Acknowledgment. This research was partially supported by a grant from the Center for Materials Research of the University of Maryland.

Registry No.—1, 10264-29-6; **4a,** 7501-79-3; **4b,** 57969-34-3; **4c,** 628-02-4; **4d,** 3418-05-1; **4e,** 628-62-6; **4f,** 79-05-0; **4g,** 10264-24-1; **7** isomer 1, 57969-35-4; **7** isomer 2, 57969-36-5; hexanal, 66-25-1.

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(10) The exchange conditions were essentially those used for a series of fatty acids. See P. E. Pfeffer and L. S. Silbert Abstracts, Middle Atlantic Regional Meeting of the American Chemical Society, Wilkes-Barre, Pa., April 23–26, 1974, paper no. 188.
(11) All photolysis reactions were accompanied by the formation of extensive amounts of polymeric materials. Irradiation of cyclohexane alone afforded small amounts of **8** as reported previously but no **9, 10,** or **11.**
(12) The formations of these secondary products is predictably inefficient. For example, the photoreduction of acetone in dioxane[9a] affords the alcohol in only 16% yield. The addition product of 1-octene to dioxane is produced in 5% yield (27% when acetone sensitizer was employed).[13] In our hands irradiation of acetaldehyde in cyclohexane gave a 7% yield of **11** (by GLC).
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Cyclopropane Ring Opening with Pyridine Hydrochloride

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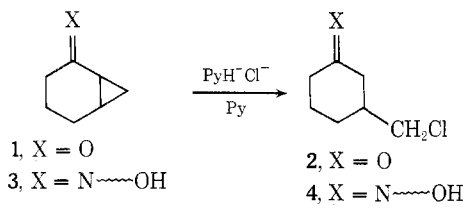
Two electron-withdrawing groups will make a cyclopropane derivative susceptible to suffer ring opening by nucleophilic attack[1-2] while monosubstituted cyclopropane rings require a strong nucleophile (like mercaptide ion[3]) or very strained systems.[4-6]

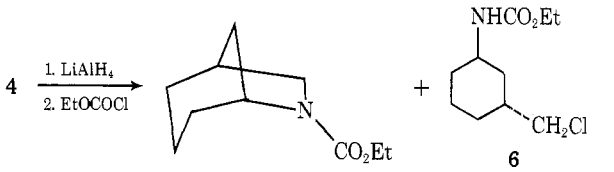
We have found that pyridine hydrochloride can produce the ring cleavage of bicyclo[4.1.0]heptan-2-one (**1**) and of its oximes **3**. When **1**[7] was refluxed in dry pyridine in the presence of pyridine hydrochloride for 20 h a high yield of 3-chloromethylcyclohexanone (**2**) was obtained.



1, X = O
3, X = N⟋OH
2, X = O
4, X = N⟋OH

Under the same conditions a syn and anti mixture of **3** furnished a syn and anti mixture of **4**. Traces of **2** were also found if the reaction medium was not perfectly dry. Interestingly, only **4** was obtained when the oximation of **1** was accomplished according to the usual procedure using hydroxylamine hydrochloride in ethanolic pyridine solution.

The structure of **4** was deduced from spectral data (ir, NMR, MS). Confirmatively *N*-carbethoxy-6-azabicyclo[3.2.1]octane (**5**) was recognized as one of the two products obtained by the lithium aluminum hydride reduction of **4** followed by treatment with ethyl chlorocarbonate; the other one was the chlorourethane **6**. An authentic sample of **5** was prepared from *m*-aminobenzoic acid according to the reported procedure.[8] **6** and its cis isomer were obtained also by catalytic hydrogenation of **4**.



5 6

We think that at least two features of the compounds **1** and **3** are determinant in the nucleophilic cyclopropane ring opening: the conjugation of the three-membered ring with a π system and the participation of the cyclopropane of a more strained system. According to this assumption bicyclo[4.1.0]heptane was recovered unchanged after an analogous treatment with pyridine hydrochloride in pyridine. In addition we found both cyclopropyl methyl ketone and its oximes to react quite slowly under the conditions used for the cleavage of **1** and **3**.

