discussed above although details of symmetry and precise molecular arrangement vary.

Most of the acids listed in Table I have been found to form salts with the composition $(NH_3)\cdot(ArCOOH)_2$ and several of the crystal structures have been determined. Such salts might be expected to be reaction intermediates when the carboxylic acids react with ammonia but we have found no evidence that they accumulate to a detectable extent. Further when platelets of the 1:2 salt of *p*-chlorobenzoic acid were treated with gaseous ammonia they appeared to react as fast as, or faster than, the initial acid (again with strongly anisotropic behavior) to form the 1:1 salt. Principles similar to those discussed for the acids seem to hold for the crystallization and reaction with ammonia of the 1:2 salts.

There remains the question of the mechanism of the incorporation of the ammonia molecules into an already fully packed crystal. A comparison of the volumes per dimer unit of the carboxylic acids with those of the 1:2 ammonium salts calculated from previously available X-ray data shows that there is a volume increase of 6–8% (Table I); earlier density measurements[3] suggest that the addition of two ammonia molecules to form the 1:1 ammonium benzoate produces a total increase of 20–25%. It is not surprising then that disordering accompanies the absorption of ammonia. To investigate this point further X-ray powder photographs of ammonium benzoate and ammonium *p*-chlorobenzoate (the 1:1 salts) were obtained. The same photographs could be obtained by mounting the product from the acid–ammonia reaction without grinding which shows that the product is formed as unoriented microcrystallites of ammonium salt. It seems highly improbable that this reaction is a simple diffusion process: instead ammonia molecules attack a crystal face and formation of ammonium salt loosens successive layers of carboxylic acid molecules in such a way as to permit accelerated diffusion of ammonia into the interior of the crystal.

To determine whether the reaction could be extended to bulkier bases the reaction of crystalline *dl*-mandelic acid[4] with *dl*-2-butylamine, bp 63°, was carried out by placing crystals of the acid in a sealed jar containing a vial of (excess) liquid amine. The vapor pressure was sufficient to permit diffusion of the amine to the acid and a quantitative yield of 1:1 salt was obtained in 96 hr; the salt gave correct microanalytical values without purification. Ammonium *dl*-mandelate, formed by the method employed with the acids in Table I, when submitted to reaction with *dl*-2-butylamine for a length of time which would have caused the free acid to react completely gave no sign of exchange of the amine for ammonia as shown by submitting the product "crystals" to nmr analysis; there was no trace of absorption in the alkyl proton region of the spectrum where the butyl protons should show absorption. Similarly, when the crystalline 2-butylammonium salt of mandelic acid prepared as above was treated with ammonia under conditions which would have caused complete reaction of mandelic acid, microanalysis of the product gave values correct for the unchanged 2-butylammonium salt and showed no indication of any amine–ammonia exchange reaction. It may be concluded that at least in this case the acid–base reactions are irreversible under the conditions employed.

It is hoped that crystal chirality may be utilized to achieve asymmetric induction in the reaction of crystalline acids with gaseous bases.[1b,j,5] Preliminary results have indicated that crystalline (*S*)-(+)-mandelic acid,[6,7] $[\alpha]$D 150° (ethanol), in its reaction with an equimolar amount of *dl*-2-butylamine gas shows a preference for the (*S*)-(+) isomer.

It is likely then that reactions between gases and molecular crystals of the sort reported here not only have synthetic value but may also provide valuable insight into the structure of crystal surfaces.

Acknowledgment. This research was supported by the Advanced Research Projects Agency of the Department of Defense.

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[3] L. Klemm and W. Klemm, *Z. Phys. Chem., Abt. A*, **151**, 71 (1930).

[4] S. Furberg, *Research* (*London*), **4**, 192 (1951); H. A. Rose, *Anal. Chem.*, **24**, 1680 (1952).

[5] Compare footnote 7 of ref 1h, and F. Wudl, D. A. Lightner, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 4099 (1967).

[6] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 89, 99.

[7] We are indebted to Professor John Wood, Department of Biochemistry, University of Illinois, for a sample of the optically active acid.

[8] Alfred P. Sloan Foundation Fellow, 1968–1970.

