

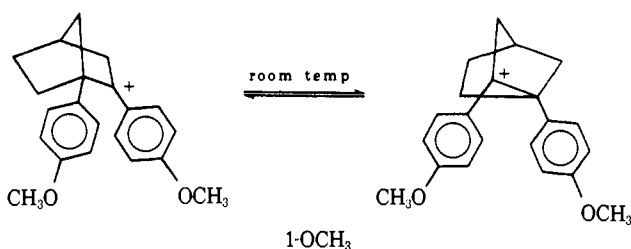
Stable Carbocations. CXLVI.<sup>1</sup>The 1,2-Diphenyl-2-norbornyl Cation. Comparison of  $\sigma$  and  $\pi$  Delocalization in Phenylnorbornyl and Related Cations

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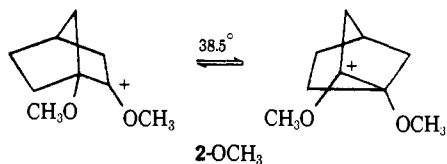
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**Abstract:** The 1,2-diphenylnorbornyl cation 1-H was prepared in  $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$  solution at  $-78^\circ$  and examined by proton and carbon-13 nmr spectroscopy. Ion 1-H is characterized as a rapidly equilibrating carbenium ion undergoing fast 1,2 Wagner–Meerwein shift. The degree of  $\sigma$  delocalization in 1-H is found to be very similar to that in the 1,2-dimethyl-2-norbornyl cation, 2- $\text{CH}_3$ .  $\sigma$  delocalization in the 2-methyl-2-norbornyl cation is found to be more significant than in the 2-phenyl-2-norbornyl cation in which  $\pi$  delocalization dominates. Reasons for differing  $\sigma$  and  $\pi$  delocalization are discussed.

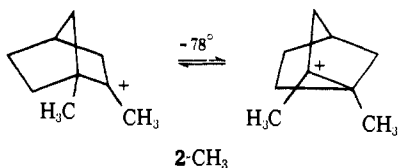
The 1,2-dianisyl-2-norbornyl cation 1- $\text{OCH}_3$  was shown by Schleyer<sup>2</sup> to possess a rapidly equilibrat-



ing classical ion structure. In his studies the absence of bridging was rationalized as resulting from the unfavorable nonbonded interactions which would exist in the bridged ion when one or both of the aryl groups were oriented as to allow overlap between aryl  $\pi$  orbital and the electron-deficient center. Nickon's study of the 1,2-dimethoxy-2-norbornyl cation 2- $\text{OCH}_3$  also



showed that the ion did not possess a bridged structure.<sup>3</sup> More recently we have reported that the 1,2-dimethyl-2-norbornyl cation 2- $\text{CH}_3$  is a rapidly equilibrating ion



having a low energy barrier for the 1,2 Wagner–Meerwein shift.<sup>4</sup> Due to less severe nonbonded interactions prevailing in 2- $\text{CH}_3$ , it was observed as a partially  $\sigma$ -

delocalized carbenium ion. The 1,2-dianisyl-2-norbornyl cation was considered to be an ion in which the  $\sigma$  delocalization was of much smaller (if of any) importance than in 2- $\text{CH}_3$ .

We report now our direct observation of the parent 1,2-diphenyl-2-norbornyl cation 1-H under stable ion conditions and its  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectroscopic investigation showing that it is a rapidly equilibrating carbenium ion similar in nature to 2- $\text{CH}_3$ , having a low energy barrier for the 1,2 Wagner–Meerwein shift and a similar degree of  $\sigma$  delocalization. Several unsymmetrically substituted 2-norbornyl cations were also examined as to gain more information on the degree of  $\sigma$  delocalization and the trend of charge delocalization.<sup>5-7</sup>

## Results and Discussion

The 1,2-diphenyl-2-norbornyl cation 1-H was prepared from 1,2-diphenyl-endo-2-norborneol<sup>2b</sup> in  $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$  ( $\text{SO}_2$ ) solution at  $-78^\circ$ . The ion was not stable when allowed to warm to above  $-50^\circ$  and gave unidentified decomposition (rearrangement) products.<sup>8a</sup> Quenching of the solution of 1-H with a slurry of  $\text{KOH}-\text{SO}_2\text{ClF}$  at  $-78^\circ$  gave 50% of 1,2-diphenyl-2-norbornene,<sup>2b</sup> besides some unidentified decomposition products.

