9**. The peak assignment was straightforward, based on the published chemical shifts. To help distinguish between the signals for the methylene and methine cyclopropyl carbons, the spectrum of **3** was also run with off-resonance decoupling. The carbon chemical shifts are listed in Table 2.

The carbon-13 chemical shifts have been used to estimate the electron density at a given site in a molecule or ion. Particularly, for uninterrupted, cyclic,  $\pi$ -delocalized systems, a linear relationship between carbon chemical shifts and the formal  $\pi$ -electron count for each individual carbon (1 for benzene, 1.2 for the cyclopentadienyl anion, 6/7 for tropylium, *etc.*) was discovered by Spiess and Schneider [18], then expanded by others, as

Table 1  
Electronic Spectra of Pyrylium Salts

Compound	R	R'	R''	Solvent [a]	$\lambda$ max ( $\epsilon$ max) [b]			
<b>1</b>	<i>c</i> -Pr	Me	<i>c</i> -Pr	EtOH	214 (21000)	229 (sh, 17200)	240 (sh, 11200)	331 (17400)
<b>2</b>	<i>c</i> -Pr	Me	Me	EtOH	208 (16600)	230 (sh, 6100)		310 (12500)
<b>3</b>	<i>c</i> -Pr	Ph	<i>c</i> -Pr	EtOH	210 (17700)	229 (20100)	331 (24900)	350 (sh, 18000)
<b>4</b>	<i>c</i> -Pr	Ph	Ph	EtOH	207 (13900)	259 (10250)	341 (16640)	377 (12490) [c]
<b>5</b> [d]	<i>i</i> -Pr	Me	<i>i</i> -Pr	water		232 (4680)		288 (34720)
<b>8</b>	<i>i</i> -Pr	Ph	Ph	EtOH	209 (19720)	254 (17420)	337 (25240)	372 (28640) [c]
<b>9</b> [e]	Me	Me	Me	EtOH	203 (5700)	231 (5600)		285 (13600)
<b>10</b> [f]	Ph	Ph	Ph	AcOH		277 (16600)	352 (39800)	407 (24500)
- [g]	Me	Ph	Ph	EtOH	208 (17900)	253 (15290)	335 (22600)	370 (26400) [c]
- [d]	Ph	Me	Ph	AcOH		236 (13800)	277 (36100)	392 (26900)
- [d]	Me	Ph	Me	water			304 (20000)	327 (23400)

[a] Water and ethanol solutions were stabilized with perchloric acid (ref [14]). [b]  $\lambda$  max in nm. The intensity of bands marked sh (shoulder) are only approximate. [c] A shoulder may be present on the high wavelength side of this band. [d] Values taken from ref [14]. [e] Lit values: 232 (4500) and 286 (9260) in EtOH, 233 (5450) and 284 (7900) in water, ref [14], were obtained with an instrument with a 220 nm cut-off. [f] Literature values: 278 (18000), 361 (30000), and 408 (24500) (ref [14]). [g] Literature values: 254 (14610), 338 (23600), and 374 (29100) in acetic acid ref [14].

Table 2  
Carbon-13 NMR Spectra of Pyrylium Salts [a]

