6,6-(2-Norbornylidene)fulvene (7). To a stirred solution of sodium metal (2.3 g, 0.1 mol) in 40 ml of absolute ethanol under nitrogen, 3.3 g (0.05 mol) of freshly distilled cyclopentadiene was added followed by 5.5 g (0.05 mol) of norcamphor. The stirring was continued for 14 h and the reaction mixture was worked up as described earlier. The product was fractionated under vacuum. The yellow, oily fraction distilling at 80–81 °C (0.5 mm) was collected, 4.2 g (53%), air-sensitive liquid. The infrared spectrum (neat) showed $\nu_{C=C}$ 1656 (s), 1620 cm^{-1} (m). The UV spectrum (cyclohexane) showed maxima at 276.5 nm (log ϵ 4.30), 283.5 (4.28), 365 (2.49), and a shoulder at 295 nm. The mass spectrum showed *m/e* 158 (100, M^+). The ^1H NMR spectrum (60 MHz, $CDCl_3$ from external capillary Me_4Si, 37 °C) showed absorptions at δ 6.8 (s, 4 H, ring protons), 3.7 (b, 1 H, bridgehead proton at 1′), 2.9 (b, 3 H, methylene protons at 3′ and bridgehead proton at 4′), 1.6–2.4 (b, 6 H, methylene protons at 5′, 6′, and 7′).

Anal. Calcd for $C_{12}H_{14}$: C, 91.14; H, 8.86. Found: C, 91.06; H, 8.90.

Preparation of Fulvenium Ions. Freshly distilled FSO_3H was dissolved in about twofold amount of SO_2ClF or SO_2F_2 at dry ice/acetone temperature (ca. −78 °) or ethanol/liquid nitrogen temperature (ca. −120 °C). To this solution was slowly added with vigorous stirring a cooled slurry of the appropriate fulvene precursor in SO_2ClF or SO_2F_2, to give an approximately 10% solution of the ion.

^1H NMR spectra were obtained on a Varian Model A56/60A spectrometer equipped with variable temperature probes and external capillary Me_4Si was used as the reference.

^{13}C NMR spectra were obtained using a Varian Model XL-100 NMR spectrometer equipped with an FT accessory with variable temperature probe as previoulsy described.[16]

The infrared spectra were obtained on a Beckman IR-10 spectrophotometer, the ultraviolet spectra were recorded on a Beckman DB-G spectrophotometer, and the mass spectra on a Du Pont Model 21-094 GC/MS system operating at a filament current of 70 eV.

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Registry No.—1, 4479-62-3; **2**, 2175-91-9; **3**, 2175-90-8; **4**, 2320-32-3; **5**, 61010-59-1; **6**, 61010-60-4; **7**, 61010-61-5; **8**, 16668-82-9; **15**, 61010-54-6; **16**, 61010-55-7; **17**, 61010-56-8; **18**, 61010-57-9; **19**, 61010-58-0; cyclopentadiene, 542-92-7; cyclopropyl methyl ketone, 765-43-5; phenyl cyclopropyl ketone, 3481-02-5; adamantanone, 700-58-3; norcamphor, 497-38-1.

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Carbon-13 Nuclear Magnetic Resonance. Steric and Electronic Effects on the α, β, and γ Shifts in Norcarane Derivatives

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Fourier transform carbon-13 nuclear magnetic resonance spectra were measured for a number of endo- and exo-7-substituted and 7,7-disubstituted norcaranes. The substituent shift parameters were calculated from a series of 7-monosubstituted norcaranes and were used for predicting the shifts of stereoisomers of some 7,7-disubstituted norcaranes. The agreement between the observed and the calculated shifts was satisfactory, proving the validity of this general approach. Interpretation of the observed substituent shifts in terms of steric and electronic effects has shown that (1) the α and β substituent effects as well as the γ gauche and anti effects are dependent on the relative orientation of the substituent on the α carbon, and (2) a long-range γ anti effect produced on the γ carbon nuclei by the exo 7 substituent can be explained more reasonably by the back-lobe interaction mechanism than by the hyperconjugative interaction mechanism. Several $^{13}C-^{19}F$ and $^{13}C-^1H$ coupling constants are also reported and interpreted in terms of the s character of the C–F and C–H bonds, respectively.