The temperature-independent ( $-135$  to  $-60^\circ$ ) pmr spectra (60 MHz, Figure 1) of 1-H in  $\text{FSO}_3\text{H}-\text{SO}_2$  solution indicate the equivalence of the two phenyl groups.<sup>8b</sup> The four equivalent methylene protons,  $\text{H}_3$  and  $\text{H}_7$ , are more deshielded ( $\delta$  3.10) than the corresponding protons ( $\delta$  2.42) in 2- $\text{CH}_3$ . The bridgehead proton ( $\text{H}_4$ ) in 1-H is also slightly more deshielded than that in 2- $\text{CH}_3$ . The  $\text{C}_6$  protons, however, show comparable absorption for both ions. The phenyl ring protons in 1-H are unresolved indicating only a small extent of

(5) (a) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969); (b) G. Frankel and D. G. Farnum, "Carbocation Ions," Vol. 1, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1968.

(6) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972); *Chem. Brit.*, **8**, 281 (1972); *Chem. Technol.*, 556 (1971); *Science*, **168**, 1298 (1970).

(7) (a) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3958 (1969); (b) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970); (c) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, **94**, 146 (1972).

(8) (a) In our hands, trifluoroacetic acid<sup>2</sup> was not a suitable solvent to obtain the stable 1,2-diphenyl-2-norbornyl cation. (b) Slightly different chemical shifts for ion 1-H in  $\text{SO}_2$  than in  $\text{SO}_2\text{ClF}$  solutions are noticed (see Table I). Better resolution is obtained in  $\text{SO}_2$  solution.

(1) (a) Part CXLV: G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **96**, 189 (1974). (b) Taken in part from the Ph.D. Thesis of G. Liang, Case Western Reserve University, 1973.

(2) (a) P. v. R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Amer. Chem. Soc.*, **85**, 479 (1963); (b) D. C. Kleinfelter and P. v. R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

(3) A. Nickon and Y. Lin, *J. Amer. Chem. Soc.*, **91**, 6861 (1969).

(4) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *ibid.*, **93**, 1442 (1971).

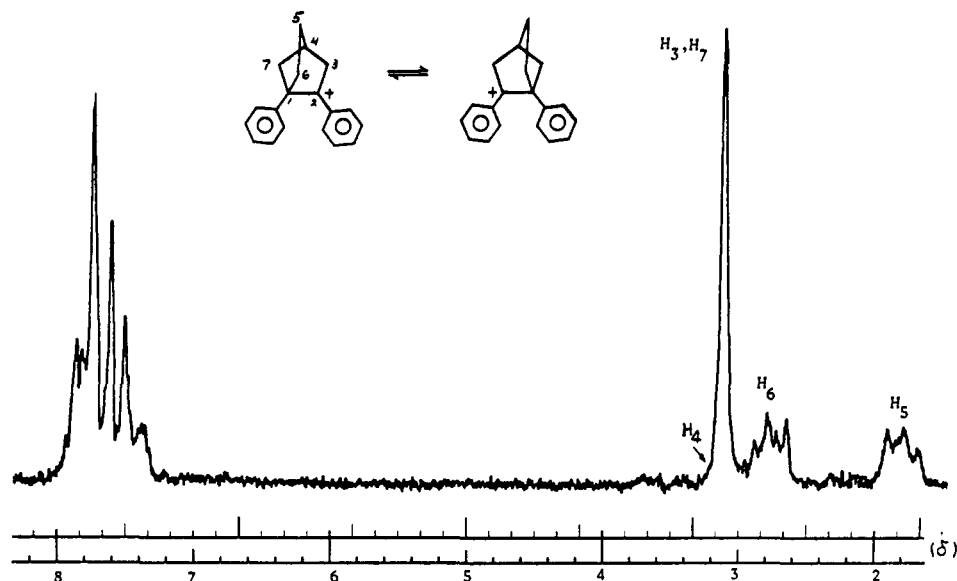
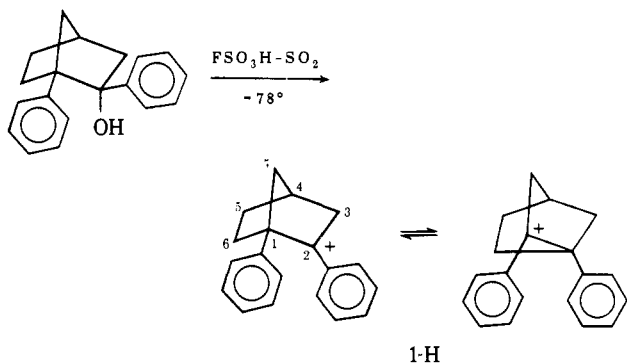


Figure 1. Pmr spectrum (60 MHz) of the 1,2-diphenyl-2-norbornyl cation in  $\text{FSO}_3\text{H-SO}_2$  solution at  $-70^\circ$ .

