

# Small-Ring Propellanes

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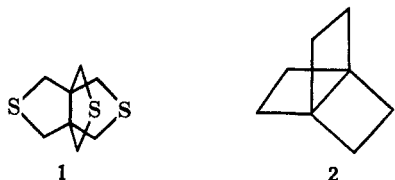
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Slowly but surely the propellane nomenclature is being accepted.<sup>1</sup>

Propellanes have been defined as tricyclic systems conjoined "in"<sup>2</sup> or "by"<sup>3</sup> a carbon-carbon single bond. In this Account we shall discuss only small-ring propellanes, defined herein as those which contain five to ten carbon atoms in their carbocyclic skeleton.<sup>4</sup>

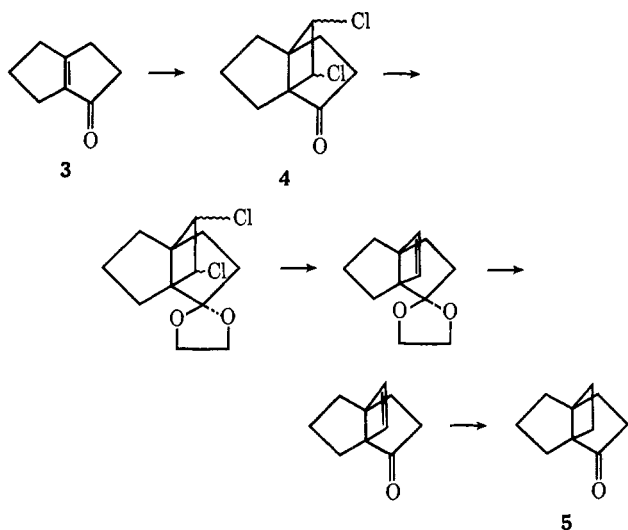
Obviously, heterocyclic propellanes having, say, eight carbon atoms in their skeleton are of larger ring size than corresponding carbocyclic propellanes which may, at least on paper, potentially be produced from them; compare **1** and **2**, C<sub>8</sub>H<sub>12</sub>S<sub>3</sub> and C<sub>8</sub>H<sub>12</sub>, respectively.



We shall see that ring contraction of a sulfur-containing five-membered ring is indeed a possible way to prepare a four-membered ring within a propellane system, but let us begin with more direct methods.

Cargill and his coworkers have studied the photochemical addition of olefins to substituted cyclopentenones. Thus, 1,2-dichloroethylene was added to

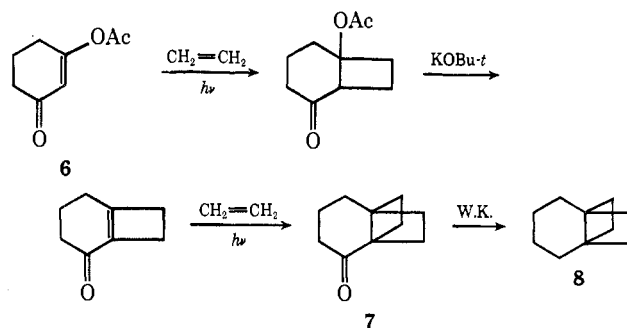
Scheme I



Professor Ginsburg was born in New York, N. Y., and educated there and in Palestine. After five years in industry in the United States, he went to Israel where, from 1948 to 1954, he was at the Weizmann Institute. He then moved to the Technion-Israel Institute of Technology. Professor Ginsburg has served as a Visiting Professor at Brandeis University, the University of Zurich, New York University, University of Saskatchewan, Weizmann Institute, McGill University, and Oxford University. Throughout his career, his research interests have remained in the areas of stereochemistry and alkaloids.

bicyclo[3.3.0]oct-1(5)-en-2-one (**3**) to give the [3.3.2]-propellane derivative **4** and the ketone **5** as shown in Scheme I.<sup>5</sup> Perhaps the most successful application of this photochemical approach involves the synthesis of [4.2.2]propellane (**8**) and its lower homolog, [3.2.2]-propellane (**9**), both of which contain two fused cyclobutane rings.<sup>1b</sup> The starting material for both products was the readily available enol acetate of cyclohexane-1,3-dione (**6**) (Scheme II). Although the

Scheme II



first photoaddition is sluggish it results in a clean product, and this route appears quite a reasonable one from the viewpoint of yield. A more strained [4.2.2]-propelladiene has been prepared in extremely low yield, but this will be discussed below.

The lower homolog was prepared by two different routes (Scheme III).<sup>1b</sup> The first employed Cargill's

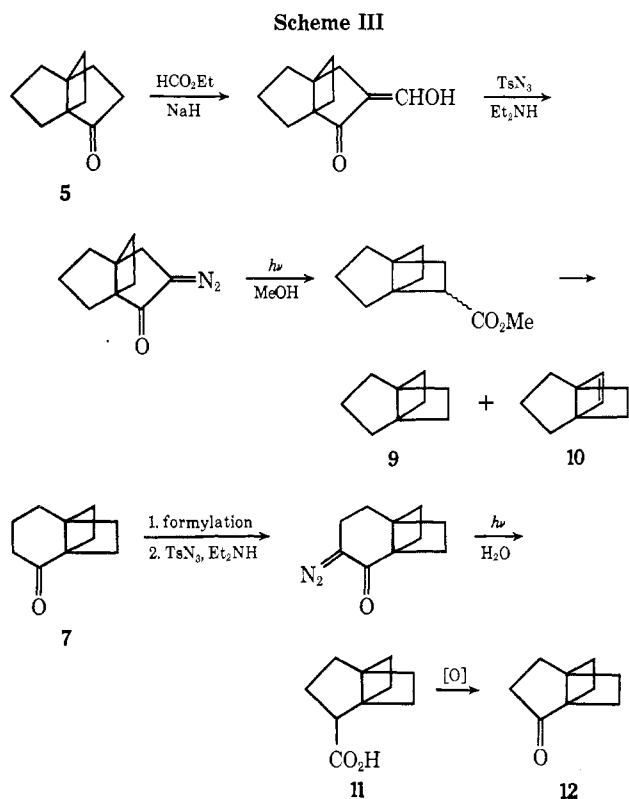
(1) (a) *Chem. Abstr.*, **70**, 26675 (1969); (b) P. E. Eaton and N. Kyi, *J. Amer. Chem. Soc.*, **93**, 2786 (1971), ref 2. Other ramparts have not fallen as drastically as reported for another case (J. B. Nun, *Joshua*, Chapter VI, Verse 20). Those erroneously alleged to be among the greatest of reactionaries, the editors of chemical journals, have also accepted this nomenclature (e.g., *Tetrahedron Lett.*, 4885 (1968); *J. Amer. Chem. Soc.*, **91**, 3973 (1969); *Accounts Chem. Res.*, **2**, 121 (1969); *Justus Liebigs Ann. Chem.*, **746**, 70 (1971)). Some purists still hold the fort (e.g., *J. Amer. Chem. Soc.*, **91**, 3372 (1969); *Tetrahedron Lett.*, 1093 (1969)).

