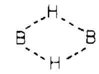
bridge bonds of 9-BBN dimer at 1570 cm^{-1} with an IR spectrometer.[1c] A detailed procedure has been described earlier. A typical example is as follows. Cyclohexane (1.3 mL), followed by $(9\text{-BBN})_2$ (36.8 mL of a 0.068 *M* solution), was added into a 100-mL round-bottom flask with the usual precautions of air protection. After the reaction mixture was equilibrated in a constant-temperature bath at 25.0 ± 0.1 °C, it was pumped through a 0.1-mm NaCl IR cell to determine the absorbance of



vibration at 1570 cm^{-1}. The reaction was initiated by adding pyridine (0.40 mL). The initial concentrations of $(9\text{-BBN})_2$ and pyridine were 0.065 *M* and 0.130 *M*, respectively. The initial absorbance increased slightly, due to a weak absorption of pyridine at 1570 cm^{-1}.

The absorbance was continuously recorded on chart paper. After 3 h, the absorbance ceased to decrease. The residual absorbance was measured as the background absorbance. The concentration of $(9\text{-BBN})_2$ at a particular reaction time was calculated as described previously and the second-order rate constants were calculated on a Hewlett-Packard 9820 calculator. The best straight line was fitted to this set of data by using the method of least squares. The rate constant was obtained numerically as the slope of the line.

Acknowledgment. We thank the National Science Foundation for Grants CHE 76-20846 and CHE 79-18881.

Registry No. $(9\text{-BBN})_2$, 70658-61-6; pyrrolidine, 123-75-1; piperidine, 110-89-4; *n*-butylamine, 109-73-9; neopentylamine, 5813-64-9; pyridine, 110-86-1; benzylamine, 100-46-9; cyclohexylamine, 108-91-8; cycloheptylamine, 5452-35-7; cyclopentylamine, 1003-03-8; *sec*-butylamine, 13952-84-6; 2-methylpyridine, 109-06-8; *N*-methylpyrrolidine, 120-94-5; di-*n*-butylamine, 111-92-2; quinuclidine, 100-76-5; *tert*-butylamine, 75-64-9; aniline, 62-53-3; cyclohexane, 110-82-7; benzene, 71-43-2; tetrahydrofuran, 109-99-9.

Photoelectron Spectra of *syn*- and *anti*-Sesquinorbornene. Evidence for Vertical σ–π Delocalization in Bicyclo[2.2.1]heptene

R. S. Brown,* J. M. Buschek,* K. R. Kopecky,* and A. J. Miller

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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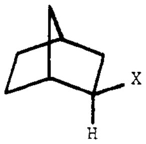
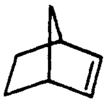
The photoelectron spectra of *syn*- and *anti*-sesquinorbornene show the π IP's to be 8.12 and 7.90 eV, respectively. Comparison of these IP's with those of other tetraalkylethylenes having the same number of carbon atoms indicates that both isomers are easier to ionize than expected for a C_{12} tetraalkylethylene. This is attributed to σ–π closed shell–closed shell repulsions between the ethano and methano bridges and the π bond. The difference of 0.2 eV in the π IP between the two is surprisingly large for two geometric isomers and is related to the molecular symmetry. The π IP of norbornene, when compared with those of a series of cis olefins, is 0.12 eV easier to ionize than is expected for a *cis*-dialkylethylene containing seven carbons. This small reduction in π IP which is attributable to vertical electronic factors may account for an increased reactivity of norbornene in processes involving electrophilic addition to the π bond.

Few systems have attracted more interest than the bicyclo[2.2.1]heptyl (norbornyl) skeleton.[1] The bulk of the controversy pertains to the high exo/endo selectivity both of its saturated derivatives (1) under solvolytic conditions and in additions (either electrocyclic or electrophilic) to the unsaturated norbornene (2).[2-5]



1



2

Although it is generally accepted that norbornene itself exhibits unusual chemical properties, insofar as we are aware no incontrovertable analysis of extant data has been made which would indicate that its π IP[6,7] is substantially different from those of other olefins which do not incorporate the bicyclo[2.2.1] framework. Indeed, norbornene has been referred to as belonging to a well-behaved series of molecules in which an ethylene π level is affected by alkyl substitution.[8] If vertical σ–π interaction[9] were