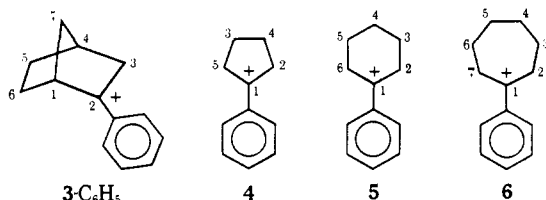
Table I. Pmr Parameters of 1,2-Diphenyl-2-norbornyl Cation and Model Cations<sup>a</sup>

Cation	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	o <sup>b</sup>	m	p	CH <sub>3</sub>
1-OH			3.35	3.35	2.10	3.02	3.35		7.6-8.2		
2-CH <sub>3</sub>			3.10 <sup>c</sup>	3.10	1.82	2.75	3.10		7.3-7.9		
3-CH <sub>3</sub>	4.64 (d, 6.5)		2.42	2.86	1.52	2.86	2.42				2.43
3-C <sub>6</sub> H <sub>5</sub>	4.83 (d, 6.5)		2.70	2.70	1.47	3.28, 1.09	1.71				3.00
4		4.09			4.09			8.66	7.90	8.44	
5		3.81				3.81		8.71	7.87	8.46	
6		4.30 <sup>d</sup>	2.42	2.20	2.20	2.42	4.30	8.70	7.89	8.50	
								9.00	8.16	8.78	

<sup>a</sup> Chemical shifts are in  $\delta$  (ppm) relative to external TMS. Cationic solutions are obtained in  $\text{FSO}_3\text{H-SO}_2\text{ClF}$  unless otherwise indicated.  
<sup>b</sup> Aromatic carbons are indicated by o = ortho carbons, m = meta carbons, and p = para carbons. <sup>c</sup> In  $\text{FSO}_3\text{H-SO}_2$ . <sup>d</sup> In  $\text{FSO}_3\text{H-SbF}_6\text{-SO}_2\text{ClF}$ .



charge delocalization into the aromatic ring which is believed to be the result of unfavorable nonbonded interaction between the two phenyl rings that forces them out of plane for  $\pi$ - $p$  overlap. To prove this latter point, several model phenylcycloalkylcarbenium ions (**3-C<sub>6</sub>H<sub>5</sub>**, **4**,<sup>9a</sup> **5**,<sup>9a</sup> and **6**<sup>9b</sup>) were studied and their pmr



(9) (a) D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969). (b) This work, see Experimental Section.

parameters are summarized in Table I. All these ions show similar characteristic phenyl ring patterns in their pmr spectra indicating substantial charge delocalization into the neighboring phenyl group. We therefore conclude that ion **1-H** is a classical carbenium ion undergoing rapid degenerate 1,2 Wagner-Meerwein shift with little charge delocalization into the phenyl rings.

The complete Fourier transform cmr spectrum of ion **1-H** was also obtained and compared with those of the 2-phenyl-2-norbornyl cation<sup>10a</sup> as well of the 1,2-dimethyl-<sup>10b</sup> and -2-methyl-2-norbornyl cations.<sup>10a</sup> Carbon shifts and corresponding coupling constants ( $J_{\text{CH}}$ ) for these ions are summarized in Table II with their assignments. The average cmr shifts for the C<sub>1</sub> and C<sub>2</sub> carbons in ion **1-H** ( $\delta_{13\text{C}} + 22.5$ ) is very close to that in the model ion **2-CH<sub>3</sub>** ( $\delta_{13\text{C}} + 26.0$ ) indicating that the former also is a rapidly equilibrating ion. The average of the cmr shifts of the C<sub>1</sub> and C<sub>2</sub> carbons in the dimethyl-*tert*-butylcarbenium ion **7** ( $\delta_{13\text{C}} - 11$ )<sup>5a</sup> could be considered a model for a rapidly equilibrating structure of ion **1**, without charge delocalization. The observed average cmr shift of 22.5 for **1-H** apparently indicates that the ion is a tertiary rapidly equilibrating structure with limited charge delocalization. C<sub>2</sub> in the 2-phenyl-2-norbornyl cation **3-C<sub>6</sub>H<sub>5</sub>** has been shown to have a