The carbon-13 magnetic resonance spectra of a number of molecules containing hetero substituents have been recorded and interpreted in terms of inductive, steric, and bond delocalization effects.[1-8] In the literature, however, there is no systematic investigation on the conformational and substituent factors, which affect carbon-13 shieldings, in cyclopropyl ring systems possessing hetero substituent(s).

Now we have determined the carbon chemical shifts for a series of norcarane derivatives. These compounds were chosen because the norcaryl skeleton provides a relatively rigid and stereochemically defined framework suitable for the investigation of substituent effects. Our aim was to determine steric and substituent shift factors and to investigate their variations due to the orientational changes of a substituent on the norcaryl skeleton. This will make it possible to test quantitatively the validity of the theories and speculations which have been advanced to explain carbon-13 shieldings on an electronic ground.

Experimental Section[9]

Materials. All 7,7-disubstituted norcaranes except 7-chloro- (and -bromo-) 7-methoxycarbonylnorcarane were obtained by the addition of the corresponding halocarbene (or carbenoid) to cyclohexene.[10] 7-Chloro- (and -bromo-) 7-methoxycarbonylnorcarane was prepared

Table I. Carbon-13 Chemical Shifts in Endo and Exo 7-Substituted Norcaranes[a]

Registry no.	Compd	X	C-7	C-1,6	C-2,5	C-3,4	Others
286-08-8	1	Nil	10.6	9.8	24.4	21.8	
				Endo Derivatives			
16646-97-2	**2a**	F	74.7 (−64.1)	11.1 (−1.3)	17.7 (6.7)	22.4 (−0.6)	
18688-22-7	**3a**	Cl	40.0 (−29.4)	12.5 (−2.7)	18.6 (5.8)	21.8 (0.0)	
1121-40-0	**4a**	Br	33.4 (−22.8)	12.3 (−2.5)	20.1 (4.3)	21.6 (0.2)	
2988-67-2	**5a**[b]	OCH_3	60.4 (−49.8)	11.6 (−1.8)	18.3 (6.1)	22.6 (−0.8)	58.0
36744-58-8	**6a**	$COOCH_3$	22.1 (−11.5)	16.6 (−6.8)	18.9 (5.5)	21.5 (0.3)	50.8, 172.1 (C=O)
10503-37-4	**7a**	Ph	22.4 (−11.8)	12.9 (−3.1)	20.4 (4.0)	21.9 (−0.1)	138.6, 128.2 (*o*), 131.3 (*m*), 125.8 (*p*)
14222-39-0	**8a**	CH_3	12.2 (−1.6)	10.4 (−0.6)	18.9 (5.5)	22.9 (−1.1)	8.3
				Exo Derivatives			
16646-98-3	**2b**	F	79.5 (−68.9)	17.0 (−7.2)	21.9 (2.5)	21.7 (0.1)	
18688-22-7	**3b**	Cl	37.9 (−27.3)	21.5 (−11.7)	22.5 (1.9)	21.4 (0.4)	
1121-41-1	**4b**	Br	25.3 (−14.7)	21.6 (−11.8)	22.7 (1.7)	21.1 (0.7)	
3101-24-4	**5b**[b]	OCH_3	66.4 (−55.8)	17.7 (−7.9)	22.7 (1.7)	22.0 (−0.2)	57.4
36744-59-9	**6b**	$COOCH_3$	25.9 (−15.3)	22.1 (−12.3)	23.1 (1.3)	21.3 (0.5)	51.2, 174.7 (C=O)
10503-36-3	**7b**	Ph	28.9 (−18.3)	22.5 (−12.7)	23.8 (0.6)	21.6 (0.2)	144.5, 125.4 (*o*), 128.2 (*m*), 125.0 (*p*)
14135-43-4	**8b**	CH_3	18.0 (−7.4)	18.4 (−8.6)	24.0 (0.4)	22.0 (−0.2)	19.0

[a] The values in parentheses are substituent shifts relative to norcarane (1), expressed in parts per million; a negative sign denotes a downfield shift on substitution. [b] The chemical shifts were obtained from the measurement for an isomeric mixture.