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(1) (a) For leading literature citations see: Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; pp 413–428. (b) Brown, H. C. *Tetrahedron* **1976**, *32*, 179–204. (c) Schleyer, P. V. R. In "The Non-Classical Ion Problem"; Brown, H. C., Ed.; Plenum: New York, 1977. (d) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41–52. (e) Sargent, G. D. In "Carbonium Ions"; Olah G. A., Schleyer, P. V. R., Eds.; Wiley: New York, 1972; Vol. III, Chapter 24. (f) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 87–96.

(2) (a) Freeman, F. *Chem. Rev.* **1975**, *75*, 439–490. (b) Traylor, T. G. *Acc. Chem. Res.* **1969**, *2*, 152–160.

(3) (a) Inagaki, H.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054–4061. (b) Wipff, G; Morokuma, K. *Tetrahedron Lett.* **1980**, 4445–4448. These authors have optimized norbornene at the STO-3G level and report the angle between the C_1–C_2–C_3–C_4 and H—C_2=C_3—H planes to be 175.1°. (c) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436–2438. These authors calculate this same angle to be 176.6°. (d) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, 2435–2438.

(4) Schleyer, P. V. R. *J. Am. Chem. Soc.* **1967**, *89*, 701–703.

(5) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Mareda, J.; Mueller, P. H.; Houk, K. *J. Am. Chem. Soc.* **1982**, *104*, 4974–4976.

(6) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745–1749.

(7) Neijzen, B. J. M.; Schmitz, R. F.; Klumpp, G. W.; de Lange, C. A. *Tetrahedron* **1975**, *31*, 873–876.

(8) Hoffmann, R.; Mollère, P. D.; Heilbronner, E. J. *J. Am. Chem. Soc.* **1973**, *95*, 4860–4862.

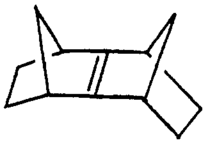
Table I. Vertical Ionization Potentials and Double Bond Stretching Frequencies in Tetrasubstituted Ethylenes and Their Molecular Ions

alkene	IP,[a] eV	$\nu_{C=C}$(M), cm^{-1}	$\nu_{C=C}$(M$^{+\cdot}$), cm^{-1}	$\Delta\nu$, cm^{-1}
3	8.12	1587	*b*	
4	7.90	1603	*b*	
cyclohexylidenecyclohexane (**7**)	8.16	1676	1210 ± 200 (0.15 eV)	470
isopropylidenecyclopentane (**8**)	8.34	1686	1370 ± 200 (0.17 eV)	420
4,5-dipropyl-4-octene (**9**)	8.11	1649	1050 ± 200 (0.13 eV)	600
1(7)-bicyclo[5.3.0]decene (**10**)	8.25	1677	1210 ± 200 (0.15 eV)	470
5	8.15	1653		
3-methylcyclohexene (**12**)	9.12	1640	970 ± 200 (0.12 eV)	870

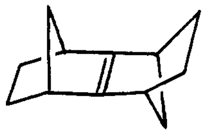
[a] Estimated error ±0.02 eV. [b] Unlike all other tetrasubstituted ethylenes of which we are aware, neither **3** nor **4** show discernible vibrational structure in their π bands.

present and substantial, the π IP of norbornene might be expected to be quite different from comparison olefins,[10a] but any such effect is obviously small enough that it has not been specifically addressed.[10c,11]

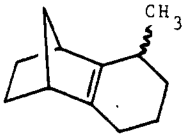
In order to cast more light on this question, we have determined the photoelectron spectra of several olefins including *syn*- and *anti*-sesquinorbornene (**3**[12] and **4**,[13] respectively). Because of the unique structure of the latter two isomers, the probe π bond formally experiences simultaneous interaction with *two* bicyclo[2.2.1] fragments such that the π IP might be expected to reflect an augmented σ–π interaction. In the following it is shown that the photoelectron spectra of these not only provide evidence for such electronic interaction but also indicate that the magnitude of such an effect depends markedly on the geometry which is in turn controlled by the molecular symmetry. With this information in hand, it is subsequently shown that the π IP of norbornene is indeed reduced by vertical σ–π delocalization.



