# Uni- and Biparticulate Electrophilic Additions to Conjugated Bis(bicyclo[1.1.0]butanes)

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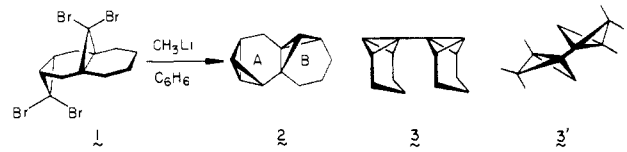
**Abstract:** The pair of hexacyclic bis(bicyclo[1.1.0]butanes) **2** and **6** react with such reagents as trifluoroacetic acid, perchloric acid, aqueous silver nitrate, and anhydrous aluminum chloride in ether with deep-seated rearrangement to give *anti*-7-norbornenyl derivatives **4** and **7**. Through deuterium labeling of the biparticulate electrophile, it was established that the initial bond cleavage occurs regiospecifically at the central bicyclobutane ring with retention of configuration. Further proof of the mechanistic cascade was gained by examining the products resulting from reaction with tetracyanoethylene and chlorosulfonyl isocyanate. Because of their uniparticulate nature, these reagents are capable of intercepting the framework isomerization prior to arrival at the 7-norbornenyl cation stage. Extensive use was made of X-ray crystallography and 2-D NMR methods to establish the structures of the adducts. The coherent mechanistic picture that has developed is presented and the underlying causative factors for the regiospecificity of attack and related phenomena are discussed.

Several years ago,[2] we observed that the tetrabromide **1** and closely related compounds are capable of twofold intramolecular cyclopropylidene C–H insertion when treated with methyllithium in an inert solvent.[3] The simplicity of the process and the remarkable regioselectivity of the dual ring formation cause **2** and similar conjugated bis(bicyclo[1.1.0]butanes) to be readily available.[2,4] The dimeric tricyclo[3.1.0.0$^{2,6}$]hexane **3** (together with a pair of lower homologs)[5] and the two stereoisomers of **3′**,[6] prepared by different routes, are the only other members of this class of molecules to have been successfully synthesized.




**1** **2** **3** **3′**

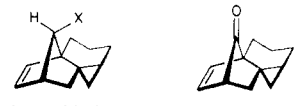
Highly strained compounds of type **2** have a total of *ten* distorted C–C $\sigma$ bonds available for cleavage by an attacking electrophile. For reasons of symmetry, the number of *different* bent bonds in **3** and **3′** is reduced appreciably. The conformational constraints imposed by amalgamation of the conjoined bicyclobutane rings into frameworks typified by **2** might limit the options, but any prediction of possible regioselective capture of the $E^+$ reagent must necessarily be viewed as speculative.

Despite the high probability for multisite attack, experimental evidence is presented herein that demonstrates ring cleavage in **2** to occur with remarkable *regiospecificity*, irrespective of the uni- or biparticulate character of the electrophile.[7] Moreover, the initiation step proceeds exclusively with retention of configuration at the reaction center, thereby enabling dipolar intermediates to undergo cyclization at various stages prior to completion of the electronic reorganization cascade. When *intramolecular* charge annihilation is not possible, the rearrangement has not proven capable of interception until arrival at the annulated 7-norbornenyl cation intermediate, notwithstanding pronounced differences in counterion nucleophilicity. Also, the length of the polymethylene tether in ring B exerts no obvious control on the deep-seated structural changes that follow capture of the electrophile.[8a]

Comparably unusual and intricate circumstances have only rarely been encountered previously.[8b] The silver ion catalyzed rearrangement of **3** and its response to treatment with HX have been extensively studied by Szeimies.[5] In this instance, conformational mobility about the interconnective C–C bond allows for total rupture of *both* bicyclo[1.1.0]butane subunits.

**Exposure to Biparticulate Electrophilic Agents.** As a consequence of the intensity with which the reaction of cycloalkenes with trifluoroacetic acid has been investigated,[9] a solution of **2** in chloroform at 20 °C was initially treated with 8.2 equiv of this reagent. A quite rapid reaction ensued to give a single trifluoroacetate (**4a**), which could be isolated in 86% yield. The 300-MHz $^1$H NMR spectrum of this oily ester clearly revealed that only one three-membered ring had been retained and that this cyclopropyl subunit was trisubstituted. Beyond that, a proton of the type H–C–O could be clearly seen, but the remaining multiplets proved not to be helpfully diagnostic of structure.

However, with arrival at parent alcohol **4b** by mild saponification, the spectral features became more sharply defined. Usefully, the pair of geminal cyclopropyl methylene protons now happen to be easily distinguished. Thus, the endo proton at $\delta$ 0.40 appears downfield of its exo counterpart ($\delta$ 0.27) and is seen to be equivalently coupled ($J$ = 4.7 Hz) to its geminal and vicinal neighbors. In contrast, the dd pattern for $H_{exo}$ ($J$ = 4.7, 8.5 Hz) features a large spin interaction that is compatible with its cis relationship to the methine proton.




**4a**, X = $OCOCF_3$
**b**, X = OH
**c**, X = $OCOCH_3$
**d**, X = Cl

**5**

(1) (a) The Ohio State University. (b) Northern Illinois University. This author is responsible for the X-ray crystallographic analyses of **12** and **17a**.

(2) (a) Paquette, L. A.; Browne, A. R.; Chamot, E. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 546. (b) Paquette, L. A.; Browne, A. R.; Chamot, E.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 643. (c) The original example of this reaction type was reported some time ago by Moore [Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019].

(3) Benzene has supplanted ether as the solvent originally employed for this step because it precludes formation of carbene (carbenoid) insertion products into the reaction medium (see the Experimental Section).

(4) Chamot, E. Ph.D. Thesis, The Ohio State University, 1978.

(5) (a) Romer, R.; Harnisch, J.; Rodu, A.; Schoffer, A.; Szeimies, G.; Germain, G.; Arrieta, J. M. *Chem. Ber.* **1984**, *117*, 925. (b) Szeimies, G.; Harnisch, J.; Stadler, K.-H. *Tetrahedron Lett.* **1978**, 243. (c) Harnisch, J.; Szeimies, G. *Ibid.* **1978**, 247. (d) Szeimies-Seebach, U.; Harnisch, J.; Szeimies, G.; Van Meerssche, M.; Germain, G.; Declercq, M.-P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 848.

(6) Moore, W. R.; Costin, C. R. *J. Am. Chem. Soc.* **1971**, *93*, 4910.

(7) Paquette, L. A.; Allen, G. R., Jr.; Broadhurst, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 4503.

(8) (a) Preliminary communication: Paquette, L. A.; Lau, C. J.; Browne, . R.; O'Brien, M. E. *J. Am. Chem. Soc.* **1986**, *108*, 8111. (b) For a recent example, consult: Paquette, L. A.; Waykole, L.; Jendralla, H.; Cottrell, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 3739.

(9) *cis*-Cyclooctene is a case in point: (a) Peterson, P. E.; Allen, G. *J. Org. Chem.* **1962**, *27*, 1505. (b) Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1982**, *104*, 3145. (c) Nordlander, J. E.; Kotian, K. D.; Raff, D. E.; Njoroge, F. G.; Winemiller, J. J. *Ibid.* **1984**, *106*, 1427. For a vinylcyclopropane study, consult: Mueller, L. G.; Lawton, R. G. *J. Org. Chem.* **1979**, *44*, 4741.

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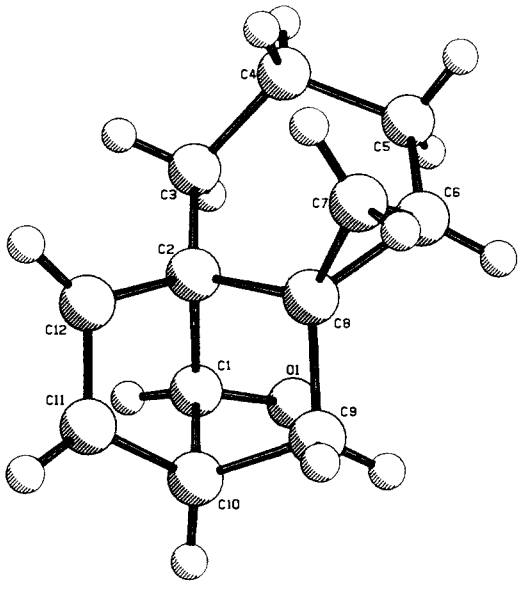



**Figure 1.** Computer-generated perspective drawing of **4b** as determined by X-ray crystallographic analysis [courtesy of Dr. Judith Gallucci (The Ohio State University) and Dr. Paul N. Swepston of Molecular Structure Corporation (College Station, TX)].

A modified 2-D INADEQUATE study[10] proved highly informative. The experiment was performed with two different values for the $1/(4J)$ refocusing time period. The first series utilized a delay of 7 ms ($J_{CC}$ = 35 Hz) and established the $J$ connectivities between each of the carbon pairs except between the two olefinic carbons ($J_{CC} \sim 70$ Hz) and between the cyclopropyl carbons ($J_{CC} \sim 12$ Hz). A second series with a refocusing delay of 10 ms ($J_{CC}$ = 25 Hz) showed all of the cyclopropyl couplings with each other and with the other ring carbons. The only interaction not observed was between the bridgehead and cyclopropyl quaternary carbons, presumably because of an insufficient relaxation delay time between pulse repetitions.

The structural assignment was further corroborated by single-crystal X-ray analysis of the *anti*-7-norbornenol. As detailed elsewhere,[11] sublimation of **4b** results in spontaneous resolution into optically pure enantiomorphically related crystals. This unprecedented observation is made possible because the racemate in this instance is a conglomerate[12] and crystallization occurs in the $P3_1$ space group. The final computer-generated three-dimensional features of **4b** are shown in Figure 1.

At this juncture, our attention was focused upon the generality of the deep-seated rearrangement. Indeed, **2** reacted with glacial acetic acid in chloroform and with 70% aqueous perchloric acid in tetrahydrofuran at room temperature to provide **4c** (70%) and **4b** (77%), respectively. When use was made of aqueous silver nitrate under comparable conditions,[13] conversion to **4b** was again observed. Swern oxidation of this alcohol furnished the 7-ketonorbornene **5**.