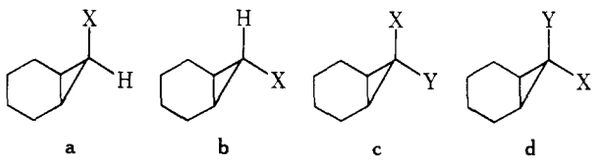
by the carbonation of 7-chloro- (or -bromo-) 7-norcaryllithium with solid carbon dioxide followed by esterification with the conventional procedure.[11] 7-Monosubstituted norcaranes were obtained by the reduction of the corresponding 7-norcaryl halides with tri-*n*-butyltin hydride.[12] Only 7-methoxynorcarane was synthesized according to the previously reported method.[13] Separation of isomers of these compounds was achieved by use either of preparative gas chromatography (GLC) or of thermal decomposition of an isomeric mixture in hot quinoline[14] Stereochemistry of the isomers was determined on the basis of their proton and fluorine magnetic resonance spectra and of the difference in rate of the thermal decomposition in hot quinoline.[14]

Spectra. ^{13}C NMR spectra were recorded on a Varian Associates CFT-20 computer-controlled spectrometer operating at 20 MHz. The Fourier transform (FT) technique was applied.[15] Samples for measurement were prepared as 0.2–0.4 M solutions in chloroform-*d* with tetramethylsilane (Me_4Si) as an internal standard. All chemical shifts were determined from proton noise decoupling (PND) spectra and are expressed in parts per million downfield from Me_4Si. The precision of the computer-measured chemical shifts is within ±0.1 ppm (4K data points in the time-domain spectra for a 200-ppm spectral width) and narrow peaks as close as 0.1 ppm can be resolved. Single frequency off-center decoupled (sfocd) (off-resonance) spectra were used to assign the resonance of carbons in questionable cases. In a few instances, spectra were taken on an isomeric mixture because of the difficulties in separation of the isomers. The resonance lines due to each component in the mixture could be readily identified from their intensities because the components were present in unequal amounts in all cases. The chemical shifts determined for an isomer alone or as an isomeric mixture were practically identical.

Results

In almost all proton noise decoupled (PND) spectra, four signals generally appeared except those due to the carbon(s) contained in the substituent because of the presence of an element of symmetry in the norcaryl system studied. The chemical shifts for the series of 7-substituted and 7,7-disubstituted norcaranes are given in Tables I and II, respectively. The assignment for four signals in the spectrum of norcarane (1) was made as follows: carbon 7 and carbons 1,6 were assigned from the off-resonance experiment because this technique splits the carbon signals according to the number of directly attached hydrogen. The assignment for carbons 2,5 and carbons 3,4 was unambiguously made on the basis of the criterion that substitution with a methyl or a methylene group causes a downfield shift at both the α and β carbons and an upfield shift at the γ carbons.[1] Further confirmation of this assignment was obtained by comparison with the relative chemical shifts of the α and β carbons in decalin.[16] In the case

Scheme I



a b c d

1, X = H
2, X = F
3, X = Cl
4, X = Br
5, X = OCH_3
6, X = $COOCH_3$
7, X = Ph
8, X = CH_3

9, X = F; Y = Cl
10, X = F; Y = Br
11, X = Cl; Y = Br
12, X = Cl; Y = Ph
13, X = Cl; Y = $COOCH_3$
14, X = Br; Y = $COOCH_3$
15, X = Y = Cl
16, X = Y = Br