(2) J. Altman, E. Babad, J. Itzhaki, and D. Ginsburg, *Tetrahedron, Suppl.*, **8**, Part 1, 279 (1966).

(3) L. A. Paquette, R. E. Wingard, Jr., J. C. Philips, G. L. Thompson, L. K. Read, and J. Clardy, *J. Amer. Chem. Soc.*, **93**, 4508 (1971).

(4) The upper limit of ten was arbitrarily and pragmatically decided upon in order to include [4.2.2]propellane and its elegant synthesis.<sup>1b</sup> We shall in practice limit ourselves even more in our discussion. [4.3.1]Propellane also has ten carbon atoms, but the "small-ring" interest in propellanes containing cyclopropane rings is the greater, the lower the number of carbon atoms in the skeleton. Thus [3.2.1]propellane, for example, would appear to be more interesting than the [4.3.1]homolog. From the point of view of strain imposed by small rings in a propellane array, there is no doubt that much effort is being expended in the synthesis of propellanes approaching the lower limit chosen arbitrarily. The fact is, at this writing, that [3.2.1]propellane has been prepared while its [2.2.2] isomer has not.

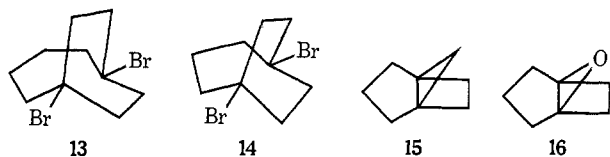
(5) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966); R. L. Cargill, A. C. Miller, D. M. Pond, P. de Mayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, *Mol. Photochem.*, **1**, 301 (1969).



ketone **5** and involves a photochemical Wolff rearrangement of a diazo ketone, affording the mixture of epimeric esters of [3.2.2]propellane which were converted into the *tert*-butyl peresters and thermolyzed at 160° to give [3.2.2]propellane (**9**) in 45% yield, accompanied by about 5% of [3.2.2]propell-6-ene (**10**).

The second route employing **7** and again involving a similar photochemical Wolff rearrangement gives the carboxylic acid derivative **11** of [3.2.2]propellane which upon conversion into **12** affords a starting material for potential ring contraction of the cyclopentanone ring in **12** to a [2.2.2]propellane. This ultimate step has evidently not yet been accomplished.

It is noteworthy from the work of Eaton and Kyi<sup>1b</sup> that both **8** and **9** are thermally stable "to at least 160°." Though the cyclobutane rings do not undergo hydrogenolysis at atmospheric pressure using Adams catalyst, they react quantitatively with bromine in carbon tetrachloride at room temperature, affording the bridgehead dibromides **13** and **14**, respectively.



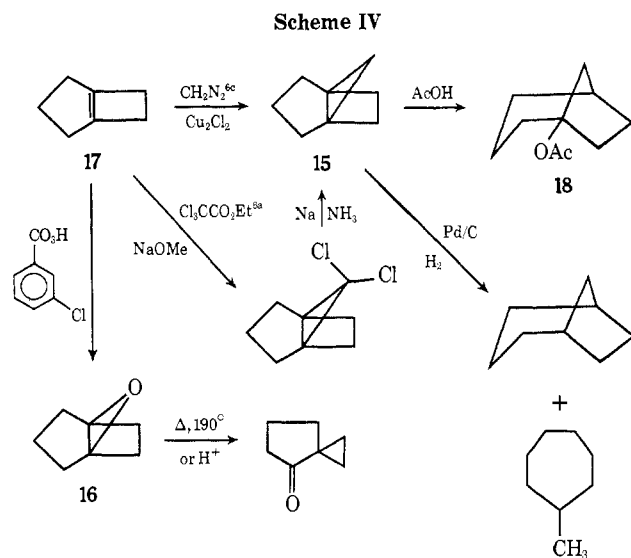
This is reminiscent of the similar case of breaking the conjoining bond in **15**<sup>6a-c</sup> and **16**.<sup>6b,d</sup>

The fact that all the atoms joined to the two bridgehead atoms in small-ring propellanes lie either in one plane or on one side of a plane passing through the

(6) (a) K. B. Wiberg and G. J. Burgmaier, *Tetrahedron Lett.*, 317 (1969); (b) K. B. Wiberg, E. C. Lupton, Jr., and G. J. Burgmaier, *J. Amer. Chem. Soc.*, **91**, 3372 (1969); (c) P. G. Gassman, A. Topp, and J. W. Keller, *Tetrahedron Lett.*, 1093 (1969); (d) K. B. Wiberg, J. E. Hiatt, and G. J. Burgmaier, *ibid.*, 5855 (1968).

bridgehead atoms, *i.e.*, they lie in one hemisphere, has been pointed out explicitly by Wiberg.<sup>6d,7a</sup> Such coercion provides a distortion of tetracoordinate carbons from the tetrahedral, and it is not surprising that Wiberg synthesized compounds such as **15** and **16** as an extension of his studies on bicyclic systems involving cyclopropane and/or cyclobutane rings in which the bridgehead carbon atoms approach  $sp^2$  character.<sup>7b</sup> This coercion obviously introduces further strain into molecules already made up of rings having innate strain themselves.

[3.2.1]Propellane (**15**) has been prepared as shown in Scheme IV. Both syntheses<sup>6a,c</sup> began with the same starting material, **17**, but one is more direct than the other. One group has reported that compound **15** is quite stable thermally; its half-life at 195° is over 20 hr.<sup>6a</sup> Treatment of **15** with dilute acetic acid at room temperature affords **18** in less than 5 min. Its heat of combustion could not be determined readily as it is attacked by oxygen to give a polymer.



The other group of investigators also reported the ease of polymerization of **15**, but it is not made clear whether or not this polymer contains oxygen. The conjoining bond in **15** is readily hydrogenolyzed, and **15** reacts so rapidly with bromine that it may be titrated at -60°.<sup>6c</sup>

The heat of combustion of **16** was measured (60 kcal/mole) and compared with 53 kcal/mole, that of bicyclo[2.1.0]pentane, the most strained moiety in **16**. In **15** it was estimated that the increased strain imposed by further distortion of the bridgehead positions in bicyclo[2.1.0]pentane must be at least 4 and possibly

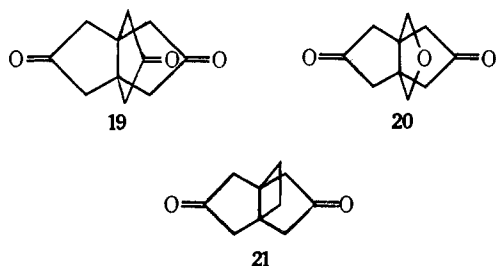
(7) (a) A referee has asked for a picture to clarify this statement. Wiberg<sup>6d</sup> has drawn formulas similar to those drawn in this Account for the pertinent compounds, *e.g.*, [2.2.1]propellane. These do not really comply with the definition in that paper,<sup>6d</sup> which appears, intuitively, reasonable. Thus [2.2.1]propellane would be drawn as



Of course, proof that this structure is correct is unavailable, as this compound has not yet been synthesized. (b) K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 193 (1968).