3[12]



4[13]



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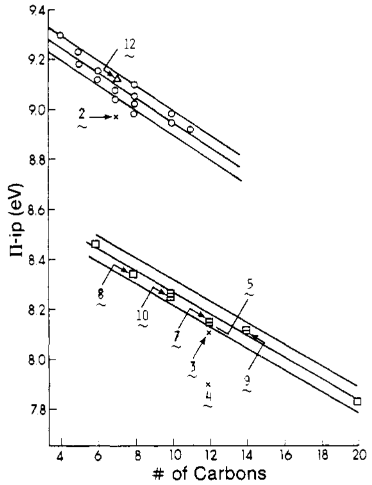

Figure 1. Plots of vertical π IP ionization energies vs. total number of C atoms for cis-disubstituted ethylenes (upper line) and tetraalkylethylenes (lower line). The data used to define the upper line include the following: *cis*-2-butene, cis C_5–C_8 cyclic olefins (Clary, D. C.; Lewis, A. A.; Morland, D.; Murrell, J. N.; Heilbronner, E. *J. Chem. Soc., Faraday Trans.* 2 **1974**, 1889–1894); 3-methyl-, 3-ethyl-, and 3-isopropylcyclopentene (McAlduff, E. J.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 105–110); *cis*-2-pentene, 3-hexene, 2-hexene, 2-octene, 3-octene (Krause, D. A.; Taylor, J. W.; Fenske, R. F. *J. Am. Chem. Soc.* **1978**, *100*, 718–723); bicyclooctene;[6] cyclononene and cyclodecene (Bischoff, P.; Heilbronner, E. *Helv. Chim. Acta* **1970**, *53*, 1677–1682). Data used to define the lower line are abstracted from ref 15a and include our value for tetra-*n*-propylethylene. Additional examples from Table I are included on the regression. (Triple lines define ±0.05 eV error limits.)

Results and Discussion

(a) *syn*- and *anti*-Sesquinorbornene. It is particularly interesting that the π IP's of *syn*- and *anti*-sesquinorbornene (Table I) are substantially different (8.12[14] and 7.90 eV, respectively). In order to gauge how these IP's compare to those of other tetrasubstituted ethylenes, we

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[9] (a) Brown, R. S.; Traylor, T. G. *J. Am. Chem. Soc.* **1973**, *95*, 8025–8032. (b) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *Ibid.* **1971**, *93*, 5715–5725. (c) Traylor, T. G.; Clinton, N. A.; Brown, R. S. *Ibid.* **1970**, *92*, 5228–5230. (d) Eaton, D. F.; Traylor, T. G. *Ibid.* **1974**, *96*, 1226–1227.

[10] (a) If such electronic (σ–π) interactions were prominent in the ground or ion states of norbornene, one might anticipate a reduced π IP of norbornene relative to some suitable nonbicyclic comparison olefin. Admittedly, the reported π IP's of **2** and cyclohexene of 8.97 and 9.11 eV, respectively,[10b] are in the direction consistent with a σ–π interaction in the former. However, it is also well-known that alkylation of the allylic positions of an olefin reduces its π IP[14] such that one might reasonably argue that the 0.1–0.15-eV difference in π IP is associated (at least in part) with changing substitution effects. A similar argument might be invoked to rationalize the reduced IP of *exo*-methylenenorbornene (9.04 eV) relative to that of methylenecyclohexane (9.13 eV).[13b] (b) Asmus, P.; Klessinger, M. *Tetrahedron* **1974**, *30*, 2477–2483. (c) We must point out that as early as 1971 Traylor et al.[9b] did address the possibility of σ–π delocalization in 2-methylenenorbornane when it was observed that its tetracyanoethylene charge-transfer λ_{max} was different from that of methylenecyclohexane. In these authors' opinion "there is probably some vertical stabilization available at the 2-position in norbornane but the studies are not sufficiently quantitative to establish the extent to which vertical stabilization contributes to the stability of the transition state in the solvolysis of norbornyl tosylate".

[11] Masclet, P.; Grosjean, D.; Mouvier, G.; Dobois, J. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 225–237.