That the same process can occur under nonprotic conditions was established by admixing **2** with 0.20 equiv of anhydrous aluminum chloride in dry ether. The only characterizable product proved to be the reactive chloride **4d**. The stereodisposition of its C–Cl bond was established by replacement of the hydroxyl group in **4b** with retention through the agency of thionyl chloride in refluxing ether.[14]

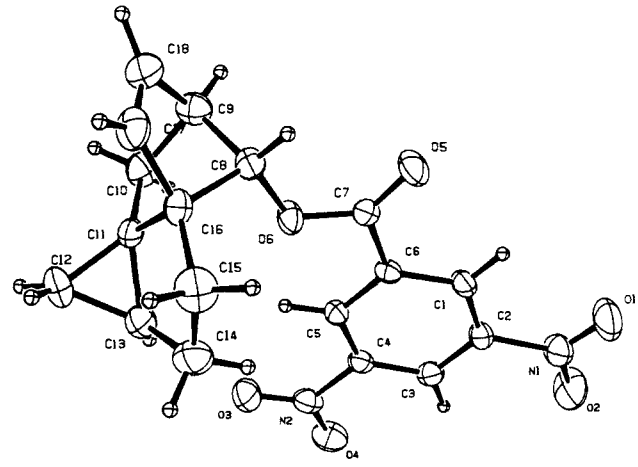
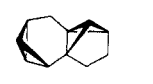
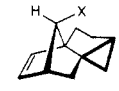



**Figure 2.** Computer-generated drawing of **7d** as determined by X-ray crystallographic analysis (see credits below Figure 1).

The response of lower homologue **6** proved identical. Analogous exposure to trifluoroacetic acid and aluminum chloride provided **7a** and **7b**. As before, the cyclopropyl methylene protons in **7a** are characteristically well separated in chemical shift [$\delta$ 0.45 (dd, $J$ = 4.9, 7.8 Hz) and 0.36 (dd, $J$ = 4.9, 4.9 Hz)] and readily distinguished. Curiously, an inversion in the relative position of this pair of protons materializes as the proximal larger ring is contracted from six- to five-membered status. This phenomenon has, however, been observed previously and commented upon.[15] In this series, the endo configuration of the three-membered ring was established by conversion of alcohol **7c** to its 3,5-dinitrobenzoate (**7d**) and X-ray crystallographic analysis of this derivative (Figure 2).

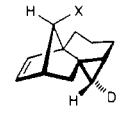


**6**

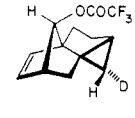



**7a**, X = $OCOCF_3$
**b**, X = Cl
**c**, X = OH
**d**, X = ODNB

The stage was now considered set for carrying out the deuterium-labeling experiments critical to mechanistic understanding. Reaction of **2** with $CF_3COOD$ as before delivered a trifluoroacetate clearly lacking only the signal at $\delta$ 0.40 so characteristic of the endo cyclopropyl proton. Conversion to **8a** had obviously materialized. Isomerically pure **8b** was similarly obtained upon mixing **2** with silver nitrate in a $D_2O$–THF solvent system.




**8a**, X = $OCOCF_3$
**b**, X = OH




**9**

In keeping with this trend, **9** was produced exclusively (within the limits of our spectral analysis) from **6** with $CF_3COOD$. Consequently, one can confidently conclude that *full retention of configuration is operational during capture of the electrophile in both series.*

**Response to Uniparticulate Electrophiles.** The preceding results are best reconciled with a mechanism in which only one specific bond in the central bicyclobutane subunit experiences electrophile-induced cleavage (see Discussion). When $H^+$ or $D^+$ is involved, a carbocationic rearrangement cascade sets in, with seemingly little opportunity for intermolecular interception. Considering the consequences of the stereodirected initiation step, we were led to explore the efficacy with which several uniparticulate electrophiles might enter into intramolecular charge annihilation at one or more intermediate stages.

(10) The modification, written by Dr. Charles Cottrell, involves the use of a 90° read pulse along with 60° phase shifts of the read pulse to separate the + and −2 coherence pathways giving quad detection in $F_1$. This is similar to a scheme proposed by D. Piveteau, M.-A. Delsuc, and J.-Y. Lallemand [*J. Magn. Reson.* **1985**, *63*, 255].
(11) Paquette, L. A.; Lau, C. J. *J. Org. Chem.* **1987**, *52*, 1634.
(12) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*; John Wiley and Sons: New York, 1981.
(13) Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, 280.
(14) Tanida, H.; Hata, Y. *J. Org. Chem.* **1965**, *30*, 977.
(15) Dauben, W. G.; Wipke, W. T. *J. Org. Chem.* **1967**, *32*, 2976.

**Table I.** Crystallographic Data for Adducts **12** and **17a**

| | **12** | **17a** |
|---|---|---|
| compd | $C_{18}H_{14}N_4$ | $C_{13}H_{14}ClNO_3S$ |
| color/shape | clear/parallelepiped | clear/parallelepiped |
| mol wt | 286.3 | 299.8 |
| space group | $P2_1/c$ | $P2_1/c$ |
| temp, °C | 20 | 20 |
| cell constants | | |
| $a$, Å | 11.713 (1) | 7.994 (2) |
| $b$, Å | 11.461 (2) | 11.789 (2) |
| $c$, Å | 10.607 (2) | 14.211 (3) |
| $\beta$, deg | 97.03 (1) | 104.50 (3) |
| cell vol, Å$^3$ | 1413.1 | 1296.7 |
| formula units/unit cell | 4 | 4 |
| $D_{calcd}$, g cm$^{-1}$ | 1.35 | 1.54 |
| $\mu$(calcd), cm$^{-1}$ | 0.47 | 4.00 |
| radiation, graphite monochromator | Mo K$\alpha$ ($\lambda$ = 0.71073) | Mo K$\alpha$ ($\lambda$ = 0.71073) |
| max cryst dimen, mm | 0.25 × 0.30 × 0.45 | 0.20 × 0.23 × 0.63 |
| scan width | 0.80 + 0.35 tan $\theta$ | 0.80 + 0.35 tan $\theta$ |
| std reflcns | 700, 020, 004 | 600, 060, 006 |
| decay of stds, % | ±0.5 | ±0.4 |
| reflcns measured | 2741 | 2562 |
| 2$\theta$ range, deg | $2 < 2\theta < 50$ | $2\ \theta\ 2\theta < 50$ |
| range of $h,k,l$ | ±13, +13, +12 | +9, +14, ±16 |
| reflcns obsd [$F_o \geq 5\sigma(F_o)$] | 1576 | 1890 |
| no. of parameters varied | 255 | 228 |
| weights | $[\sigma(F_o)^2 + 0.00008F_o^2]^{-1}$ | $[\sigma(F_o)^2 + 0.00002F_o^2]^{-1}$ |
| GOF | 0.68 | 1.58 |
| $R$ | 0.038 | 0.037 |
| $R_w$ | 0.039 | 0.038 |

The recognized ionic character of tetracyanoethylene (TCNE) additions to a large number of alkenes,[16] strained unsaturated hydrocarbons,[17-19] and cyclic polyolefins[20] qualifies this reagent as a highly useful uniparticulate electrophile.[7] The events which occur during reaction of benzvalene[21] and homobenzvalene[22] with TCNE have been elucidated. Tricyclo[4.1.0.0$^{2,7}$]heptane (**10**), a substrate closely allied to **2** and **6**, reacts with TCNE to give the unusual product **11** in 38% yield.[22]


10 11

Admixture of **2** with an excess of TCNE in ethyl acetate at 0 °C resulted in formation of the pair of 1:1 adducts **12** and **13** in purified yields of 17 and 30%, respectively. The 300-MHz $^1$H NMR spectra of both compounds contain no absorptions attributable to olefinic protons. Furthermore, the large number of $^{13}$C signals at higher field than 30 ppm suggested that several of the original strained rings had been retained in these products. The exceptional crystallinity of **12** enabled its structure to be elucidated by X-ray methods (Table I). As can be seen in Figure 3, the entire bicyclobutane segment of the A ring has remained intact. The chemical event that transpired in ring B is comprised of TCNE insertion into one bicyclobutane edge bond.[33]

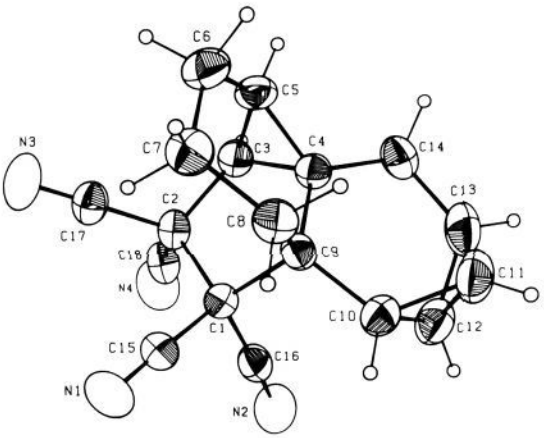
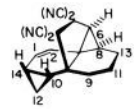
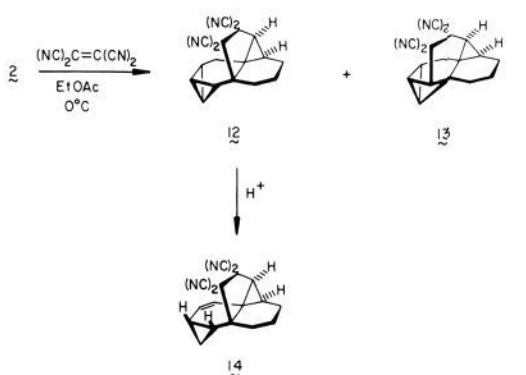



**Figure 3.** Computer-generated perspective drawing of **12** as determined by X-ray crystallography. The atomic numbering is arbitrary.

