199.

Anal. Calcd for $C_{20}H_{34}O_3S_2$: C, 62.13; H, 8.86. Found: C, 62.50; H, 8.62.

10-Nor-9,11-seco-9,11-dideoxy-9,11-epidithioprostaglandin H_2 (3). A slightly turbid solution of **22** (0.091 g, 0.24 mmol) in *tert*-butyl alcohol (2.5 mL) and 3 N aqueous potassium hydroxide (0.78 ML, 2.3 mmol) was stirred at room temperature for 6 h. Hydrolysis was complete by TLC analysis. The solution was poured into 10% aqueous sodium bisulfate (40 mL) and extracted with ethyl acetate (400 mL total). The extract was washed with brine (3 × 40 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by HPLC over 17.1 g of acid-washed silica gel (Mallincrodt CC-4). The column was eluted with 5:1 hexane-ethyl acetate. Fractions of 20 mL volume were collected. The product (**3**, 0.054 g, 62%) was eluted in fractions 2-18 as a pale yellow oil: IR (cm^{-1}, neat), 3600-2300, 2940, 1710, 1455, 1405, 1240, 970, and 725; ^1H NMR (δ, $CDCl_3$) 5.45 (m, 4 H, olefinic protons), 0.89 (t, 3 H, J = 5 Hz, $-CH_3$); high-resolution mass spectrum (TMS derivative, m/e) 516.2593 (M^+, calcd for $C_{25}H_{48}Si_2O_3S_2$: 516.2583), 501, 483, 445, 435, 426, 393, 361, 355, 341, 337, 313, 199 and 173.

Preparation of Human Platelet Rich Plasma. Human platelet rich plasma (PRP) was prepared by withdrawing blood directly into 0.1 volumes of 3.8% (v/v) trisodium citrate, followed by centrifugation at 200xg for 10 min at room temperature.

Analysis of Endoperoxide Analogue Aggregatory Activity. To assess the influence of the endoperoxide analogues on human platelet aggregation, 1.0 mL of PRP was prewarmed to 37 °C and stirred at 1100 rpm in a Payton Aggregometer, Payton Associates, Buffalo, NY. Following the warming period, dose-response curves were constructed by using the endoperoxide analogues and these responses were then compared with the dose-response curve of authentic PGH_2. In cases where the analogue did not exert agonist activity, platelets were preincubated for 2 min with the appropriate analogue and then challenged with PGH_2. This test uncovered any potential antagonism of PGH_2 by the analogues. Aggregation data are reported as percent transmission.

Rat Aorta Constricting Activity. The intrinsic agonist activity of the analogues was tested by using spirally cut strips of rat aorta according to the method of Furchgott.[21] The tissues were placed in 10-mL tissue baths at 37.5 °C; one end of the strip was fixed, and the other was attached to an isometric transducer (Grass FT .03) with an initial tension of 2 g. During a 1-h equilibration period, the tissue relaxed to an average basal tension of 1.55 ± 0.05 g. The Krebs solution contained 1.0 μg/mL of indomethacin to inhibit endogenous prostaglandin synthesis. Dose-response curves were constructed for the various agonists, and the data reported as ED_{50} in ng/mL.

Registry No. 1, 80559-54-2; **1** tetrakis(TMS), 80572-40-3; **2**, 80559-55-3; **2** bis(TMS), 80559-56-4; **3**, 80559-57-5; **3** bis(TMS), 80559-58-6; **4**, 31753-19-2; **5**, 80559-59-7; **5** bis(TMS), 80559-60-0; **6**, 13261-27-3; 10α-hydroxy-**5**, 80559-61-1; 10α,11α-epoxy-**6**, 80559-62-2; **7**, 80559-63-3; **7** tris(TMS), 80559-84-8; **8**, 80559-64-4; **8** TMS, 80572-41-4; **9**, 80559-65-5; **9** bis(TMS), 80559-66-6; **10**, 80559-67-7; **11**, 36323-03-2; **11** epoxide isomer 1, 38310-85-9; **11** epoxide isomer 2, 38344-07-9; **11** epoxide TMS, 80559-68-8; **12**, 80559-69-9; **12** bis(TMS), 80559-70-2; **13**, 80559-71-3; **14**, 80559-72-4; **15**, 80559-73-5; **15** bis(TMS), 80559-74-6; **16**, 80559-75-7; **17**, 80559-76-8; **18**, 80559-77-9; **18** TMS, 80559-78-0; **19**, 80559-79-1; **20**, 50559-80-4; **21**, 80559-81-5; **22**, 80559-82-6; **22** TMS, 80559-83-7.