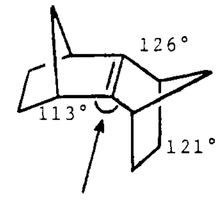
[12] Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553–7559.

[13] (a) Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383–1390. (b) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. M. *Ibid.* **1981**, *103*, 2022–2031.

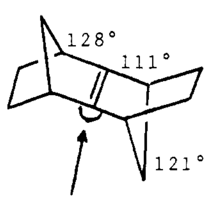
[14] A value of 8.27 eV for the π IP of **3** (determined in the laboratories of R. Gleiter) is reported in ref 12. Although we have no explanation for the apparent discrepancy in IP between this number and ours, careful and repeated determinations of the photoelectron spectrum of **8** (referencing against MeI and Ar) have convinced us that the true value is 8.1–8.15 eV.

have plotted the vertical π IP vs. the total number of carbons for a series of tetrasubstituted ethylenes chosen in such a way that they contain no severe steric or strain factors (Figure 1).[15] An excellent linear regression of π IP (eV) = 8.70 − 0.043 $\sum C$ exists (r = 0.994). The π IP's of both **3** and **4** lie below the best fit line by 0.08 and 0.29 eV, respectively. Thus electronic features exist in these molecules which facilitate their ionizations relative to "normal" unstrained tetrasubstituted ethylenes having 12 carbons. This is particularly surprising since a closely related molecule, **5**, which also contains 12 carbons shows a π IP of 8.15 eV, close to the linear regression shown in Figure 1. Clearly, the additional ring closure required to produce **3** or **4** from **5** is reflected i n the IP. The difference of 0.2 eV in the π IP's of **3** and **4** is unusually large for two compounds which are ostensibly geometric isomers and are therefore expected to have very similar inductive and strain effects.

However, it has been definitively established by X-ray crystallography that whereas derivatives of **4** have an essentially flat π bond, the double bond of the syn derivatives is distorted from planarity by some 16–18°.[13b] Recent EH calculations on **3** indicate that the distortion results from σ–π interactions and leads to an increased π IP.[16] In order to relieve destabilizing σ–π interactions, compound **3** experiences distortion of the σ framework and pyramidalization of the π bond. Importantly, the latter mode is not available to **4** for reasons of symmetry. The experimental angles are indicated in **6a** and **6b**.[13b] (See, however, Note Added in Proof.[29])



6a θ = 162°



6b θ ≈180°

It is not unreasonable to suggest that geometric distortion and π IP differences between **3** and **4** are related to the same electronic factors. In the absence of π deformation, it would be anticipated that similar electronic repulsions would exist in both **3** and **4** such that their π IP's would be reduced relative to other tetrasubstituted ethylenes (Figure 1). However, pyramidalization of the π bond in **3** not only reduces the overall electron repulsion[16] but also injects more s character into the rehybridized π orbital. Both factors should lead to an increase in π IP relative to **4** as is observed. It is particularly curious but not expected in the light of the above analysis that the isomer which is most geometrically distorted is in fact the one whose π IP appears to be most like a normal tetrasubstituted ethylene. The IP difference between **3** and **4** might therefore be taken as experimental verification for the theoretically based suggestion that the distortion in **3** actually leads to stabilization of the π level.[16]

Although the above experimental IP data refer to isolated gas-phase molecules, it is interesting to note that the difference in ionization energy between the syn and anti isomers is manifested in solution as well. Cyclic voltamograms of **4** and **3** in CH_2Cl_2 solution[17] show electrochemically reversible waves at scan rates of 600 mV/s, the oxidation potentials being 1.33 and 1.47 V, respectively.