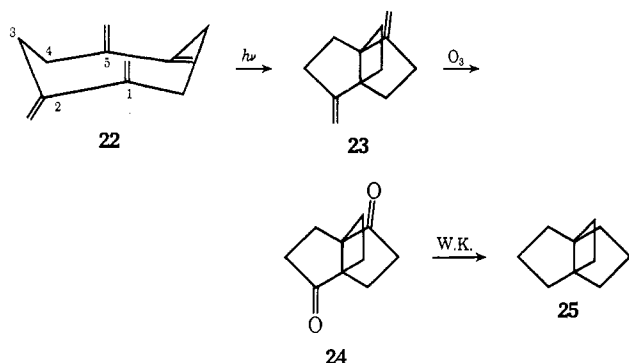
as much as 10 kcal/mole. Since the addition of a cyclopentane ring to the bicyclo[2.1.0]pentane component should increase the strain by 3 kcal/mole, the minimum strain energy of **15** should be 60 kcal/mole.<sup>6b</sup> The oxapropellane **16** is quite stable thermally, but at 190° its half-life was 4 hr and it afforded spiro[2.4]-heptan-4-one, which is also formed very rapidly when **16** is treated with dilute acid.<sup>6d</sup>

Let us now return to a discussion of the potential synthesis of propellanes containing cyclobutane rings by contraction of precursor cyclopentanone rings. Several approaches are of course possible: photochemical extrusion of carbon monoxide or ground-state chemical means, *e.g.*, the Favorski rearrangement. We have seen above that ketone **12** is a potential precursor for the synthesis of [2.2.2]propellane.<sup>1b</sup> In a previous Account<sup>8</sup> we have discussed a number of ketones, *e.g.*, **19**,<sup>9</sup> as a photochemical precursor of **2**.



It was, however, not possible to effect mercury-photo-sensitized decarbonylations of **19** at a temperature low enough to permit isolation of **2**.<sup>10</sup> Three moles of carbon monoxide was obtained along with polymeric material.<sup>11</sup> Similar failure was observed for **20**<sup>9</sup> and **21**.<sup>12</sup>

Borden and coworkers have prepared a diketone, **24**, which they intend to use as a substrate for ring-contraction reactions which might lead to **2**.<sup>13a</sup> Thus 1,2,5,6-tetramethylenecyclooctane (**22**) was irradiated



with a high-pressure mercury lamp in degassed hexane solution. A number of products unrelated to propel-

(8) D. Ginsburg, *Accounts Chem. Res.*, **2**, 121 (1969).

(9) J. Altman, E. Cohen, T. Maymon, J. B. Petersen, N. Reshef, and D. Ginsburg, *Tetrahedron*, **25**, 5115 (1969).

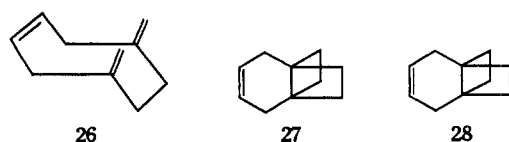
(10) "That the will is infinite, and the execution confined; that the desire is boundless, and the act a slave to limit" (W. Shakespeare, "Troilus and Cressida," Act 3, Scene II).

(11) M. Kaufman, unpublished results from this laboratory.

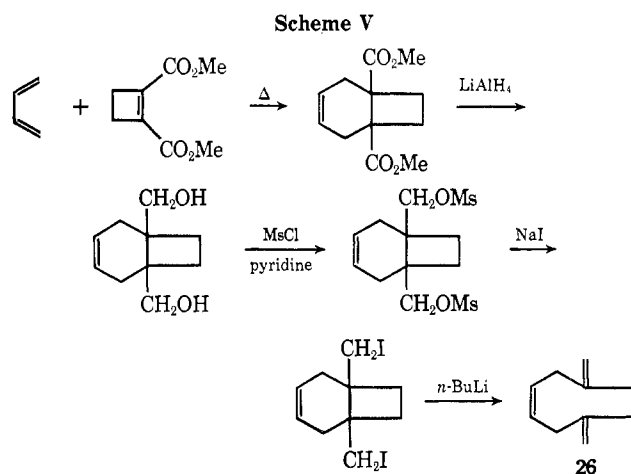
(12) D. Tatarsky, unpublished results from this laboratory.

(13) (a) W. T. Borden, I. L. Reich, L. A. Sharpe, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 3808 (1970); (b) W. T. Borden, L. Sharpe, and I. L. Reich, *Chem. Commun.*, 461 (1970).

lanes are obtained,<sup>13b</sup> as well as **23** in 50% yield, produced by a 1,5-transannular [2 + 2] cycloaddition. The diketone **24**, a positional isomer of **21**, was obtained by ozonolysis of the exocyclic olefinic bonds remaining in **23**. A model shows the excellent geometry of the two double bonds in 1,5 disposition, permitting the formation of **23**. The parallelism of the 1,4-disposed exocyclic double bonds in 4,7-dimethylenecyclooctene (**26**) is seen in a model to be similar to that of the 1,4-disposed bonds in **22** which were shown not to have interacted directly on irradiation.<sup>13b</sup> In the case of **26** as well, these exocyclic bonds did not interact transannularly and the hoped-for **27** was not obtained.<sup>11</sup>

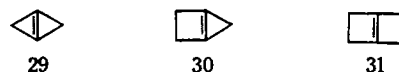


The synthesis of **26** is described in Scheme V.



Although conditions were not found for efficient formation of **27** by irradiation of **26**, there is little doubt that **27**, if prepared, would be stable enough to permit its isolation. We have already seen that its dihydro derivative **8** is quite stable.<sup>1b</sup> A related, undoubtedly more strained product, **28**, has been prepared in very low yield<sup>14</sup> (see below).