**Table II.** $^{13}$C–$^1$H Correlation for **14**




| | multiplicity | proton shift, $\delta$ | location |
|---|---|---|---|
| 129.3 | d | 6.17 | 1 |
| 125.0 | d | 4.70 | 2 |
| 112.0, 111.1, 110.0, 109.4 | s | | C≡N |
| 65.5 | s | | 3 |
| 49.6 | s | | 4 |
| 44.6 | s | | 5 |
| 36.8 | d | 2.06 | 6 |
| 34.1 | s | | 7 |
| 33.4 | d | 1.86 | 8 |
| 32.7 | t | 2.10, 2.02 | 9 |
| 23.1 | d | 1.58 | 10 |
| 19.2 | t | 1.95, 1.42 | 11 |
| 16.2 | t | 1.19, 0.52 | 12 |
| 16.0 | t | 2.34, 2.29 | 13 |
| 14.1 | d | 1.78 | 14 |




12 13

14

Chemical evidence for the presence of a residual bicyclobutane ring was provided by the sensitivity of **12** to standing in $CDCl_3$ solution at room temperature. Evidently, the adventitious acid contained therein induced facile isomerization to vinylcyclopropane **14**. Of the two stereoisomeric options possible, only that pathway

(16) Bartlett, P. D. *Q. Rev., Chem. Soc.* **1970**, *24*, 473.
(17) The following citations are illustrative: (a) Nishida, S.; Moritani, I.; Teraji, T. *J. Chem. Soc. D* **1971**, 36. (b) Baldwin, J. E.; Peavy, R. E. *J. Org. Chem.* **1971**, *36*, 1441. (c) Baldwin, J. E.; Pinschmidt, R. K., Jr. *Tetrahedron Lett.* **1971**, 935. (d) Noyori, R.; Hayashi, N.; Kato, M. *J. Am. Chem. Soc.* **1971**, *93*, 4948.
(18) (a) Okamura, W. H.; Osborn, T. W. *J. Am. Chem. Soc.* **1970**, *92*, 1061. (b) Baxter, C. S.; Garratt, P. J. *J. Am. Chem. Soc.* **1970**, *92*, 1062; *Tetrahedron* **1971**, *27*, 3285.
(19) (a) Paquette, L. A.; Broadhurst, M. J.; Lee, C.; Clardy, J. *J. Am. Chem. Soc.* **1972**, *94*, 630. (b) Clardy, J.; Read, L. K.; Broadhurst, M. J.; Paquette, L. A. *Ibid.* **1972**, *94*, 2904. (c) Paquette, L. A.; Broadhurst, M. J.; Reed, L. K.; Clardy, J. *Ibid.* **1973**, *95*, 4639.
(20) See, for example: Löffler, H.-P.; Martini, T.; Musso, H.; Schröder, G. *Chem. Ber.* **1970**, *103*, 2109.
(21) Christl, M.; Brunn, E.; Lanzendorfer, F. *J. Am. Chem. Soc.* **1984**, *106*, 373.
(22) Christl, M.; Lang, R.; Herzog, C.; Stangl, R.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 611.
(23) The subject of thermal addition of carbon–carbon multiple bonds to strained carbocyclics has been reviewed: Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128.

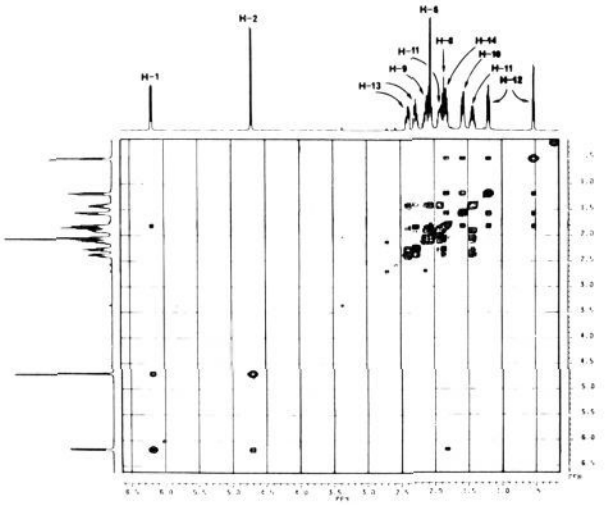


**Figure 4.** 500-MHz COSY spectrum of **14** (see Table II for numbering scheme).

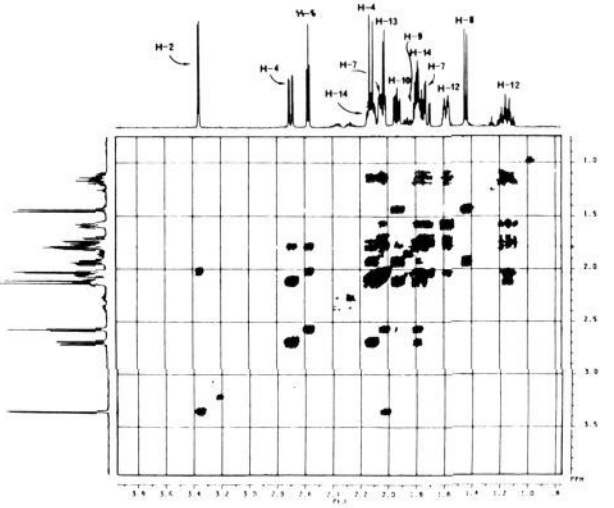
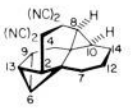


**Figure 5.** 500-MHz COSY spectrum of **13** (see Table III for numbering scheme).

**Table III.** $^{13}C-^{1}H$ Correlation for **13**



| carbon shift, ppm | multiplicity | proton, shift, $\delta$ | location |
|---|---|---|---|
| 113.0, 112.3, 110.8, 109.7 | s | | C≡N |
| 46.1 | s | | 1 |
| 45.6 | d | 3.36 | 2 |
| 44.0 | s | | 3 |
| 40.5 | t | 2.69, 2.12 | 4 |
| 37.0 | s | | 5 |
| 33.0 | d | 2.57 | 6 |
| 28.5 | t | 2.07, 1.73 | 7 |
| 27.2 | d | 1.44 | 8 |
| 26.1 | d | 1.78 | 9 |
| 23.8 | d | 1.93 | 10 |
| 23.2 | s | | 11 |
| 19.8 | t | 1.58, 1.14 | 12 |
| 19.0 | d | 2.02 | 13 |
| 14.8 | t | 2.12, 1.76 | 14 |

leading to the anti-cyclopropyl system operated. The results of a number of sophisticated NMR studies on **14** including C–H correlation (Table II), $^{13}C$ gated decoupling, NOE, COSY (Figure 4), and NOSY were in agreement uniquely with the indicated stereochemical outcome.[24]

A similar battery of spectroscopic techniques including 2-D INADEQUATE was applied to resolving the bond connectivities in **13** (C–H correlation: Table III, Figure 5). In this fashion, definitive evidence was gained for the fact that carbocationic rearrangement of the framework had materialized prior to zwitterion charge annihilation. Specifically, one of the dicyano-substituted carbons in **13** is connected to an atom further removed from the point of initial peripheral bond cleavage. Also, the strained bicyclobutane segment of ring A has undergone expansion to a bicyclopentane unit.

Owing to the symmetry of tetracyanoethylene, certain points of detail relevant to the above reactions might be considered unclear. Therefore, attention was next directed to the unsymmetrical reagent chlorosulfonyl isocyanate (CSI). Like TCNE, CSI is widely recognized to be highly reactive toward acyclic[25]

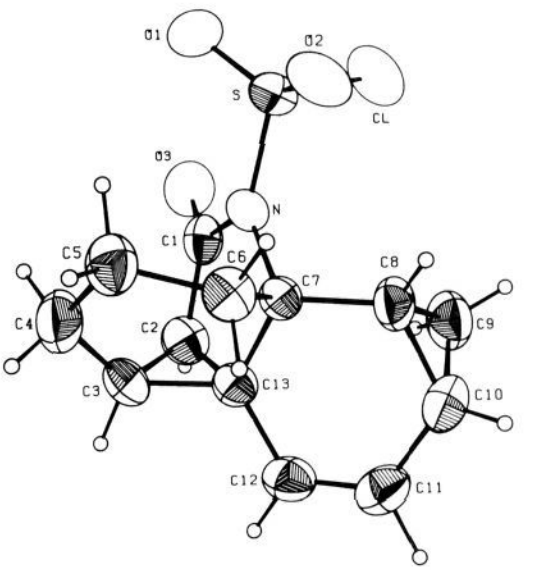
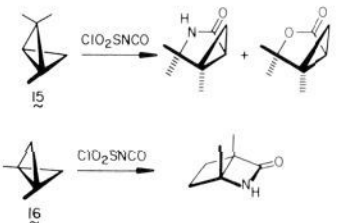


**Figure 6.** Computer-generated perspective drawing of **17a** as determined by X-ray crystallography. The atomic numbering is arbitrary.

and cyclic olefins[19,26] as well as strained hydrocarbons. In the latter category, the reactions with **15** and **16** are representative.[6,27]



(24) For more specific detail, consult: Lau, C. J. Ph.D. Thesis, The Ohio State University, 1987.

(25) (a) Graf, R. *Chem. Ber.* **1956**, *89*, 1071. (b) Graf, R. *Angew. Chem.* **1968**, *80*, 179. (c) Moriconi, E. J. *Mech. React. Sulfur Compd.* **1968**, *3*, 131. (d) Rasmussen, J. K.; Hassner, A. *Chem. Rev.* **1976**, *76*, 389.

(26) Some representative examples are: (a) Paquette, L. A.; Barton, T. J.; Whipple, E. B. *J. Am. Chem. Soc.* **1967**, *89*, 5481. (b) Paquette, L. A.; Krow, G. R.; Malpass, J. R.; Barton, T. J. *Ibid.* **1968**, *90*, 3600. (c) Paquette, L. A.; Krow, G. R. *Ibid.* **1968**, *90*, 7149. (d) Paquette, L. A.; Malpass, J. R. *Ibid.* **1968**, *90*, 7151. (e) Paquette, L. A.; Malpass, J. R.; Krow, G. R.; Barton, T. J. *Ibid.* **1969**, *91*, 5296. (f) Paquette, L. A.; Krow, G. R.; Malpass, J. R. *Ibid.* **1969**, *91*, 6107. (g) Paquette, L. A.; Malpass, J. R.; Krow, G. R. *Ibid.* **1970**, *92*, 1980. (h) Paquette, L. A.; Kakihana, T. *Ibid.* **1968**, *90*, 3897. (i) Paquette, L. A.; Philips, J. C. *Ibid.* **1968**, *90*, 3898. (j) Paquette, L. A.; Kakihana, T.; Hansen, J. F.; Philips, J. C. *Ibid.* **1971**, *93*, 152. (k) Paquette, L. A.; Broadhurst, M. J. *Ibid.* **1972**, *94*, 632. (l) Pasto, D. J.; Chen, A. F.; Ciurdaru, G.; Paquette, L. A. *J. Org. Chem.* **1973**, *38*, 1015. (m) Paquette, L. A.; Broadhurst, M. J. *Ibid.* **1973**, *38*, 1886, 1893. (n) Paquette, L. A.; Broadhurst, M. J.; Lee, C.; Clardy, J. *J. Am. Chem. Soc.* **1973**, *95*, 4647.