Supplementary Material Available: A description of the X-ray crystallographic method used, tables of torsion angles, anistropic thermal parameters, hydrogen bonds and close intermolecular distances, hydrogen coordinates, and distances involving hydrogens, and a figure showing two views of compound **7** (8 pages). Ordering information is given on any current masthead page.

(21) R. F. Furchgott in "Methods in Medical Research", Vol. 8, H. D. Bouner, Ed., The Yearbook Publishers: Chicago, IL, 1960, pp 177-186.

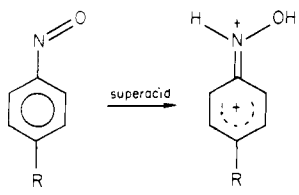
Preparation and ^{13}C and ^{15}N NMR Spectroscopic Study of Cyanocarbenium Ions. Substituent Effects on the Extent of Mesomeric Nitrenium Ion Character in Cyanodiphenylmethyl Cations. The Search for Related Stable α-Cyanocarbenium Ions[1]

George A. Olah,* Massoud Arvanaghi, and G. K. Surya Prakash

Contribution from the Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90007. *Received August 24, 1981*

Abstract: A series of para-substituted cyanodiphenylmethyl cations have been prepared by the ionization of the corresponding benzophenone cyanohydrins in superacid solutions at -78 °C. The ^{13}C and ^{15}N NMR spectroscopic data on these ions indicate that the extent of mesomeric nitrenium character largely depends on the electronic effect of the substituent on the aryl ring. The 7-cyano-7-norbornenyl cation was found to be of bishomoaromatic nature with some charge delocalization into the cyano group. Attempts to prepare the related α-cyanocarbocations from acyclic, cyclic, bicyclic, and tricyclic precursors were, however, unsuccessful.

Nitrenium ions with divalent positive nitrogen have been claimed as intermediates in the reactions of some nitrogen-containing organic compounds.[2,3] Attempted generation of them as distinct species under long-lived stable ion conditions has thus far been unsuccessful.[4] Protonation of nitrosobenzenes **1**-R in superacidic media has led only to benzeniumiminium dications **2**-R.[4,5]



1-R 2-R

(1) (a) Stable Carbocations, Part 239. For Part 238 see: G. A. Olah, G. K. S. Prakash, and T. Nakajima, *J. Am. Chem. Soc.*, in press. (b) Appeared as a preliminary communication: G. A. Olah, G. K. S. Prakash, and M. Arvanaghi, *ibid.*, **102**, 6640-6641 (1980).

(2) P. G. Gassman, *Acc. Chem. Res.*, **3**, 26-33 (1970).

(3) P. G. Gassman and G. D. Hartman, *J. Am. Chem. Soc.*, **95**, 449-454 (1973).

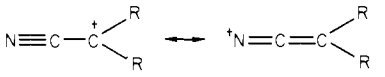
0002-7863/82/1504-1628$01.25/0

Table I. ^{13}C NMR[a] and ^{15}N NMR[b] Chemical Shifts of Cyanocarbenium Ions in $CDCl_3/FSO_3H/SO_2ClF$ Solution at −80 °C