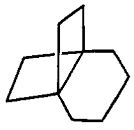
Rodger S. Miller, David Y. Curtin,* Iain C. Paul[8]
Department of Chemistry and Materials Research Laboratory
University of Illinois, Urbana, Illinois 61801

Received March 4, 1971

[4,2,2]- and [3,2,2]Propellanes[1]

Sir:

Propellanes are compounds having three rings fused along a common edge.[2] Although a variety of such compounds are known,[3] we report here the first examples containing two fused cyclobutane rings; namely, the [4.2.2]propellane (**1**) and [3.2.2]propellane (**2**) systems. The skeletal requirements of these propellanes are probably best accommodated by near-sp^2 hybridization of the quaternary bridgehead atoms; the central bond, then formed to a degree by σ overlap of p orbitals, would be expected to be longer and weaker than the usual carbon–carbon bond.[1,3d]



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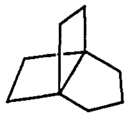

2

Photocycloaddition of ethylene to the enol acetate **3**[4] of cyclohexane-1,3-dione in ether produces the bi-

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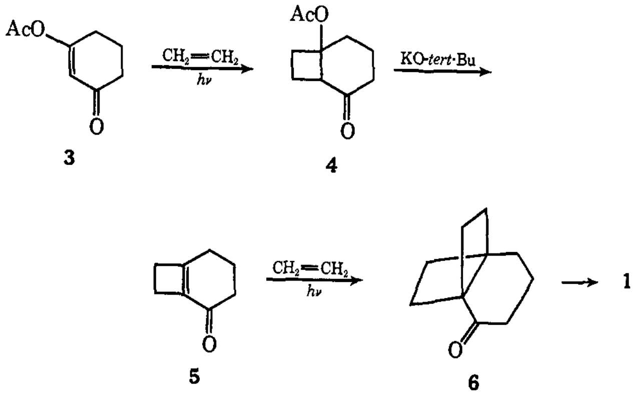
[1] (a) Taken in part from the Ph.D. Thesis of Kayson Nyi, The University of Chicago, 1970; (b) a preliminary report of part of this work was presented by one of us (E) at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] The propellane nomenclature for such compounds was introduced by Ginsburg[3a] and apparently has been accepted by the arbiters of such things (see *Chemical Abstracts*). The title compounds, in the Baeyer system, are tricyclo[4.2.2.0]decane and tricyclo[3.2.2.0]nonane, respectively.

[3] For example, (a) J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron, Suppl.*, **8** (1), 279 (1966); (b) D. Ginsburg, *Accounts Chem. Res.*, **2**, 121 (1968), and references therein: (c) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966); (d) K. B. Wiberg, E. C. Lupton, Jr., and G. J. Burgmaier, *ibid.*, **91**, 3372 (1969); (e) K. B. Wiberg and G. J. Burgmaier, *Tetrahedron Lett.*, 317 (1969); P. G. Gassman, A. Topp, and J. W. Keller, *ibid.*, 1093 (1969); (f) W. T. Borden, I. L. Reich, L. A. Sharpe, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 3808 (1970).

[4] This derivative of 2-cyclohexenone and relatives bearing an oxygen atom bound to the β carbon of the chromophore undergo photocycloaddition reactions very much more sluggishly than cyclohexenones bear-

cyclic keto acetate **4** [bp 105–110° (1 mm); ir (CCl_4) ν 5.74, 5.84, and 8.5 μ]. The reaction is run at −70 to −90° to obtain a workable concentration of ethylene (>3 *M*). The addition is very slow; about 1.5 g of **4** can be obtained from each day of irradiation.[5] Fortunately, the reaction is clean, and with suitable refrigeration equipment[6] 10-day runs can be carried out without bother. Elimination[4a] of acetic acid from **4** using potassium *tert*-butoxide-*tert*-butyl alcohol in ether at 0° gives (85%) the enone **5**, purified by molecular distillation at room temperature [ir (CCl_4) ν 5.95 μ; uv (cyclohexane) λ 232 (ϵ 9200) and 336 nm (ϵ 38); nmr ($CDCl_3$, 100 MHz) δ 2.7 (4 H) and 2.2 ppm (6 H)]. This cyclobutene derivative is quite heat sensitive; above 50° it dimerizes rapidly, apparently *via* 2,3-dimethylenecyclohexanone. A second photocycloaddition of ethylene,[7] now to the enone **5**, gives (50%) the [4.2.2]propellane **6** [bp 108.6–109° (11 mm); mp 30–32°; ir (film) ν 5.88 μ]. This photoaddition reaction is very much more facile than the addition of ethylene to **3**; however, the reaction is still best carried out at low temperature. The pure propellane ketone **6** is a waxy solid, smelling very much like camphor. Wolff–Kishner reduction of **6** by way of the Huang–Minlon modification gives the hydrocarbon **1**, [4.2.2]propellane, mp 58–60° The 100-MHz nmr spectrum of **1** is reproduced in Figure 1a.