(10) (a) Only partial cmr spectra were previously given for these ions.<sup>4,7a,b</sup> (b) Minor corrections of cmr assignments are made: C<sub>3</sub> in **2-CH<sub>3</sub>** have carbon shifts  $\delta_{13\text{C}} + 146.0$  ( $J_{\text{CH}} = 134.5$  Hz) instead of the previously reported value,  $\delta_{13\text{C}} + 179$ .

carbon shift of  $\delta_{13C} - 63.5$  and  $C_1$  has a carbon shift of  $\delta_{13C} 134.0$ . Correcting the  $C_1$  shift for the phenyl substituent effect (approximate deshielding of 15–20 ppm is expected<sup>11</sup>) gives an estimated carbon shift of  $\delta_{13C} + 109$  for  $C_1$  in **1-H**. The average of these two shifts ( $C_1 + 109$  and  $C_2 - 63.5$ ) is  $+22.8$  which gives the estimated average cmr shift for  $C_1$  and  $C_2$  in the rapidly equilibrating ion **1-H**. This estimated value is almost identical with the experimentally observed one. In addition, carbon shifts of  $C_3$ ,  $C_4$ ,  $C_5$ , and  $C_6$  in ion **1-H** are very close to the corresponding shifts in the rapidly equilibrating ion **2-CH<sub>3</sub>** (Table II). We therefore conclude that both ions **1-H** and **2-CH<sub>3</sub>** are rapidly equilibrating carbenium ions with a similar degree of charge delocalization.

The most noticeable aspect of the cmr spectrum of **1-H** (Figure 2) is that only a small degree of the positive charge has been delocalized into the two equivalent phenyl rings. This is seen from both ortho and para carbon resonances in **1-H** which are more shielded than those in the model cations **3-6**. The ortho carbon shifts in typical phenylcarbenium ions are all about  $\delta_{13C} + 50$  to  $+55$ , and the para carbon shifts are about  $\delta_{13C} + 40$ . In **1-H** the ortho and para carbon shifts are found at  $\delta_{13C} 58.9$  and  $52.5$ , respectively. Apparently, charge delocalization into the phenyl rings in **1-H** is restricted by the unfavorable nonbonded interaction existing between the phenyl rings, due to which none of them can reach the desired planar geometry for effective charge delocalization. In **3-C<sub>6</sub>H<sub>5</sub>** such interaction is not expected to be substantial and effective charge delocalization into the phenyl ring is observed. The energy barrier for the 1,2 Wagner–Meerwein shift in ion **1-H** is therefore expected to be as low as that in the rapidly equilibrating ion **2-CH<sub>3</sub>**. This is also seen from the experimental fact that the rapid equilibration process in **1-H** cannot be frozen out on the nmr time scale even at  $-135^\circ$ . The Wagner–Meerwein shift in the 1,2-dianisyl-2-norbornyl cation as shown by Schleyer, *et al.*,<sup>2</sup> and in the 1,2-dimethoxy-2-norbornyl cation as shown by Nickon, *et al.*,<sup>3</sup> could be slowed down or frozen out at low temperatures. In the case of 1,2-dimethyl- or -diphenyl-2-norbornyl cations, there was no indication of similar “freezing out” of the pmr shifts even at  $-135^\circ$ . The positive charge is therefore expected to be substantially localized on oxygen in both the dimethoxy- and dianisyl-substituted 2-norbornyl cations and thus increases the barrier for the 1,2 Wagner–Meerwein shift.

Since the phenyl rings in **1-H** are not delocalizing the positive charge by significant conjugative interaction, the difference of the averaged carbon shifts of  $C_1$  and  $C_2$  between **1-H** and **2-CH<sub>3</sub>** ( $\delta_{13C} 3.5$  ppm) can be accounted for by the difference of the inductive effect between the phenyl and methyl groups.<sup>12</sup>

A detailed analysis of the pmr spectrum of the 2-phenyl-2-norbornyl cation has been previously given,<sup>7a,10a</sup> and showed no indication of nonequivalence of the ortho protons. The total Fourier transform cmr spectrum of **3-C<sub>6</sub>H<sub>5</sub>** reveals, however, that the two ortho phenyl ring carbons are nonequivalent (Table II). In order

(11) G. A. Olah, R. Waack, M. A. Doran, and E. B. Baker, *J. Amer. Chem. Soc.*, **88**, 1272 (1966).

