Ring Enlargements by Thallium(III) Oxidation of Double Bonds. Applications to Adamantane Systems

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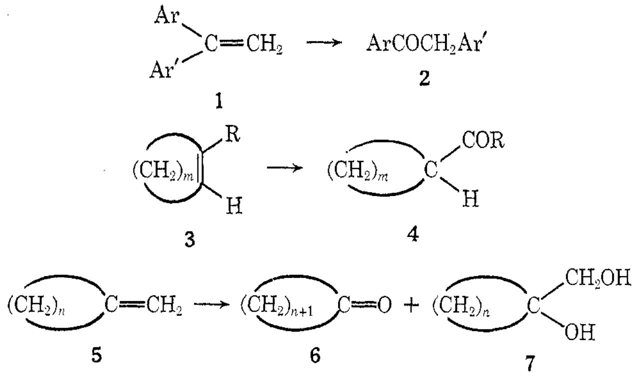
The synthetic potential of a new homologization procedure based on the thallium(III) oxidation of exocyclic olefins was explored. The four- and five-membered ring systems, **9**, **10**, **11**, and **13**, gave moderate yields of ring-expanded ketones. The method was found to suffer from incompleteness of oxidation on one hand and the sensitivity of the ketone products toward further oxidation on the other. In the case of 2-methyleneadamantane, a six-membered system less prone to ring expansion, side reactions predominated, and unsatisfactory yields of 4-homodiamantanone (**15**) were obtained. The high ratio of methylene over methine migration (85:1) in the oxidation of 2-methylenenorbornane (**13**) to **29** and **30** suggests the intermediacy of 2-*exo*-hydroxy-2-thallomethylnorbornane (**35**) rather than its endo epimer, **36**.

Rearrangements characterize the reaction of olefins with thallium(III) salts.[2–6] Deoxybenzoins (**2**) are obtained from 1,1-diarylethylenes (**1**),[3] and cycloalkanes (**3**) give ring-contracted aldehydes and ketones (**4**).[3–6] Recently, Abley, Byrd, and Halpern have shown that exocyclic olefins (**5**) undergo ring expansion by thallic oxidation in aqueous solution.[6]

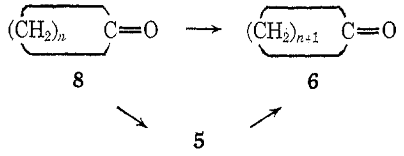
We wished to explore the potential of this reaction as an alternative method for ring enlargement of cyclic ketones, **8** → **6**. Of the homologation methods normally employed, the reaction with diazomethane[7] is the most direct, but often gives poor results with cyclobutanones[8,9] and cyclopentanones.[10,11] These either are unreactive, or give complex mixtures of mono- and polyhomologated products.[7,8,10,11] The Tiffeneau–Demyanov procedure involves three steps: cyanohydrin formation, reduction to an amino alcohol, and nitrous acid deamination.[12] Because of unfavorable equilibria, the formation of cyanohydrins from ketones is often unfavorable. While methods are now available which overcome this drawback,[13,14] the overall yields of homologated ketones (**8** → **6**) are seldom good.[12–14]



a, $n = 3$; **6**:**7** = 8:2

b, $n = 4$; **6**:**7** = 8:2

c, $n = 5$; **6**:**7** = 3:7



Since the methylenecycloalkanes (**5**) can be obtained from ketones **8** by the Wittig reaction,[15] the conversion **8** → **6** using thallium oxidation would be a two-step process. However, the procedure used by Halpern, *et al.*[6] (oxidation of olefin with thallic perchlorate in 0.1–1 *M* aqueous perchloric acid) was designed for analytical and kinetic purposes and is unsuitable for synthetic work on larger systems with very low water solubility.

Results

Five representative olefins, **9**–**13**, were chosen for study. These included 3-methylenecyclobutanecar-

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[1] Sabbatical leave at Princeton University, 1971–1972.

[2] A. McKillop and E. C. Taylor, *Chem. Brit.*, 4 (1973).