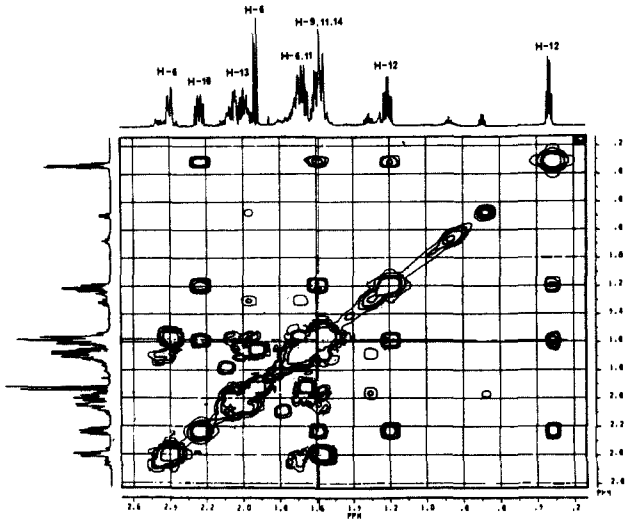
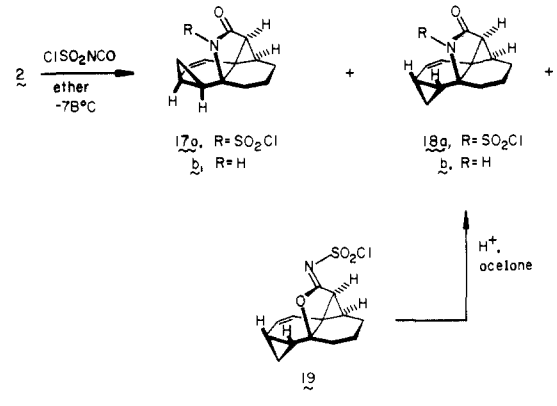



**Figure 7.** Expanded scale upfield region of the 500-MHz COSY spectrum of **18** (the numbering is identical with that for **14**, see Table II).

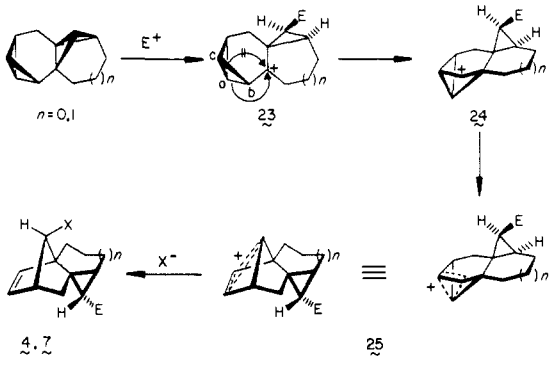
When CSI was added dropwise to a cold (−78 °C) ethereal solution of **2**, the three products **17a** (22%), **18a** (11%), and **19** (15%) could be isolated. That the most prevalent adduct was an *N*-(chlorosulfonyl) lactam was immediately apparent from its infrared carbonyl stretching frequency (1745 $cm^{-1}$). In addition, the $^1H$ and $^{13}C$ NMR spectra indicated a vinylcyclopropane unit to be present. More extensive 2-D NMR analysis provided evidence that the substance possessed structure **17a**, and this conclusion was ultimately corroborated by X-ray crystallography (Table I, Figure 6).

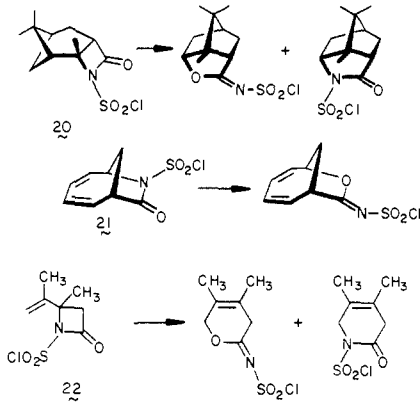



The $^1H$ NMR spectrum of **18a** exhibits many similarities to that of **14** and is completely consistent with its formulation as the anti vinylcyclopropane isomer. Independent confirmatory evidence was subsequently derived from a combination of COSY (Figure 7), NOSY, DEPT, and NOE measurements.[24]

The third substance was unusual in that it exhibited no infrared carbonyl stretch, yet it was clearly isomeric with **17a** and **18a** (mass spectral analysis). Since *N*-(chlorosulfonyl)imino ethers are known to result from cycloadditions involving CSI[28] and **19** did show the expected infrared band at 1575 $cm^{-1}$, the decision was made to effect hydrolysis under the acidic conditions earlier developed by Malpass.[28b] This treatment gave rise to a separable mixture of **18a** and **18b**, quite unlike the customary eventuality of lactone formation. Although several examples of the isomerization of *N*-(chlorosulfonyl) lactams (e.g., **20–22**) into *N*-(chlorosulfonyl)imino ethers have been documented,[28] the **19** → **18** conversion would appear to be the first instance where the reverse process occurs. We attribute its facile operation in the present circumstances to the relative ease of formation of the requisite cyclopropylcarbinyl cation intermediate.

**Scheme I**




The hydrolysis of **17a** to **17b** was accomplished efficiently by stirring with a solution of triethylamine in methanol for 1 h.

## Discussion

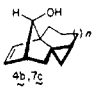
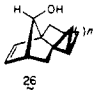
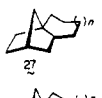
One of the major features of the biparticulate additions to **2** and **6** is the striking tendency for framework isomerization to a somewhat complex 7-norbornenyl carbocation prior to covalent capture by the counteranion or solvent. Advocacy of initial regiospecific electrophilic attack *only* at the central and not the flanking bicyclobutane subunit takes its justification largely from the internal consistency of the scheme and its accommodation of product structure, including the site and stereospecificity of deuterium incorporation.

In terms of the generalized reagent $E^+$, its proper capture must necessarily give rise to **23** as shown in Scheme I. Detailed elsewhere[29,30] is the fact that two pathways can operate to deliver the stereochemical features demanded by this pivotal intermediate. The first of these is, of course, regiospecific edge bond cleavage. Alternatively, unidirectional SE2-like cleavage of the internal bicyclobutane bond can take place, followed by rapid Wagner–Meerwein shift within the newly generated cyclobutyl cation. Although the direct and indirect routes cannot be differentiated here, the evidence requires that product formation be triggered via **23**.

At this crucial point, the systems respond by migrating bond a–b of the second bicyclobutane ring to the exclusion of bond b–c. This distinction does not appear to be stereoelectronically driven since molecular models indicate that both bonds bisect the carbocationic center to a comparable degree. We note that rearrangement according to the first option delivers **4** or **7**, while the second would lead instead to **26**. MM2 calculations (Table IV) of this isomer pair denote the latter compounds with their exo-fused cyclopropane rings to be significantly less thermodynamically

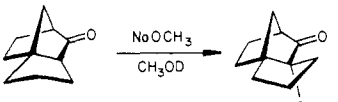
(27) Volz, W. E.; Paquette, L. A.; Rogido, R. J.; Barton, T. J. *Chem. Ind. (London)* **1974**, 771.
(28) (a) Moriconi, E. J.; Meyer, W. C. *J. Org. Chem.* **1971**, *36*, 2841. (b) Malpass, J. R. *Tetrahedron Lett.* **1972**, 4951. (c) Moriconi, E. J.; Hummel, C. F.; Kelly, J. F. *Ibid.* **1969**, 5325.
(29) Wiberg, K. B.; Szeimies, G. *J. Am. Chem. Soc.* **1970**, *92*, 571.
(30) (a) Zon, G.; Paquette, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 215. (b) Paquette, L. A.; Zon, G. *Ibid.* **1974**, *96*, 224 and pertinent references cited therein.

**Table IV.** Calculated Gas-Phase Heats of Formation[a]

| compd | $\Delta H°_f$ (25 °C) $n = 0$ | $n = 1$ |
|---|---|---|
|  4b,7c | 7.36 | -3.44 |
|  26 | 13.44 | -0.51 |
|  27 | -15.40 | -26.64 |
|  28 | -8.84 | -24.83 |

[a] MMP2 (QCPE 395).

stable. This ordering is entirely comparable to that estimated for the somewhat simpler hydrocarbons **27** and **28**.[31,32] Additionally, there exists full agreement with the facility with which ketone **29** undergoes epimerization to **30**.[33] It is, of course, this migratory event that determines the ultimate spatial orientation of the 7-norbornenyl cation in **25** relative to the cyclopropane ring. We presume that this facet of the rearrangement is one where the transition state resembles the products.




29 30

The determination of deuterium stereochemistry in **8** and **9** shows that initial cleavage of the appropriate strained bond occurs with retention. The results involving silver(I) ion catalysis are equally well accommodated by this scheme and require only that protonolysis or deuterolysis of the C–Ag bond also occur with retention where applicable.[34]

When TCNE is the electrophile in question, the proposed mechanism requires that **23** [E = $C(CN)_2\bar{C}(CN)_2$] arise early in the sequence. As a direct consequence of the dipolar nature of this intermediate and its access to a five-membered cyclization pathway, collapse to **12** can and does occur. However, the rate of formation of **12** is not overwhelmingly rapid, since isomerization to a second zwitterionic species, viz **24** [E = $C(CN)_2\bar{C}(CN)_2$], occurs competitively and leads ultimately to **13**. We have turned up no evidence for thermal equilibration between **12** and **13** and therefore conclude that their 1:2 distribution is a direct consequence of kinetic control. The considerable release of strain that materializes upon ring expansion of **23** to the bicyclopentyl cation **24** is the probable major accelerative facet of this step in the overall sequence. Normally, the speed of this rearrangement is such that intermolecular trapping of **23** and **24** is not effective. When intramolecular processes are possible, as in the TCNE example, the rates of cyclization and isomerization become comparable.