No.	R	R'	R''	C(2)	C(3)	C(4)	C(5)	C(6)	Substituent at		
									C(2)	C(4)	C(6)
1	<i>c</i> -Pr	Me	<i>c</i> -Pr	183.31	120.87	173.17	120.97	183.31	18.00 (1') 16.26 (2')	23.88	[b]
2	<i>c</i> -Pr	Me	Me	186.23	122.02	174.65	123.10	177.20	18.16 (1') 17.36 (2')	23.72	21.08
3	<i>c</i> -Pr	Ph	<i>c</i> -Pr	183.04	116.19	166.60	116.19	183.04	18.24 (1') 15.87 (2')	133.43 (1') 130.18 (2') 131.72 (3') 136.92 (4')	[b]
4	<i>c</i> -Pr	Ph	Ph	184.17	117.53	167.67	114.75	172.59	18.87 (1') 17.44 (2')	133.77 (1') 130.27 (2') 131.83 (3') 137.19 (4')	129.76 (1') 129.04 (2') 131.70 (3') 137.19 (4')
5 [c]	<i>i</i> -Pr	Me	<i>i</i> -Pr	187.01	122.40	177.91	122.40	187.01	36.02 (1') 20.34 (2')	24.42	[b]
6	<i>i</i> -Pr	Me	Me	188.13	122.53	178.08	125.27	180.42	36.22 (1') 20.63 (2')	24.46	21.78
7	<i>i</i> -Pr	Ph	<i>i</i> -Pr	187.43	117.56	170.77	117.56	187.43	36.67 (1') 20.75 (2')	133.60 (1') 130.75 (2') 132.06 (3') 137.95 (4')	[b]
8	<i>i</i> -Pr	Ph	Ph	185.64	117.15	169.73	116.10	174.62	36.46 (1') 20.89 (2')	133.89 (1') 130.46 (2') 131.69 (3') 137.58 (4')	129.81 (1') 129.56 (2') 131.76 (3') 137.65 (4')
9 [d]	Me	Me	Me	179.89	124.64	176.99	124.64	179.89	21.44	23.83	[b]
10 [c]	Ph	Ph	Ph	173.16	115.63	168.88	115.63	173.16	129.64 (1') 129.38 (2') 131.65 (3') 137.42 (4')	133.92 (1') 130.02 (2') 131.73 (3') 137.23 (4')	[b]

[a] In trifluoroacetic acid-deuteriodichloromethane (80:20); chemical shifts (ppm) are based on the deuteriodichloromethane solvent signal, taken as 53.80 ppm. [b] Same values as for the substituent at C(2). [c] From ref. [17b], corrected (-0.25 ppm). [d] The values measured by us and listed here were upfield from those in ref. [17b] by 0.25 ppm on the average.

new charged aromatic carbocycles were synthesized and studied [19]. In what we consider liberties taken with the correlation, average chemical shifts of systems with non-equivalent carbon atoms were placed on the same straight line [18], then the correlation was used to predict average electron densities in these systems, even though it was mentioned that carbon-13 chemical shifts reflect trends of charge density only when hybridization and substitution are invariant [20]. Such extensions included alkyl- and aryl-substituted aromatic ions [19a], polycyclic aromatic ions [21], methano-bridged annulenes and ions [22], and even alkenyl and phenylmethyl anions [23]. We believe that the results of these correlations are no more than first approximations. The evaluation of charge density changes involves a comparison of chemical shifts in at least two systems. It is important that structure and substitution pattern be kept constant at the atom examined, and at the atoms bonded directly to it; in other words, no  $\alpha$  or  $\beta$  substituent should be added or removed [24].

We have proposed the application of  $^{13}\text{C}$  chemical shifts for C(4) in 2,6-disubstituted pyrylium salts for comparing the electron-donating ability of various substituents [25]. The relationship between the substituent at C(2) or C(6) and the ring carbon C(4) is the same as between a substituent and a meta position in a benzene ring, where no shielding or deshielding effect is observed [24]. On the other hand, in the pyrylium ring the charge is manifested at positions 2, 4, and 6, and an increase in the electron-donating ability of substituents bonded to C(2) and C(6) reduces the positive charge density at C(4). Therefore, the chemical shift change of C(4) reflects the variation in electronic effect of substituents.

The availability of symmetrical 2,6-disubstituted pyrylium salts allowed us to compare several substituents [25]. The data presented in Table 2 confirm a key finding of the other study, namely that the electron-donating ability of substituents increases in the order alkyl < Ph < *c*-Pr. This trend appears clearly upon comparing the

chemical shifts for C(4) in **7** (170.77), **10** (168.88), and **3** (166.60), as well as upon examining the nonsymmetrical cations **8** (169.73), **10**, and **4** (167.67).

Consideration of both electronic and C-13 nmr spectra indicate that cyclopropyl is a better electron donor than phenyl in the ground state, but phenyl is better at stabilizing the excited state by conjugative effects.