(b) Norbornene. Also shown in Figure 1 is a plot for several cis-disubstituted ethylenes, the linear regression being π IP (eV) = 9.44 − 0.49 $\sum C$ (r = 0.945). The olefins used to define the linear regression were chosen on the basis of two criteria: first, that no "unusual" strain effects are present, which excludes such candidates as cyclopropene and cyclobutene, and second, that the two ends of the olefin differ in total number of carbons by no more than 4 units, thus excluding such compounds as 2-nonene. Admittedly, there is considerable scatter in the plot, but a large amount of this is undoubtedly due to the fact that the data are drawn from several sources and therefore are not as internally consistent in terms of cross-referencing as one would like. Nevertheless, if we put error limits of ±0.05 eV on the best-fit line, it can be seen that the π IP's of virtually all olefins lie acceptably close to the line. However, that of norbornene (**2**) lies 0.12 eV lower than would be anticipated for a C_7 cis olefin, and it is in fact 0.14 eV lower than that of 3-methylcyclohexene (indicated by a Δ on Figure 1). Thus, by this criterion, it would appear that norbornene is indeed easier to ionize than comparison olefins having the same number of carbons.

We believe that the reduction in π IP of norbornene is explicable in terms of e–e repulsion between the σ framework and the π orbital similar to that operative in **3** and **4**. Although many workers have suggested such an interaction,[3–5,9] the reported π IP of 8.97 eV[6] for **2** has apparently not been considered to be abnormally low. Norbornene appears to be one of those olefins for which the π IP is not sufficiently different from that of a given comparison olefin to be definitively attributed to any obvious effect.[18] The advantage of treating the IP data as in Figure 1 rests in the fact that one avoids comparison with any single imperfect model.

Originally Traylor pointed out that vertical stabilization of cationic states should be manifested in chemical processes in which rate-limiting generation of a a positive charge adjacent to a delocalizable or hyperconjugating σ bond occurs.[9] For electrophilic additions to norbornene, if the transition state involves rate-limiting generation of a positive charge at C_2, it is expected that those vertical factors which decrease the π IP of **2** will also contribute to an increase in reaction rate. This, as well as other factors which become more prominent as the nucleii move toward the transition-state geometry,[3d,4,5] seems to account for the observation that in a wide variety of electrophilic additions, including bromination,[2a] oxymercuration,[2b] acid-catalyzed hydration,[19a] and even with 1,3-dipolaro-

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(15) (a) The PES data for tetrasubstituted olefins comes from: Mollere, P. D.; Houk, K. N.; Bomse, D. S.; Morton, T. H. *J. Am. Chem. Soc.* **1976**, *98*, 4732–4736. (b) Although a much larger set of tetrasubstituted olefin IP data exists,[11] the reported values appear to be adiabatic and not vertical and so are not directly compatible with our values unless the vibrational spacing is known. (c) The approach of plotting the π IP against the total number of carbons has been used before.[11] Houk[15a] has used this approach to show that tetraisopropylethylene and adamantylideneadamantane are "normal olefins" in terms of π IP.

(16) Gleiter, R.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, *23*, 927–930. According to these calculations, the puckering of the π unit in **3** leads to reduced interaction between the π and σ frameworks and therefore leads to a net stabilization of the π level.

(17) Conventional cyclic voltametry was performed in CH_2Cl_2 solution containing 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte. Potentials were measured vs. a silver wire immersed in the solution as a reference electrode. We thank Dr. B. Speiser and Prof. S. Pons of this department for determining the values.

(18) We are certain that the reported IP of norbornene must have been carefully scrutinized by many groups, particularly that of T.G. Traylor, with the intent of ascertaining whether it could be used as a criterion for assessing the importance of vertical delocalization of the C_1–C_6 σ bond to an electron-deficient center at C_2. However, we are unaware of any literature discussion of the IP of norbornene itself,[10c] which pertains to this issue.

(19) (a) Chwang, W. K.; Nolan, V. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1977**, *99*, 7233–7238. (b) Huisgen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. *Ibid.* **1980**, *102*, 3951–3953.

philes[19b] norbornene reacts ~10^1–10^4 faster than does cyclohexene.[20]

Conclusions

(1) The π IP's of *syn*- and *anti*-sesquinorbornene (**3** and **4**) are lower than that expected for a "normal" tetrasubstituted ethylene containing 12 carbons. The observed reductions in the π IP result from electronic features attributable to the symmetry of the molecular structures.

(2) Similarly, we conclude the π IP of norbornene is also low for a cis C_7 olefin relative to a regression defined by cis olefins.