carbocation	C+	C-1	C-2	C-3	C-4	C-5	C-6	-C≡N	miscellanious	^{15}N shift
5-4-OCH_3	147.6	132.9	145.8	122.4	179.2	122.4	145.8	113.1	OCH_3 60.6	260.2
5-4-CH_3	161.8	137.7	147.3	136.8	172.9	136.8	144.2	113.1	CH_3 25.3	273.4
5-H	168.8	138.2	148.2	133.7	153.3	133.7	143.8	112.1		283.0
5-4-Cl	164.8	137.5	145.6	135.6	162.6	135.6	145.6	112.2		
5-4-F	163.6	136.7	150.7	124.6 (J_{C-C-F} = 23.7 Hz)	180.6 (J_{C-F} = 297.8 Hz)	124.6 (J_{C-C-F} = 23.7 Hz)	150.7	113.1		279.2
6	84.5	50.9	135.9 (J_{C-H} = 177.6 Hz)	135.9 (J_{C-H} = 177.6 Hz)	50.9	21.6	21.6	114.00		

[a] ^{13}C chemical shifts are in ppm from external capillary tetramethylsilane. [b] ^{15}N chemical shifts are in ppm from external anhydrous ammonia.

The ambivalent nature of a α-cyano functionality on a carbocationic center has been recently demonstrated by the solvolytic work of Gassman and co-workers.[6-8] Inductively, the cyano group is strongly destabilizing. However, the major portion of this effect is offset by the stabilizing effect of mesomeric nitrenium ion structure **4**. This effect has also been evaluated theoretically.[9]

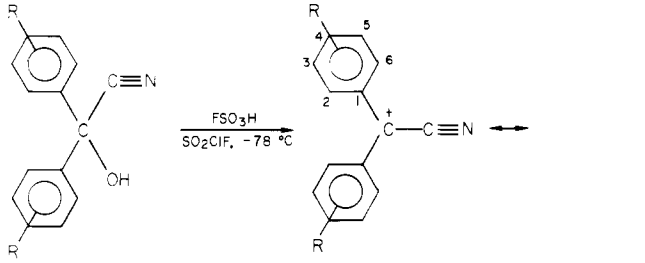


3 4

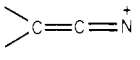
Recently in a preliminary communication[1b] we reported that the cyanodiphenylmethyl cation **5**-H has significant mesomeric nitrenium ion character inspite of competitive aryl ring charge delocalization. Interested in the preparation of the still elusive nitrenium ions, we wish to report preparation and ^{13}C and ^{15}N NMR spectroscopic investigation of a series of para-substituted cyanodiphenylmethyl cations **5**-R under long-lived stable ion conditions. Attempts to prepare other analogous α-cyano-substituted cations met with little success except for the 7-cyano-7-norbornenyl cation **6**.

Results and Discussion

The substituted cyanodiphenylmethyl cations **5**-R were prepared by the ionization of the corresponding cyanohydrins **7**-R[10] in



7-R 5-R



5-R(b)

R = 4-OCH_3, 4-CH_3, H, 4-Cl, 4-F, 4-CF_3, 3,5-$(CF_3)_2$

FSO_3H/SO_2ClF at −78 °C. The ^{15}N NMR spectra were obtained by ionizing 10% ^{15}N-enriched cyanohydrin precursors. The 7-cyano-7-norbornenyl cation **6** was prepared from the cyanohydrin **8**.[7] Attempts to prepare α-cyano-substituted cations starting from cyanohydrins **9**–**15** under a variety of superacid conditions were,

