Electroorganic Chemistry. X. Anodic Allylic Substitution

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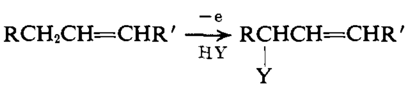
Abstract: Allylically substituted products were obtained in the anodic oxidation of some olefins, such as cyclohexene, cyclopentene, methylcyclohexenes, and octenes, in acetic acid or methanol. α- or β-pinene gave ring-opened products and norbornene yielded transannularly interacted product, 3-substituted nortricyclene. Isotope effect for anodic acetoxylation of cyclohexene was 1.6. The current efficiency decreased with lowering of oxidation potential of supporting electrolyte. The cation radical formed from one-electron oxidation of the substrate was the initial reactive species and an allylic cation was the main intermediate in the product-determining step.

In recent years, much interest has been attracted to the electrochemical synthesis of organic compounds. However, much attention has been concentrated on the anodic oxidation of aromatic compounds,[1] and very little study has been accomplished on the electrochemical reaction of aliphatic olefins.[2] Previously, it was preliminarily reported in this series that the anodic oxidation of an olefin in a nucleophilic solvent gave an allylically substituted product.[3]



$$RCH_2CH{=}CHR' \xrightarrow[HY]{-e} \underset{\displaystyle Y}{RCH}CH{=}CHR'$$

Although many kinds of the allylic substitution reaction using organic peroxides[4] or metallic oxidizing agents[5] have been known, they are not necessarily favorable for the synthetic purposes. On the other hand, the present electrochemical allylic substitution reaction has a remarkable feature to be carried out under a very mild condition. In this paper, we wish to describe the detailed mechanism of the anodic allylic substitution of olefins.

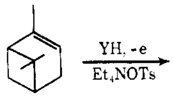
Results

Preparative Electrooxidation of Olefins. First, the anodic allylic substitutions of some olefins were studied in a preparative scale, and the results are shown in Table I, in which the reactions were not necessarily carried out under the optimum condition. All of the reactions were performed at room temperature using carbon rod electrodes under the condition of constant current, and the supporting electrolyte was tetraethylammonium *p*-toluenesulfonate (0.30 mol/l.). After 2.0 *F*/mol of electricity was passed, the current efficiency was determined by gas chromatography using an internal standard.

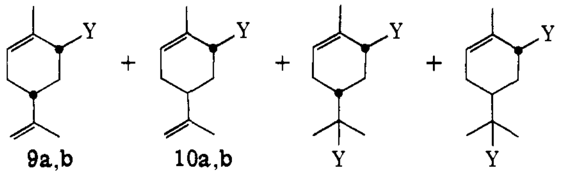
As shown in Figure 1, in the anodic oxidation of cyclohexene in acetic acid, the plot of the yield of 3-acetoxycyclohexene *vs.* the amount of passed electricity indicates that the current efficiency in the early stage is considerably high and the yield reaches to a maximum value at the point where a theoretical amount of electricity is given.

Current density change, within the range of 20–60 mA/cm^2, showed no apparent effect on the current efficiency, whereas this efficiency is affected considerably by the nature of the anionic part of the supporting electrolyte. The oxidation potential of the supporting electrolyte may play an important role in this phenomenon (Table II).

Electrooxidation of Pinenes. Under a similar condition, the electrooxidation of α-pinene in acetic acid gave carveol and *p*-menth-6-ene-2,8-diol derivatives **9–12**.

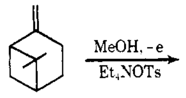


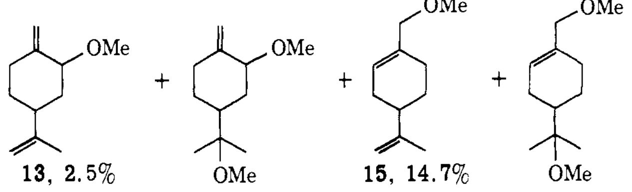
a, Y = OAc
b, Y = OMe



9a,b	**10a,b**	**11a,b**	**12a,b**
7.6%	16.8%	3.1%	9.0%
3.0%	18.8%	11.4%	29.4%

β-Pinene gave the following result by the similar oxidation in methanol.





13, 2.5% **14**, 7.4% **15**, 14.7% **16**, 23.4%

Electrooxidation of Methylcyclohexenes, Octenes, and 5,5-Dimethylcyclohexadiene-1,3. The electrooxidation of three methylcyclohexenes or two octenes gave mixtures of isomeric allylic acetoxy olefins. Table

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(1) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, 68, 449 (1968).

(2) (a) A. J. Baggaley and R. Brettle, *J. Chem. Soc. C*, 2055 (1968); (b) K. Fleischmann and D. Pletcher, *Tetrahedron Lett.*, 6255 (1968); (c) G. Faita, M. Fleischmann, and D. Pletcher, *J. Electroanal. Chem.*, 25, 455 (1970).

(3) (a) T. Shono and T. Kosaka, *Tetrahedron Lett.*, 6207 (1968); (b) T. Shono, A. Ikeda, and Y. Kimura, *ibid.*, 3599 (1971).

(4) (a) G. Sosnovsky and S. O. Lawesson, *Angew. Chem.*, 76, 218 (1964); (b) C. Djerassi, *Chem. Rev.*, 43, 271 (1948).

(5) (a) K. B. Wiberg, "Oxidation in Organic Chemistry," Academic Press, New York, N. Y., 1965, p 105, 337; (b) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, 29, 3353 (1964).