[3] A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Lett.*, 5275 (1970); A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Amer. Chem. Soc.*, **95**, 3635 (1973).

[4] J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971).

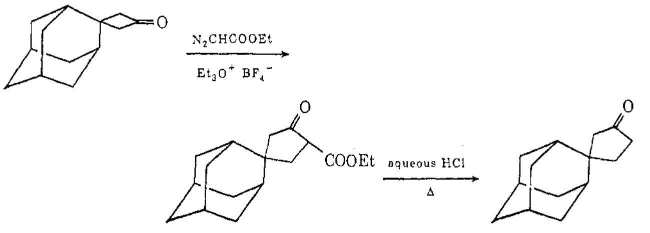
[5] E. J. Corey and T. Ravindranathan, *Tetrahedron Lett.*, 4753 (1971).

[6] P. Abley, J. E. Byrd, and J. Halpern, *J. Amer. Chem. Soc.*, **95**, 2591 (1973); also see J. E. Byrd and J. Halpern, *ibid.*, **95**, 2586 (1973).

[7] C. D. Gutsche, *Org. React.*, **8**, 364 (1954); C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, Chapter IV.

[8] J. Jaz and J. P. Davreux, *Bull. Soc. Chim. Belg.*, **74**, 370 (1965).

[9] This problem can be circumvented by employing diazoacetic ester and triethyloxonium fluoroborate catalyst: W. L. Mock and M. E. Hartman, *J. Amer. Chem. Soc.*, **92**, 5767 (1970). The ring-expanded β-keto ester can be hydrolyzed and decarboxylated to the parent ketone. By this procedure, we have carried out the following homologation in 94% yield.



[10] A. P. Giraitis and J. L. Bullock, *J. Amer. Chem. Soc.*, **59**, 951 (1937); J. T. Lumb and G. H. Whitham, *Tetrahedron*, **21**, 499 (1965).

[11] (a) R. R. Sauers and R. J. Tucker, *J. Org. Chem.*, **28**, 876 (1963); (b) G. Fachinetti, F. Pietra, and A. Marsili, *Tetrahedron Lett.*, 393 (1971).

[12] P. A. S. Smith and D. R. Baer, *Org. React.*, **11**, 157 (1960); ref 7b, Chapter III.

[13] U. Schöllkopf and F. Gerhart, *Angew. Chem., Int. Ed. Engl.*, **7**, 805 (1968); *Tetrahedron Lett.*, 6231 (1968).

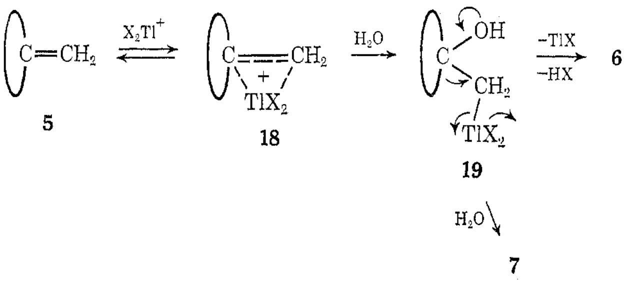
[14] H. Gerlach, *Helv. Chim. Acta*, **55**, 2962 (1972).

[15] U. Schöllkopf in "Newer Methods of Preparative Organic Chemistry," Vol. 3, W. Foerst, Ed., Academic Press, New York, N. Y., 1964, p 111; A. Maercker, *Org. React.*, **14**, 270 (1965).

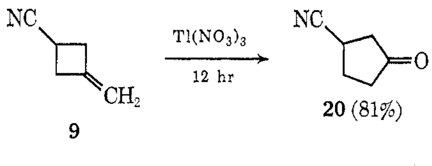
bonitrile (**9**)[16] and 2-methylenenorbornane (**13**)[17] as model substrates for four- and five-membered ring systems. 2-Methyleneadamantane (**12**),[18] a six-membered ring example, was expected to be less prone toward ring expansion. The conversion of adamantanone (**14**) to 4-homoadamantanone (**15**) has already been carried out by diazomethane[19] and Tiffeneau–Demyanov[20] procedure, so that a direct comparison of all three methods was possible. The ring-expanded ketones, **16** and **17**, from the two tetracyclic adamantane derivatives, **10** and **11** (obtained from the ketones **21**[21] and **22**[22]), were desired in order to prepare the parent hydrocarbons.