The isolation of **17–19** from the reaction of **2** with CSI suggests that intramolecular closure within **23** [E = $C(O)\bar{N}SO_2Cl$] is so efficient that the system never advances to **24**. The vinylcyclopropane nature of these products reflects only the difficulty of maintaining acid-free conditions with this reagent. The independent isomerization of **12** to **14** points up the well-recognized acid lability of the bicyclobutane ring in this type of molecule.

This ring opening can follow one of two courses, leading to exo (e.g., **17**) or endo (e.g., **14**, **18**, **19**) isomers. A plausible attribution to the specificity observed in the **12** → **14** isomerization is the requirement that an exo cyclopropane ring would necessarily experience serious nonbonded steric interactions with at least one cyano group. The effective planarity associated with the *N*-(chlorosulfonyl) lactam or *N*-(chlorosulfonyl)imino ether bridges in **17–19** produce less in the way of steric demands. As a consequence, the exo/endo partitioning in these examples is rather equitable.

Finally, the regiochemistry of attack on **2** and **6** is likely determined by several factors including the localization of the HOMOs,[35] the coefficients on the carbon atoms in the HOMO, steric interactions, and strain relief. For bicyclo[1.1.0]butane in particular, the valence orbital energies are well recognized to be closely tied to the particular dihedral angle between the two cyclopropane rings.[36]

## Experimental Section

**Octahydro-1,2,3:4a,5,8a-dimethenonaphthalene (2).** A flame-dried one-necked flask was blanketed with nitrogen and tetrabromide **1** (2.00 g, 4.19 mmol) was added to dry benzene (26 mL). The magnetically stirred solution was cooled to 10–12 °C and methyllithium (7.85 mL of 1.6 M in ether, 12.6 mmol) was introduced dropwise over 10 min. After 3.5 h, the reaction mixture was poured slowly into 50 mL of an ice–water mixture. The organic phase was separated, dried, and concentrated to give 560 mg (79%) of **2**. For the spectral properties of **2**, see ref 2b.

**Reaction of 2 with Trifluoroacetic Acid.** To a magnetically stirred solution of **2** (250 mg, 1.58 mmol) in chloroform (10 mL) at room temperature was added dropwise a solution of trifluoroacetic acid (0.4 mL, 5.2 mmol) in chloroform (2 mL). A slight exothermicity was observed and the reaction mixture took on a purple coloration. After 2.5 h of stirring at room temperature, the solvent was evaporated to leave a dark oil that was flash distilled at 0.1 Torr to give 369 mg (86%) of **4a** as a pale yellow liquid which was further purified by preparative gas chromatography: IR (neat, $cm^{-1}$) 3070, 2940, 1780, 1225, 1160; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.08 (dd, $J$ = 6.05, 3.5 Hz, 1 H), 5.97 (dd, $J$ = 6.05, 0.65 Hz, 1 H), 4.59 (s, 1 H), 2.86 (br d, $J$ = 2.7 Hz, 1 H), 1.92 (dd, $J$ = 11.5, 3.7 Hz, 1 H), 1.81 (m, 1 H), 1.58 (m, 3 H), 1.41 (m, 1 H), 1.32 (d, $J$ = 11.5 Hz, 1 H), 1.28 (m, 2 H), 0.40 (dd, $J$ = 4.9, 4.9 Hz, 1 H), 0.32 (dd, $J$ = 8.5, 4.9 Hz, 1 H); $^{13}C$ NMR (75 MHz, $CDCl_3$) 140.2, 131.9, 90.0, 49.8, 44.1, 36.4, 23.5, 17.6, 17.5, 13.8 ppm (3 carbons not observed); mass spectrum, $m/z$ ($M^+$) calcd 272.1024, obsd 272.1031.

Anal. Calcd for $C_{14}H_{15}F_3O_2$: C, 61.76; H, 5.55. Found: C, 61.91; H, 5.70.

**Saponification of 4a.** To a magnetically stirred solution of **4a** (365 mg, 1.34 mmol) in methanol (15 mL) was added potassium carbonate (0.25 g, 1.81 mmol). Within 2 h, dissolution of the solid had occurred and stirring was maintained overnight. The solvent was evaporated to furnish a thick yellow oil, which was partitioned between ether and water. The aqueous phase was extracted twice with ether, and the combined ethereal extracts were washed with brine and dried. Solvent evaporation left 230 mg of a yellow oil which was purified by MPLC on silica gel (elution with 15% ethyl acetate in petroleum ether) to give **4b** (108 mg, 46%) as a white solid: mp 71–72 °C; IR ($CDCl_3$, $cm^{-1}$) 3590, 3055, 2930, 1390, 1065; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.05 (dd, $J$ = 6.1, 3.4 Hz, 1 H), 5.92 (d, $J$ = 6.1 Hz, 1 H), 3.46 (s, 1 H), 2.52 (s, 1 H), 1.97 (dd, $J$ = 11.8, 3.7 Hz, 1 H), 1.79 (m, 1 H), 1.6–1.5 (series of m, 4 H), 1.30 (d, $J$ = 11.8 Hz, 1 H), 1.29 (m, 1 H), 1.21 (m, 1 H), 0.40 (dd, $J$ = 4.7, 4.7 Hz, 1 H), 0.27 (dd, $J$ = 8.5, 4.7 Hz, 1 H); $^{13}C$ NMR (75 MHz, $CDCl_3$) 141.0, 132.6, 88.5, 50.2, 46.5, 36.8, 24.0, 23.7, 23.0, 18.0, 17.4, 13.2 ppm.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.82; H, 9.09. Found: C, 81.46; H, 9.08.

**Reaction of 2 with Acetic Acid.** A magnetically stirred solution of **2** (1.5 g, 9.5 mmol) in chloroform (50 mL) at room temperature was treated dropwise with a solution of glacial acetic acid (2.4 mL, 42 mmol) in chloroform (10 mL). The consumption of **2** was complete after stirring at room temperature for 2.5 h. The solvent was evaporated to leave a yellow oil that was flash distilled at 0.05 mmHg through a short path distillation head. There was isolated 1.89 g (91%) of a 3:1 (GC analysis) mixture of acetate products as a slightly yellow liquid.

For major component **4c**: IR (neat, $cm^{-1}$) 3060, 2930, 1735, 1450, 1375, 1240, 1045; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.02 (dd, $J$ = 6.1, 3.4 Hz, 1 H), 5.91 (d, $J$ = 6.1 Hz, 1 H), 4.41 (s, 1 H), 2.71 (d, $J$ = 2.2 Hz,

(31) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.
(32) Osawa, E.; Aigami, K.; Takaishi, N.; Inamoto, Y.; Fujikura, Y.; Majerski, Z.; Schleyer, P. v. R.; Engler, E. M.; Farcasiu, M. *J. Am. Chem. Soc.* **1977**, *99*, 5361.
(33) Klester, A. M.; Ganter, C. *Helv. Chim. Acta* **1985**, *68*, 104, 734.
(34) Paquette, L. A.; Ward, J. S.; Boggs, R. A.; Farnham, W. B. *J. Am. Chem. Soc.* **1975**, *97*, 1101.
(35) Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 197.
(36) Bischof, P.; Gleiter, R.; Müller, E. *Tetrahedron* **1976**, *32*, 2769.

1 H), 2.05 (s, 3 H), 1.91 (dd, $J$ = 11.2, 3.8 Hz, 1 H), 2.1–1.1 (series of m, 7 H), 1.21 (d, $J$ = 11.2 Hz, 1 H), 0.33 (dd, $J$ = 4.8, 4.8 Hz, 1 H), 0.24 (dd, $J$ = 8.4, 4.8 Hz, 1 H); $^{13}$C NMR (20 MHz, $CDCl_3$) 170.9, 140.4, 132.2, 87.4, 49.4, 44.5, 36.9, 23.9, 23.8, 21.4, 17.9, 17.5, 13.9 ppm.

The minor component remains unidentified: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.56 (d, $J$ = 3.8 Hz, 1 H), 5.41 (dd, $J$ = 7.2, 2.3 Hz, 1 H), 2.57 (dd, $J$ = 13.8, 2.5 Hz, 1 H), 2.05 (s, 3 H), 2.1–1.1 (series of m, 8 H), 0.80 (t, $J$ = 5.2 Hz, 1 H), 0.55 (m, 1 H), 0.47 (m, 1 H), 0.39 (q, $J$ = 4.5 Hz, 1 H).

**Reaction of 2 with Silver Nitrate.** To a magnetically stirred solution of silver nitrate (0.07 g, 0.4 mmol) in 1.25 mL of water and 3.75 mL of tetrahydrofuran was added dropwise a solution of **2** (0.25 g, 1.58 mmol) in 2.5 mL of tetrahydrofuran. One hour after addition, a silver mirror formed and reaction was complete. Pentane (8 mL) was added followed by brine, and the aqueous layer was extracted with pentane. The combined pentane layers were dried and evaporated to afford 0.27 g of a green liquid. Flash column chromatography of the material on TLC grade silica gel (elution with 13% ethyl acetate in petroleum ether) gave 0.11 g (40%) of **4b**.

**Reaction of 2 with Aqueous Perchloric Acid.** A magnetically stirred solution of **2** (50 mg, 0.32 mmol) in tetrahydrofuran (2 mL) at room temperature was treated sequentially with 0.1 mL of water and 0.1 mL of a solution of 0.03 mL of 70% perchloric acid in 0.5 mL of tetrahydrofuran. Reaction was allowed to proceed for 2 h before pentane (3 mL) and saturated sodium bicarbonate solution were added. This mixture was extracted twice with pentane and the combined organic phases were dried and evaporated. There was isolated 43 mg (77%) of **4b**.