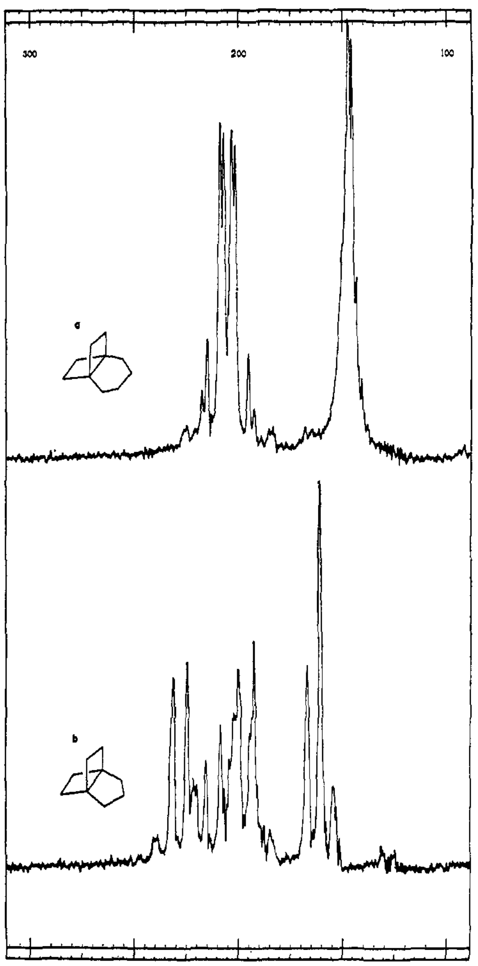
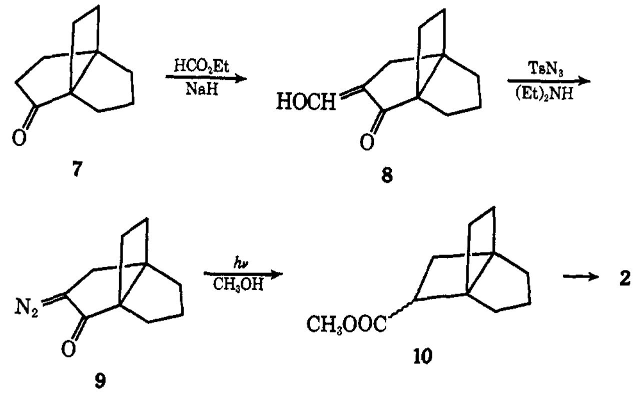


Figure 1. The 100-MHz spectra of (a) [4.2.2]propellane and (b) [3.2.2]propellane in $CDCl_3$ solution. The scale is hertz downfield from tetramethylsilane. The high-field absorption in spectrum a arises from all eight protons of the six-membered ring of [4.2.2]-propellane. Only four of the six protons of the five-membered ring of [3.2.2]propellane are accounted for in the high-field absorption in spectrum b; the resonance of the central methylene protons of this ring lies within the lower field group of absorptions, centered at about 2 ppm.

Two paths to [3.2.2]propellanes have been developed. Both involve ring contraction *via* photochemically induced Wolff rearrangement of a diazo ketone,[8] the first in the [3.3.2]propellane series and the second in the [4.2.2] series. Formylation of the ketone **7**, prepared as described by Cargill and coworkers,[3c] with ethyl formate–sodium hydride gives (85%) the hydroxymethylene derivative **8**, mp 84–85°. Reaction of **8** with tosyl azide and diethylamine[9] produces (95%) the liquid α-diazo ketone **9**. Photolysis of **9** in anhydrous methanol leads (60%) to a mixture of the epimeric esters **10**, bp 41–45° (0.2 mm).[10] Thermolysis[11] of the corre-



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ing a carbon substituent at the β position. However, such compounds have been used productively a number of times; see, for example (a) K. Lin, Ph.D. Dissertation, The University of Chicago, 1966; (b) T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, **34**, 509 (1969); (c) B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. DeMayo, *ibid.*, **34**, 794 (1969).