The peculiarity of pyridine hydrochloride[9] in such a hydrochloric acid addition to a cyclopropane ring appears clearly. Bicyclo[4.1.0]heptane was reported to react with 12 M HCl in equimolar ratio at room temperature. After 6 h a mixture of olefins and chlorides was obtained.[10] Actually we found that both **1** and **3** remained unreacted under the same conditions. However, α-cyclopropyl ketones are known to give ring cleavage in HBr–AcOH at room temperature.[11]

The ring opening is selective. The C_1–C_7 bond cleavage observed is consistent with a previous report according to which this bond is the weakest because of its large orbital overlap with the adjacent π system.[12] This selectivity, the high yield obtained, and the possibility of the hydroxyiminic function preservation can get this sequence of reactions regarded as a useful synthetic route to the azabicycloalkanes.

Experimental Section

General. GC analyses were performed on a Carlo Erba Fractovap GI gas chromatograph equipped with a column of Apiezon L (60 m × 0.25 mm) and on a Carlo Erba Fractovap GV gas chromatograph equipped with a column of 4% OV 17 (2 m × 3 mm). Infrared spectra were obtained on a Perkin-Elmer 257 Infracord instrument. Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R32 90-MHz spectrometer, using Me_4Si as an internal standard. Mass spectra were obtained on an AEI-MS12 spectrometer at an ionization potential of 70 eV. GC–MS spectra were obtained using a column of 2% OV 17 (2 m × 2 mm).

Oximes of Bicyclo[4.1.0]heptan-2-one (3). A solution of 2.2 g (20 mmol) of **1**,[7] 2.1 g (30 mmol) of hydroxylamine hydrochloride, and 3.2 g of $CH_3COONa{\cdot}3H_2O$ in 16 ml of ethanol was heated under reflux for 6 h. To the cooled mixture a saturated NaCl solution was added. Extraction with ether followed by evaporation afforded a residue of 1.9 g (76%) of **3**: mp 83–86 °C (petroleum ether); the GC analysis showed two partially overlapped peaks of similar areas, whose GC–MS spectra were nearly identical; ir (CCl_4) 3600, 3250, 3090, 3010 cm^{-1}; NMR (CCl_4) δ 0.4–1.1 (m, 3

H), 1.1–2.7 (m, 7 H), 8.5 (s, 1 H); MS *m/e* 125 (parent and base peak).

Treatment of 1 with Py·HCl in Py. A mixture of 1.75 g (16 mmol) of 1 and 3.7 g (32 mmol) of pyridine hydrochloride (freshly prepared[13]) in 40 ml of dry pyridine was refluxed during 20 h. After extraction, washing with saturated NaCl solution, drying, and evaporation of the organic phase, 1.76 g (76%) of **2** was obtained: bp 103–107 °C (15 mm);[14] ir (CCl_4) 1720 cm^{-1}; NMR (CCl_4) δ 3.45 (m, CH_2Cl); MS *m/e* 148 (isotopic), 146 (parent), 97 (base peak). Treatment of the crude ketone with hydroxylamine hydrochloride afforded exclusively **4**.

Treatment of 3 with Py·HCl in Py. As described above, 2.0 g (16 mmol) of **3** was treated with 3.7 g (32 mmol) of pyridine hydrochloride in 40 ml of pyridine to give 2.0 g (77%) of **4**: bp 80–85 °C (1 mm);[14] NMR (CCl_4) δ 3.45 (m, CH_2Cl); MS *m/e* 163 (isotopic), 161 (parent), 126 (base peak).

Treatment of Bicyclo[4.1.0]heptane, Cyclopropyl Methyl Ketone, and Cyclopropyl Methyl Ketone Oximes with Py·HCl in Py. The title compounds, obtained by WBL, Fluka, and according to a reported procedure,[15] respectively, were treated as above. NMR and GC analyses showed that none of them suffered a detectable transformation.

Treatment of 1 with NH_2OH·HCl in the Presence of Py. A mixture of 2.2 g (20 mmol) of 1 and 2.1 g (30 mmol) of hydroxylamine hydrochloride in 15 ml of ethanol and 15 ml of pyridine was refluxed for 3 h. Water was added and the solution was extracted with ether. Upon washing with 2 N HCl and water, drying, and evaporation of the organic phase 480 mg (15%) of **4** remained as a yellowish oil, purity 85% (GC); the remaining 15% was the ketone **2**.

Treatment of 2 and 4 with 12 M HCl. An equimolar mixture of **2** or **4** and 12 M HCl was shaken for 6 h at room temperature. After the usual work-up the GC and ir analyses showed only the presence of **2** or **4**, respectively.