1,2-Dimethoxyethane was chosen as cosolvent to increase olefin solubility and decrease reaction time,[23] but studies of the reaction conditions indicated that a mixed solvent containing a large excess of water gave better results. The effect of other parameters, like acidity and reaction time, was also investigated, but a truly comprehensive search for the best reaction conditions was not carried out; it might be possible to improve the results reported here. However, our experience in difficult cases was not encouraging in this respect.

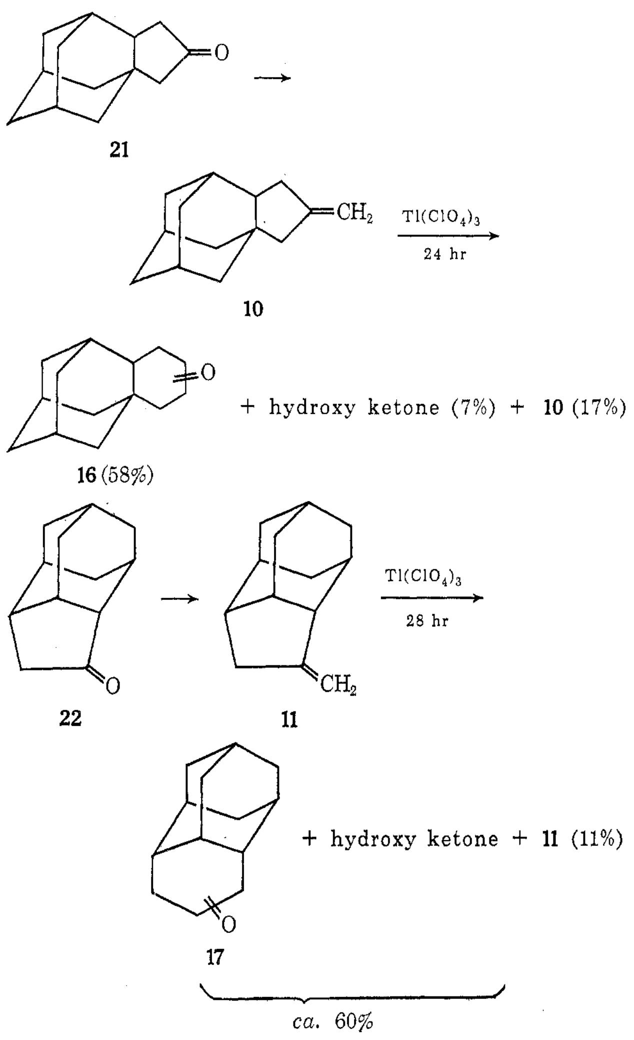
The mechanism of these reactions generally involves initial formation of a cyclic thallonium ion (**18**), followed by trans attack by water to give an intermediate **19** in which the thallium can function as leaving group.[4,6,24]

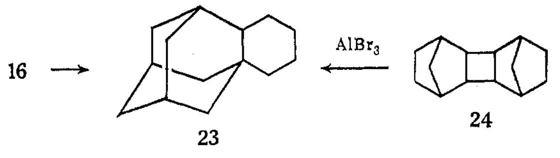


Nucleophilic displacement by water on **19** can give diol **7**, but, in favorable instances where ring strain can be relieved, rearrangement to ring-expanded ketone **6** predominates. Thus, methylenecyclobutanecarbonitrile (**9**) gave 3-cyanocyclopentanone (**20**) as the only product observed.