(5) A Hanovia 450-W mercury arc was used; the output was filtered through Pyrex glass.

(6) We used a dual cascade system with a thermal capacity of 800 Btu/hr at −100° specially constructed by Cincinnati Sub-Zero Products, Inc.

(7) We have used numerous olefins other than ethylene, both at this stage and in the earlier photoaddition; these lead to propellanes bearing substituents on the four-membered ring(s).

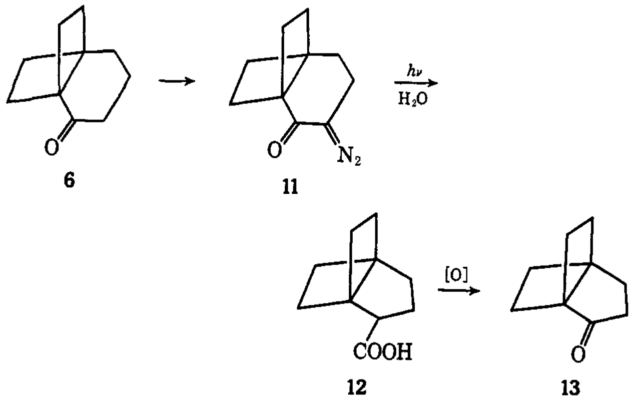
(8) For other examples of the use of this reaction for the production of strained systems see (a) L. Horner and E. Spietschka, *Chem. Ber.*, **88**, 934 (1955); (b) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Amer. Chem. Soc.*, **83**, 3998 (1961); (c) M. P. Cava and E. Moroz, *ibid.*, **84**, 115 (1962); J. Meinwald, G. G. Curtis, and P. G. Gassman, *ibid.*, **84**, 116 (1962); J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966).

(9) Following the scheme of M. Rosenberger, P. Yates, J. B. Hendrickson, and W. Wolf, *Tetrahedron Lett.*, 2285 (1964).

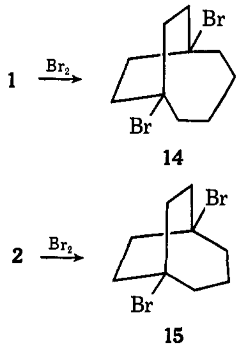
(10) As we shall show in the full paper, the major isomer (80%) is the exo epimer.

sponding *tert*-butyl peresters in 1,3,5-triisopropylbenzene at 160° gives **2**, [3.2.2]propellane, in 45% yield.[12] The pure hydrocarbon is a mobile liquid, fp 11°; the 100-MHz nmr spectrum of **2** is reproduced in Figure 1b.

The sequence from **7** works well and permits production of substantial amounts of the hydrocarbon **2**, yet it does not provide suitable intermediates for attempts at the preparation of the elusive [2.2.2]propellane system *via* another ring contraction.[13] Our second approach to [3.2.2]propellanes is without this subtle deficiency. Formylation of the [4.2.2]propellane **6** and subsequent reaction of the α-hydroxymethylene ketone with tosyl azide and diethylamine yields the α-diazo ketone **11**. Irradiation of **11** in aqueous dioxane gives (63%) the [3.2.2]propellane acid **12**, mp 79°. We have converted **12** to the ketone **13** [ir (CCl_4) ν 5.77 μ] and are trying now to bring about contraction of **13** to a [2.2.2]-propellane.



The [4.2.2]- and [3.2.2]propellane hydrocarbons are thermally stable to at least 160°. Neither reacts at a significant rate with hydrogen at atmospheric pressure over Adams catalyst. On the other hand, [4.2.2]- and [3.2.2]propellane react quantitatively with bromine[14] to give the tertiary dibromides **14**, mp 44–45°, and **15**, mp 143–143.5°, respectively, rare and useful examples of a bicyclo[4.2.2]decane and a bicyclo[3.2.2]nonane substituted at the bridgeheads.



The propellane ketone **6** and the corresponding alcohol, mp 117.5–118.5°, are thermally stable, but both react very rapidly with acid.[15] We shall discuss these reactions in future reports along with the thermochemical and X-ray data now being gathered for the [4.2.2]- and [3.2.2]propellane systems.