**Reaction of 2 with Aluminum Chloride.** Into a flame-dried 10-mL two-necked flask fitted with a septum and nitrogen inlet was placed aluminum chloride (0.03 g, 0.22 mmol) and ether (4 mL). To this magnetically stirred mixture was slowly added via syringe a solution of **2** (100 mg, 0.63 mmol) in ether (2 mL). The reaction mixture, which became yellow, was stirred for 3 h, at which point 2 mL of saturated sodium bicarbonate solution was introduced. The product was extracted into ether and dried. Concentration left a thick yellow oil (103 mg) which was purified by MPLC on silica gel (elution with petroleum ether) or by Kugelrohr distillation. Purification by either method afforded **4d** as a slightly yellow liquid (35 mg, 29%) that was not subjected to combustion analysis because of its inherent instability: IR ($CDCl_3$, cm$^{-1}$) 3060, 2990, 2930, 2855, 1450, 1270, 835; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.14 (dd, $J$ = 6.1, 3.4 Hz, 1 H), 6.04 (d, $J$ = 6.1 Hz, 1 H), 3.72 (s, 1 H), 2.73 (s, 1 H), 2.28 (dd, $J$ = 11.3, 3.6 Hz, 1 H), 1.79 (m, 1 H), 1.69–1.60 (series of m, 3 H), 1.55 (m, 1 H), 1.36 (m, 1 H), 1.26 (d, $J$ = 11.3 Hz, 1 H), 1.23 (m, 1 H), 0.45 (dd, $J$ = 4.8, 4.8 Hz, 1 H), 0.15 (dd, $J$ = 8.3, 4.8 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 141.7, 133.6, 75.5, 51.8, 47.5, 36.8, 23.8, 23.3, 23.2, 18.6, 17.0, 11.9 ppm; mass spectrum, $m/z$ ($M^+$) calcd 194.0862, obsd 194.0864.

**Chlorination of 4b.** Into a flame-dried 10-mL two-necked flask fitted with a condenser, nitrogen inlet, and septum was placed a solution of **4b** (75 mg, 0.426 mmol) in 2 mL of ether. To this magnetically stirred solution was added thionyl chloride (0.045 mL, 0.61 mmol), and the reaction mixture was immediately heated at the reflux temperature for 10 min. After the mixture was cooled, saturated sodium bicarbonate solution (2 mL) was introduced, and the product was extracted into ether and dried. Concentration left a dark liquid (0.1015 g) which was purified by preparative GC at 150 °C to afford 27 mg (50%) of **4d**.

**Oxidation of 4b.** To a cold (−60 °C), magnetically stirred solution of oxalyl chloride (0.027 mL, 0.31 mL) in dichloromethane (0.71 mL) was added via syringe a solution of dimethyl sulfoxide (0.048 mL, 0.68 mmol) in dichloromethane (0.14 mL). After 15 min, a solution of **4b** (50 mg, 0.28 mmol) in dichloromethane (0.28 mL) was added, soon to be followed by triethylamine (0.2 mL). The reaction mixture was allowed to warm to room temperature and water (1 mL) was added. The product was extracted with dichloromethane and the combined organic phases were washed with brine, dried, and concentrated. The residue was triturated with hexane and ether. Solvent removal from the soluble portion afforded **5** (8 mg, 32%): IR ($CDCl_3$, cm$^{-1}$) 3050, 2930, 1770, 1450, 1265; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.56 (dd, $J$ = 6.8, 3.6 Hz, 1 H), 6.36 (dd, $J$ = 6.8, 0.7 Hz, 1 H), 2.90 (t, $J$ = 3.6 Hz, 1 H), 2.0–1.88 (series of m, 3 H), 1.47–1.19 (series of m, 5 H), 1.38 (d, $J$ = 11.6 Hz, 1 H), 0.50 (dd, $J$ = 5.0, 5.0 Hz, 1 H), 0.38 (dd, $J$ = 8.6, 5.0 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 206.3, 139.2, 132.6, 50.0, 47.5, 35.2, 24.0, 22.2, 19.9, 19.0, 18.3, 17.9 ppm; mass spectrum, $m/z$ ($M^+$ − CHO) calcd 145.1017, obsd 145.0996.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.71; H, 8.23.

**Hexahydro-1,3a,7a:4,5,6-dimethenoindane (6).** *anti*-4,4,11,11-Tetrabromotetracyclo[4.3.1.0$^{1,7}$.0$^{3,5}$]undecane (20.0 g, 43 mmol) dissolved in 1 L of anhydrous benzene was treated with 66.45 mL of 1.55 M methyllithium in hexane (103 mmol) at 10–12 °C during 30 min. Workup as described above and distillation at 58–64 °C (1.6 torr) afforded 970 mg (16%) of **6**. For spectral properties, see ref 2b.

**Reaction of 6 with Trifluoroacetic Acid.** A magnetically stirred solution of **6** (250 mg, 1.73 mmol) in chloroform (10 mL) at room temperature was treated dropwise with a solution of trifluoroacetic acid (1.0 mL, 12.9 mmol) in chloroform (2.5 mL). The reaction was complete after 30 min, at which point the solvent was evaporated to leave a dark oil that was flash distilled at 0.1 Torr through a short-path distillation column. There was isolated 0.26 g (58%) of **7a** as a pale yellow liquid that was used without further purification: IR (neat, cm$^{-1}$) 3060, 2940, 1780, 1385, 1335, 1220, 1160; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.14 (dd, $J$ = 6.1, 3.5 Hz, 1 H), 6.08 (d, $J$ = 6.1 Hz, 1 H), 4.54 (s, 1 H), 3.02 (br d, $J$ = 2.4 Hz, 1 H), 2.09 (dd, $J$ = 12, 3.7 Hz, 1 H), 1.96 (m, 1 H), 1.82 (dd, $J$ = 8.9, 2.8 Hz, 1 H), 1.78 (m, 1 H), 1.49–1.35 (series of m, 2 H), 1.44 (d, $J$ = 12 Hz, 1 H), 0.45 (dd, $J$ = 7.8, 5.0 Hz, 1 H), 0.36 (dd, $J$ = 5.0, 5.0 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 137.1, 132.7, 88.7, 62.5, 46.6, 35.5, 30.3, 29.9, 21.9, 20.8, 10.2 ppm; mass spectrum, $m/z$ ($M^+$) calcd 258.0868, obsd 258.0873.

Anal. Calcd for $C_{13}H_{13}F_3O_2$: C, 60.46; H, 5.07. Found: C, 60.76; H, 5.30.

**Reaction of 6 with Aluminum Chloride.** Into a flame-dried 15-mL two-necked flask fitted with a septum and nitrogen inlet was placed aluminum chloride (10 mg, 0.07 mmol) and chloroform (2 mL). To this magnetically stirred mixture was slowly added via syringe a solution of **6** (53 mg, 0.37 mmol) in chloroform (0.75 mL). The reaction mixture became yellow and was stirred for 1 h, at which point 2 mL of saturated sodium bicarbonate solution was introduced. The product was extracted into chloroform and dried. Concentration left **7c** as a thick yellow oil (42 mg, 63%). This material was subjected to preparative GC in order to obtain a sample for NMR: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.19 (dd, $J$, = 6.2, 3.4 Hz, 1 H), 6.14 (d, $J$ = 6.2 Hz, 1 H), 3.67 (s, 1 H), 2.89 (s, 1 H), 2.39 (dd, $J$ = 11.6, 3.6 Hz, 1 H), 2.35 (m, 1 H), 2.14 (m, 1 H), 1.82 (m, 2 H), 1.40 (m, 2 H), 0.38 (dd, $J$ = 8.2, 4.3 Hz, 1 H), 0.28 (dd, $J$ = 4.3, 4.3 Hz, 1 H).

**Saponification of 7a.** To a magnetically stirred solution of **7a** (230 mg, 0.89 mmol) in methanol (10 mL) at room temperature was added potassium carbonate (0.18 g, 1.30 mmol). Within 2 h the solid had dissolved and the solution was stirred for an additional 2 h. The solvent was evaporated to give a thick yellow oil, which was partitioned between ether and water. The aqueous layer was extracted twice with ether and the combined organic phases were washed with brine and dried. Evaporation of the ether left 0.13 g of a yellow oil which was purified by MPLC on silica gel (elution with 13% ethyl acetate in petroleum ether). Alcohol **7c** (82 mg, 57%) was obtained as a clear oil: IR (neat, cm$^{-1}$) 3400, 3050, 2930, 2860, 1060, 710; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.08 (dd, $J$ = 6.0, 3.4 Hz, 1 H), 5.99 (d, $J$ = 6.0 Hz, 1 H), 3.37 (s, 1 H), 2.68 (s, 1 H), 2.08 (dd, $J$ = 12.1, 3.7 Hz, 1 H), 2.06 (m, 1 H), 1.93 (br s, 1 H), 1.78 (d, $J$ = 9.0 Hz, 1 H), 1.75 (dd, $J$ = 8.8, 1.9 Hz, 1 H), 1.46–1.25 (series of m, 2 H), 0.40 (dd, $J$ = 7.9, 4.8 Hz, 1 H), 0.32 (dd, $J$ = 4.8, 4.8 Hz, 1 H); $^{13}$C NMR (125 MHz, $CDCl_3$) 137.8, 133.6, 87.7, 62.8, 49.2, 35.2, 30.3, 30.2, 21.8, 20.3, 9.8 ppm; mass spectrum, $m/z$ ($M^+$) calcd 162.1044, obsd 162.1052.

Conversion to the 3,5-dinitrobenzoate proceeded in quantitative yield to give yellow crystals of **7d**: mp 122–126 °C (from hexane–chloroform); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.22 (t, $J$ = 2.1 Hz, 1 H), 9.13 (d, $J$ = 2.1 Hz, 2 H), 6.19 (dd, $J$ = 6.2, 3.6 Hz, 1 H), 6.13 (dd, $J$ = 6.2, 0.7 Hz, 1 H), 4.73 (s, 1 H), 3.06 (br d, $J$ = 1.9 Hz, 1 H), 2.20 (dd, $J$ = 12.0, 3.7 Hz, 1 H), 1.94–1.79 (series of m, 3 H), 1.52–1.43 (series of m, 2 H), 1.52 (d, $J$ = 12 Hz, 1 H), 0.54 (dd, $J$ = 7.8, 5.0 Hz, 1 H), 0.43 (dd, $J$ = 5.0, 3.8 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) 162.0, 148.8, 137.3, 134.3, 133.0, 129.2, 122.3, 87.7, 62.6, 47.1, 36.1, 30.8, 30.5, 21.9, 20.7, 10.4 ppm.