Table I. Preparative Anodic Allylic Substitution of Olefins

Olefin	mol/l.	Solvent	Current density, mA/cm²	Anode potential, V *vs.* sce	Product	Current efficiency, %
Cyclohexene	1.75	CH_3COOH	32	2.0 ∼ 2.25	3-Acetoxycyclohexene (**1**)	55
Cyclohexene	1.75	CH_3OH	16	1.6 ∼ 1.7	3-Methoxycyclohexene (**2**)	24
Cyclohexene	0.36	$H_2O–CH_3CN$[a]	23	1.9 ∼ 2.4	3-Hydroxycyclohexene (**3**)	14
Cyclohexene	0.36	$CH_3CN–H_2O$[b]	92	2.05 ∼ 2.45	3-Acetoaminocyclohexene (**4**)	17[c]
Cyclopentene	1.75	CH_3COOH	23	2.15 ∼ 2.35	3-Acetoxycyclopentene (**5**)	41
Cyclopentene	1.75	CH_3OH	28	1.55 ∼ 1.7	3-Methoxycyclopentene (**6**)	28
1-Methylcyclohexene	1.75	CH_3COOH	36	2.1 ∼ 2.3	Acetoxymethylcyclohexenes	30
3-Methylcyclohexene	0.88	CH_3COOH	40	2.15 ∼ 2.4		24
4-Methylcyclohexene	1.75	CH_3COOH	36	2.1 ∼ 2.35		37
2-Octene	0.88	CH_3COOH	22	2.1 ∼ 2.25[d]	Acetoxyoctenes	47
1-Octene	0.88	CH_3COOH	22	2.4 ∼ 2.55		1
Norbornene	1.75	CH_3COOH	24	2.1 ∼ 2.3	3-Acetoxynortricyclene (**7**)	11
Norbornene	1.75	CH_3OH	24	1.6 ∼ 1.7	3-Methoxynortricyclene (**8**)	7

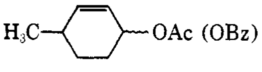
[a] H_2O/CH_3CN = 1/1 (mol/mol). [b] CH_3CN/H_2O = 80/1 (mol/mol). [c] Isolated yield. [d] Although the anode potential is slightly lower than the half-wave oxidation potential, it is sufficient to oxidize the olefin on the basis of Figure 2.

Table II. Effect of Supporting Electrolyte on the Current Efficiency of the Formation of **1**

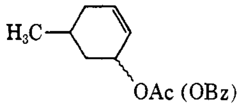
Supporting electrolyte	mol/l.	Cyclohexene, mol/l.	Anode potential, V *vs.* sce	Current density, mA/cm²	Current efficiency, %
$(C_2H_5)_4NSO_3C_6H_4CH_3$	0.30	1.75	2.0 ∼ 2.25	32	55
$LiSO_3C_6H_4CH_3$[a]	0.38	1.10	2.2 ∼ 2.4	28	53
$(C_2H_5)_4NClO_4$[a]	0.47	1.59	2.0 ∼ 2.3	25	55
$LiClO_4$	0.30	1.75	1.95 ∼ 2.2	21	53
$(C_2H_5)_4NBF_4$[a]	0.36	1.07	2.2 ∼ 2.45	24	35
$LiBF_4$[a]	0.49	1.05	2.25 ∼ 2.4	13	24
$(C_2H_5)_4NNO_3$	0.42	1.75	1.85 ∼ 2.3	42	17
$LiNO_3$[a]	0.30	1.37	1.8 ∼ 2.2	24	16
$(C_2H_5)_4NCl$	0.32	1.75	1.75 ∼ 1.9	34	15
$(C_2H_5)_4NBr$	0.29	1.67	1.8 ∼ 1.95	35	9
$(C_2H_5)_4NI$[a]	0.31	1.59	1.5 ∼ 1.6	35	7
CH_3COONa	1.28	1.28	1.8 ∼ 2.2	37	8

[a] A small amount of acetonitrile was added as a cosolvent.

III shows the distribution of isomers and those of the isomeric benzoyloxy olefins obtained by the Kharasch–Sosnovsky reaction in which the allylic substitution is known to involve an allylic cation as the intermediate. The qualitative similarity of the product distribution shown in Table III would suggest the resemblance of the product-determining steps of these two reactions. Comparing with the Kharasch reaction, a remarkable stereospecificity was observed in some of the acetoxylated methylcyclohexenes



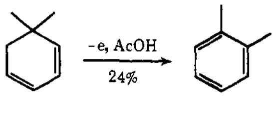
cis/trans = 2.8–3.4 (0.23–0.27)



cis/trans = 4.5 (2.6)

The number shown in parentheses is the corresponding ratio observed in the Kharasch reaction.

Anodic oxidation of 5,5-dimethylcyclohexadiene-1,3 in acetic acid yielded *o*-xylene as the major product indicating the 1,2-methyl migration in the reaction intermediate.



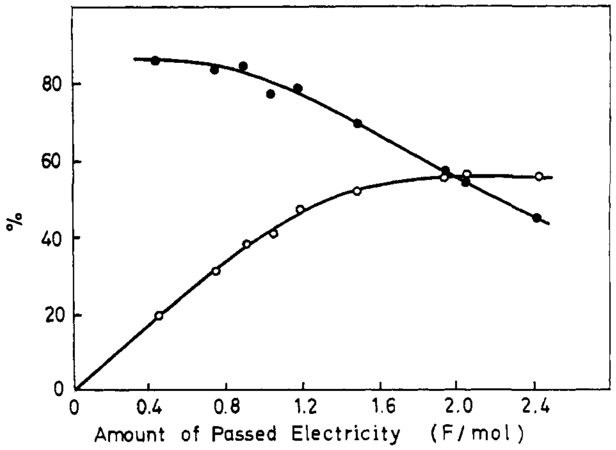
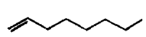
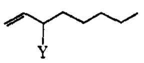
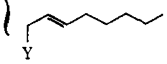
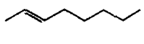
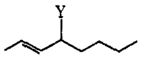
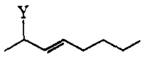
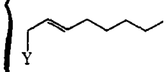
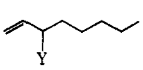
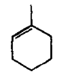
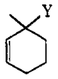
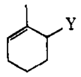
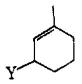
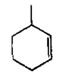
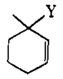
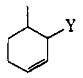
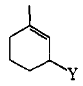
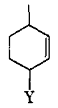
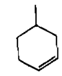
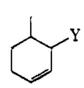
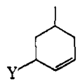
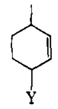


Figure 1. Yield (—○—) and current efficiency (—●—) of 3-acetoxycyclohexene in the anodic oxidation of cyclohexene in acetic acid.