Table II. Carbon-13 Chemical Shifts in Some 7,7-Disubstituted Norcaranes

Registry no.	Compd	C-7	C-1,6	C-2,5	C-3,4	Others
16646-94-9	**9c**	95.7	22.8	17.5	21.1	
16646-93-8	**9d**	101.7	21.2	20.5	18.4	
19144-91-3	**10c**	85.2	23.7	17.4	21.1	
19144-90-2	**10d**	97.1	22.0	20.3	19.6	
24321-25-3	**11c**	51.8	26.7	19.1	20.5	
24321-26-4	**11d**	58.2	26/9	20.1	20.6	
6434-79-3	**12c**	55.2	21.4	19.3	21.2	145.1, 127.1 (*o*), 128.3 (*m*), 127.1 (*p*)
6508-78-7	**12d**[a]	48.5	24.7	20.7	20.6	138.0, 128.8 (*o*), 130.9 (*m*), 128.0 (*p*)
37863-38-0	**13c**	56.9	24.6	18.8	21.0	52.9, 179.8 (C=O)
38213-17-1	**14d**	32.2	25.9	19.6	20.7	52.6, 172.7 (C=O)
823-69-8	**15**	67.5	26.2	19.0	20.4	
2415-79-4	**16**	40.4	27.2	20.2	20.7	

[a] See footnote *b*, Table I.

Table III. ^{13}C–^{19}F Coupling Constants in Fluoro Compounds[a]

Compd	$^1J_{CF}$	$^2J_{CF}$	$^3J_{CF}$	$^4J_{CF}$
2a	221.6	10.6	4.8	1.1
2b	221.6	10.6	3.4	0
9c	289.8	11.0	2.8	2.0
9d	282.4	11.3	2.7	0
10c	305.6	10.2	3.1	1.7
10d	295.6	10.5	2.6	0

[a] All coupling constants are in hertz.

Table IV. ^{13}C–^1H Coupling Constants on 7 Carbon in Some 7-Substituted Norcaranes[a] **(RX**[b]**)**

		J_{CH}	
Compd	X	Endo-X	Exo-X
1	H	154.6	
2	F	196.8	194.5
3	Cl	189.0	186.5
4	Br	187.8	c
5	OCH_3	179.5	177.4

[a] See footnote *a*, Table III. [b] R stands for 7-norcaryl group. [c] No value could be obtained owing to overlapping with other signals.

of fluorinated compounds, 7-fluoronorcarane (**2**), 7-chloro-7-fluoronorcarane (**9**), and 7-bromo-7-fluoronorcarane (**10**), the observation of C–F coupling constants and the dependence of their magnitude on the number of intervening bonds made a straightforward assignment possible for all carbon nuclei (Table III). The α carbon, C-7, has the largest J value, followed by the β carbons, C-1,6, and the γ carbons, C-2,5. The δ carbons, C-3,4, have the smallest or zero J value. The assignment presented here clearly demonstrates the great utility of fluorine substitution for the identification of carbon-13 resonances. Sfocd experiments were not performed on these fluoro compounds since several carbon signals were split by fluorine nucleus, giving a complex sfocd spectrum. The assignment for carbon resonances in spectra of nonfluorinated compounds was made by comparison with those of 7-fluoronorcarane. The δ carbons (C-3,4) were readily assigned since they are distant from the 7 substituent(s) enough to be invariant in their chemical shift. In exo 7-substituted norcaranes, however, the assignment for the γ and δ carbons cannot be decisive because their shifts are too close for certainty. For the differentiation of the α carbon (C-7) from the β carbons (C-1,6), their relative intensities could be a good aid in addition to the larger downfield shift on the α carbon caused by the 7 substituent(s). The assignment was further confirmed from the sfocd experiments.