(12) (a) G. J. Ray, A. K. Colter, D. G. Vavis, D. E. Wisnosky, and R. J. Kurlander, *Chem. Commun.*, 815 (1968); (b) G. J. Ray, R. J. Kurlander, and A. K. Colter, *Tetrahedron*, **27**, 735 (1971).

Table II. Cmr Parameters of 1,2-Diphenyl-2-norbornyl Cation and Model Cations in  $FSO_3H-SO_2ClF^a$

Ion	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$	$C_7$	$q^b$	o	m	p	$CH_3$	
<b>1-H</b>	22.5 (s)	22.5 (s)	145.5 (t, 140.7)	158.7 (d, 150.7)	171.8 (t, 130.4)	160.8 (t, 136.5)	145.5 (t, 140.7)	56.5 (s)	58.9 (165.0)	62.5 (160.5)	52.5 (198.0)		
<b>2-CH<sub>3</sub></b>	26.0 (s)	26.0 (s)	146.0 (t, 134.5)	152.5 (d, 152.6)	169.4 (t, 137.4)	154.0 (t, 148.5)	146.0 (t, 134.5)						176.0 (q, 130.5)
<b>3-CH<sub>3</sub></b>	113.0 (d, 169.5)	-77.3 (s)	138.2 (t, 135.4)	165.5 (d, 175.1)	158.0 (t, 132.8)	153.6 (t, 150.2)	170.2 (t, 140.2)						150.9 (q, 151.2)
<b>3-C<sub>6</sub>H<sub>5</sub></b>	134.0 (d, 158.4)	-63.5 (s)	142.8 (t, 138.6)	153.7 (d, 154.7)	159.2 (t, 142.6)	152.0 (t, 136.6)	168.0 (t, 137.9)	59.9 (s)	51.8 (162.4)	61.0 (168.3)	41.1 (164.3)		
<b>4</b>	-74.6 <sup>c</sup>	145.5	166.6	166.6	145.4			57.1	51.1 (166.3)	61.3	39.5		
<b>5</b>	-65.8 <sup>c</sup>	148.1	152.0	166.0	152.0	148.0		57.0	54.9	61.9	40.1		
<b>6</b>	-66.3 <sup>c</sup>	147.0	163.8	165.1	165.1	163.8	147.0	54.1	53.4	63.9	39.9		

<sup>a</sup> Cmr chemical shifts are calculated directly from external  $CS_2$  signal ( $\delta_{13C} 0$ ). Multiplicities and coupling constants (in Hz) are shown in parentheses: s = singlet, d = doublet, and t = triplet. Aromatic carbons are indicated by q = quaternary carbon, o = ortho carbons, m = meta carbons, and p = para carbons. In off-resonance cmr spectra o, m, and p carbons display as doublets, while q carbons are singlets. <sup>c</sup> Phenylcycloalkyl cations are generated in  $FSO_3H-SbF_6-SO_2ClF$  solutions from their corresponding tertiary alcohols (coupling constants are not shown).

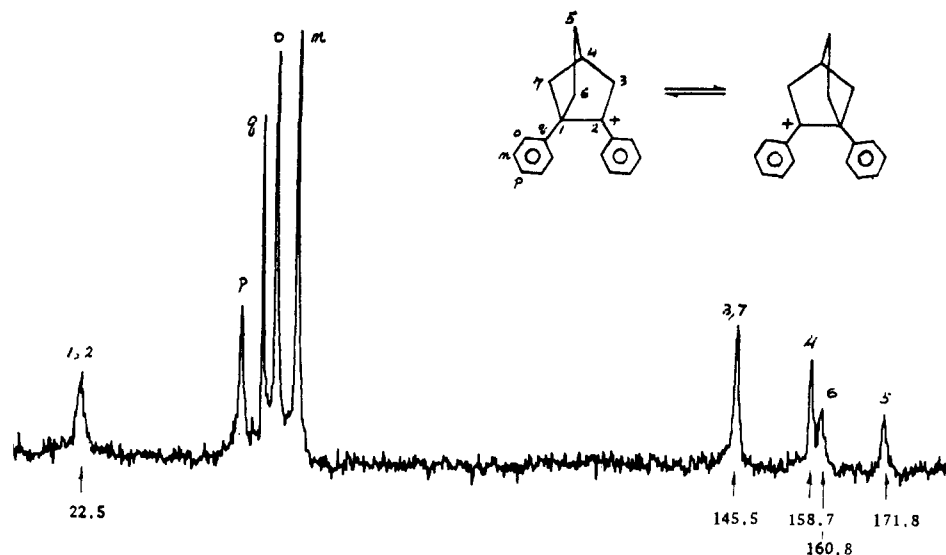
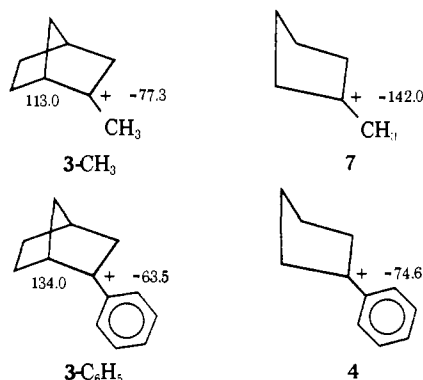