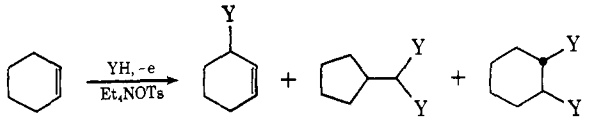
Oxidative Addition Reaction. Under the above-mentioned reaction condition, an oxidative addition reaction was observed in addition to the allylic substitution reaction. A typical example obtained in the oxidation of cyclohexene in acetic acid or methanol was as follows.

When tetraethylammonium chloride or bromide was used as the supporting electrolyte, the anodic oxidation

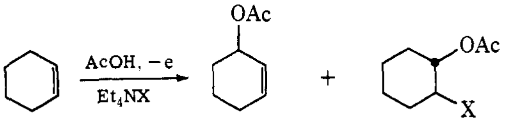
Table III. Distribution of Allylically Substituted Products in Anodic Acetoxylation or Kharasch Reaction of Octenes and Methylcyclohexenes

Olefin	Product	Anodic acetoxylation (Y = OAc)	Kharasch reaction (Y = OBz)
		71	86
		29	14
		12	
		50	
		14	
		24	
		0[a]	0
		49	75
		51	25
		0[a]	0
		52	32
		15	26
		33	42
		18	22
		61	55
		21	23

[a] That no acetoxylation occurred at the tertiary position may be explainable by a steric hindrance, which was frequently observed in the electrode reaction.



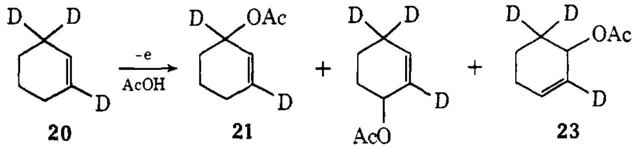
a, Y = OAc **1**, 55% **17a**, 2.6% **18a**, 1.1%
b, Y = OMe **2**, 24% **b**, 23% **b**, 2.5%



1 **19a,b**
a, X = Cl 14.8% 6.5% (36%)
b, X = Br 9.0% 14.2% (82%)

of cyclohexene in acetic acid gave 1-halo-2-acetoxycyclohexane (**19**) along with allylically substituted product **1**. The numbers in the parentheses indicate the yields based on the supporting electrolyte.

Isotope Effect. The anodic oxidation of cyclohexene-*1,3,3*-d_3 (**20**) in acetic acid gave a mixture of three isomeric 3-acetoxycyclohexenes **21**, **22**, and **23**. The distribution of the product was determined by nmr and the isotope effect (k_H/k_D) in anodic allylic acetoxylation was found to be 1.6.



20 **21** **22** **23**

Discussion

In the present reaction system, the anodically oxidizable species are the anionic part of supporting electrolyte, solvent, and substrate. Thus, the initiation stage of the reaction may be classified into the following two categories I and II. Category I, a radical species (S·) generated by the anodic oxidation of the supporting electrolyte or solvent, initiates the reaction. Category II, the cation radical formed from one-electron oxidation of the substrate, is the initiating reactive species.

The initiation step of the anodic aromatic or benzylic substitution reaction has mainly been explained from the similar standpoint to the latter category.[1] However, because of the rather higher oxidation potentials of aliphatic olefins than those of aromatic hydrocarbons, the elucidation of the first step of anodic allylic substitution needs further detailed discussion.

In category I, the abstraction of an allylic hydrogen from the substrate by the radical species S·, followed by the anodic one-electron oxidation of the resulting allylic radical to the allylic cation, would be the most probable pathway.

Category I[6]

$S^- \xrightarrow{-e} S\cdot$

$RCH_2CH{=}CHR' \xrightarrow{S\cdot}$

$$\begin{tikzcd} R\dot{C}HCH{=}CHR' \arrow[d, "-e"] \arrow[rd, dashed, "Y\cdot"] & \\ R\overset{+}{C}HCH{=}CHR' \arrow[r, "YH"] & R\overset{Y}{C}HCH{=}CHR' \end{tikzcd}$$

As for category II, the allylic cation may be generated from the corresponding cation radical by further one-electron transfer concerted with the proton

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(6) In categories I and II, the allylic rearrangement is not shown.

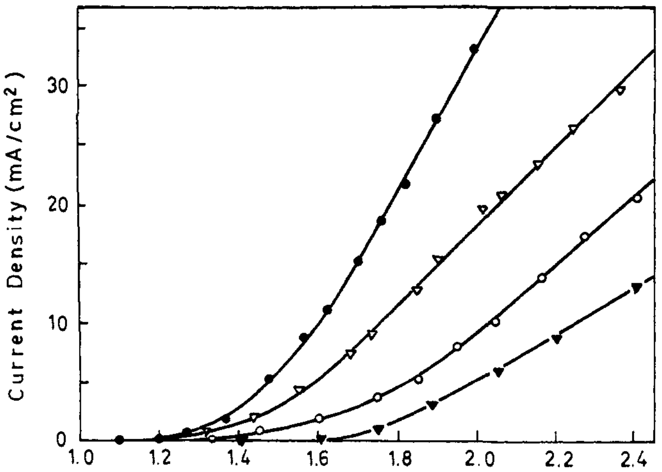


Figure 2. Plots of current *vs.* anode potential for solution of 0.30 *M* tetraethylammonium *p*-toluenesulfonate in acetic acid: (—▼—) without olefin; (—○—) with 1-octene (1.75 *M*); (—▽—) with 2-octene (1.75 *M*); (——●——) with cyclohexene (1.75 *M*) (at 18°).

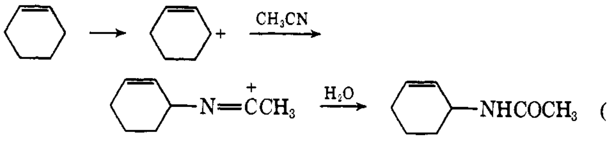
ejection or by one-electron oxidation subsequent to the proton elimination.