The expansion of methylenecyclopentanes to cyclohexanones is still favorable thermodynamically, and this is reflected in our results with **10** and **11**; no unrearranged oxidation products were observed. However, the reactions were rather slow, evidently owing to the poor solubility of these compounds, and starting olefin was recovered. At the same time, some overoxidation to the corresponding α-hydroxy ketones occurred.[25] It is probably significant that **11** reacted more slowly than **10** and gave the larger amount of α-hydroxy ketone. We found no way of avoiding incomplete oxidation without increasing overoxidation. The Wolff–Kishner reduction of ketone **16** gave the parent hydrocarbon, **23**, identical with that obtained by disproportionation from the [2 + 2] norbornene dimer, **24** (precursor of diamantane).[26]





In 2-methyleneadamantane (**12**)[18] the double bond is exocyclic to a six-membered ring, and ring expansion would increase strain. Oxidation with Tl(III) gave a mixture of 4-homoadamantanone (**15**)[19,20] (15–20%), 2-

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[16] H. N. Cripps, J. K. Williams, and W. H. Sharkey, *J. Amer. Chem. Soc.*, **80**, 751 (1958); **81**, 2723 (1959).

[17] O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **470**, 62 (1929).

[18] P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961).

[19] P. v. R. Schleyer, E. Funke, and S. H. Liggero, *J. Amer. Chem. Soc.*, **91**, 3965 (1969); R. M. Black and G. B. Gill, *J. Chem. Soc. C*, 671 (1970).

[20] J. E. Nordlander, F. Y. H. Wu, and S. P. Jindall, *J. Amer. Chem. Soc.*, **91**, 3962 (1969); J. L. M. A. Schlatmann, J. G. Korsloot, and J. Schut, *Tetrahedron*, **26**, 949 (1970).

[21] J. K. Chakrabarti, S. S. Szinai, and A. Todd, *J. Chem. Soc. C*, 1303 (1970). The same ketone was obtained in better yield from 2-adamantylmethyl diazomethyl ketone: D. Fărcaşiu, unpublished observations.

[22] W. Thielecke and D. Fărcaşiu, unpublished observations.

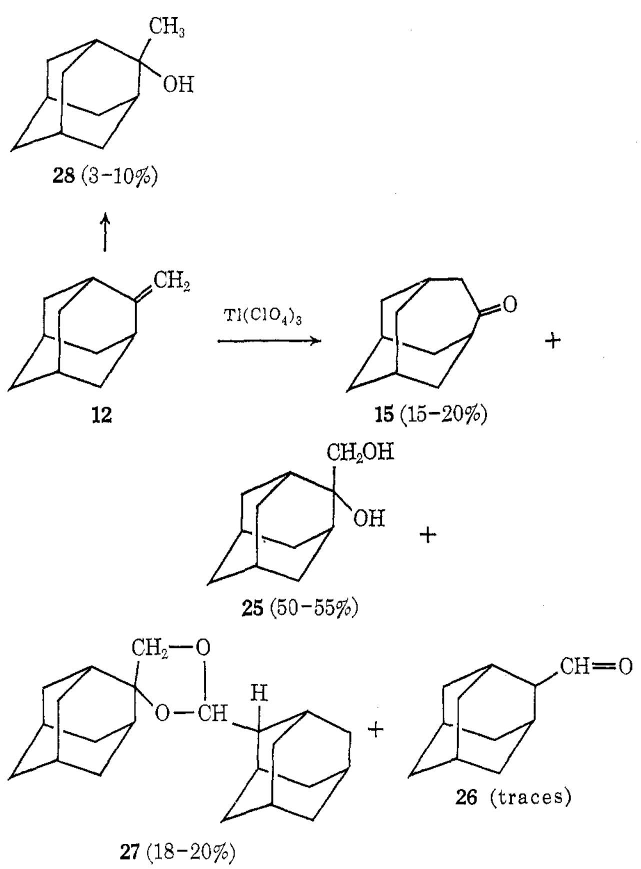
[23] E. C. Taylor, personal communication.

[24] P. M. Henry, *J. Amer. Chem. Soc.*, **87**, 990 (1965).