It has been discussed in literature that the carbon resonances of the cyclopropyl group itself are influenced by a positively charged group bonded to it, but that the actual chemical shifts are particularly dependent upon the nature of the charged group [26,27]. The compounds made by us can be used to test this theoretical representation. By maintaining the charged group constant (pyrylium) and changing substituents at C(4) and C(6), more than three bonds away, in the 2-cyclopropylpyrylium, we can check whether the cyclopropyl carbon chemical shifts are a measure of the demand for electrons by the charged system. The electron pull from a three-membered ring in position 2 decreases as substituents in positions 4 and 6 become better donors.

The chemical shifts presented in Table 2 for C( $\alpha$ ) show little variation with the change in substituents. The C( $\beta$ ) signal is more sensitive, and for closely related pairs (**1** and **2** or **3** and **4**) it moves upfield when the other substituents are better donors. The differences [ $\delta$ (C- $\alpha$ ) -  $\delta$ (C- $\beta$ )], however, vary consistently for the five examples of 2-cyclopropylpyrylium cations that we have investigated:

Substituent at C(4):	Me	H	Ph	Me	Ph
Substituent at C(6):	Me	<i>c</i> -Pr	Ph	<i>c</i> -Pr	<i>c</i> -Pr
$\delta$ C( $\alpha$ )- $\delta$ C( $\beta$ ) at C(2):	0.08	1.37[25]	1.43	1.74	2.37

Considering the order of electron-releasing power: H < Me < Ph < *c*-Pr established before [25] and confirmed here, the results show that the chemical shift difference becomes smaller (less positive) as the electron demand increases. Likewise, for the series cyclopropyltropylium, 1,4-dicyclopropyltropylium, and 1,3,5-tricyclopropyltropylium, the corresponding differences are 3.6, 4.1, and 5.7 ppm, respectively [3a].

## EXPERIMENTAL

### General Procedures.

Reagent grade chemicals and solvents were used as purchased. Proton nmr spectra were run at 60 and 90 MHz. The <sup>13</sup>C-nmr spectra were recorded at 62.896 MHz.

### Cyclopropanecarboxylic Anhydride (**11**).

This compound was prepared by the reaction of the acid and the acid chloride with pyridine [28], but in toluene rather than in benzene solution as recommended, bp 110-111° at 12 torr.

### 1,3-Diphenyl-2-buten-1-one (**15**).

This compound was obtained by the self-condensation of acetophenone, catalyzed by aluminum chloride [29].

### Pyrylium Perchlorates.

Cyclopropanecarboxylic anhydride (**11**) or isobutyric anhydride (**16**) (160 mmoles) was mixed with the substrate for acylation, **12**, **13**, **14** or **15** (20 mmoles) in a dry round-bottomed flask equipped with a magnetic stirring bar, dropping funnel, and calcium chloride drying tube. The mixture was cooled to 0° and 72% perchloric acid (20 mmoles) was added dropwise over a period of 30 minutes, with stirring. The solution was stirred for another 30 minutes in the ice-bath, then at room temperature overnight. The dark, viscous mixture was cooled again in ice, and a three-fold volume of ether was added. Stirring was continued for 1 to 2 hours, until the product solidified (in a few cases it was necessary to decant the solvent off and repeat washing with fresh ether). The salt was purified by precipitation from ethanol containing a small amount of perchloric acid (one drop for 50 ml) with ether, or from acetone with ether or pentane. **1** and **3** could also be recrystallized from alcohol (containing perchloric acid), whereas **4** and **8** could be recrystallized from acetic acid. The salts prepared by monoacylation of **14** are dark and remain off-white or tan even after the melting point reaches the value for the pure material. The IR spectra in KBr pellets were consistent with the pyrylium perchlorate structure [30]. The yields indicated below are for materials after one cycle of purification, unless indicated otherwise, and were not optimized.

### 2,6-Dicyclopropyl-4-methylpyrylium Perchlorate (**1**).

This compound was obtained in 33% yield, mp 221-222°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>15</sub>ClO<sub>5</sub>: C, 52.47; H, 5.50; Cl, 12.91. Found: C, 52.45; H, 5.66; Cl, 13.08.