Category II[6]

$$\begin{tikzcd} RCH_2CH{=}CHR' \arrow[r, "-e"] & {} \\ RCH_2\overset{+}{C}H\overset{\bullet}{C}HR' \arrow[r, "-H^+"] \arrow[d, "-e"', "-H^+"] & RCH{=}CH\overset{\bullet}{C}HR' \arrow[dl, "-e"'] \arrow[d, dashed, "Y\cdot"'] \\ RCH{=}CH\overset{+}{C}HR' \arrow[r, "YH"] & RCH{=}CH\overset{\overset{Y}{|}}{C}HR' \end{tikzcd}$$

Product-Determining Step. As shown above, the initiation reaction yields the allylic radical or cation as the reaction intermediate. Thus, the allylically substituted product may be formed by either radical or cation pathway or both. However, the radical route, that is the recombination of the allylic radical with a radical (Y·) generated from solvent, would be unlikely from the following points of view.

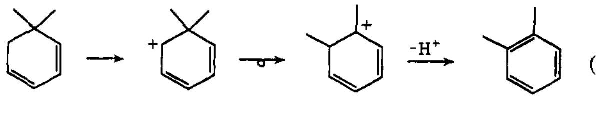
(1) As shown in Figure 1, the initial current efficiency for the formation of 3-acetoxycyclohexene was sufficiently high. It is, however, unreasonable that the recombination of the acetoxy radical, the extremely short-lived radical, with the allylic radical gives such high current efficiency. (2) The oxidation of cyclohexene in acetonitrile containing a small amount of



(1)

4

water resulted in the allylic acetoamidation (eq 1). This reaction is accountable only by the cationic mechanism resembling the Ritter reaction. (3) The migration of the methyl group observed in the anodic oxidation of 5,5-dimethylcyclohexadiene-1,3 strongly supports the contribution of a cationic intermediate (eq 2).



(2)

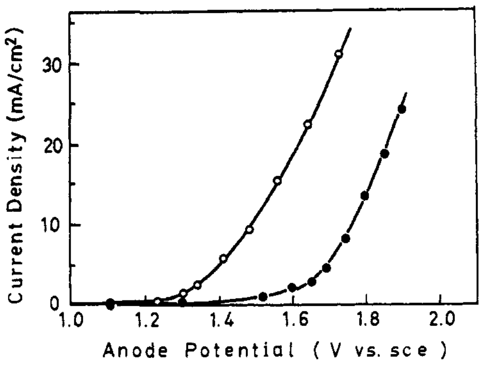
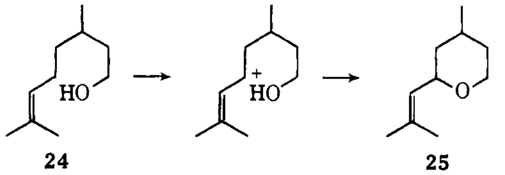


Figure 3. Plots of current *vs.* anode potential for solution of 0.30 *M* tetraethylammonium *p*-toluenesulfonate in methanol: (—●—) without cyclohexene; (—○—) with cyclohexene (1.75 *M*) (at 18°).

(4) The formation of rose oxide (**25**) in anodic oxidation of citroneroll (**24**) would eliminate the radical mechanism (eq 3).[3b]



(3)

24 **25**

Initiation Step. The oxidation potentials of some olefins and the anodic limits of the supporting electrolytes are shown in Table IV, implying that the olefins are more oxidizable than perchlorate or tosylate anion. The current *vs.* anode potential curve measured in acetic acid under the preparative condition (Figure 2) demonstrates that the addition of cyclohexene into the solvent-supporting electrolyte system brought a remarkable increase in the current at a given anode potential and that a smaller extent of the similar increase in the current was observed for 2-octene, whereas 1-octene caused only a slight increase. Furthermore, a similar remarkable current increase was observed in the addition of cyclohexene to the methanol-supporting electrolyte system in which the anode potential was considerably lower than that in acetic acid (Figure 3).

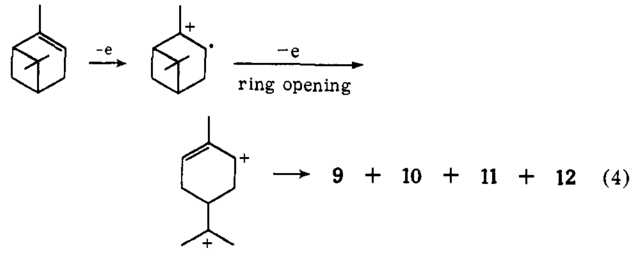
Table IV. Oxidation Potentials of Some Olefins and Anodic Limits of Some Supporting Electrolytes in Acetonitrile

Olefin or supporting electrolyte	Oxidation potential,[a] V *vs.* sce
α-Pinene	1.41
1-Methylcyclohexene	1.70
β-Pinene	1.89
Cyclopentene	1.96
Norbornene	2.02
Cyclohexene	2.14
2-Octene	2.3[b]
1-Octene	2.8[b]
Tetraethylammonium perchlorate	2.9[c]
Methyltriethylammonium *p*-toluenesulfonate	3.3[c]

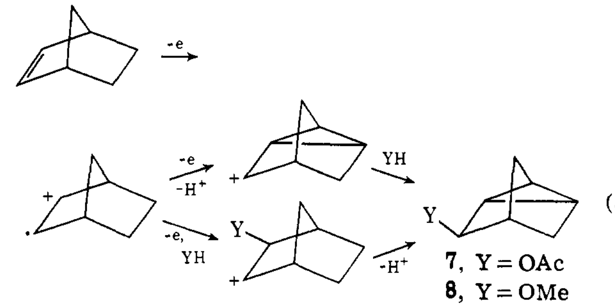
[a] Supporting electrolyte: lithium perchlorate. [b] Estimated from the oxidation potential[2b] in CH_3CN-Et_4NBF_4 *vs.* Ag|Ag⁺. [c] Anodic limit: S. Andreades and E. W. Zahnow, *J. Amer. Chem. Soc.*, **91**, 4181 (1969).

Thus, such experimental evidence strongly suggests that the initiation step classified as category II, that is the one-electron oxidation of olefin to a cation radical, is a reasonable mechanism.