Figure 2.  $^{13}\text{C}$  spectrum of the 1,2-diphenyl-2-norbornyl cation.

to achieve p- $\pi$  overlap between the phenyl  $\pi$  system and the electron-deficient center, the phenyl ring in **3**- $\text{C}_6\text{H}_5$  must orient itself so that the two ortho carbon atoms are becoming nonequivalent. The carbon shifts of the two meta carbon atoms are equivalent. The energy barrier for rotation along the carbon-phenyl ring bond must be high since we could not observe any spectral change up to temperatures above  $+45^\circ$ , when ion **3**- $\text{C}_6\text{H}_5$  starts to decompose. This observation also indicates that conjugative delocalization by the phenyl ring is the major factor in stabilizing ion **3**- $\text{C}_6\text{H}_5$ . The 2-methyl-2-norbornyl cation **3**- $\text{CH}_3$  has also been shown to be a tertiary carbenium ion stabilized by partial  $\sigma$  delocalization.  $\text{C}_1$  in ion **3**- $\text{CH}_3$  has a carbon shift of  $\delta_{^{13}\text{C}} + 113.0$  (d,  $J_{^{13}\text{C}} = 169.5$  Hz), while  $\text{C}_1$  in **3**- $\text{C}_6\text{H}_5$  is about 20 ppm more shielded ( $\delta_{^{13}\text{C}} + 134.0$ ,  $J_{^{13}\text{C}} = 158.4$ ). Much less  $\sigma$  delocalization is therefore involved in **3**- $\text{C}_6\text{H}_5$  than in **3**- $\text{CH}_3$ . Ion **3**- $\text{C}_6\text{H}_5$  has



been considered to be a completely classical 2-substituted 2-norbornyl cation.<sup>7a,9a</sup> We have now compared the carbon shifts for the carbenium center in **3**- $\text{C}_6\text{H}_5$  ( $\delta_{^{13}\text{C}} - 63.5$ ), **4** ( $\delta_{^{13}\text{C}} - 74.6$ ), **5** ( $\delta_{^{13}\text{C}} - 65.8$ ), and **6** ( $\delta_{^{13}\text{C}} - 66.3$ ) showing that ion **3**- $\text{C}_6\text{H}_5$  has a slightly shielded carbon shift for the carbenium center compared with those in the other ions. A limited degree of  $\sigma$  delocalization might thus also be operative in **3**- $\text{C}_6\text{H}_5$ . It is further possible to utilize the ring shifts, particularly the para carbon shift as a guide for charge distribution in the phenylcarbenium ions (*i.e.*, in the

phenyl group directly attached to the carbenium center). A good linear relationship between electron densities and chemical shifts can be assumed (the para shifts being generally not affected by steric factors). A comparison between the para shifts in the 1,2-diphenyl-2-norbornyl cation **1**-H and 2-phenyl-2-norbornyl cation **3**- $\text{C}_6\text{H}_5$  shows a only slightly deshielded para shift ( $\delta_{^{13}\text{C}} 52.5$ ) in **1**-H, but a substantially more deshielded para shift ( $\delta_{^{13}\text{C}} 41.1$ ) in **3**- $\text{C}_6\text{H}_5$ .