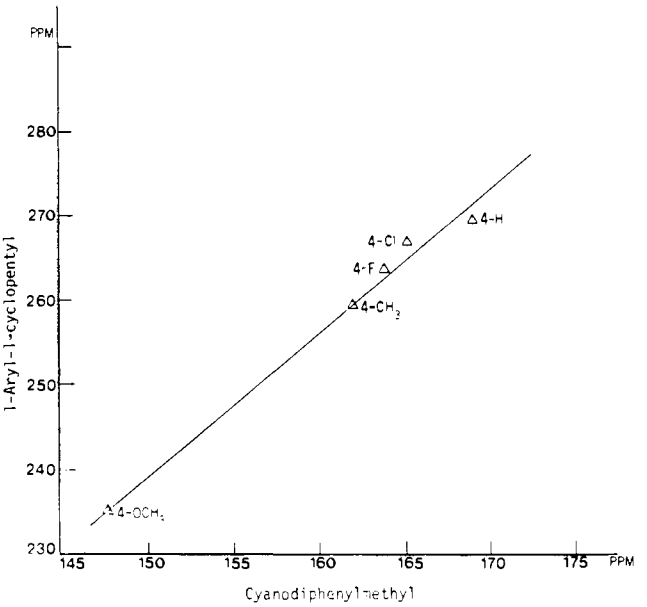


Figure 1. A plot of ^{13}C NMR chemical shifts of the cationic center in cyanodiphenylmethyl cations **5**-R vs. those in 1-aryl-1-cyclopentyl cations.

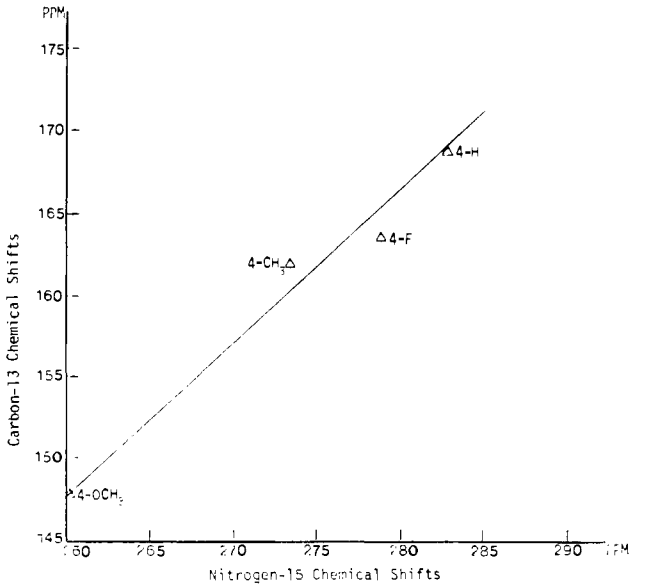
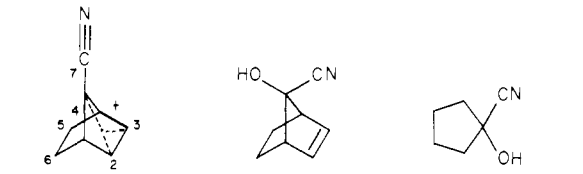
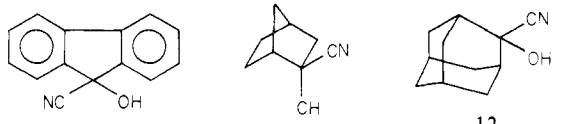


Figure 2. A plot of ^{15}N NMR chemical shifts of the cyanonitrogen vs. the ^{13}C NMR chemical shifts of the cationic center in cyanodiphenylmethyl cations **5**-R.

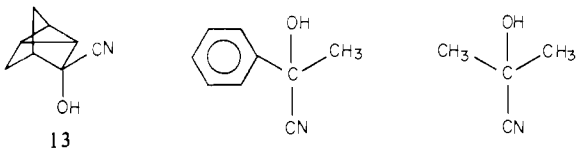
(4) G. A. Olah and D. J. Donovan, *J. Org. Chem.*, **43**, 1743–1750 (1978).
(5) (a) T. Okamoto, K. Shudo, and T. Ohta, *J. Am. Chem. Soc.*, **97**, 7184–7185 (1975). (b) T. Ohta, K. Shudo, and T. Okamoto, *Tetrahedron Lett.*, 101–104 (1977). (c) K. Shudo, T. Ohta, Y. Endo, and T. Okamoto, *ibid.*, 105–108 (1977).
(6) P. G. Gassman and J. J. Talley, *J. Am. Chem.*, **102**, 1214–1216 (1980).
(7) P. G. Gassman and J. J. Talley, *ibid.*, **102**, 4138–4143 (1980).
(8) (a) P. G. Gassman, K. Saito, and J. J. Talley, *ibid.*, **102**, 7613–7615 (1980). (b) An earlier report on the solvolysis of α-cyanotosylates can be found in a senior thesis of Professor Schleyer's group; E. A. Hyson, Senior Thesis, Princeton University, May 1971.
(9) D. A. Dixon, P. A. Charlier, and P. G. Gassman, *ibid.*, **102**, 3957–3959 (1980).
(10) P. G. Gassman and J. J. Talley, *Tetrahedron Lett.*, 3773–3776 (1978).