### 2-Cyclopropyl-4,6-dimethylpyrylium Perchlorate (**2**).

This compound was made in 20% yield, mp 160.5-161.5°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>13</sub>ClO<sub>5</sub>: C, 48.30; H, 5.27; Cl, 14.26. Found: C, 48.25; H, 5.27; Cl, 13.80.

### 2,6-Dicyclopropyl-4-phenylpyrylium Perchlorate (**3**).

This compound was prepared in 16% yield, mp 194-195°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>17</sub>ClO<sub>5</sub>: C, 60.63; H, 5.09; Cl, 10.53. Found: C, 60.56; H, 5.07; Cl, 10.84.

### 2-Cyclopropyl-4,6-diphenylpyrylium Perchlorate (**4**).

This compound was isolated in 52% yield (crude product, mp 230-242°), mp 259-260°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>13</sub>ClO<sub>5</sub>: C, 64.44; H, 4.60; Cl, 9.50. Found: C, 64.42; H, 4.50; Cl, 9.63.

### 2-Isopropyl-4,6-dimethylpyrylium Perchlorate (**6**).

This compound was synthesized in 29% yield (lit 12% [8e]), mp 120-122°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>15</sub>ClO<sub>5</sub>: C, 47.91; H, 6.03; Cl, 14.15. Found: C, 48.16; H, 6.08; Cl, 13.83.

### 2,6-Diisopropyl-4-phenylpyrylium Perchlorate (**7**).

This compound was secured [7b] in 20% yield (fully purified material), mp 215-217°.

### 2,4-Diphenyl-6-isopropylpyrylium Perchlorate (**8**).

This compound was likewise obtained in 19% yield of analytically pure material, mp 274-275°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>19</sub>ClO<sub>5</sub>: C, 64.09; H, 5.11; Cl, 9.46. Found: C, 64.02; H, 4.98; Cl, 9.43.

Acknowledgments.

We are indebted to Sandoz Research Institute, East Hanover, N. J. 07936 for elemental analyses, and to Dr. Alexander Susan and Dr. Sandor Barcza for support and helpful discussions; to Glen Miller for running the C-13 nmr spectra, and to the students in the Advanced Organic Chemistry Laboratory course at Clarkson, Fall 1989, for the synthesis of **15**. Preliminary work on the synthesis of **1** was done by Ed Dix and John Seaburg. The NR250 NMR instrument was a gift from IBM Corporation to Clarkson University.

[4a] K. Komatsu, I. Tomioka, and K. Okamoto, *Tetrahedron Letters*, **21**, 947, (1980); [b] R. A. Moss and R. C. Munjal, *ibid.*, **21**, 1221 (1980).

[5a] A. T. Balaban, W. Schroth, and G. Fischer, *Adv. Heterocyclic Chem.*, **10**, 241 (1969); [b] A. T. Balaban, A. Dinculescu, G. N. Dorofeenko, G. W. Fischer, A. V. Koblik, V. V. Mezheritskii, and W. Schroth, *Adv. Heterocyclic Chem.*, Suppl. **2**, 1982.

[6] M. Regitz and S. G. Khbeis, *Chem. Ber.*, **117**, 2233 (1984).

[7a] A. T. Balaban and C. D. Nenitzescu, *Liebigs Ann. Chem.*, **625**, 74 (1959); *J. Chem. Soc.*, 3553 (1961); *Org. Synth.*, **44**, 98 (1964); [b] C. Uncuta, M. D. Gheorghiu, F. Chiraleu, M. Plaveti, M. Elian, and A. T. Balaban, *Rev. Roum. Chim.*, **33**, 719 (1988).