It is further possible to use the difference of the carbenium carbon shifts in a series of carbocations to understand the extent of charge delocalization. For instance, the differences of the carbenium carbon resonances between **3**- $\text{C}_6\text{H}_5$  and **4**, **3**- $\text{C}_6\text{H}_5$  and **5**, as well as **3**- $\text{C}_6\text{H}_5$  and **6** are 11.1 ppm, 2.3 ppm, and 2.8 ppm, respectively (Table II). All these phenylcarbenium ions are therefore expected to experience a similar degree of charge delocalization through p- $\pi$  conjugation between the phenyl ring and the electron-deficient center. In contrast, the difference of the carbenium carbon resonances between the 2-methyl-2-norbornyl cation **3**- $\text{CH}_3$  and 1-methyl-1-cyclopentyl cation **7** is very significant (*i.e.*, 64.7 ppm). If one assumes that a similar degree of conjugation through the phenyl ring exists in **3**- $\text{C}_6\text{H}_5$  and **4**, and a similar degree of hyperconjugative effect through methyl group exists in **3**- $\text{CH}_3$  and **7**, then the large difference (64.7 ppm) in carbon shifts found in the case of the latter pair of ions must be accounted for by  $\text{C}_1$ - $\text{C}_6$   $\sigma$  delocalization operating in the 2-methyl-2-norbornyl cation. A small difference (11.4 ppm) in carbon shifts existing in the case of the former pair of ions can be accounted for by a limited degree of  $\text{C}_1$ - $\text{C}_6$   $\sigma$  delocalization operating in the 2-phenyl-2-norbornyl cation.

The  $^{13}\text{C}$  nmr study of the 2-phenyl- (**3**- $\text{C}_6\text{H}_5$ ) and 1,2-diphenyl-2-norbornyl (**1**-H) cations when compared with the related 2-methyl- (**3**- $\text{CH}_3$ ) and 1,2-dimethyl-2-norbornyl (**2**- $\text{CH}_3$ ) cations allows a comparison of  $\pi$  and  $\sigma$  delocalization in substituted 2-norbornyl cations. **3**- $\text{C}_6\text{H}_5$  clearly is a typical tertiary phenylcarbenium ion with substantial charge delocalization into the phenyl ring and with only very limited  $\text{C}_1$ - $\text{C}_6$   $\sigma$  delocalization. In contrast,  $\pi$  delocalization into the

phenyl ring in 1-H is drastically reduced due to unfavorable nonbonded interaction between the two phenyl groups.  $\pi$  delocalization consequently in this ion is substantially taken over by  $\sigma$  delocalization of the C<sub>1</sub>-C<sub>6</sub> bond and induces the fast 1,2 Wagner-Meerwein shift. We suggest that consideration of the complete cmr spectra of carbocations allows further differentiation of the nature of charge delocalization. This point can be well illustrated when comparison is made between the 2-methyl- and 2-phenyl-2-norbornyl cations. The C<sub>2</sub> carbon shifts are  $\delta_{13C}$  -77.3 and -63.5, respectively. If only these shifts would be compared, the phenyl group could be considered only slightly more effective in delocalizing charge than the methyl group. This conclusion would, however, be very misleading. In fact the charge is substantially delocalized through p- $\pi$  conjugation into the phenyl ring in ion 3-C<sub>6</sub>H<sub>5</sub>, and charge delocalization in 3-CH<sub>3</sub> is the result of C<sub>1</sub>-C<sub>6</sub>  $\sigma$ -bond hyperconjugation. The effect of the methyl group (*i.e.*, C-H hyperconjugation) is small when compared with that of the C<sub>1</sub>-C<sub>6</sub> bond (*i.e.*, C-C hyperconjugation) as is shown by the comparison of CH<sub>3</sub> carbon shifts in several methyl-substituted carbenium ions.<sup>5a</sup> We have recently commented on the continuity of charge delocalization in carbocations with or without significant bridging.<sup>13</sup> The partial  $\sigma$ -bond delocalization observed in the 2-methyl-2-norbornyl cation 3-CH<sub>3</sub> can be readily explained without the necessity of symmetrical bridging.