6 8 9



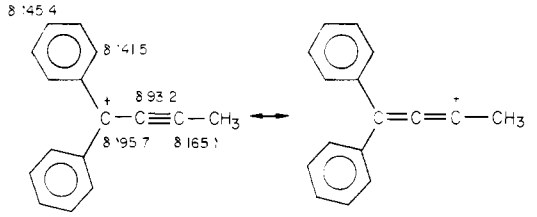
10 11 12



13 14 15

however, unsuccessful. It was also not possible to generate **5**-4-CF_3 or **5**-3,5-$(CF_3)_2$ under long-lived stable ion conditions. The ^{13}C and ^{15}N NMR data of the prepared cyanocarbocations are listed in Table I. Figure 1 shows a plot of cationic center chemical shifts of ions **5**-R with those of the model 1-aryl-1-cyclopentyl cations.[11] Figure 2 depicts a plot of ^{15}N NMR chemical shifts of **5**-R vs. their ^{13}C NMR chemical shifts of the cationic center.

Cyanodiphenylmethyl Cation 5-H. The deep orange solution obtained upon addition of a solution of benzophenonecyanohydrin **7**-H into FSO_3H/SO_2ClF at −78 °C showed a ^{13}C NMR spectrum, wherein the cationic center carbon absorbed at $\delta(^{13}C)$ 168.8 followed by para carbon at $\delta(^{13}C)$ 153.3. The cyano carbon absorbed at $\delta(^{13}C)$ 112.1, about 9 ppm shielded over that in the neutral progenitor.[12] The substantial deshielding of both ortho and para carbons (Table I) and some shielding of cyano carbon are indicative of extensive charge delocalization into the aromatic ring as well as into the cyano group through the mesomeric nitrenium ion form **5**-H(b). The cation **5**-H is comparable to the related 1,1-diphenyl-2-butynyl cation **16**[13] (which also has significant mesomeric vinyl cation contribution) although the charge delocalization into the aromatic ring is considerably less in the latter.



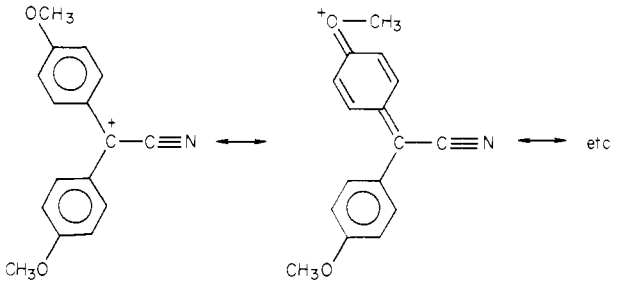
16-a 16-b

In the ^1H NMR spectrum, the aromatic protons are observed as a multiplet at $\delta(^1H)$ 7.6–8.6 which is substantially deshielded over that in the neutral precursor[13] (≈1 ppm).

To ascertain the extent of mesomeric nitrenium ion character in **5**-H, we prepared 10% ^{15}N-enriched ion from the ^{15}N-enriched precursor. In the ^{15}N NMR spectrum of the ion **5**-H at −80 °C, the cyano nitrogen was observed at $\delta(^{15}N)$ 283.0, which is 30 ppm deshielded over that in the neutral precursor ($\delta(^{15}N)$ 253.0). The lack of any proton coupling with the nitrogen clearly supports the formation of cyanodiphenylmethyl cation **5**-H and not the nitrilium ion. As a matter of fact, a substantial ^{15}N shielding is observed for nitrilium ions (R—C=NH^+) over the neutral nitrile precursors.[14] The observed 30-ppm deshielding clearly indicates significant carbon–nitrogen double-bond character. The observed ^{15}N NMR chemical shift is more comparable to that of an imine (observed around $\delta(^{15}N)$ 318).[15] The observed ^{15}N chemical shift data clearly support substantial mesomeric nitrenium ion contribution to the overall structure of the cation **5**-H, in spite of competing aryl ring charge delocalization.