Moreover, the following experimental results also supported the contribution of category II. (1) As was mentioned previously, the acetoxylation of cyclohexene indicated sufficiently high initial current efficiency. The explanation of this good current efficiency by the initial formation of a radical species (S·) from the solvent or supporting electrolyte (category I) would unreasonably require an almost quantitative interaction of the radical S· with olefin. (2) The formation of ring-opened products by the anodic oxidation of α- or β-pinene is explainable by the mechanism of category II (eq 4). (3) The electrochemical oxidation of norbornene bearing a less reactive allylic hydrogen gave transannularly interacted products, 3-substituted nortricyclene **7** and **8**, implying the initial intermediacy of a cation radical generated by the one-electron oxidation of a double bond (eq 5). A similar result was observed in the anodic oxidation of *endo*-norbornenemethanol (eq 6).[3b] (4) The possibility of the anodic substitution of an aliphatic saturated hydrocarbon would be expected from the participation of the radical S· (category I). The treatment of cyclohexane, methylcyclohexane, or adamantane, however, gave no substituted product.

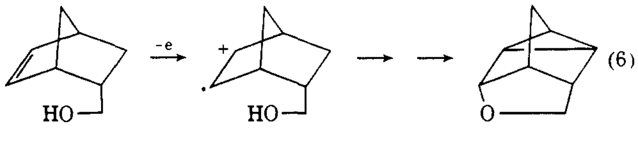


→ **9** + **10** + **11** + **12** (4)



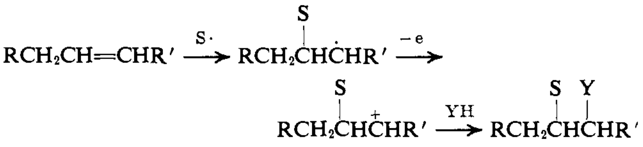
(5)

7, Y = OAc
8, Y = OMe



(6)

Although the adequacy of the initiation step classified as category II was almost established, the employment of a supporting electrolyte possessing relatively low anodic limit may result in the competitive oxidation of the supporting electrolyte. The detection of an oxidative addition product in the reaction mixture obtained by employing a supporting electrolyte containing a halide anion would suggest the exceptional contribution of the radical S· generated probably from the halide anion



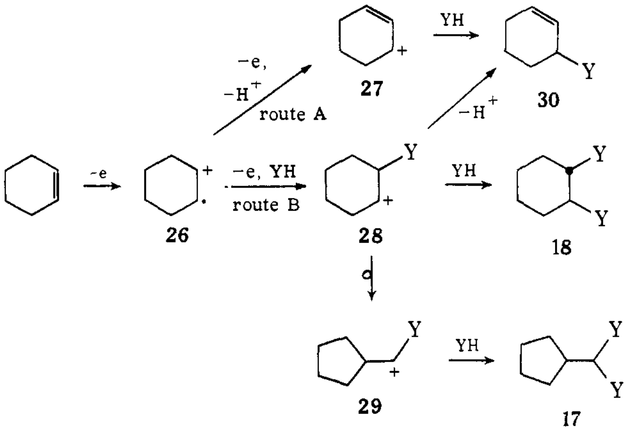
$$RCH_2CH{=}CHR' \xrightarrow{S\cdot} RCH_2\overset{S}{\overset{|}{C}}H\dot{C}HR' \xrightarrow{-e} RCH_2\overset{S}{\overset{|}{C}}H\overset{+}{C}HR' \xrightarrow{YH} RCH_2\overset{S}{\overset{|}{C}}H\overset{Y}{\overset{|}{C}}HR'$$

The extent of the participation of the radical S· would depend on the relative value of the oxidation potentials of the supporting electrolyte and olefin.

In a particular case where a solvent of sufficiently low oxidation potential is used and the radical species generated from the solvent possesses a long enough lifetime, the minor route passing through the addition of the solvent radical to the olefin may not be denied.

Finally, the main reaction pathway is indicated in Scheme I in which cyclohexene is shown as the substrate. A cation radical **26** is generated by the one-electron oxidation of the unsaturated bond adsorbed on the anode, and subsequently a second electron is transferred in concert with the proton elimination from the allylic position (route A) or with the nucleophilic attack of the solvent (route B). The cation **27** give **30**, while **28** yields both substitution and addition products. The fact that the allylic substitution was the main pathway in the acetoxylation, while a considerable amount of the addition product was detected in the methoxylation, would imply that the relative degree of route A and route B depends on the nucleophilicity of the solvent.

Scheme I



Experimental Section

Supporting Electrolyte. Tetraethylammonium *p*-toluenesulfonate,[7] tetraethylammonium perchlorate,[8] tetraethylammonium tetrafluoroborate,[8] tetraethylammonium nitrate,[9] and lithium tetrafluoroborate[10] were prepared by the reported methods.

Preparative Anodic Oxidation of Olefins in Acetic Acid. General. In a 100-ml cylindrical cell equipped with a reflux condenser, a thermometer, and two carbon-rod electrodes (diameter, 0.8 cm) was placed a solution of 0.10 mol of olefin, 60 g (1.0 mol) of acetic acid, and 5.15 g (0.017 mol) of tetraethylammonium *p*-toluenesulfonate as a supporting electrolyte. This solution, which was stirred magnetically and kept at around room temperature by cooling externally with water, was electrolyzed under the condition of constant current between 0.1 and 0.2 A until 2 *F*/mol of electricity was passed. Sometimes the anode potential was measured using a saturated calomel electrode as a reference electrode. After

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[9] D. N. Kevill and N. H. Cromwell, *ibid.*, **29**, 499 (1964).

[10] A. G. El'kenbard, *Sb. Statei Obshch. Khim.*, 2, 1239 (1953); *Chem. Abstr.*, **49**, 2931*d* (1955).

the electrolysis was completed, most of the acetic acid was evaporated under reduced pressure. The residue was neutralized with sodium bicarbonate solution and extracted with ether. After drying with anhydrous magnesium sulfate, the ether was removed by distillation. Each product was isolated by fractional distillation and preparative gas chromatography and identified by spectroscopic methods, elemental analysis, and/or comparison with the authentic sample. The yields were determined by gas chromatography using an internal standard.

Cyclohexene gave 3-acetoxycyclohexene (**1**) (55%): bp 64–66° (16 mm) [lit.[11] 58° (9 mm)]; nmr (CCl_4) τ 3.9–4.5 (m, 2 H, CH=), 4.7–5.0 (m, 1 H, CHOAc), 8.03 (s, 3 H, $OCOCH_3$), 7.7–8.7 (m, 6 H, aliphatic); ir (film) 3025 (HC=), 1735 (C=O), 1650 (C=C), 1365, 1240 (CO), 1025 (CO), 725 cm^{-1}. *Anal.* Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.47; H, 8.90.