[8a] W. Dilthey, *J. Prakt. Chem.*, **94**, 53 (1916); W. Dilthey and R. Taucher, *Ber.*, **53**, 252 (1920); W. Dilthey and B. Burger, *Ber.*, **54**, 825 (1921); [b] W. Schneider and A. Ross, *Ber.*, **55**, 2775 (1922); [c] O. Diels and K. Alder, *Ber.*, **60**, 716 (1927); [d] K. Dimroth, *Angew. Chem.*, **72**, 331 (1960); [e] C. Uncuta and A. T. Balaban, *Rev. Roum. Chim.*, **21**, 251 (1976).

[9] N. C. Deno, W. E. Billups, D. La Vietes, P. C. Scholl, and S. Schneider, *J. Am. Chem. Soc.*, **92**, 3700 (1970).

[10] P. F. G. Prail and A. I. Whitear, *Proc. Chem. Soc.*, 312 (1959); *J. Chem. Soc.*, 3573 (1961).

[11] J. A. Durden and D. G. Crosby, *J. Org. Chem.*, **34**, 1684 (1965).

[12] R. Elderfield and T. King, *J. Am. Chem. Soc.*, **76**, 5437 (1954), and references therein.

[13] R. Wizinger and K. Wagner, *Helv. Chim. Acta.*, **34**, 2290 (1951), and subsequent papers.

[14] A. T. Balaban, V. E. Sahini, and E. Keplinger, *Tetrahedron*, **9**, 163 (1963).

[15] M. A. Battiste, M. W. Couch, and R. J. Rehberg, *J. Phys. Chem.*, **81**, 64 (1977).

[16] A. T. Balaban, G. R. Bedford, and A. R. Katritzky, *J. Chem. Soc.*, 1646, (1964).

[17a] A. T. Balaban and V. Z. Wray, *Z. Naturforsch.*, **30b**, 654 (1975); [b] A. T. Balaban and V. Z. Wray, *Org. Magn. Reson.*, **9**, 16 (1977); [c] G. Cerichelli, G. Doddi, and G. Ercolani, *Gazz. Chim. Ital.*, **118**, 291 (1988).

[18] H. Spiessicke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).

[19] Examples are: [a] G. A. Olah and G. D. Mateescu, *J. Am. Chem. Soc.*, **92**, 1430 (1970); [b] J. F. M. Oth, U. Smith, and G. Schröder, *Angew. Chem., Int. Ed. Engl.*, **12**, 327 (1973).

[20] G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.*, **97**, 1539 (1975).

[21a] D. A. Forsyth and G. A. Olah, *J. Am. Chem. Soc.*, **98**, 4086 (1976); [b] G. A. Olah and B. P. J. Singh, *J. Org. Chem.*, **48**, 4830 (1983).

[22] R. J. Hunadi, *J. Am. Chem. Soc.*, **105**, 6889 (1983).

[23a] D. H. O'Brien, A. J. Hart and C. R. Russell, *J. Am. Chem. Soc.*, **97**, 4410 (1975); [b] The paper does not explain why arylmethyl anions should obey the Spiessicke-Schneider relationship, whereas the corresponding cations do not: G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Am. Chem. Soc.*, **93**, 464 (1971); [c] G. A. Olah and P. W. Westerman, *ibid.*, **95**, 7530 (1973).

[24] J. B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972.

[25] D. Fărcasiu and S. Sharma, *J. Org. Chem.*, in press.

[26] G. A. Olah and G. Liang, *J. Org. Chem.*, **40**, 2108 (1975).

[27] The nmr spectra of cyclopropanes have been reviewed by D. G. Morris in ref [2a], pp 101-172. In view of errors in transcribing chemical shifts which we found in a couple of cases, the reader is advised to check in original references.

[28] C. F. H. Allen, C. J. Kibler, D. M. McLachlin, and C. V. Wilson, *Org. Synth., Coll. Vol.*, **3**, 28 (1955). A. Vogel, *Practical Organic Chemistry*, 4th Ed, Longman, Harlow, Essex, UK, 1987, p 499.

[29] N. O. Calloway and L. D. Green, *J. Am. Chem. Soc.*, **59**, 809 (1937).

[30] A. T. Balaban, G. D. Mateescu, and M. Elian, *Tetrahedron*, **18**, 1083 (1968).