LiAlH$_4$ Reduction of 4. A solution of 1.92 g (12 mmol) of **4** in 30 ml of anhydrous ethyl ether was added dropwise to a refluxing mixture of 1.8 g (48 mmol) of lithium aluminum hydride in 40 ml of ethyl ether. After 3 h of reflux, work-up, and treatment with ethyl chloroformate,[16] the GC of the urethanes mixture showed two peaks. The product with the shorter retention time (55%) was recognized as **5** on the basis of the GC and GC–MS comparison with an independently prepared sample,[8] MS *m/e* 183 (parent), 140 (base peak). The other product (45%) showed the same retention time and fragmentation pattern as the chlorourethane **6**, one of the two isomers obtained in the catalytic reduction of **4** (see below), MS *m/e* 221 (isotopic), 219 (parent), 90 (base peak).[17]

Catalytic Hydrogenation of 4. A solution of 2.1 g (13 mmol) of **4** in 13 ml of acetic acid (distilled on $KMnO_4$), 6 ml of water, and 2.2 ml of concentrated HCl was hydrogenated at 50 psi at room temperature for 20 h in the presence of 150 mg of PtO_2. The filtrate was extracted and the crude product was treated with ethyl chloroformate[16] to afford 1.96 g (69%) of a 57:43 mixture of **6** and its cis isomer: bp 135–140 °C (1 mm);[14] ir (CCl_4) 3450, 1725 cm^{-1}; NMR (CCl_4) δ 1.2 (t, CH_3 of Et), 4.0 (q, CH_2 of Et), 4.6 (broad, NH), 3.35 (m, CH_2Cl); MS *m/e* 221 (isotopic), 219 (parent), 90 (base peak).[17] If the crude product of hydrogenation was made alkaline and allowed to stand at room temperature for several hours before the treatment with ethyl chloroformate, only **5** and **6** were detected.

Acknowledgment. National Research Council (CNR) Rome is gratefully acknowledged for partial financial support and Mr. A. Santi for mass spectra recording.

Registry No.—**1**, 5771-58-4; **2**, 57719-96-7; *syn*-**3**, 57719-97-8; *anti*-**3**, 57719-98-9; *syn*-**4**, 57719-99-0; *anti*-**4**, 57720-00-0; **5**, 57720-01-0; **6**, 57720-02-2; **6**, cis isomer, 57720-03-3; hydroxylamine hydrochloride, 5470-11-1; pyridine hydrochloride, 628-13-7; lithium aluminum hydride, 16853-84-3.

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A New Method for the Synthesis of Biscyclododecylidene Cycloalkylidene Triperoxides

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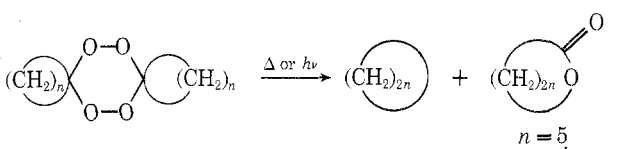
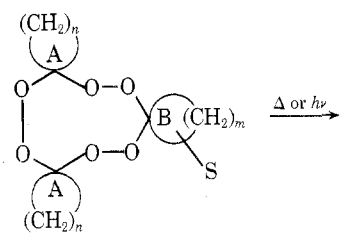
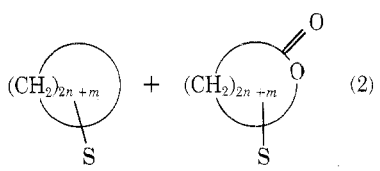
Story and co-workers[1] discovered that the thermal and photochemical decomposition of cyclic ketone peroxides produces macrocyclic lactones and hydrocarbons. This can be illustrated by eq 1 and 2.



(1)



II



(2)

Easy access to the appropriate precursor peroxides constitutes a key step for the synthesis of the desired macrocyclic compounds. Availability of peroxides of type II where $n \neq m$ will obviously broaden the scope of the reaction in terms of varying the size and introduction of the desired functionality in the macrocyclic ring.

A limited number of mixed peroxides of type II have earlier been synthesized by Criegee[2] and the process has been extended by Oldekop[3] and co-workers. Story and co-workers[4] also utilized Criegee's[2] procedure for synthesizing several mixed peroxides. Criegee's procedure essentially consists of treating 1,1′-dihydroperoxydicycloalkyl peroxide with an excess of the appropriate ketone in the presence of anhydrous $CuSO_4$ (eq 3) over an extended reaction period of 1–2 weeks.

Criegee's procedure suffers from the drawback that it

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