Effect of Substituents on the Aryl Ring. To demonstrate the contribution of mesomeric nitrenium ion character further, we decided to vary the electron demand of the cationic center by substituting the phenyl ring with electron-releasing as well as electron-withdrawing groups at the para position. As mentioned earlier, we were unable to prepare either **5**-4-CF_3 or **5**-3,5-$(CF_3)_2$ cations.

The cation **5**-4-OCH_3, wherein the para substituent is strongly

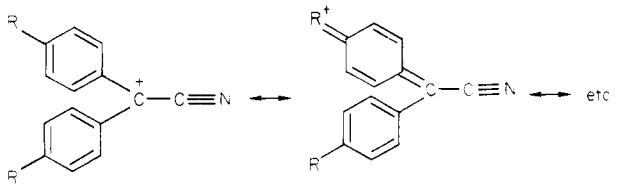


5-4(OCH_3)

electron releasing, showed the following ^{13}C NMR chemical shifts (Table I). The cationic center was observed at $\delta(^{13}C)$ 147.6, substantially shielded over that in **5**-H. The para carbon was seen at $\delta(^{13}C)$ 179.2, indicating significant charge delocalization into the aryl ring through the para-quinoidal forms. However, the cyanocarbon is observed at $\delta(^{13}C)$ 113.1 and is deshielded by only 1 ppm as compared to that in the ion **5**-H. The cyano carbon chemical shift appears to be relatively insensitive to the enhanced aryl ring charge delocalization. The most crucial evidence for the decrease in mesomeric nitrenium ion contribution in **5**-4-OCH_3 comes from the ^{15}N NMR data. Infact, the ^{15}N shift for **5**-4-OCH_3 is observed at $\delta(^{15}N)$ 260.2, about 23 ppm shielded over that in the parent ion **5**-H.

Varying the para substituent to a methyl group, the ion **5**-4-CH_3 shows an intermittent behavior. In the ^{13}C NMR spectrum the cationic center is observed at $\delta(^{13}C)$ 161.8. The para carbon and cyano carbon are seen at $\delta(^{13}C)$ 172.9 and 113.1, respectively. Again the cyano carbon chemical shift is insensitive to the substituent on the aryl ring. The ^{15}N NMR shift of the ion **5**-4-OCH_3 falls in between those of **5**-4-OCH_3 and **5**-H. The ^{15}N shift is observed at $\delta(^{15}N)$ 273.4 which is about 10 ppm shielded over that in the parent ion **5**-H, but 13 ppm deshielded over that in **5**-4-OCH_3.

For comparison we also prepared the para-chloro and para-fluoro substituted cations **5**-4-Cl and **5**-4-F. In both cases there



5-R
R = Cl, F

is significant charge delocalization into the aryl ring through the

(11) D. G. Farnum, R. E. Botto, W. T. Chambers, and B. Lam, *J. Am. Chem. Soc.*, **100**, 3847–3855 (1978).

(12) The benzophenonecyanohydrin had the following spectral data: ^{13}C NMR shifts Ci δ 142.5, Co,Cp δ 128.7, Cm δ 125.9, CN δ 125.9, C_α δ 75.1; $\delta(^{15}N)$ 253; ^1H NMR δ 7–7.6 (m, 10 H, aromatic), 6.8 (s, 1 H, OH). The ^1H NMR spectra were obtained on a Varian Associates Model A56/60 NMR spectrometer.