The small but nevertheless significant reduction of the π IP also results from vertical electronic factors inherent in the bicyclo[2.2.1] skeleton. The reduction in the vertical IP is consistent with the enhanced chemical reactivity of norbornene in a variety of electrophilic reactions.

Experimental Section

Materials and Methods. All He(I) photoelectron spectra were recorded on an instrument constructed at the University of Alberta. Typical resolution was ≤40 meV for Ar. Spectra were referenced internally and externally against Ar and Ar plus CH_3I. Raman spectra (neat) were recorded on a Beckman Model 700 laser Raman spectrometer by using the 488.0-nm exciting line from a Coherent Radiation Model 52 argon laser. ^1H NMR spectra were recorded on a Bruker WP-80 CW spectrometer with $(CH_3)_4Si$ as an internal standard. Mass spectra were taken on an AEI MS50 mass spectrometer with an electron impact of 70 eV. Melting points and boiling points are uncorrected. Elemental analyses were performed in the microanalytical laboratories in the chemistry department under the supervision of Mrs. Darlene Mahlow.

syn- and *anti*-sesquinorbornene (**3**[12] and **4**[13a]) were prepared by published procedures while isopropylidenecyclopentane[21] and 1(7)-bicyclo[5.3.0]decene[22] were available from previous studies. Cyclohexylidenecyclohexane [mp 54–55 °C (lit.[23] mp 55 °C)] was prepared by Dr. J. A. Lopez Sastre from the corresponding diol[24] by decomposition of the mixed orthoformate ester.[25]

4,5-Dihydroxy-4,5-dipropyloctane. Treatment of 4-heptanone with aluminum amalgam in CH_2Cl_2[24] and hydrolysis of the resulting mixture produced the diol, mp 74–75 °C (lit.[26] mp 68 °C). Anal. Calcd for $C_{14}H_{30}O_2$: C, 72.98; H, 13.13. Found: C, 72.73; H, 13.05.

4,5-Dipropyl-4-octene (9). A mixture of 5.0 g (0.22 mol) of the above diol, 3.2 g (0.22 mol) of triethyl orthoformate, and a few crystals of benzoic acid was heated[25] to 130 °C for 15 h, when ~2 mL of distillate had been formed. The reaction mixture was then heated at 180 °C for 1 h and cooled, and the liquid was chromatographed through a short column of basic alumina. The residual oil remaining after removal of pentane from the eluent was distilled to give 3.5 g (81%) of a colorless oil: bp 99–101 °C (13 torr), ^1H NMR ($CDCl_3$) δ 1.95 (m, 8 H), 1.35 (m, 8 H), 0.87 (m, 12 H); MS, calcd for $C_{14}H_{28}$ *m/e* 196.2191, obsd 196.2191. Anal. Calcd for $C_{14}H_{28}$: C, 85.63; H, 14.39. Found: C, 85.78; H, 14.28.

5-Methyl-1,4,4a,5,6,7,8,8a-octahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylic Anhydride. A solution of 15 g (0.091 mol) of bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylic anhydride[27] and 20 mL of 70% technical grade 1,3-pentadiene in 50 mL of benzene was heated at 80 °C for 27 h, cooled, and concentrated. The residue was crystallized from methanol to give 14 g (66%) of a white solid: mp 79–80 °C; ^1H NMR ($CDCl_3$) δ 5.70 (m, 2 H), 3.10–1.12 (overlapping m, 14 H) (the CH_3 doublet was centered at δ 1.37). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.33; H, 6.94. Found: C, 72.56; H, 6.97.

The stereochemistry of the methyl group is unknown. The exo stereochemistry was assigned to the methano bridge in analogy to the stereochemistry of the Diels–Alder reactions of the starting anhydride with cyclopentadiene.[13a]

5-Methyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylic Anhydride. The above unsaturated anhydride in ethyl acetate was hydrogenated over 5% Pd/C under 20 psi of H_2 in a Parr apparatus. The product was recrystallized from methanol: mp 73–74.5 °C; ^1H NMR ($CDCl_3$) δ 2.65 (m, 1 H), 2.35 (m, 1 H), 2.17–1.35 (m, 13 H), 1.20 (d, J = 7 Hz, 3 H. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.86; H, 7.70.