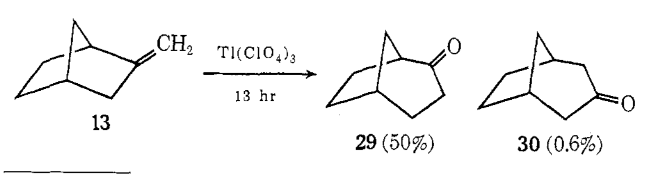
[25] A. McKillop, J. D. Hunt, and E. C. Taylor, *J. Org. Chem.*, **37**, 3381 (1972).

[26] T. M. Gund, V. Z. Williams, Jr., E. Osawa, and P. v. R. Schleyer, *Tetrahedron Lett.*, 3877 (1970); *cf.* E. Engler and P. v. R. Schleyer, *MTP Rev. Sci.*, in press. Also see ref 37.

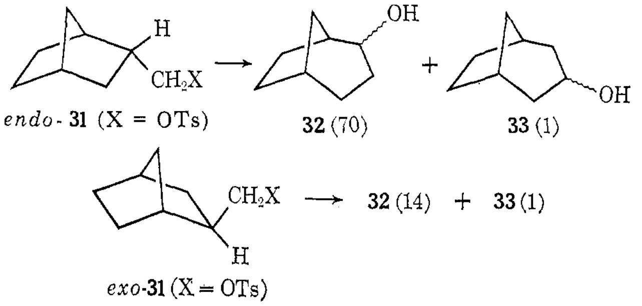
hydroxy-2-hydroxymethyladamantane (**25**)[27] (50–55%), a trace of 2-adamantanecarboxaldehyde (**26**),[27] the acetal of **25** with **26** (**27**) (18–20%), and 2-methyl-2-adamantanol (**28**)[18] (3–10%). The carbinol **28** is formed by the concurrent hydration of the double bond, as proved by allowing **12** to react with aqueous perchloric acid under the same conditions. Thus, the products in which the polycyclic skeleton is preserved (**25**–**27**) are favored over the ring-expanded product (**15**) by a factor of about 4 (compare **5c** → 30% **6c** + 70% **7c**).[6] In this case, the alternative diazomethane[19] and cyanohydrin reduction–deamination[20] homologation procedures are preferable.

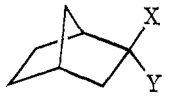


The positions of the keto groups in **16** and **17** were not established. The oxidation of **11** gave a mixture of **17** and hydroxy ketone which was only incompletely separated by column chromatography, and the nmr spectrum was complex. However, the question of regiospecificity of the ring-expansion step, **19** → **6**, was investigated with 2-methylenenorbornane (**13**).[17] The oxidation products from **13**, bicyclo[3.2.1]octan-2-one (**29**) and bicyclo[3.2.1]octan-3-one (**30**), were identified by comparison of the ir spectra (**29**) and glc retention times (**30**) with those of authentic samples.[28,29] No diol was obtained, and hydration of **13** appeared to be the only side reaction.

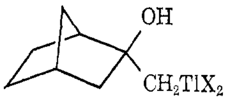


The high ratio of methylene over methine migration in the oxidation of **13** (**29**:**30** 85:1) is near to that found for the solvolysis of *endo*-2-norbornylmethyl tosylate (*endo*-**31**) {ratio of bicyclo[3.2.1]octan-2-ol (**32**): bicyclo[3.2.1]octan-3-ol (**33**) = 70} and significantly larger than the ratio obtained from *exo*-**31** (**32**:**33** = 14).[11a] Similar differences were observed in the deamination of *exo*- and *endo*-2-norbornylmethylamines (**31**, X = NH$_2$)[30] and particularly in the deamination of amino alcohols **34a** and **34b**, which gave ratios of **29**:**30** of 20 and 2, respectively.[31] These data suggest that the rearrangement step of thallic oxidation takes place from intermediate **35** rather than **36**.