Another potentially useful approach to the synthesis of small-ring propellanes appears quite ambitious and perhaps too optimistic in view of the strain expected in the starting materials **29**, **30**, and **31**. If it were



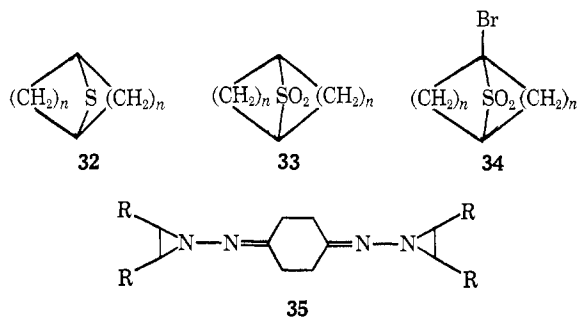
possible to prepare these compounds and treat them with carbene precursors, we might be able to prepare [1.1.1]-, [2.1.1]-, and [2.2.1]propellane, respectively. Alternatively, photochemical additions of ethylene might give [2.1.1]-, [2.2.1]-, and [2.2.2]propellane, respectively.

Corey<sup>15</sup> was interested in preparing compounds of this type and studied the extrusion of the sulfur bridge

(14) L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **93**, 4522 (1971).

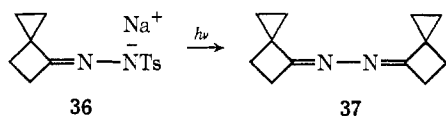
(15) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969).

in compounds of type **32**, **33**, and **34**. In principle,



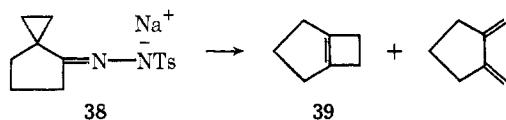
transannular single-bond formation may occur in the former cases and a transannular double bond may form in the latter case. Although for **34**,  $n = 3$ , bicyclo[3.3.0]oct-1(5)-ene was prepared in 81% yield, when  $n = 1$ , none of the desired **31** could be obtained under a variety of experimental conditions.<sup>15</sup> The Ramberg-Bäcklund reaction has, however, been applied more widely in the synthesis of propellanes (see below).

Although Professor Albert Eschenmoser urged us to use compounds of type **35** to prepare **31** or its electronic equivalent, this reaction had not yet been carried out successfully<sup>10, 16</sup> by the time that Wiberg and his coworkers communicated the results of their not-dissimilar approach.<sup>17</sup> Wiberg<sup>6d</sup> had previously shown that irradiation of a suspension of the sodium salt of spiro[2.3]hexan-4-one tosylhydrazone (**36**) in diglyme



gave the azine **37** rather than the hoped-for **31**. Nor was the desired product obtained when a homogeneous solution in dimethyl sulfoxide was irradiated.

When **38**, the higher homolog of **36**, was heated under



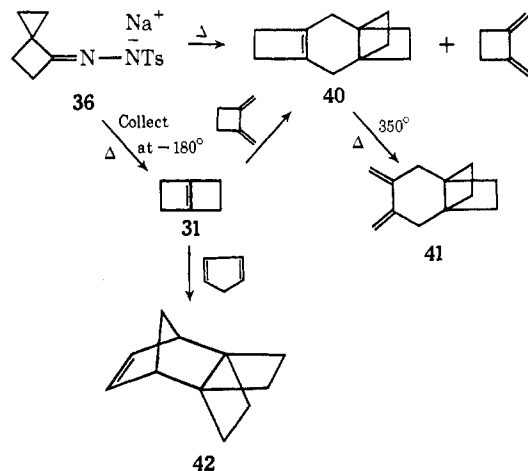
high vacuum without solvent a good yield of **39**, the higher homolog of **31**, was obtained with very little of its ring-opened product 1,2-dimethylenecyclopentane. When these conditions were applied to **36** the volatile products were collected in a trap cooled by liquid nitrogen. An exothermic reaction occurred as the contents of the trap was allowed to warm to room temperature. Two compounds were isolated, 1,2-dimethylenecyclobutane (15% yield) and a dimer (50% yield) (Scheme VI).

The dimer **40** was shown to be the Diels-Alder adduct of bicyclo[2.2.0]hexene (**31**) and 1,2-dimethylenecyclobutane. Note that it is a substituted [4.2.2]-propellane, as is its thermolysis product **41**. That **31** was indeed present in the liquid-nitrogen-cooled reaction mixture before the latter was warmed to room temperature was shown by adding cyclopentadiene.

(16) J. Altman, unpublished results in this laboratory.

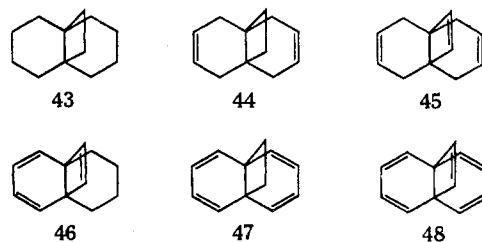
(17) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *J. Amer. Chem. Soc.*, **93**, 246 (1971).

## Scheme VI



This reacted preferentially in a Diels-Alder reaction with **31** and afforded **42**, which is also a propellane which contains two cyclobutane rings. Thus bicyclo[2.2.0]hex-1(4)-ene "has at least moderate thermal stability"<sup>17</sup> and perhaps it may interact *in situ* with molecules other than 1,2-dimethylenecyclobutane and cyclopentadiene to give some of the elusive small-ring propellanes mentioned above. We await Professor Wiberg's further results with impatient anticipation. It appears that his approach, of all those tried heretofore, has the best chance of success for the preparation of the small-ring propellanes. Let us hope that the Troilus postulate<sup>10</sup> will not hold in this case.

Let us now discuss the heterocyclic approach to the synthesis of small-ring propellanes. This has already been mentioned in passing.<sup>15</sup> The most detailed investigations regarding the use of a five-membered sulfur-containing ring as a precursor for a cyclobutane ring have been published by Paquette. This approach has been highly successful in the preparation of the propellanes **45**, **46**, and **48**, containing one four-mem-



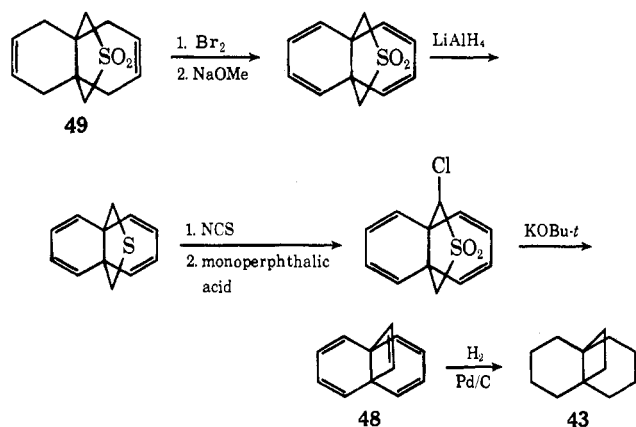
bered ring,<sup>18</sup> although such propellanes were already known. The derivatives **43**, **44**, and **47** were prepared by an alicyclic approach.<sup>2, 19</sup> Paquette's approach,<sup>18</sup> as Corey's,<sup>15</sup> involved the Ramberg-Bäcklund alkaline ring contraction of an  $\alpha$ -halo sulfone.