5-Methyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylic Acid. A solution of 6 of the above saturated anhydride and 4 g of NaOH in 50 mL of CH_3OH was heated at 130 °C for 8 h, cooled, and poured into water, and the resulting solution was acidified. The precipitate was filtered, washed with water, and recrystallized from CH_3OH to yield 6 g (92%) of white needles: mp 136–137 °C dec; ^1H NMR ($CDCl_3$) δ 10.5 (br s, 2 H), 2.87–1.12 (overlapping m, 15 H), 0.87 (d, J = 7 Hz, 3 H). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.78; H, 8.33.

Methyl Hydrogen 5-Methyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylate. When the above hydrolysis was carried out at 80 °C, the main product was the monomethyl ester: mp 145–146 °C dec; ^1H NMR ($CDCl_3$) δ 10.3 (br s, 1 H), 3.64 (s, 3 H), 2.55–1.88 (m, 5 H), 1.88–1.13 (m, 10 H), 0.88 (d, J = 7 Hz, 3 H). Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.59; H, 8.33. Found: C, 67.67; H, 8.35.

The position of the carbomethoxy group was not determined.

5-Methyl-1,2,3,4,5,6,7,8-octahydro-1,4-methanonaphthalene (5). A solution of 2.25 g of the above diacid in 20 mL of pyridine was heated to 70 °C, and 4 g of $Pb(OAc)_4$ was added at once.[28] Vigorous gas evolution began immediately and became slow after 8 min when the reaction mixture was poured into ice–HNO_3. The usual workup[28] gave an oil which was chromatographed through a short column of basic alumina with pentane as the eluent. Removal of the pentane and distillation of the residue gave 0.340 g (24%) of a colorless oil: bp 93 °C (15 torr); ^1H NMR ($CDCl_3$) δ 2.75 (m, 1 H), 2.55 (m, 1 H), 2.30 (m, 1 H, 1.90 (m, 2 H), 2.62 (m, 4 H), 1.25 (s, 3 H), 1.10 (m 3 H), 0.95 (d, J = 7 Hz, 3 H); MS, calcd for $C_{12}H_{18}$ *m/e* 162.1409, obsd 162.1409. Anal. Calcd for $C_{12}H_{18}$: C, 88.83; H, 11.17. Found: C, 88.72; H, 10.77.

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[20] Freeman[2a] recognized that a relationship between IP and rate could be established for electrophilic additions to double bonds. Unfortunately, the IP values chosen for his relationships were based on earlier measurements and are not the currently accepted vertical values determined by PES. In particular, the chosen values for cyclohexene and norbornene were 8.94 and 8.94 eV, respectively. Certainly, had the currently accepted values been used, more attention would have been focussed on the electronic factors inherent in norbornene as being logically responsible for its increased chemical reactivity in electrophilic processes.

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(29) **Note Added in Proof**: A different derivative of the anti alkene **4** has been found to have the double bond distorted by 13°, as determined by X-ray diffraction, and force field calculations indicate that the double bond of unsubstituted **4** itself is greatly distorted: Ermer, O.; Bödecker, C.-D. *Helv. Chim. Acta.* **1983**, *66*, 943–959. These calculations disagree with the assumption made in the present paper that the π bond of **4** cannot be pyramidalized because of symmetry. If the double bond of **4** is indeed distorted, then our explanation for the difference in the π IP's between **3** and **4** requires modification. However, such will have to await the determination of the gas-phase structures. The force field calculations of Ermer and Bödecker indicate that two equivalent interconverting structures of **4** with a nonplanar double bond would have a barrier to interconversion of ~8 kcal/mol. We have attempted to detect such an interconversion in **4** by variable-temperature ^{13}C NMR at 400 MHz but found no evidence of line broadening even at −90 °C. A number of other molecules containing the norbornene skeleton have been found very recently to have distortions of from 4° to 8° about the double bond: Paquette, L. A.; Schaefer, A. G.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *104*, 3642–3649.

In addition we are grateful to Prof. S. Huzinaga and D. M. Klobukowski for performing Gaussian 80 calculations and to Prof. S. Pons. and Dr. B. Speiser for electrochemical studies.