34a, X = OH; Y = CH$_2$NH$_2$
b, X = CH$_2$NH$_2$; Y = OH



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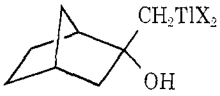

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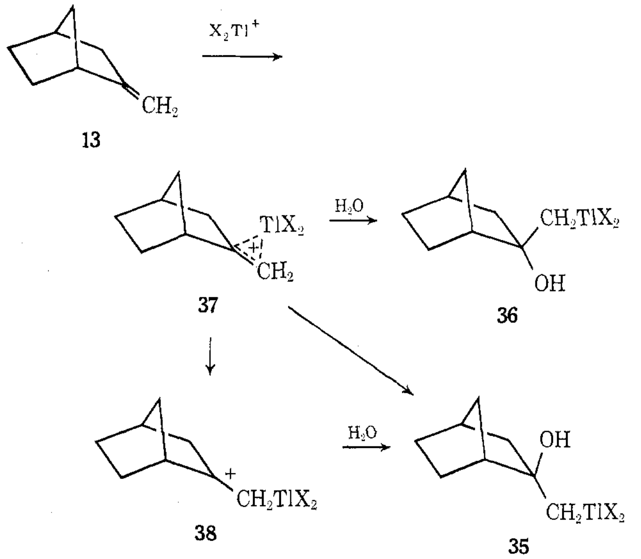
Since the attack of the double bond in **13** by Tl(III) takes place most probably from the exo side,[32] trans attack by a water molecule (as represented in **18** → **19**)[6,24] should give rise to **36**. Formation of **35**



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[27] Identical with a sample prepared from 2-epoxymethyleneadamantane: (a) D. Fărcaşiu, *Synthesis*, 615 (1972); (b) J. A. Bone, J. R. Pritt, and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 1*, 2644 (1972).

[28] W. Kraus, *Justus Liebigs Ann. Chem.*, **685**, 97 (1965); we are indebted to Dr. Kraus for the ir spectrum of authentic **29**.

[29] C. W. Jefford, J. Gunsher, D. T. Hill, P. Brun, J. LeGras, and B. Waegell, *Org. Syn.*, **51**, 60 (1971); we are indebted to Professor Jefford for a sample of **30**.

[30] J. A. Berson and P. Reynolds-Warnhoff, *J. Amer. Chem. Soc.*, **86**, 595 (1964); J. A. Berson and D. Willner, *ibid.*, **86**, 609 (1964).

[31] E. Volpi and F. Pietra, *Tetrahedron Lett.*, 4867 (1972).

[32] H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, p 181 ff.

suggested by the high ratio of **29**:**30** agrees better with the intermediacy of an "open" ion, **38**, which, even if classical (like the 2-methyl-2-norbornyl cation), is attacked by a water molecule from the exo side;[33] alternatively, a referee has suggested that **37** might be attacked by water directly from the front side to give **35**.

In conclusion, we found thallic oxidation useful for ring expanding cyclic systems in which a double bond is exocyclic to a four- or five-membered ring, but not to a six-membered ring. Even for five-membered rings, the yields are limited by side reactions and the method does not appear to be so promising a general synthetic procedure as we had hoped based on results for the simple methylenecycloalkanes.[6]

Experimental Section

The ir spectra were determined using a Perkin-Elmer 237 B spectrometer. The nmr spectra were recorded on a Varian A-60A instrument. Chemical shifts are given in δ units from internal TMS. Mass spectra were determined at 70 eV on an AEI-MS9 spectrometer. Microanalyses were performed at Hoffmann-La Roche, Nutley, N. J.

Wittig Reactions.—The literature procedure[34] was followed, except for the manner of drying the DMSO[27a] and the amount of methylenetriphenylphosphorane employed (2:1 molar ratio to the ketone). After reaction, the mixture was poured into ice–water and extracted with pentane, and the crude product was purified by chromatography on silica gel with pentane. 2-Methyleneadamantane (**12**) (70% yield) and the following olefins were prepared in this manner.