(13) (a) G. A. Olah, R. J. Spear, P. W. Westerman, and J.-M. Dennis, *J. Am. Chem. Soc.*, *96*, 5855–5859 (1974). (b) G. K. S. Prakash, Ph.D. Dissertation, University of Southern California, 1978.

(14) G. C. Levy and R. L. Lichter "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley Interscience: New York, 1979, p 67.

(15) G. A. Olah, G. Liang, and V. K. Mo, *J. Org. Chem.*, **39**, 2394–2398 (1974).

halogen back donation.[15] In the ^{13}C NMR spectra the cationic center of **5**-4-Cl and **5**-4-F are observed at $\delta(^{13}C)$ 164.8 and 163.6, respectively, with substantial deshielding of the para carbons ($\delta(^{13}C)$ 162.6 and 180.6, respectively). We also managed to get the ^{15}N NMR data on the ion **5**-4-F. It has a ^{15}N chemical shift of $\delta(^{15}N)$ 279.2.

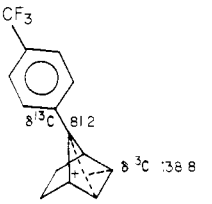
Recently we have demonstrated[16] that the ^{13}C NMR chemical shifts of the cationic center of α-aryl-substituted classical carbenium ions correlate well with those of model 1-aryl-1-cyclopentyl cations[11] with almost unit slope. Slopes considerably less than unity was attributed[16] to the presence of an additional charge delocalizing mechanism present in the system such as the interaction of either a cyclopropyl group or a phenyl ring with the electron-deficient carbocationic center. To test this hypothesis in our α-cyano-substituted cations **5**-R, we plotted their ^{13}C NMR chemical shifts of the cationic center vs. those of the model 1-aryl-1-cyclopentyl cations (Figure 1). With the limited number of substituents studied, we get a good correlation ($r = 0.988$). The most interesting aspect of the plot is the observed slope. The slope is 0.57 which is considerably less than the one observed for the similarly substituted 1,1-diarylethyl cation (slope 0.71).[11] In fact the observed slope 0.57 is close to those observed[16] for 1-aryl-1-cyclopropylethyl and 1-aryl-1-cyclopropylpropyl cations (0.55 and 0.59, respectively). In these cations there is additional charge delocalization to the cyclopropane ring. The observed slope, thus, definitely indicates the charge delocalizing ability of the α-cyano group.

Also we plotted the ^{13}C NMR chemical shifts of the cationic center of ions **5**-R vs. the ^{15}N NMR chemical shifts of the cyano nitrogen (Figure 2). Again a good correlation ($r = 0.975$) is obtained, indicating the cationic center carbon chemical shift and the cyano nitrogen chemical shift react similarly to the nature of the substituent on the aryl ring. This further reinforces the mesomeric charge delocalizing ability of the cyano substituent.

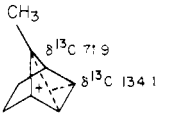
7-Cyano-7-Norbornenyl Cation 6. Dissolution of 7-cyano-7-*anti*-norborneol (**8**) in FSO_3H/SO_2ClF at −78 °C gave a deep red solution, whose ^{13}C NMR spectra showed peaks at $\delta(^{13}C)$ 135.9 (d, $J_{C-H} = 177.6$ Hz), 114.4 (s), 84.5 (s), 50.9 (d), and 21.6 (t).

From the observed symmetry and multiplicities the ion is readily assigned to 7-cyano-7-norbornenyl cation **6**. The olefinic carbons are assigned to the peak at $\delta(^{13}C)$ 135.9. The cationic center and the cyano carbon are assigned to peaks at $\delta(^{13}C)$ 84.5 and 114.4, respectively. In fact the cationic center chemical shift is close to that observed for the progenitor cyanohydrin carbon.[17] The ion is clearly of bishomoaromatic nature[18] with some charge delocalization into the cyano carbon through the mesomeric nitrenium form. The observed ^{13}C NMR data of the ion **6** can be compared to those in 7-substituted-7-norbornenyl cations **17**[18] and **18**.[19] The cyano carbon in **6** is deshielded by a ppm as compared to those in aryl-substituted analogues **5**-R.