Though a fuller discussion of these [4.4.2]propellanes is not in order,<sup>4</sup> we shall use the synthesis of **48** as an example to illustrate this ring-contraction method (Scheme VII).<sup>18c</sup> It is also noteworthy that the

(18) (a) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967); (b) *Chem. Commun.*, 681 (1969); (c) *J. Amer. Chem. Soc.*, **91**, 3973 (1969); (d) L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *ibid.*, **93**, 4516 (1971).

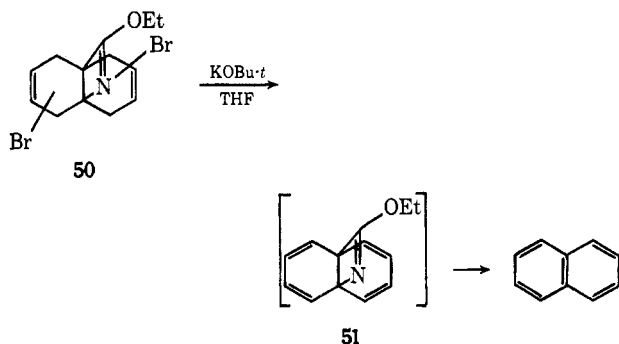
(19) (a) E. Vogel, W. Maier, and J. Eimer, *Tetrahedron Lett.*, 655 (1966); (b) J. J. Bloomfield and J. R. S. Irelan, *ibid.*, 2971 (1966).

Scheme VII



fragmentation of **48** into naphthalene and acetylene is unlikely to occur thermally in a concerted fashion. The compound was in fact thermally stable.<sup>18c</sup> The reaction is photochemically allowed, and irradiation indeed caused fragmentation to occur.<sup>18c</sup> It is of interest also that, in the case of **47**, naphthalene is formed both thermally and photochemically.<sup>20</sup>

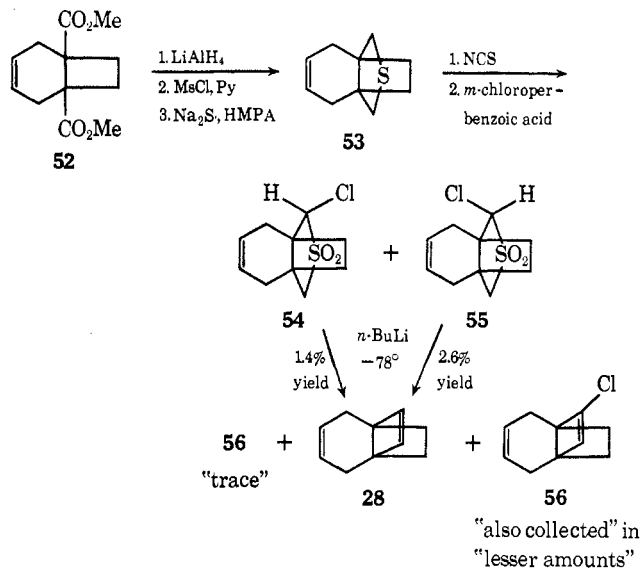
Insofar as **51** is formed on alkaline dehydrobromination of **50**, it is also most unstable thermally, as naphthalene, rather than **51**, is produced.<sup>21</sup>



The results which are more germane to this Account involve precursors other than **49** or **50**. They involve **52** as starting material, and this was produced in a Diels-Alder reaction of 1,2-dimethyl cyclobutenedicarboxylate and butadiene (Scheme V). We have seen that this diester has already featured in the field of propellanes in the synthesis of **26**, nor is this the only time it has been used. Its photochemical addition to olefins will be discussed below (*e.g.*, preparation of **62**). In the present case the dimesylate which appears in Scheme V was treated with sodium sulfide in anhydrous hexamethylphosphoramide, affording the sulfide **53** (Scheme VIII).<sup>14</sup> Chlorination and oxidation afforded a mixture of epimeric  $\alpha$ -chloro sulfones **54** and **55** in the ratio of roughly 2:1. When treated with *n*-butyllithium at low temperature the highly strained [4.2.2]-propella-3,7-diene (**28**) was obtained in extremely low yield.<sup>14</sup>

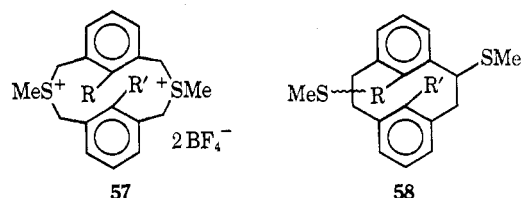
The method of establishing the configuration of the

Scheme VIII



$\alpha$ -chlorine atom in these and other propellane  $\alpha$ -chloro sulfones as well as directive effects in the chlorination of thiapropellanes have been described,<sup>3,14</sup> but fall outside the scope of this review, interesting though they are. Three stereochemical descriptors are required for the unequivocal assignment of the configuration of a given substituent in a propellane which contains three different rings. This too has been discussed (footnote 14 in ref 3).

The last approach we shall discuss also involves ring contraction of a thiacyclopentane ring derivative to a cyclobutane ring. It involves our own work and is discussed last not in the context of "last but not least" but rather in the context of "last and least successful." Yet it includes the preparation of several small-ring propellanes and some strain-relieving acrobatics of these compounds.<sup>22</sup> The approach follows in the footsteps of Boekelheide and his coworkers who used it in the synthesis of certain metacyclophanes.<sup>23</sup> To be sure, in their substrates the formation of a carbanion  $\alpha$  to a sulfonium ion was easily effected as the  $\alpha$  carbon is at the same time benzylic (*cf.* **57** *en route* to **58**).



Even though this was not the case in our substrates,<sup>22</sup> we hoped that the analogy **60**  $\rightarrow$  **61** might hold. In the event it did not, but this is putting the end before the beginning. In order to test whether **60** may be converted into **61** it is first necessary to prepare 3-thia-[3.2.2]propellane (**59**).

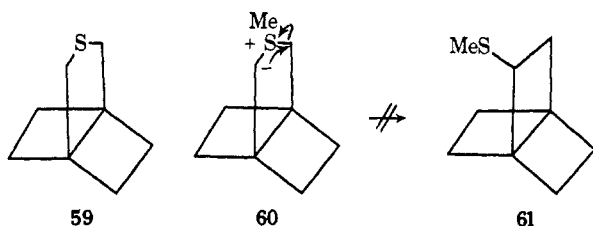
We return to our popular starting material, 1,2-

(20) J. Altman, E. Babad, D. Ginsburg, and M. B. Rubin, *Israel J. Chem.*, **7**, 435 (1969).