Registry No. **2**, 498-66-8; **3**, 73321-28-5; **4**, 73679-39-7; **5**, 86954-77-0; **7**, 4233-18-5; **8**, 765-83-3; **9**, 57984-32-4; **10**, 7125-60-2; **12**, 591-48-0; 4,5-dihydroxy-4,5-dipropyloctane, 86954-78-1; 5-methyl-1,4,4a,5,6,7,8,8a-octahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylic anhydride, 86954-79-2; 5-methyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylic anhydride, 86954-80-5; 5-methyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylic acid, 86954-75-8; methyl hydrogen 5-methyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylate, 86954-76-9.

Peroxy Esters. 8. Base-Catalyzed Rearrangement of Peroxy Esters: Formation of Alkoxyacetic Acid Derivatives[1]

Akira Nishinaga,* Koichi Nakamura, and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

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p-Peroxyquinol esters derived from base-catalyzed oxygenation of 4-alkyl-2,6-*tert*-butylphenols followed by Schotten–Baumann acylation undergo a novel base-catalyzed rearrangement with *t*-BuOK in *N*,*N*-dimethylformamide to give *p*-quinoxyacetic acid derivatives in excellent yield. The same base-catalyzed rearrangement was also observed with *tert*-butyl peroxy esters. The base-catalyzed reaction of peroxy esters depended strongly on the nature of the acyl group in the esters and the base used and is suggested to involve homolysis of the peroxy bond.

Reactions of organic peroxides have received intensive study because knowledge of their properties and reactivity is of the highest importance in a wide range of organic chemistry.[2] Reactions of peroxy esters with bases have been demonstrated to result in fragmentation through an ionic cleavage of the peroxy bond either by direct attack of bases on the peroxy bond[3-6] or by deprotonation from a C–H bond in the α-position to the peroxy group followed by concerted ionic decomposition.[7] Hydroxy anion is known to attack the carbonyl group in peroxy esters, leading to hydrolysis.[8]

The present paper deals with a novel base-catalyzed rearrangement of peroxy esters **1** derived from 4-alkyl-2,6-di-*tert*-butylphenols (**4**) to give *p*-quinoxyacetic acid derivatives **2** in excellent yield. Similar rearrangement was also observed in the base-catalyzed reaction of *tert*-butyl peroxy esters. A mechanism involving homolysis of the peroxy bond is discussed.

Table I. *t*-BuOK-Catalyzed Reaction of Peroxy Esters **1**[a]

	product yield,[b] %			
1	**2**	**3**	**4**	**5**
1a	81	3	4	0
1a (MeOH)	19	60	21	0
1b	91	1	0	0
1c	94	0	4	1
1d	53	15	2	17
1e	38	35	9	0
1f	34	0	7	0
1g	0	77	0	0
1h[c]	0		54	

[a] **1** (4 mmol), *t*-BuOK (16 mmol), DMF (15 mL) at -60 °C. [b] Determined by ^{1}H NMR. [c] In addition to phenol **4a**, a hydrolyzed product, 2,6-di-*tert*-butyl-4-(hydroperoxy)-4-methyl-2,5-cyclohexadienone, was obtained in 12% yield.

Results

Base-Catalyzed Reaction of 4-Alkyl-2,6-di-*tert*-butyl-4-(acylperoxy)-2,5-cyclohexadienones (*p*-Quinol Peroxy Esters) (1).

Peroxy esters **1** were readily obtained by the Schotten–Baumann acylation of 4-alkyl-2,6-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadienones, which were derived quantitatively from base-catalyzed oxygenation of 4-alkyl-2,6-di-*tert*-butylphenols.[9] Peroxy esters **1** except **1b** and **1f** (see Chart I) were not obtained as crystals, but TLC and NMR analyses of their reaction mixture showed the quantitative formation of **1**. The peroxy esters **1** were thermally stable, could be stored at 5 °C without decomposition for a year, but were susceptible to light. It is noted that compound **1a** could be purified by a vacuum distillation at 105 °C.

When a solution of **1** in *N*,*N*-dimethylformamide (DMF) containing *t*-BuOK was stirred at –60 °C under nitrogen atmosphere, the starting material disappeared normally in 2 h. Acidic workup followed by TLC separation of the

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