Table III compiles the C–F coupling constants observed for several fluoro compounds. The J_{CF} values on 7-fluoronorcarane (**2**) were in good agreement with those found for the other two fluoronorcaranes with exception of the one-bond coupling constant $^1J_{CF}$, which had a value of 221.6 Hz. An additional polar substituent caused a further increase in the algebraic sense in the $^1J_{CF}$ value (assumed to be of negative sign[17]) and this increase was similar to the one observed in other studies on the series of fluoromethanes.[18,19] The geminal and vicinal coupling constants, $^2J_{CF}$ and $^3J_{CF}$, were slightly different between the endo- and the exo-fluoro isomers. Carbons more than three bonds apart (the δ carbons) can be coupled with the fluorine nucleus when they are close together in space. Thus, a long-range coupling occurred on the endo-fluoro isomers with a value of 1.1–2.0 Hz and on the exo counterparts with a zero value. This variation in $^4J_{CF}$ has an important bearing on the theory of coupling constants between heavy nuclei, because it shows that a through-space interaction contributes significantly to the overall effects.[20]

Table IV lists the direct C–H coupling constants determined from natural-abundance experiments of some 7-substituted norcaranes.

Discussion

The data given in Tables I and II demonstrate that a substituent can have a substantial influence on the chemical shifts for the α (C-7), β (C-1,6), and γ (C-2,5) carbons but very little effect on that for the δ (C-3,4) carbons. Though smaller and subtler changes at the δ carbons may be proved of significance in the future, we will discuss here the α, β, and γ effects alone.

The α and β Effects. Table I shows that in the norcarane systems studied the electronegativity and the anisotropy of the substituents affect the α and β shifts in such a way as can be expected from the previous studies on acyclic[1] and other alicyclic[1,21-23] systems. To be noted is, however, that the magnitudes of the α and β effects are somewhat smaller than those observed in acyclic systems.[1]

Especially significant is the fact that the orientation of the substituent on the norcaryl skeleton has a profound effect on the magnitudes of the α and β shifts as well as of the γ shifts. As is shown in Table I, the shifts caused by the endo substituents are consistently smaller by 2–10 ppm than those by the exo substituents except for chlorine and bromine. It is not possible to decide whether this difference comes from an electronic basis or is caused by slight difference in the mo-

lecular geometry, since the endo substituents may introduce additional steric interaction which could be partially relieved by some distortion of the norcaryl skeleton. However, the difference between the effects for endo and exo orientations of 7 substituents is much larger than that observed in 2-substituted norbornanes.[8] Such a situation can be attributed to the steric elongation of the C_α–C_β bond due to an endo substituent. Elongation of this bond will, according to the theory of Litchman and Grant,[24] produce upfield shifts at the α and β carbons.

In the case of 7,7-disubstituted norcaranes, as given in Table II, an additional polar substituent has a major effect on the chemical shifts for the α, β, and γ carbons in this order but has little effect on the δ carbons. One of the most important features is the fact that the chemical shift for the α carbon is in good agreement with the one calculated from a set of the corresponding substituent parameter compiled in Table I and the chemical shift of the 7 carbon in the parent compound. For example, the observed shift for the α carbon in *exo*-7-bromo-*endo*-7-fluoronorcarane (**10c**) is 85.2 ppm and the calculated value is 89.4 ppm, which is the sum of 64.1 ppm for endo-7-fluorine substitution, 14.7 ppm for exo-7-bromine substitution, and 10.6 ppm for the 7 carbon in norcarane. In all cases except 7-chloro-7-fluoronorcarane, the deviation of the calculated from the observed values falls within the difference between the chemical shifts for the α carbon in each set of stereoisomers. Thus, the chemical shift calculated from the data in Table I allows stereochemical assignment to these related compounds, which otherwise is often very troublesome.