**Reaction of 2 with Trifluoroacetic Acid-*d*.** Treatment of **2** (250 mg, 1.58 mmol) in chloroform (10 mL) with $CF_3COOD$ (1.0 mL, 12.9 mmol) as before afforded 260 mg (75%) of **8a** after flash distillation. This material was further purified by preparative GC prior to spectral analysis. The 300-MHz $^1$H NMR spectrum was identical with that of **4a** except for the signal at ~0.40 which integrated to approximately one-half its original intensity.

**Reaction of 2 with Silver Nitrate in Deuterium Oxide–Tetrahydrofuran.** Treatment of **2** (100 mg, 0.63 mmol) with silver nitrate (35 mg, 0.21 mmol) in a solvent system consisting of $D_2O$ (0.6 mL) and tetrahydrofuran (3 mL) for 3 h and workup in the predescribed manner provided 130 mg of a yellow liquid. Flash chromatography of this material on silica gel (elution with 13% ethyl acetate in petroleum ether) afforded 50 mg (44%) of pure **8b**. The 300-MHz $^1$H NMR spectrum was identical with that of **4b** except that no signal was present at $\delta$ 0.40 and the peak at $\delta$ 0.25 was now a doublet ($J$ = 8.5 Hz).

**Reaction of 6 with Trifluoroacetic Acid-*d*.** A solution of **6** (250 mg, 1.73 mmol) in chloroform (10 mL) was treated dropwise with a solution

of $CF_3COOD$ (1.0 mL, 12.9 mmol) in the same solvent (2.5 mL). After 30 min, workup and distillation was carried out as previously described to give 260 mg (58%) of **9**. The 300-MHz $^1H$ NMR spectrum was identical with that of **7a** except for the signal at $\delta$ 0.36 which integrated to approximately one-half its original intensity.

**Reaction of 2 with TCNE.** A cold (0 °C), magnetically stirred solution of **2** (1.0 g, 6.3 mmol) in 75 mL of ethyl acetate was treated dropwise during 1 h with a solution of TCNE (1.3 g, 10.1 mmol) in 50 mL of the same solvent. The reaction mixture was stirred overnight and evaporated to leave a heavy brown oil (3.11 g). Trituration with 30% ethyl acetate in petroleum ether left a solid. The soluble portion was chromatographed on silica gel (elution with 30% ethyl acetate in petroleum ether) to give 530 mg (30%) of **13** as an unstable yellowish solid, mp 112–113 °C: IR ($CHCl_3$, $cm^{-1}$) 3025, 2950, 2870, 1455, 1050; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.36 (d, $J$ = 4.2 Hz, 1 H), 2.69 (dd, $J$ = 12.6, 3.2 Hz, 1 H), 2.57 (t, $J$ = 4.9 Hz, 1 H), 2.12 (d, $J$ = 12.6 Hz, 1 H), 2.12 (m, 1 H), 2.07 (m, 1 H), 2.02 (m, 1 H), 1.93 (td, $J$ = 10.0, 3.4 Hz, 1 H), 1.78 (m, 1 H), 1.76 (m, 1 H), 1.73 (td, $J$ = 15.0, 3.9 Hz, 1 H), 1.58 (m, 1 H), 1.44 (d, $J$ = 8.7 Hz, 1 H), 1.14 (tq, $J$ = 4.4, 12.7 Hz, 1 H); $^{13}C$ NMR (75 MHz, $CDCl_3$) 113.0 (s), 112.3 (s), 110.8 (s), 109.7 (s), 46.1 (s), 45.6 (d), 44.0 (s), 40.5 (t), 37.0 (s), 33.0 (d), 28.5 (t), 27.2 (d), 26.1 (d), 23.8 (d), 23.2 (s), 19.8 (t), 19.0 (d), 14.8 (t) ppm; mass spectrum, $m/z$ ($M^+$) calcd 286.1218, obsd 286.1212.

The less soluble material was purified by filtration through a column of silica gel (dichloromethane elution) followed by recrystallization from acetone. There was isolated 310 mg (17%) of **12** as colorless crystals, mp 213–214 °C; $^1H$ NMR (300 MHz, acetone-$d_6$) $\delta$ 2.99 (q, $J$ = 3.1 Hz, 1 H), 2.72 (q, $J$ = 2.8 Hz, 1 H), 2.44 (d, $J$ = 9.1 Hz, 1 H), 2.40–2.0 (series of m, 5 H), 1.95–1.60 (series of m, 8 H), 1.34 (septet, 2 H); $^{13}C$ NMR (75 MHz, acetone-$d_6$) 113.9, 112.4, 111.8, 111.5, 62.7, 51.8, 47.4, 47.3, 40.1, 39.0, 32.2, 29.4, 27.2, 18.3, 16.2, 10.2, 5.7 ppm; mass spectrum, $m/z$ ($M^+$) calcd 286.1218, obsd 286.1190.

**X-ray Crystallographic Determination of 12.** A transparent single crystal of **12** was mounted on a pin and transferred to the goniometer. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 23 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. The space group was determined to be the centric $P2_1/c$ from the systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the $\theta$–$2\theta$ scan technique. A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[37] Neutral atom scattering factors for N, C, and H were taken from ref 38.

The non-hydrogen atoms were located with the direct methods program MULTAN.[39] Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.107$.

The hydrogen atoms were located from a difference Fourier map and fully refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.038$ and $R_w = 0.039$. A final difference Fourier showed no feature greater than 0.2 $e^-/Å^3$. No systematic variation of $w(|F_o| - |F_c|)$ versus $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in the supplementary material.

**Acid-Catalyzed Rearrangement of 12.** When solutions of **12** in $CDCl_3$ were allowed to stand at room temperature, quantitative isomerization to **14** was seen: colorless solid, mp 146–148 °C; IR ($CDCl_3$, $cm^{-1}$) 3040, 2990, 1470, 1115, 825; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.17 (dd, $J$ = 10.0, 4.7 Hz, 1 H), 4.70 (d, $J$ = 10.0 Hz, 1 H), 2.32 (m, 2 H), 2.06 (m, 2 H), 2.06 (d, $J$ = 9.3 Hz, 1 H), 1.97–1.78 (series of m, 3 H), 1.58 (m, 1 H), 1.42 (m, 1 H), 1.19 (ddd, $J$ = 8.5, 8.5, 5.0 Hz, 1 H), 0.52 (ddd, $J$ = 5.0, 5.0, 5.0 Hz, 1 H); $^{13}C$ NMR (75 MHz, $CDCl_3$) 129.3 (d), 125.0 (d), 112.0 (s), 111.1 (s), 110.0 (s), 109.4 (s), 65.6 (s), 49.6 (s), 44.6 (s), 36.8 (d), 34.1 (s), 33.4 (d), 32.7 (t), 23.1 (d), 19.2 (t), 16.2 (t), 16.0 (t), 14.1 (d) ppm; mass spectrum, $m/z$ ($M^+$) calcd 286.1218, obsd 286.1197.

Anal. Calcd for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93. Found: C, 75.56; H, 5.09.

**Reaction of 2 with CSI.** Into a flame-dried 100-mL three-necked flask fitted with a thermometer, addition funnel with a nitrogen inlet, and septum was placed 1.2 g (7.6 mmol) of **2** and 60 mL of ether. To this magnetically stirred solution at −78 °C was added 0.6 mL of CSI in 12 mL of ether dropwise during 30 min. The reaction mixture was maintained at −78 °C for an additional hour, allowed to warm to room temperature where it was kept for 24 h, and finally filtered. The filtrate was washed with water (40 mL) followed by brine (40 mL) and then dried. Solvent removal left a thick yellow oil (2.202 g), which was passed through silica gel by elution with dichloromethane. The resulting material (1.88 g) was separated into its components by MPLC on silica gel (elution with 30% ethyl acetate–petroleum ether).

The earliest characterizable material to elute was a 2:1 mixture of **17a** and **18a** (753 mg, 33%). Analytical HPLC led to their separation (elution with 15% ethyl acetate in heptane).

For **17a**: white solid, mp 123–125 °C: IR ($CDCl_3$, $cm^{-1}$) 1745, 1410, 1175, 1050; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.25 (dd, $J$ = 9.8, 5.0 Hz, 1 H), 4.73 (d, $J$ = 9.8 Hz, 1 H), 2.46 (m, 1 H), 2.09 (m, 1 H), 1.99 (d, $J$ = 9.1 Hz, 1 H), 1.97 (m, 1 H), 1.82 (m, 1 H), 1.77–1.63 (series of m, 4 H), 1.58 (td, $J$ = 8.8, 2.6 Hz, 1 H), 1.31 (ddd, $J$ = 8.4, 8.4, 4.8 Hz, 1 H), 0.69 (ddd, $J$ = 6.0, 4.8, 4.8 Hz, 1 H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 170.6 (s), 130.3 (d), 121.5 (d), 69.3 (s), 33.2 (s), 32.3 (d), 31.5 (t), 27.8 (d), 21.6 (d), 17.9 (t), 17.5 (t), 16.3 (t), 14.9 (d) ppm; mass spectrum $m/z$ ($M^+$) calcd 299.0382, obsd 299.0367.

For **18a**: IR ($CDCl_3$, $cm^{-1}$) 2950, 1745, 1410, 1180, 1050; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.22 (dd, $J$ = 9.8, 3.9 Hz, 1 H), 4.82 (d, $J$ = 9.8 Hz, 1 H), 2.39 (dd, $J$ = 10.0, 2.6 Hz, 1 H), 2.23 (octet, 1 H), 2.02 (m, 2 H), 1.93 (d, $J$ = 9.4 Hz, 1 H), 1.74–1.55 (series of m, 5 H), 1.21 (ddd, $J$ = 9.0, 9.0, 4.7 Hz, 1 H), 0.33 (ddd, $J$ = 6.0, 4.7, 4.7 Hz, 1 H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 170.1 (s), 130.4 (d), 124.3 (d), 69.0 (s), 34.1 (s), 33.6 (d), 31.7 (t), 29.3 (d), 18.1 (t), 18.0 (t), 17.9 (d), 17.0 (t), 13.0 (d) ppm; UV $\lambda_{max}C_2H_5OH$ 210 nm ($\epsilon$ 17 340); mass spectrum, $m/z$ ($M^+$) calcd 299.0383, obsd 299.0401.