(21) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, *J. Amer. Chem. Soc.*, **93**, 152 (1971).

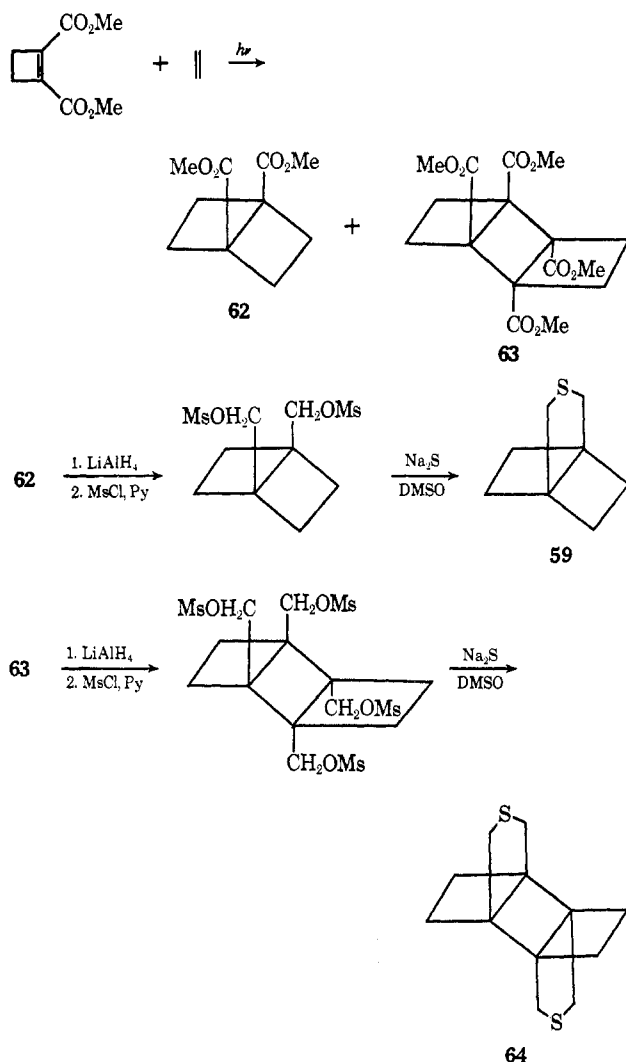
(22) I. Lantos and D. Ginsburg, *Tetrahedron*, **28**, 2507 (1972).

(23) (a) R. H. Mitchell and V. Boekelheide, *Tetrahedron Lett.*, 1197 (1970); (b) V. Boekelheide and P. H. Anderson, *ibid.*, 1207 (1970).



dimethyl cyclobutenedicarboxylate. Although it was added photochemically to a number of olefins (as well as to itself) we shall discuss only its product of photoaddition with ethylene (**62**)<sup>22,24</sup> and its dimer **63**<sup>22,25</sup> (Scheme IX). Reduction of **62** and **63** afforded a diol

Scheme IX



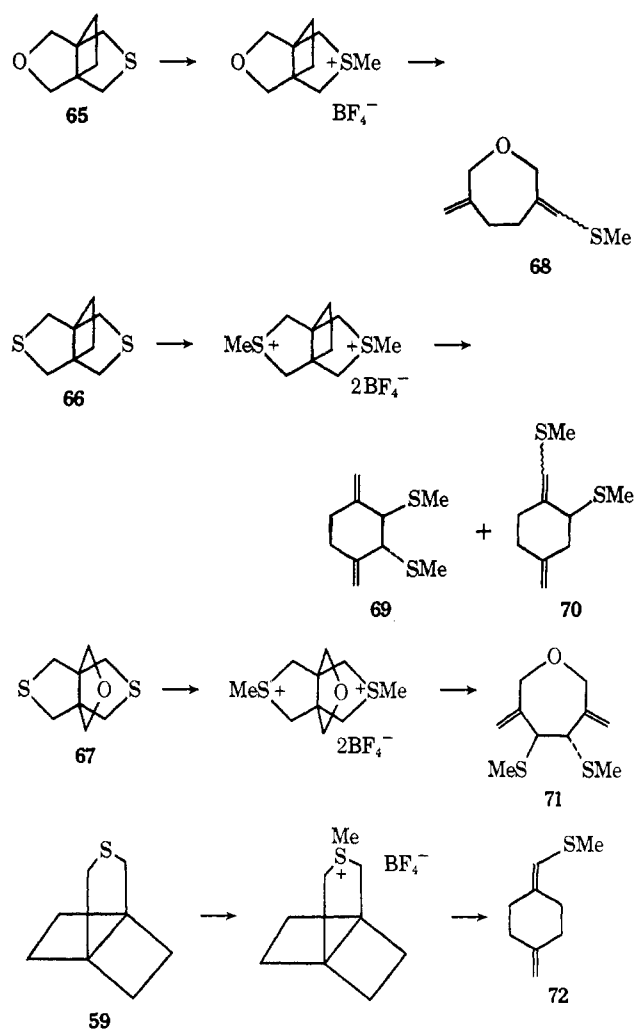
and tetrol which were converted into a dimesylate and a tetramesylate, respectively. The desired 3-thia-[3.2.2]propellane (**59**) was obtained from the former, and the pentacyclic dithiapropellane **64** of the same structural type was obtained from the latter. These as well as other thiapropellanes, **65–67**, which were used as model compounds, were converted into their respective methylsulfonium fluoroborates and the latter were then subjected to the action of bases (Scheme X).<sup>22</sup>

The common denominator in all of these reactions of

(24) D. C. Owsley and J. J. Bloomfield, *J. Amer. Chem. Soc.*, **93**, 782 (1971).

(25) E. Vogel, O. Roos, and K. H. Disch, *Justus Liebigs Ann. Chem.*, **653**, 55 (1962).