3-Methylenetetracyclo[6.3.1.1^{6,10}.0^{1,5}]tridecane (**10**) was a liquid: yield 87% from **21**;[21] nmr (CCl_4) δ 4.82 (2 H, m, $CH_2{=}$), 2.55–1.00 (18 H, complex); ir (neat) 3051, 1656, 873 cm^{-1}.

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.04; H, 10.63.

3-Methylenetetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodecane (**11**) was a liquid: yield 78% from **22**;[22] nmr δ 4.83–4.63 (2 H, broad, $CH_2{=}$), 2.57–2.21 (3 H, complex), 2.21–1.10 (13 H, complex); ir (neat) 3045, 1650, 874 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.29; H, 10.36.

Thallic Oxidations. Method A.—A solution of $Tl(ClO_4)_3$ in $HClO_4$ [made by dissolving 9.2 g (20 mmol) of Tl_2O_3 in 50 ml of 71% $HClO_4$ and 25 ml of water with heating] was added in small portions at room temperature to 5 mmol of alkene suspended in a magnetically stirred mixture of 20–30 ml of 1,2-dimethoxyethane, 220–230 ml of water, and 2–3 ml of 71% $HClO_4$. Each aliquot (1–2 ml) of Tl(III) solution was added when the previous one had reacted completely (KI–starch paper). The reaction was discontinued when the rate of Tl(III) consumption decreased markedly [usually a little less than the calculated amount of Tl(III) was used]. The total reaction time varied from 10 to 30 hr for different compounds. Solid Na_2CO_3 (30 g) was added and the reaction mixture was extracted with pentane. The crude product was chromatographed on silica gel (80 g). Elution with pentane gave the unreacted alkene; the oxidation products were then eluted with ether.

Method B.[35]—To a solution of 1 g (10.9 mmol) of 3-methylenecyclobutanecarbonitrile (**9**)[16] in 20 ml of dimethoxyethane, $Tl(NO_3)_3 \cdot 3H_2O$ (5.8 g, 12 mmol) dissolved in water (20 ml) was added dropwise with stirring. The reaction was slightly exothermic and after 20 min a white precipitate appeared [Tl(I) salt]. The reaction mixture was stirred overnight, poured into saturated aqueous NaCl, and extracted three times with chloroform. The chloroform solution was washed with 5% aqueous sodium bicarbonate, dried (Na_2SO_4), and eluted through a short (5 cm) column with silica gel to remove any inorganic salts. The residue after evaporation of solvent (1.2 g still containing some solvent) contained only one product, 3-cyanocyclopentanone (**20**) (glc on a 5% Carbowax column, 3 m × 6 mm o.d., at 175°). Preparative glc gave a product showing ν 2240 ($C{\equiv}N$), 1755 cm^{-1} ($C{=}O$) (in $CDCl_3$); nmr ($CDCl_3$) δ 3.43–2.95 (complex, 1 H, CHCN), 2.65–2.14 (complex, 6 H). Integration of the gas chromatogram of the crude reaction mixture indicated a yield of 81% of **20**.

Oxidation of 10 (0.78 g, 4.15 mmol) was conducted by method A as above. The residue from the pentane extract weighted 0.70 g. Extraction with $CHCl_3$ of the residual water solution (*vide infra*) gave no additional organic material (diol). The crude product was chromatographed on silica gel. Elution with pentane gave 0.135 g (17.5%) of **10**. Elution with pentane–ether (25:75) gave 0.50 g (58%) of **16**, ir (CCl_4) 1715 cm^{-1}, nmr complex pattern at δ 2.55–1.10. Further elution gave (after 0.051 g of a mixture of **16** and hydroxy ketone) 0.063 g (7%) of hydroxy ketone, ir 1705, 3050 cm^{-1}, mass spectrum *m/e* 220 (M^+). Owing to the small amount of material, this was not further investigated.