Finally, 346 mg (15%) of **19** was obtained as colorless crystals: mp 120–121 °C (from hexane–dichloromethane); IR ($CDCl_3$, $cm^{-1}$) 1575, 1380, 1180; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.26 (dd, $J$ = 9.8, 4.0 Hz, 1 H), 4.95 (d, $J$ = 9.8 Hz, 1 H), 2.70 (br 1 H), 2.24 ($J$ = 14.0, 5.0 Hz, 1 H), 2.05 (m, 3 H), 1.69 (m, 6 H), 1.20 (ddd, $J$ = 9.0, 9.0, 4.7 Hz, 1 H), 0.31 (ddd, $J$ = 6.0, 4.7, 4.7 Hz, 1 H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 131.5 (d), 122.2 (d), 37.7 (d), 31.8 (t), 19.7 (t), 19.0 (d), 16.6 (t), 15.0 (t), 12.5 (d) (3 carbons not seen) ppm; mass spectrum, $m/z$ ($M^+$) calcd 299.0382, obsd 299.0348.

**X-ray Crystallographic Determination of 17a.** A clear single crystal of **17a** was mounted on a pin and transferred to the goniometer. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. The space group was determined to be the centric $P2_1/c$ from the systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the $\theta$–$2\theta$ scan technique. A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[37] Neutral atom scattering factors for Cl, S, O, N, C, and H were taken from ref 38.

The non-hydrogen atoms were revealed with use of the direct methods program MULTAN.[39] A subsequent difference Fourier map readily revealed the positions of the hydrogen atom. Least-squares refinement with isotropic thermal parameters without refining the hydrogen atoms led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.126$.

Refinement of the non-hydrogen atoms with anisotropic temperature factors and the hydrogen atoms with isotropic thermal parameters led to final values of $R = 0.037$ and $R_w = 0.038$. A final difference Fourier showed no feature greater than 0.3 $e^-/Å^3$. The weighting scheme was based on $[\sigma(F_o)^2 + pF_o)^2 + pF_o^2]^{-1}$ where $p = 0.00002$; no systematic variation of $w(|F_o| - |F_c|)$ versus $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in the supplementary material.

**Acidic Hydrolysis of 19.** A magnetically stirred solution of **19** (0.243 g, 0.8 mmol) in acetone (25 mL) at room temperature was treated with 0.5 N hydrochloric acid (2.5 mL) and gently refluxed for 4 h. The cooled reaction mixture was diluted with saturated sodium bicarbonate solution (5 mL), the acetone was removed by evaporation, and the residual liquid was extracted with ether (2 × 15 mL). The combined ethereal phases were washed with brine (3 mL), dried, and evaporated. There was obtained 0.21 g of a yellow oil, chromatography of which on silica gel (elution with 30% ethyl acetate–petroleum ether) resulted in clean separation of the two components.

First to elute was **18a** (112 mg, 46%).

Subsequently, 56 mg (34%) of **18b** was isolated as a white solid: mp 160–162 °C: IR ($CDCl_3$, $cm^{-1}$) 3410, 3195, 2950, 1675, 1120; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.83 (br 1 H), 6.05 (dd, $J$ = 9.8, 4.0 Hz, 1 H), 4.79 (d, $J$ = 9.8 Hz, 1 H), 2.05 (dd, $J$ = 15.0, 4.9 Hz, 1 H), 1.87 (m, 1 H), 1.65 (d, $J$ = 9.2 Hz, 1 H), 1.62–1.21 (series of m, 8 H), 0.98 (ddd, $J$ = 6.0, 4.7, 4.7 Hz, 1 H); $^{13}C$ NMR (75 MHz, $CDCl_3$) 175.5, 128.6, 125.8,

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(38) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1972, Vol. IV, pp 72, 99, 149.

(39) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 368.

54.1, 35.3, 33.8, 32.6, 28.7, 21.5, 19.9, 17.7, 16.6, 12.5 ppm; UV $\lambda_{max}C_2H_5OH$ 220 nm ($\epsilon$ 7539); mass spectrum, $m/z$ ($M^+$) calcd 201.1153, obsd 201.1140.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.31; H, 7.55.

**Hydrolysis of 17a.** To a magnetically stirred solution of **17a** (16 mg, 0.054 mmol) in ether (2 mL) at room temperature was added a solution of triethylamine (0.02 mL, 0.14 mmol) in methanol. The reaction mixture was stirred for 1 h, the volatiles were evaporated, and the residue was passed through a small column of silica gel (elution with ethyl acetate) to give **17b** as a white solid (9 mg, 82%): IR ($CDCl_3$, $cm^{-1}$) 3420, 3200, 2950, 1680; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.19 (br, 1 H), 6.15 (dd, $J$ = 9.8, 5.1 Hz, 1 H), 4.78 (d, $J$ = 9.8 Hz, 1 H), 1.98 (m, 1 H), 1.75 (d, $J$ = 8.8 Hz, 1 H), 1.71-1.30 (series of m, 9 H), 1.04 (ddd, $J$ = 8.4, 8.4, 4.8 Hz, 1 H), 0.50 (ddd, $J$ = 6.0, 4.8, 4.8 Hz, 1 H); $^{13}C$ NMR (75 MHz, $CDCl_3$) 174.3, 129.3, 123.3, 54.1, 33.1, 31.9, 26.7, 23.7, 18.0, 17.5, 16.8, 14.0 ppm; mass spectrum, $m/z$ ($M^+$) calcd 201.1154, obsd 201.1150.

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**Supplementary Material Available:** Tables of bond distances and angles, final fractional coordinates, thermal parameters, and least-squares planes for **12** and **17a** (10 pages). Ordering information is given on any current masthead page.

# Diphenylacetaldehyde and Its Enol: Determination of the Keto-Enol and Hydration Equilibrium Constants and the p$K_a$'s of the Aldehyde, Enol, and Hydrate. Comparison with Sterically Hindered Systems

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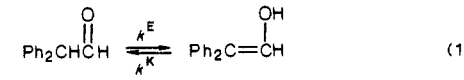
**Abstract:** The enol isomer of diphenylacetaldehyde was generated in aqueous solution from its potassium salt, formed by treating the aldehyde with potassium hydride, and rates of ketonization of this enol were measured at 25 °C in perchloric acid and sodium hydroxide solutions and acetic acid and bicarbonate ion buffers. These data, coupled with rates of enolization of the aldehyde measured at 25 °C in acetic acid buffer and sodium hydroxide solutions, lead to duplicate independent determinations of the keto-enol equilibrium constant, $K_E = (1.04 \pm 0.10) \times 10^{-1}$, $pK_E = 0.98 \pm 0.04$, the acid dissociation constant of the enol ionizing as an oxygen acid, $K_a^E = (4.03 \pm 0.11) \times 10^{-10}$ M, $pK_a^E = 9.40 \pm 0.01$, and the acid dissociation constant of the aldehyde ionizing as a carbon acid, $K_a^K = (3.80 \pm 0.12) \times 10^{-11}$ M, $pK_a^K = 10.42 \pm 0.02$. The equilibrium constant for formation of the aldehyde hydrate, $K_h = 4.7 \pm 0.2$, was also determined by two independent methods, and the acid dissociation constant of the hydrate ionizing as an oxygen acid, $K_a^h = (7.1 \pm 0.4) \times 10^{-14}$ M, $pK_a^h = 13.15 \pm 0.02$, was evaluated from kinetic data. The unusually large values of $K_E$ and $pK_a^x$ for this system are attributed to stabilization of the carbon-carbon double bonds of the enol and enolate ion by the phenyl substituents. Comparison with literature data on sterically hindered, stable, "Fuson" enols bearing mesityl substituents suggests that a substantial portion of the thermodynamic stability of Fuson enols is provided by similar phenyl group stabilization of their double bonds; the methyls of the mesityl substituents of Fuson enols, however, do appear to play a critical role in conferring kinetic stability upon these substances.

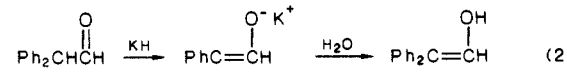
The enol isomers of simple monofunctional aldehydes and ketones are generally quite unstable and revert to their carbonyl tautomers rapidly. A notable exception to this behavior is provided by a group of crowded enols studied by Fuson in a classic series of investigations some 40 years ago.[1] Fuson's enols have bulky aryl substituents, such as mesityl or duryl, attached to their carbon-carbon double bonds. They are stable substances that can be isolated, and, if the crowding is sufficiently severe, they resist conversion to their keto isomers strongly. Keto-enol equilibrium constants for some of these crowded systems have been determined only recently,[2] and these new studies have shown that these enols are stable, not only because the barriers for their keto-enol interconversions are high but also because the enols themselves have unusual thermodynamic stability.

It would be of interest to compare the behavior of these crowded enols with that of enols containing unsubstituted phenyl groups on their carbon-carbon double bonds. We report here the beginning of such a study using the diphenylacetaldehyde keto-enol system (eq 1). We have measured rates of enolization of the



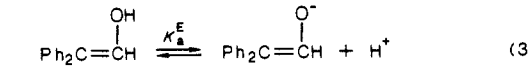
(1)

aldehyde, $k^E$, as well as ketonization of the enol, $k^K$, with the latter substrate generated from its potassium salt (eq 2); this has provided



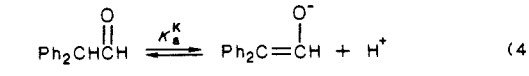
(2)

the keto-enol equilibrium constant for the system as the ratio of specific rate constants for these two reactions: $K_E = k^E/k^K$. Analysis of the rate data obtained in basic solutions has also given the acid dissociation constant of the enol ionizing as an oxygen acid, $K_a^E$ (eq 3), as well as that of the aldehyde ionizing as a carbon



(3)

acid, $K_a^K$ (eq 4). Diphenylacetaldehyde is extensively hydrated



(4)

in aqueous solution, and we have therefore also determined the

(1) For a recent summary of this work, see: Hart, H. *Chem. Rev.* **1979**, *79*, 515-528.

(2) (a) Miller, A. R. *J. Org. Chem.* **1976**, *41*, 3599-3602. (b) Biali, S.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1007-1015. Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 3669-3676. (c) Nadler, E. B.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 2112-2127.

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