Other products were the diacetate of cyclopentanecarboxaldehyde (**17a**)[12] (2.6%) and *trans*-1,2-diacetoxycyclohexane (**18a**)[13,14] (11%). Ir and nmr spectra of these compounds were identical with those of the authentic samples synthesized independently.

In the case using tetraethylammonium chloride or bromide as a supporting electrolyte, *trans*-2-haloacetoxycyclohexane was produced (**19a,b**). *trans*-2-Bromoacetoxycyclohexane (**19b**) was identical with the authentic sample prepared by acetylation of *trans*-2-bromocyclohexanol.[14] The structure of **19a** was determined by the comparison of mass, nmr, and ir spectra with those of **19b**: bp 95–97° (5 mm) [lit.[15] 77–80° (2 mm)]; nmr (CCl_4) τ 5.0–5.4 (d of t, *J* = 4.5 and 9 Hz, 1 H, CHOAc), 5.9–6.3 (d of t, *J* = 4.5 and 9 Hz, 1 H, CHBr), 7.95 (s, 3 H, $OCOCH_3$), 7.6–8.8 (m, 8 H, aliphatic); ir (film) 1735 (C=O), 1445, 1372, 1360, 1235 (CO), 1045, 1035, 960, 905, 890, 852, 837, 795, 690 cm^{-1}; mass spectrum *m/e* (rel intensity) 222 (0.05, P^+), 220 (0.05, P^+), 180 (10), 178 (10), 162 (46), 160 (47), 99 (52), 98 (43), 81 (100), 43 (89).

trans-2-Chloroacetoxycyclohexane (**19a**): bp 105–107° (15 mm) [lit.[16] 100–100.3° (12 mm)]; nmr (CCl_4) τ 5.0–5.5 (d of t, *J* = 4.5 and 9 Hz, CHOAc), 6.0–6.45 (d of t, *J* = 4.5 and 9 Hz, 1 H, CHCl), 8.00 (s, 3 H, $OCOCH_3$), 7.6–8.8 (m, 8 H, aliphatic); ir (film) 1735 (C=O), 1447, 1374, 1360, 1230 (C—O), 1045, 1035, 960, 905, 890, 858, 838, 798, 735 cm^{-1}; mass spectrum *m/e* (rel intensity) 178 (0.3, P^+), 176 (0.8, P^+), 136 (25), 134 (80), 118 (39), 116 (95), 98 (91), 81 (95), 43 (100).

Cyclopentene yielded 41% of 3-acetoxycyclopentene (**5**).[17]

Norbornene gave 3-acetoxynortricyclene (**7**)[18] (6.9%), *exo,anti*-2,7-diacetoxynorbornane (**31a**)[19] (6.6%), and *exo,syn*-2,7-diacetoxynorbornane (**32a**)[19] (5.2%). The nmr and ir spectra of the products **5**, **7**, **31a**, and **32a** were identical with those of the authentic samples.

Methylcyclohexenes, 1-octene, and **2-octene** gave mixtures of isomeric allylic acetoxy olefins. The distribution was determined according to the following method. The ethereal extract obtained according to the general work-up was condensed and hydrogenated on palladium/charcoal (10%). The hydrogenated products were analyzed with gas chromatography (Golay column) and compared with authentic samples. Cis and trans isomers of 3- or 4-acetoxymethylcyclohexane, which were prepared from corresponding alcohols,[20] were separated by gas chromatography, whereas two isomers of 2-acetoxycyclohexane showed the same retention time.

Reaction of Methylcyclohexene or 1-Octene with *tert*-Butylperbenzoate in the Existence of Copper Catalyst (Kharasch Reaction). Into a stirred mixture of the olefin (0.096 mol) and a small amount of cuprous chloride was added *tert*-butylperbenzoate (12.5 g, 0.065 mol) at the refluxing temperature under 1 atm of nitrogen. Heating was continued for 2 hr after the addition of perester was completed. The mixture was extracted with a 2 *N* solution of sodium bicarbonate to remove the catalyst and benzoic acid. The organic layer was treated with a solution of excess potassium iodide containing a trace amount of ferric chloride in order to decompose the remaining perester. Next, the organic phase was washed with a solution of sodium bicarbonate, dried over magnesium sulfate, and evaporated. The residue was hydrolyzed with alcoholic potassium hydroxide to yield a mixture of allylic alcohols, which were acetylated by acetyl chloride. The distribution of the acetates was determined in a similar manner to the electrooxidation.

Anodic Oxidation of Olefins in Methanol. Anodic oxidation was carried out in a similar manner to that in acetic acid.

Cyclohexene gave 3-methoxycyclohexene (**2**) (24%), dimethylacetal of cyclopentanecarboxaldehyde (**17b**) (23%), and *trans*-1,2-dimethoxycyclohexane (**18b**) (2.5%).

2: bp 136° (1 atm) [lit.[21] 139° (1 atm)]; nmr (CCl_4) τ 4.0–4.6 (m, 2 H, CH=), 6.2–6.6 (m, 1 H, CHOMe), 6.73 (s, 3 H, OCH_3), 7.7–8.8 (m, 6 H, aliphatic); ir (film) 3020 (HC=), 1640 (C=C), 1095 (CO), 720 cm^{-1}. *Anal.* Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.81; H, 10.65.

17b: bp 58–60° (18 mm) [lit.[12] 65–66° (22 mm)]; nmr (CCl_4) τ 6.00 (d, *J* = 7 Hz, 1 H, $CH(OMe)_2$), 6.75 (s, 6 H, OCH_3), 7.5 ~ 8.3 (m, 1 H, $CHCH(OMe)_2$), 8.3 ~ 8.6 (m, 8 H, aliphatic); ir (film) 2835 (OMe), 1455 (cyclopentane CH_2), 1120 (CO) cm^{-1}. *Anal.* Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.33; H, 11.24.