The γ Effects. As shown in Table I, the γ shifts are most easily recognized for overall series of endo 7-substituted norcaranes. In these compounds, the substituent at the 7 carbon is syn to the γ carbons (C-2,5). The effect on the γ carbons is clearly steric in origin and is essentially analogous to that observed in other studies.[6-8,25,26] The magnitude of this γ gauche effect is given in Table I. However, it does not correlate simply with the bulkiness of substituents nor with their electronic property; e.g., chlorine and methoxycarbonyl groups have the effect of the same order of magnitude, in spite of the substantial difference in electronegativity. These results suggest the dependence of the γ gauche effect on the nonbonded distance between the hydrogen attached to the γ carbon and an interacting substituent. This distance, which has been measured using a Dreiding stereomodel, is nicely correlated with the magnitude for the observed γ gauche effect.

On the other hand, the data compiled in the lower half of Table I clearly demonstrate that the signal of the γ carbon nucleus anti to a polar substituent generally appears at a significantly higher field than that of the parent compound. The γ carbons (C-2,5) in exo 7-substituted norcaranes are invariably shielded by the exo substituents. It is evident that this effect cannot be explained in terms of sterically nonbonded interactions discussed above. The upfield shift of this type has also been observed in the studies on several other compounds.[8,27,28] To our best knowledge, two mechanisms have been proposed to explain the γ anti effect. The first mechanism[8,27] involves back-lobe interactions of the bonding orbitals on the γ carbon with those on the α carbon used to bind a polar substituent, by analogy with the model used to explain long-range spin–spin coupling through a "W" arrangement of bonds.[29] The other is hyperconjugative interactions of free-electron pairs on a substituent with the C_α–C_β bond accompanied by a subsequent alternation of the electron density at the γ anti carbon. The latter mechanism was recently suggested by Eliel et al.[28] for the apparently unique role which the second-row heteroatoms (e.g., N, O, and F elements) do play but the third-row elements (e.g., Cl and S elements) do not in the γ anti effect. At a glance of the data in Table I, it can be noted that almost all substituents have a profound effect on the chemical shifts for the γ anti carbons. The magnitude of the upfield shift due to chlorine or bromine is nearly identical with that due to the methoxy group, and even other groups (i.e., methoxycarbonyl and phenyl groups) have nonnegligible effects. The order of the γ anti effect in magnitude appears to correlate roughly with the electronic nature of the substituents and this correlation has also been found in norbornane derivatives.[8] Consideration of such situations led us to prefer the back-lobe interaction mechanism for explaining the γ anti effect, although we do not have tools available to unravel the physical basis for this. The contrast between our data and those obtained by Eliel and his coworkers,[28] which apparently lack the γ shielding due to antiperiplanar third-row heteroatoms, seems to be due to the slight difference in rigidity of molecular framework. The results obtained here would provide a further opportunity to examine the mechanistic interpretation of the γ anti effect.

^{13}C–^{19}F and ^{13}C–^{1}H Coupling Constants. Table III demonstrates that the one-bond coupling constants $^1J_{CF}$ are markedly affected by additional substitution and that $^1J_{CF}$ and the long-range couplings $^4J_{CF}$ are dependent on the relative orientation of the C–F bond on the norcaryl skeleton. Previously, it was suggested that the largest $^1J_{CF}$ value occurs for the most strongly deshielded fluorine nucleus and there is a tendency for $^1J_{CF}$ (assumed to be of negative sign[17]) to decrease, i.e., to become more positive, with increasing ^{19}F shielding.[18] This is not necessarily the case. Endo fluorinated compounds have larger $^1J_{CF}$ values than exo counterparts, whereas in their ^{19}F NMR spectra[30] the endo-fluorine nucleus is invariably more strongly shielded than the exo one. This trend is analogous to that found for the direct C–H couplings (Table IV) but the relative signs are opposite. It seems that the major factor contributing to $^1J_{CF}$ includes the s character of the carbon orbital in the C–F bond; the $^1J_{CF}$ value decreases in magnitude with increase of the s character. In the case of vicinal couplings $^3J_{CF}$, the carbons at the position cis to fluorine have larger coupling constants than the ones trans to fluorine. An apparently similar trend can be noted with the vicinal H–H[31] or H–F[32] coupling in the cyclopropyl ring systems. Of more importance is that the long-range coupling of carbon nuclei separated by four bonds with fluorine occurs in endo fluorinated compounds. This is closely related with their proximity in space, which indicates the contribution of through-space interactions to this effect.