Conclusions reached concerning the relative ability of phenyl and methyl groups to affect  $\pi$  and  $\sigma$  delocalization, respectively, are also in accordance with results of solvolytic studies.<sup>14,15</sup> Brown has solvolyzed *exo*- and *endo*-2-aryl-2-norbornyl derivatives and found that the relative rates of the *exo* isomers with respect to the corresponding *endo* isomers remain essentially constant as the electron demand of the cationic center is increased over the same range by varying substituents on the phenyl ring.<sup>14a,b,d</sup> Consequently, he concluded that no significant  $\sigma$  participation can be present in the 2-aryl-2-norbornyl system. According to our cmr studies,  $\sigma$  delocalization in 3-C<sub>6</sub>H<sub>5</sub> is indeed found to be much smaller than that in 3-CH<sub>3</sub>, and therefore no significant  $\sigma$  participation in the solvolytic reaction of 2-aryl-2-norbornyl derivatives is expected, as the stabilization of the developing carbenium ion center in solvolytic reactions also comes mainly from aryl ring and not from the  $\sigma$  bond. For the same reason the *exo/endo* rate ratio is not expected to change significantly. If  $\sigma$  participation is found to be limited in the related carbenium ions under stable ion conditions, it is expected to be even more limited in solvolytic reactions. The same is, however, not expected to be applicable in tertiary 2-alkyl-2-norbornyl systems, since  $\sigma$  participation in

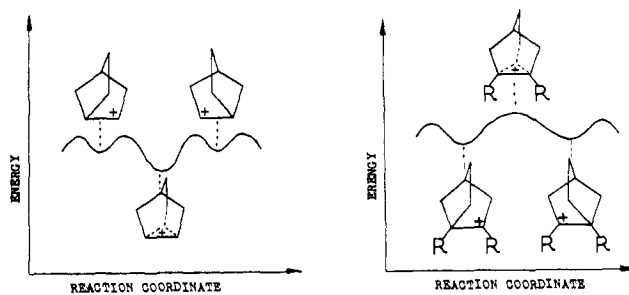


Figure 3.

ion 3-CH<sub>3</sub> is indeed found to be significant. A change in the *exo/endo* rate ratio is therefore expected.

### Conclusions

Although no solvolytic studies were reported for 1,2-diphenyl-2-norbornyl derivatives, the results of solvolysis of related 1,2-dimethyl-2-norbornyl derivatives are instructive.<sup>15</sup> Evidence has shown the importance of  $\sigma$  delocalization in the solvolysis of secondary norbornyl systems.<sup>16</sup> This factor is becoming less dominant affecting rates of solvolysis in tertiary norbornyl derivatives. The stable 2-norbornyl cation has been shown at low temperature to be completely bridged (nonclassical).<sup>6</sup> Tertiary 2-substituted 2-norbornyl cations only show partial  $\sigma$  delocalization, and even much less  $\sigma$  delocalization is found in 1,2-diaryl- (alkyl) or 2,3-dialkyl-2-norbornyl<sup>1a</sup> cations where 1,2 Wagner-Meerwein or 3,2-hydrogen shifts can be extremely fast. The symmetrically  $\sigma$ -bridged 2-norbornyl cation must be consequently represented as an energy minimum (intermediate) on the potential energy diagram of the related solvolysis reactions, while such bridged ions can be considered either only as transition states (energy maxima) or metastable intermediates with very shallow minima on a flat energy profile (see Figure 3) in 1,2-diaryl(alkyl)-2-norbornyl systems (*i.e.*, 1-H and 2-CH<sub>3</sub>).

### Experimental Section

**1,2-Diphenyl-*endo*-2-norborneol** was prepared according to the procedure of Schleyer, *et al.*,<sup>2b</sup> mp 108–110°.

**Preparation of the 1,2-Diphenyl-2-norbornyl Cation 1-H.** 1,2-Diphenyl-*endo*-2-norborneol in SO<sub>2</sub> (or SO<sub>2</sub>ClF) solution precooled at -78° was slowly added to a freshly prepared FSO<sub>3</sub>H-SO<sub>2</sub> (SO<sub>2</sub>ClF) solution at Dry Ice-acetone bath temperature (with vigorous stirring) to give an approximately 20% solution of the ion.

**Quenching of a solution of the 1,2-diphenyl-2-norbornyl cation** was carried out by adding the solution of the cation 1-H to an excess of KOH-SO<sub>2</sub>(SO<sub>2</sub>ClF) at -78°. The resulting solution was slowly allowed to warm to 0°, poured into ice, extracted with ether, and then washed to neutral. The ether extract was dried (MgSO<sub>4</sub>) and concentrated and the products were identified by glc and pmr.

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectroscopic studies were carried out the same way as reported previously.<sup>1a</sup>

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