Scheme X



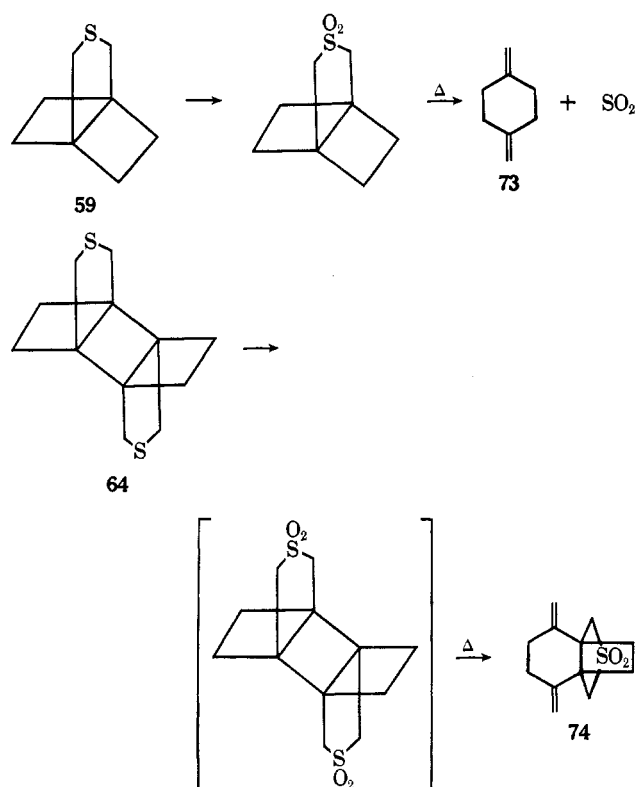
sulfonium salts is that they took the course leading to compounds in which two exocyclic double bonds had been formed rather than to the desired ring contractions.<sup>10</sup> The sulfones of **59** and **64** were prepared and thermolyzed. Here also compounds **73** and **74** similar in structure to the products described in Scheme X were obtained. Nor did low-temperature photolysis of the sulfone of **59** lead to the desired [2.2.2]propellane (**2**).<sup>22</sup>

It is now necessary to intersperse an apparent tangent concerning the not fully understood mechanism of the Stevens rearrangement, as this will form a bridge to the theoretical results and predictions of Hoffmann and Stohrer.<sup>26</sup> Ionic species have been written as intermediates in the Stevens rearrangement.<sup>27</sup> Recent papers have raised the possibility that radicals may be intermediates. CIDNP effects have been observed in the Stevens rearrangement of sulfonium ylides<sup>28a</sup> as well as in that of amine imides.<sup>28b</sup> In the latter case,

(26) (a) R. Hoffmann and W. D. Stohrer, *J. Amer. Chem. Soc.*, in press; (b) W. D. Stohrer and R. Hoffmann, *ibid.*, **94**, 779 (1972). We are grateful to Professor Hoffmann for giving us copies of these manuscripts before publication.

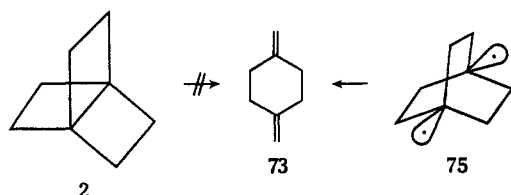
(27) (a) J. H. Brewster and M. W. Kline, *ibid.*, **74**, 5179 (1952). (b) S. H. Pine, *Org. React.*, **18**, 406 (1970).

(28) (a) U. Schöllkopf, G. Ostermann, and J. Schossig, *Tetrahedron Lett.*, 2619 (1969); (b) R. W. Jemison and D. G. Morris, *Chem. Commun.*, 1276 (1969); (c) H. P. Benecke and J. H. Wikel, *Tetrahedron Lett.*, 3479 (1971); (d) J. Jacobus, *Chem. Commun.*, 709 (1970).



intermediate radicals have been trapped by scavengers.<sup>28c</sup> A warning has, however, been published regarding the possibility that such CIDNP effects may be artifacts and therefore cannot be taken as conclusive evidence for the actual intermediacy of radicals in the rearrangement step proper. The warning appears justified for the particular case cited.<sup>28d</sup>

Hoffmann and Stohrer<sup>26</sup> have discussed the electronic structure of [2.2.2]propellane and other small propellanes. They point out that the  $2_s + 2_s$  fragmentation of **2** to give **73** is forbidden, but the conversion of the diradical **75** into **73** is symmetry allowed and indeed



may be thermodynamically favored. The intramolecular recombination of **75** to afford **2** is also a symmetry-forbidden process. Their<sup>26</sup> CNDO/2 and INDO calculations predict that **2** is more stable than **75**. All this taken together leads to the synthetic consequence that if **75** were generated it would not constitute an intermediate *en route* to **2** but, rather, it would be likely to undergo the thermodynamically favored fragmentation leading to 1,4-dimethylenecyclohexane (**73**).

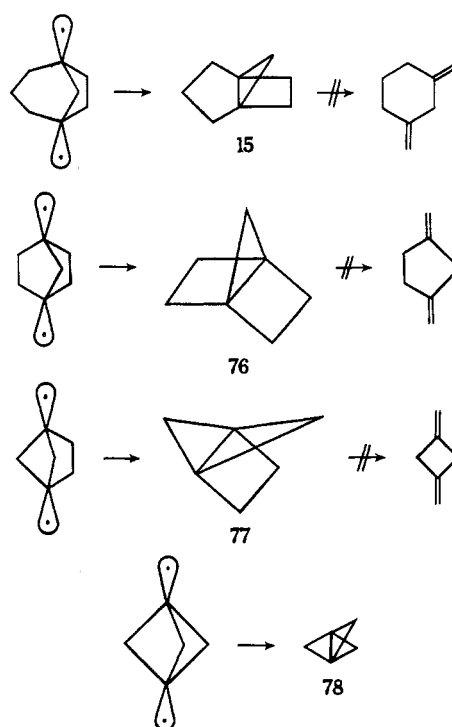
The foregoing discussion does not, of course, prove that we are dealing with radical intermediates in certain steps of the Stevens rearrangements listed in Scheme X. We have nevertheless been rather successful in synthesizing compounds containing exocyclic methylene

groups, *e.g.*, **68–74**, rather than attaining the much desired and highly elusive **2**.

Stohrer and Hoffmann have also predicted<sup>26b</sup> on the basis of their calculations that small-ring propellanes are susceptible to acid and to radical attack at the conjoining bond (acid rearrangements of propellanes are known even when the rings are all five membered or six membered).<sup>9</sup> Their calculations show, however, that small-ring propellanes should be relatively inert to the action of base. We are aware of a number of experimental approaches now in progress which should test the possibility of synthesis of small-ring propellanes employing basic reagents at their last stages.<sup>29</sup>

We have emphasized, perhaps undeservedly, attempts to synthesize [2.2.2]propellane. Stohrer and Hoffmann<sup>26b</sup> also devote more space to the discussion of this compound because of their interest in its possibilities for through-bond coupling. Scheme XI sum-

Scheme XI



marizes their conclusions for [3.2.1]-, [2.2.1]-, [2.1.1]-, and [1.1.1]propellanes, **15**, **76**, **77**, and **78**, respectively. They believe that the species written as diradicals are nothing but stretched conformations of the collapsed respective  $\sigma$ -bonded propellanes. In contrast to the diradical **75** (which is actually an isomer of **2** and not its unstable conformation), which is allowed to undergo the  $2_s + 2_s$  fragmentation to give 1,4-dimethylenecyclohexane (**73**), analogous fragmentations of **15**, **76**, and **77** to give 1,3-dimethylenecycloalkanes are forbidden as shown in Scheme XI.