Acknowledgments. Support of this work by the National Science Foundation and by the Institute for General Medical Sciences of the National Institutes of Health is recognized with gratitude. Badische Anilin-und-Soda-Fabrik AG was kind enough to provide generous gifts of bicyclo[3.3.0]oct-1(5)-en-2-one. We thank Mr. G. H. Temme for his help.

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(11) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958). See ref 8b and P. E. Eaton and T. W. Cole, Jr. (*ibid.*, **86**, 3157 (1964)) for examples of applications of this method.

(12) [3.2.2]Propell-6-ene is a minor product (*ca.* 5%).

(13) We have examined also a number of routes proceeding from relatives of 7 carrying functional groups on both five-membered rings, for example, from [3.3.2]propella-2,6-dione produced (*cf.* ref 3f) by way of photoaddition of ethylene to simple derivatives of bicyclo[3.3.0]oct-1(5)-ene-2,6-dione whose preparation will be described elsewhere. To date, these paths have offered no special advantages.

(14) The reactions were carried out at room temperature in carbon tetrachloride initially 1 *M* in each reactant and were complete in 10–20 min.

(15) An early, verbal report[1b] that halogen acids add across the central bond of 6 is in error; unfortunately, this interpretation has been quoted in the literature [W. F. Erman and T. W. Gibson, *Tetrahedron*, **25**, 2493 (1969)].

(16) Witco Chemical Co. Fellow, 1967–1968; American Chemical Society–Petroleum Research Fund Graduate Fellow, 1968–1969; National Institutes of Health Predoctoral Fellow, 1969–1970.

Philip E. Eaton,* Kayson Nyi[16]
Searle Chemistry Laboratory, Department of Chemistry
The University of Chicago, Chicago, Illinois 60637

Received December 19, 1970

Discovery and Electron Spin Resonance Spectra of Matrix-Stabilized Hydronium Radicals H_3O and D_3O[1]

Sir:

Bernstein[2] was the first to publish on the possible existence of H atom adducts such as H_3O and NH_4. By estimations based on thermodynamic cycles and vibrational frequencies, he predicted the bond dissociation energies for such species in the gas phase to range from 7 to 33 kcal/mol. If so, H_3O would be stable relative to H + H_2O and should be observable. Further interest in the significance of H_3O was stimulated by Magee,[3] who proposed it as an intermediate in the radiolysis of water. Sworski[4] extended this view to argue that H_3O was the probable precursor of molecular hydrogen in water radiolysis. About this time, Martin[5] began to search for H_3O and NH_4 using a special palladium catalyst and mass spectrometer apparatus. He was encouraged in this effort by Soldano[6a] and Lossing.[6b] These experiments failed because the emission of spontaneous positive ions from the catalyst when exposed to either ammonia or water precluded using an electron beam of variable energy to detect transient free radicals. However, after witnessing

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(1) This work was made possible by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2825 and by Vanderbilt University. The esr apparatus used was purchased through Vanderbilt's Centers of Excellence Award sponsored by the National Science Foundation. We also thank Professor R. E. Rummel for adapting the photochemical apparatus for esr work and for drawing our figures. Parts of this study were first reported at the Ninth Informal Conference on Photochemistry, The Ohio State University, Columbus, Ohio, Sept 1–4 1970 and at the International Symposium on Atomic, Molecular and Solid-State Theory and Quantum Biology, University of Florida, Sanibel Island, Fla, Jan 18–23, 1971.

(2) H. J. Bernstein, *J. Amer. Chem. Soc.*, **85**, 484 (1963).

(3) J. L. Magee, *Radiat. Res. Suppl.*, **4**, 20 (1964).

(4) T. J. Sworski, *J. Amer. Chem. Soc.*, **86**, 5034 (1964).

(5) T. W. Martin, *J. Chem. Phys.*, **43**, 1422 (1965).

(6) (a) Dr. B. A. Soldano of the Oak Ridge National Laboratory predicted the existence and possible theoretical significance of the hydronium radical in private conversations with Martin during the summer of 1958. (b) Dr. F. P. Lossing of the National Research Council of Canada brought Bernstein's paper to his attention and independently suggested the catalyst experiments.