Compound **18b** was identified by the comparison with an authentic sample prepared by methylation of the corresponding diol.[13]

Cyclopentene yielded 28% of 3-methoxycyclopentene (**6**).[17] **Norbornene** gave a mixture of 3-methoxynortricyclene (**8**)[22] (11.0%), *exo,anti*-2,7-dimethoxynorbornane (**31b**)[23] (7.0%), and *exo,syn*-2,7-dimethoxynorbornane (**32b**)[23] (5.8%). The structures of **6**, **8**, **31b**, and **32b** were established by comparison of their spectral data with those of authentic samples.

Anodic oxidation of α-**pinene** in acetic acid gave 2-acetoxy-*p*-mentha-6,8-diene (*cis*-**9a**, 7.6%) (*trans*-**10a**, 16.8%) and 2,8-diacetoxy-*p*-menth-6-ene (*cis*-**11a**, 3.1%) (*trans*-**12a**, 9.0%). Products in methanol were the corresponding four methoxy derivatives **9b** (3.0%), **10b** (18.8%), **11b** (11.4%), and **12b** (29.4%). Anode potential and current density were 1.95–2.2 V (*vs.* sce), 28 mA/cm² in acetoxylation, 1.4–1.5 V (*vs.* sce), 27 mA/cm² in methoxylation. The concentration of α-pinene was 1.75 mol/l. in both cases. The identification of **9a**, **10a**, **9b**, and **10b** was accomplished by comparison of their nmr data, ir spectra, and retention times of gas chromatography with those of authentic samples.[24]

9a: bp 92–94° (4 mm) [lit.[24] 108–108.5° (10 mm)]; nmr (CCl_4) τ 4.2–4.6 (m, 1 H, CH=), 4.4–4.8 (m, 1 H, CHOAc), 5.2–5.35 (m, 2 H, H_2C=), 7.98 (s, 3 H, $OCOCH_3$), 8.27 (m, 3 H, CH_3), 8.37 (m, 3 H, CH_3), 7.5–8.8 (m, 5 H, aliphatic); ir (film) 3090 (=CH_2), 3020 (=CH), 1735 (C=O), 1645 (C=C), 1455, 1435, 1240 (CO), 1020 (CO), 970, 920, 890, 808 cm^{-1}. *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.25; H, 9.44.

10a: bp 95–96° (5 mm) [lit.[24] 106–106.5° (9 mm)]; nmr (CCl_4) τ 4.25–4.5 (m, 1 H, CH=), 4.65–4.95 (m, 1 H, CHOAc), 5.2–5.4 (m, 2 H, =CH_2), 7.98 (s, 3 H, $OCOCH_3$), 8.2–8.4 (m, 6 H, CH_3), 7.5–8.7 (m, 5 H, aliphatic); ir (film) 3090 (=CH_2), 3020 (=CH), 1735 (C=O), 1645 (C=C), 1440, 1240 (CO), 1020 (CO), 965, 950, 910, 885, 805 cm^{-1}; mass spectrum *m/e* (rel intensity) 194 (0.54 P^+), 152 (66), 134 (8), 119 (97), 109 (85), 84 (100).

The authentic sample of **9b** or **10b** was prepared by methylation of corresponding carbeol.[24]

9b: bp 94–96° (15 mm); nmr (CCl_4) τ 4.45–4.7 (m, 1 H, CH=), 5.31 (broad s, 2 H, CH_2=C<), 6.1–6.5 (m, 1 H, CHOMe), 6.70 (s, 3 H, OCH_3), 8.27 (broad t, 3 H, CH_3), 8.35 (m, 3 H, CH_3), 7.7–8.8 (m, 5 H, aliphatic); ir (film) 3085 (=CH_2), 2815 (OMe), 1640 (C=C), 1100 (CO), 880, 805 cm^{-1}. *Anal.* Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.44; H, 10.95.

10b: bp 104–106° (17 mm); nmr (CCl_4) τ 4.4–4.6 (m, 1 H, CH=), 5.27 (broad s, 2 H, CH_2=C<), 6.5–6.7 (m 1 H, CHOMe), 6.65 (s, 3 H, OCH_3), 8.25 (broad s, 6 H, CH_3), 7.7–8.8 (m, 5 H, aliphatic); ir (film) 3095 (=CH_2), 2820 (OMe), 1645 (C=C), 1090 (CO), 885, 805 cm^{-1}. *Anal.* Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.73; H, 10.89.

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The structures of **11** and **12** were determined by comparison of ir and nmr spectra with those of **9** and **10**.

11a: bp 83–85° (0.18 mm); nmr (CCl_4) τ 4.3–4.9 (m, 2 H, CH=C and CHOAc), 8.00 (s, 3 H, $OCOCH_3$), 8.08 (s, 3 H, $OCOCH_3$), 8.40 (broad s, 3 H, $CH_3C\leqslant$), 8.56 (s, 3 H, CH_3), 8.60 (s, 3 H, CH_3), 7.7–8.9 (m, 5 H, aliphatic); ir (film) 3025 (HC=), 1730 (C=O), 1450, 1435, 1240 (CO), 1020 (CO), 970, 925, 805 cm^{-1}. *Anal.* Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.28; H, 8.64.

12a: bp 83–85° (0.18 mm); nmr (CCl_4) τ 4.2–4.6 (m, 1 H, CH=C<), 4.7–5.0 (m, 1 H, CHOAc), 8.00 (s, 3 H, $OCOCH_3$), 8.10 (s, 3 H, $OCOCH_3$), 8.32 (broad s, 3 H, $CH_3C\leqslant$), 8.58 (broad s, 3 H, CH_3), 8.62 (broad s, 3 H, CH_3), 7.7–8.7 (m, 5 H, aliphatic); ir (film) 3020 (HC=), 1730 (C=O), 1440, 1240 (CO), 1020 (CO), 965, 950, 915, 805 cm^{-1}. *Anal.* Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.32; H, 8.53.

11b: bp 115–117° (17 mm); nmr (CCl_4) τ 4.5–4.7 (m, 1 H, CH=), 6.2–6.5 (m, 1 H, CHOMe), 6.69 (s, 3 H, OCH_3), 6.85 (s, 3 H, OCH_3), 8.35 (m, 3 H, $CH_3C\leqslant$), 8.91 (s, 6 H, CH_3), 7.7–9.0 (m, 5 H, aliphatic); ir (film) 2825 (OMe), 1380, 1365, 1105 (CO), 810 cm^{-1}. *Anal.* Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.45; H, 11.33.