The above theoretical conclusions are supported by experimental results which are cited.<sup>26b</sup>

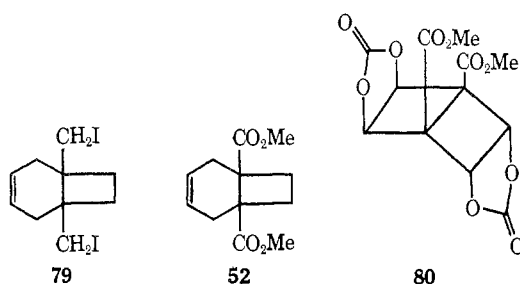
**Miscellaneous.** For the sake of completeness several other points formally belong to or are related to the

(29) *Inter alia*, H. Bohm, work in progress in this laboratory.

subject and scope of this Account. Several heterocyclic propellanes, having less than ten carbon atoms in their skeleton, have been described.<sup>9,30</sup> Calculations regarding the type of bonding in the central, conjoining, bond of **2** are in progress.<sup>31</sup>

Two photodimers, that of 2-methoxynaphthalene<sup>32</sup> and that of biphenylene,<sup>33</sup> have been alleged to contain a substituted [2.2.2]propellane core. The first claim<sup>32</sup> has already been retracted. The second claim,<sup>33</sup> like the first, questioned an earlier literature report on the specific reaction concerned. This does not mean, of course, that the second report<sup>33</sup> is incorrect.

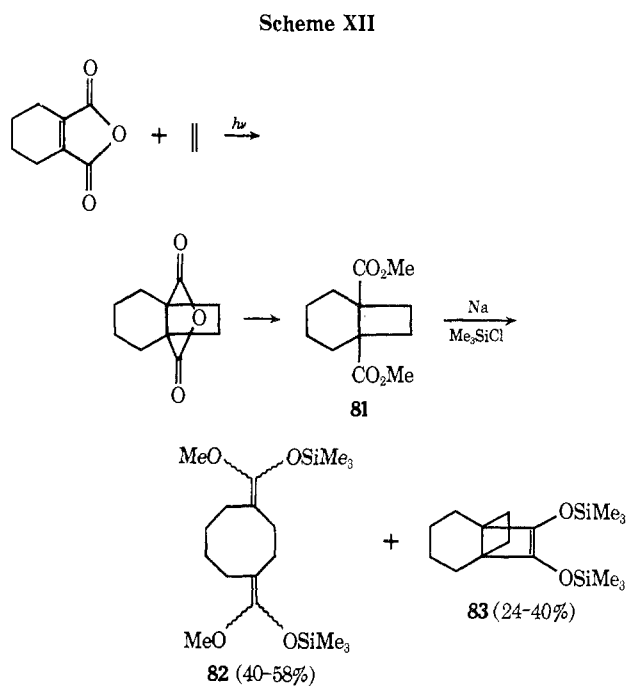
Finally, it is not surprising that Wurtz conditions or standard acyloin reaction conditions or those concurrently employing trimethylchlorosilane did not afford a [4.2.2]propellane derivative when applied to **79** or **52**, respectively.<sup>11</sup> Nevertheless, it would be interesting to try the latter reaction on **80** whose



synthesis has recently been reported.<sup>34,35</sup> However, a preprint of a paper received after this Account was submitted contains material much related to this point.<sup>36</sup>

The diester **81** (dihydro **52**) was prepared by photochemically sensitized addition of ethylene to 3,4,5,6-tetrahydrophthalic anhydride followed by esterification. When **81** was submitted to the conditions of the acyloin condensation using sodium in the presence of trimethylchlorosilane, a mixture of the propellane **83** and the cyclooctane derivative **82** was obtained (Scheme XII).

The acyloin **84** was obtained by methanolysis of freshly distilled **83** under nitrogen with dry oxygen-free methanol. Scheme XIII summarizes the reactions of the acyloin. Prolonged treatment of **83** with methanol or rapid treatment by using a catalytic amount of



acid adds methanol to the central conjoining bond. If acid is used in tetrahydrofuran solution both **83** and **84** give **86** by corresponding addition of water to the conjoining bond. Finally **84** may be oxidized to give another C-10 propellane, **87**. This type of ring opening has already been discussed.<sup>5,37</sup>

*It is a pleasure to express my gratitude for stimulation to all those authors whose papers concerning small-ring propellanes have been cited in this Account. It has been a pleasure to be associated with Dr. Ivan Lantos, who has borne the brunt of the attempts to synthesize **2** in our laboratory. Dr. Morris Kaufman and David Tatarsky have also contributed.*

(30) (a) E. Buchta and S. Billenstein, *Justus Liebig's Ann. Chem.*, **702**, 38 (1967); (b) E. Buchta and A. Kröniger, *Chimia*, **22**, 430 (1968); (c) K. Weinges and A. Wiesenhütter, *Justus Liebig's Ann. Chem.*, **746**, 70 (1971).

(31) Footnote 13 in J. M. Schulman and G. J. Fisanick, *J. Amer. Chem. Soc.*, **92**, 6653 (1970).

(32) M. Sterns and B. K. Selinger, *Aust. J. Chem.*, **21**, 2131 (1968).

(33) N. L. Goldman and R. S. Ruden, *Tetrahedron Lett.*, 3951 (1968).

(34) J. Tancredi and M. Rosenblum, *Synthesis*, 219 (1971).

(35) It is all too easy to transfer one's own blame to, say, a typesetter. However, footnote 5 in ref 8 must be corrected herein. Despite *Ecclesiastes*, Chapter 1, Verse 2, it is *Ecclesiastes* and not *Ecclesiasticus* that must be cited there as well.

(36) J. J. Bloomfield, R. A. Martin, and J. M. Nelke, *J. Chem. Soc., Chem. Commun.*, 96 (1972). We thank Professor Bloomfield for this information which can at least be attached at the end, although it includes aspects which are reminiscent of the behavior of other small-ring propellanes<sup>5</sup> and might have been discussed earlier in the paper.

(37) This preprint<sup>36</sup> also cites unsuccessful attempts to prepare a [3.2.2]propellane derivative from dimethyl bicyclo[3.2.0]heptane-1,5-dicarboxylate (Scheme XIII, **88**): D. C. Owsley and J. J. Bloomfield, *Org. Prep. Proced. Int.*, **3**, 61 (1971); *J. Org. Chem.*, in press.