Attempted Generation of Other α-Cyano-Substituted Cations. Attempted generation of 1-cyano-1-cyclopentyl, 9-cyano-9-fluorenyl, 2-cyano-2-norbornyl, 2-cyano-2-adamantyl, 3-cyano-3-nortricyclyl, 1-cyano-1-methylethyl cations from the corresponding cyanohydrins **9–15** under a variety of superacid conditions at low temperatures was unsuccessful. They generally gave the corresponding protonated ketones along with decomposition products. These observations seem to indicate that as the contribution of the mesomeric nitrenium ion form to the overall structure increases, the ion tends to get unstable and decomposes. The decomposition products probably arise from the reaction of nitrenium ion structure (singlet form).



17



18

Conclusion

^{13}C and ^{15}N NMR spectroscopic studies on substituted cyanodiphenylmethyl cations **5**-R and 7-cyano-7-norbornenyl cation **6** clearly demonstrate the mesomeric stabilizing nature (through the nitrenium form) of a α-cyano substituent on the cationic center. An increase in the contribution of the mesomeric nitrenium form to the overall structure, however, tends to destabilize the system as was observed in the case of cyanohydrins **9–15**. Our studies are in accord with the theoretical and solvolytic work of Gassman and co-workers.[6-9]

Experimental Section

All the cyanohydrins utilized in our study were prepared from the respective carbonyl compounds and trimethylsilyl cyanide using the procedure of Gassman and Talley.[10] The 10% ^{15}N-enriched trimethylsilyl cyanide was prepared[20] from enriched silver cyanide and trimethylsilyl chloride. The enriched silver cyanide was obtained by reacting aqueous silver nitrate solution with aqueous enriched sodium cyanide. All the new cyanohydrins prepared in this study gave satisfactory spectroscopic data.

Preparation of Ions. The appropriate cyanohydrin precursor dissolved in SO_2ClF or $CDCl_3$, precooled at −70 °C (dry-ice/acetone bath) is slowly added with vigorous stirring to a freshly prepared solution of a fourfold excess of the appropriate superacid in SO_2ClF maintained at −78 °C or −130 C in a 10-mm NMR tube so as to obtain approximately 10–15% solution of the ion.

The ^{13}C and ^{15}N NMR Spectroscopic Studies were carried out on a Varian Associates Model FT-80 spectrometer equipped with a variable-temperature broad-band probe. The ^{13}C NMR chemical shifts are in parts per million from external capillarly tetramethylsilane. The ^{15}N NMR chemical shifts are referenced to external anhydrous ammonia signal.

Acknowledgment. Support of our work by the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

Registry No. 5 (R = 4-OCH_3), 80721-26-2; **5** (R = 4-CH_3), 80721-27-3; **5** (R = H), 75670-43-8; **5** (R = 4-Cl), 80721-28-4; **5** (R = 4-F), 80721-29-5; **6**, 80800-11-9; **7** (R = 4-OCH_3), 80721-30-8; **7** (R = 4-CH_3), 80721-31-9; **7** (R = H), 4746-48-9; **7** (R = Cl), 80721-32-0; **7** (R = 4-Cl), 80721-33-1; **8**, 80721-34-2.

(16) G. A. Olah, A. L. Berrier, and G. K. S. Prakash, *Proc. Natl. Acad. Sci. U.S.A.*, **78**, 1998–2002 (1981).

(17) The cyano carbon in **8** was observed at $\delta(^{13}C)$ 123 followed by cyanohydrin carbon at $\delta(^{13}C)$ 83.0.

(18) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **97**, 6803–6806 (1975) and references cited therein.

(19) G. A. Olah, A. L. Berrier, M. Arvanaghi, and G. K. S. Prakash, *J. Am. Chem. Soc.*, **103**, 1122–1128 (1981).

(20) D. A. Evans, G. L. Carroll, and L. K. Truesdale, *J. Org. Chem.*, **39**, 914–917 (1974).