12b: bp 115–117° (17 mm); nmr (CCl_4) τ 4.4–4.6 (m, 1 H, CH=), 6.5–6.7 (m, 1 H, CHOMe), 6.67 (s, 3 H, OCH_3), 6.86 (s, 3 H, OCH_3), 8.28 (broad s, 3 H, $CH_3C\leqslant$), 8.91 (s, 6 H, CH_3), 7.7–9.0 (m, 5 H, aliphatic); ir (film) 2825 (OMe), 1360, 1380, 1080 (CO), 800 cm^{-1}. *Anal.* Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.61; H, 10.89.

Electrooxidation of β-pinene (1.75 mol/l.) in methanol (1.45–1.55 V *vs.* sce, 23 mA/cm^2) yielded 2-methoxy-*p*-mentha-1(7),8-diene (**13**) (2.5%), 2,8-dimethoxy-*p*-menth-1(7)-ene (**14**) (7.4%), 7-methoxy-*p*-mentha-1,8-diene (**15**) (14.7%), and 7,8-dimethoxy-*p*-menth-1-ene (**16**) (23.4%).

13: bp 62–63° (5 mm); nmr (CCl_4) τ 5.1–5.3 (m, 2 H, C^1 methylene), 5.25–5.4 (m, 2 H, C^8 methylene), 6.39 (t, J = 3 Hz, 1 H, CHOMe), 6.87 (s, 3 H, OCH_3), 8.30 (t, J = 1 Hz, 3 H, CH_3), 7.5–9.0 (m, 7 H, aliphatic); ir (film) 3090 (=CH_2), 2825 (OMe), 1640 (C=C), 1110, 1090 (CO), 885 cm^{-1}. *Anal.* Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.27; H, 10.70.

14: bp 77–80° (5 mm); nmr (CCl_4) τ 5.15–5.35 (m, 2 H, =CH_2), 6.40 (t, J = 3 Hz, 1 H, CHOMe), 6.87 (s, 6 H, OCH_3), 8.97 (s, 6 H, CH_3), 7.6–8.9 (m, 5 H, aliphatic); ir (film) 3085 (=CH_2), 2825 (OMe), 1650 (C=C), 1380, 1365, 900 (=CH_2) cm^{-1}; mass spectrum *m/e* (rel intensity) 198 (0.3, P$^+$), 166 (4), 151 (8), 134 (7), 73 (100).

15: bp 66–68° (5 mm); nmr (CCl_4) τ 4.3–4.5 (m, 1 H, CH=), 5.30 (broad s, 2 H, =CH_2), 6.30 (broad s, 2 H, CH_2OMe), 6.82 (s, 3 H, OCH_3), 8.27 (broad s, 3 H, CH_3), 7.7–9.1 (m, 7 H, aliphatic); ir (film) 3095 (=CH_2), 3025 (HC=), 1670 (C=C), 1645 (C=C), 1100 (CO), 885 (H_2C=), 815 cm^{-1}; mass spectrum *m/e* (rel intensity) 166 (18, P$^+$), 134 (51), 93 (100).

16: bp 79–82° (5 mm); nmr (CCl_4) τ 4.3–4.5 (m, 1 H, CH=), 6.30 (broad s, 2 H, CH_2OMe), 6.81 (s, 3 H, OCH_3), 6.88 (s, 3 H, OCH_3), 8.93 (s, 6 H, CH_3), 7.8 ~ 8.6 (m, 7 H, aliphatic); ir (film) 2825 (OMe), 1380, 1360 (Me_2C), 1080 (CO), 810 cm^{-1}. *Anal.* Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.93; H, 11.18.

Anodic oxidation of cyclohexene in water–acetonitrile (1:1 mol/mol) gave 3-hydroxycyclohexene (**3**). This compound was identical with the authentic sample, which was prepared by hydrolysis of **1**.

Electrooxidation of cyclohexene in acetonitrile containing 0.23 mol/l. of water yielded 3-acetoaminocyclohexene (**4**): mp 78°; nmr (CCl_4) τ 2.5–3.1 (m, 1 H, NH), 4.0–4.7 (m, 2 H, CH=), 5.45, 4.9 (m, 1 H, CHN), 8.10 (s, 3 H, $COCH_3$), 7.8–8.7 (m, 6 H, aliphatic); ir (KBr) 3290 (NH), 3070, 3020 (HC=), 1640 (C=O), 1550 (NH), 1370 (CN), 730 cm^{-1}. *Anal.* Calcd for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 68.94; H, 9.55; N, 9.78.

Isotope Effect. Cyclohexene-*1,3,3*-d_3 (**20**) (purity is almost 100% by nmr) was prepared from cyclohexanone by the method of R. C. Fahey.[25] Anodic acetoxylation of **20** was carried out in a similar manner to cyclohexene. The content of deuterium at the C_3 position of the obtained 3-acetoxycyclohexene was determined by nmr to be 39% indicating the deuterium effect (k_H/k_D) of 1.6.

The current *vs.* anode potential curve was obtained by the following method. Anode potential was measured at constant temperature as a function of electrolysis current, which was supplied in both the ascending and descending directions. The results were independent of the sequence in which the current was varied.

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A Comparative Molecular Orbital Study of Protonated Adenine Tautomers and Their Intermolecular Interactions

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Abstract: Electronic structures of several neutral and protonated adenine tautomers were calculated using the CNDO/2 and MINDO methods. Substantial changes in net atomic charges and σ and π charge distributions and large increases in ionization potentials were noted upon protonation. The effect of protonation on base–base interactions was qualitatively evaluated taking into account monopole–monopole, monopole–induced dipole, and dispersion terms.

There are numerous calculations in the literature on the electronic structure of adenine.[1] No such calculations are to be found on protonated DNA bases other than one on cytosine.[2] As part of our systematic study of the electronic structures of protonated DNA bases, nucleosides, and nucleotides we have performed calculations on N-7-H and N-9-H tautomers and their N-1 protonated analogs—the N_7-methyl and N_9-methyladenines and corresponding N-1 protonated structures—always maintaining the amino configuration at N-10.

For these calculations we have employed the well-documented CNDO/2[3] and MINDO[4] methods using

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