As shown in Table IV, the magnitudes of the direct C–H coupling constants are dependent upon the nature of 7 substituents and are in good agreement with those reported for other monosubstituted cyclopropanes.[33] The magnitudes, furthermore, depend slightly on the relative orientation of the C–H bond with respect to the cyclopropyl ring, though the difference is relatively small. It is well known that the coupling constant J_{CH} correlates with the s character of carbon in the C–H bond of interest: the equation $J_{CH} = a(\%\,s) - b$ generally applies though the values of a and b vary with the author.[34] If the approximate relationship $J_{CF} = (5.70)(\%\,s) - 18.4$[35] is used to estimate the s characters of the 7-carbon atoms in these compounds, they fall in the range of 30.4–37.8%, which corresponds to the hybridization state of $sp^{2.3}$–$sp^{1.7}$. These values may be regarded as satisfactory.

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Electrochemical Oxidation of Tropanes

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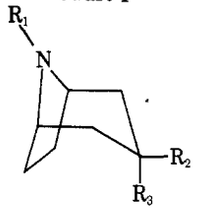
Tropane and nortropane were selected as examples of the tropane alkaloids for study of their anodic reactions. The tertiary amine, tropane, undergoes anodically induced dealkylation, and, like nortropane, does not show further cleavage of carbon–nitrogen bonds, presumably because of the presence of bridgehead carbon atoms α to nitrogen. Instead, reactions that involve formation of carbon–nitrogen and of nitrogen–nitrogen bonds are observed. These reactions involve reaction of the solvent, acetonitrile, with electrochemically generated intermediates. Evidence is presented to support a proposed reaction scheme that involves electrochemical reaction of the amine and of hydroxide ion.

The electrochemical oxidation of saturated aliphatic amines in wet acetonitrile proceeds through the aminium cation radical which typically loses a proton from an α carbon atom to form an intermediate that ultimately undergoes hydrolytic cleavage between the nitrogen atom and the adjacent carbon atom.[1,2] Thus a symmetrically substituted tertiary straight chain alkylamine forms the secondary amine and the aldehyde corresponding to the cleaved alkyl group. The process can be successively repeated to form a primary amine, ammonia, and nitrogen. By contrast, anodic oxidation of aromatic or olefinic amines may lead to formation of relatively stable intermediates owing to delocalization of the unpaired electron. In some cases, radical intermediates with appreciable lifetimes are observed; in others, products from coupling and polymerization are found.[3-6]

Complex amines of both aliphatic and aromatic character are formed in plants and animals. Those of plant origin fall in the general classification of alkaloids. The physiological function of alkaloids is often obscure, but it is generally accepted that chemical and enzymatic redox reactions occur. Electrochemistry provides a tool with which to study redox reactions of biogenic compounds outside living systems.[7-11]

The tropane alkaloids are nonaromatic bicyclic amines. The parent compounds of the series are nortropane (I) (8-azabicyclo[3.2.1]octane) and tropane (II) (8-methyl-8-azabicyclo[3.2.1]octane). Many compounds of this class exist; some, such as atropine, scopolamine, and cocaine, are very well known. Our attention has been attracted to them because of their pharmacological importance. Compounds studied in the work are identified in Chart I and Table I.

Chart I



Experimental Section

Apparatus. Electrolyses were performed with conventional potentiostats. Hydrogen–nitrogen gas coulometers or electronic integrators were used for current integration.[12] Cyclic voltammograms were obtained at a platinum button anode on a PAR Model 173 potentiostat equipped with a H-P model 300A function generator and an X-Y recorder.