Tetracyclo[7.3.1.1^{7,11}.0^{1,6}]tetradecane (**23**).—The Wolff–Kishner reduction of **16** (0.48 g) by the procedure of Whitlock and Siefken[36] gave 0.26 g (59% yield) of **23** (oil). For analysis it was purified by column chromatography on silica gel (25 g, elution with pentane). The nmr (complex pattern, δ 2.40–0.85), ir, and mass spectra[37] were identical with those of the disproportionation product from **24**.[26,37]

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.36; H, 11.64.

Oxidation of 11 (0.74 g, 4.25 mmol) conducted by procedure A as above gave 0.71 g of crude product. Column chromatography gave 0.085 g (11%) of unreacted **11**, eluted with pentane; then elution with ether gave 0.05 g (6%) of **17** [ir (CCl_4) 1705–1715 cm^{-1}] and 0.47 g (*ca.* 55% yield) of a product exhibiting in the ir spectrum a broad absorption at 1705–1725 cm^{-1} and the ν_{OH} centered at 3380 cm^{-1} (CCl_4). In the mass spectrum intense peaks were present both at *m/e* 206 (mol wt of hydroxy ketone) and at *m/e* 190 (mol wt of **17**). Therefore, this product was probably a mixture of **17** and hydroxy ketone.

Oxidation of 2-methyleneadamantane (**12**) (0.74 g, 5 mmol) was conducted by procedure A as above. When the pentane extract was concentrated, a small amount of diol **25** precipitated. The remaining solution was chromatographed on 25 g of silica gel. Elution with hexane gave the acetal **27** (after small amounts of unreacted **12**). Elution with hexane–benzene mixtures (with increasing benzene content) gave the carbinol **28**, the ketone **15**, and the aldehyde **26** (eluted in this sequence). An approximate analysis of the residue from the pentane extract was provided by integrating the nmr spectrum using the CH_2O signal for **25**, the CHO_2 signal for **27**, the CH_3 signal for **28**, and the $CH{=}O$ signal for **26**; the amount of **15** was calculated by difference.

2-Hydroxymethyl-2-hydroxyadamantane (**25**).—The aqueous solution from oxidation of **12** (after extraction with pentane) was extracted four times with chloroform. After drying, evaporation of the solvent gave *ca.* 45–48% yield of **25** (combined with the diol recovered from the pentane extract, 50–55%). (The same product was obtained by shaking an ether solution of 2-epoxymethyleneadamantane[27a] with an aqueous acid solution.) **25** was obtained as white needles (from benzene): mp 211.9–213.0° (sealed tube); nmr ($CDCl_3$) δ 3.95 (s, 2 H, CH_2O), 2.05 (2 H, OH), 2.50–1.50 (14 H, complex).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.48; H, 9.95. Found: C, 72.18; H, 9.65.

Acetal of 25 and 26 (**27**).—To 0.71 g (3.84 mmol) of diol **25**, a benzene solution of aldehyde **26** (prepared from 4.26 mmol of 2-epoxymethyleneadamantane[27a]) and 10–15 mg of *p*-toluenesulfonic acid were added. After dilution with benzene to 45 ml, the solution was refluxed for 18 hr, using a Dean–Stark trap to remove water. The flask was cooled in ice–water, 0.5 ml of concentrated ammonia and a few drops of water were added, and the resulting mixture was then stirred for 1 hr at room temperature. Anhydrous Na_2SO_4 was added and the stirring was continued for 30 min. The solid was filtered off and washed with benzene. The residue from evaporating the benzene solution was dissolved in pentane (no residue was left) and evaporated again to give an almost quantitative yield of **27** (based on **25**), mp 220–

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[33] P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967); H. L. Goering, C. Brown, and C. B. Schewene, *ibid.*, **90**, 6214 (1968).

[34] R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

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223° (slight decomposition). For analysis, a sample was sublimed at 140° (0.3 mm): nmr δ 5.12 (1 H, d, J = 7.5 Hz, CHO_2), 3.70 (2 H, AB pattern, CH_2O), 2.45–0.85 (29 H, complex); mass spectrum m/e 328 ($M\cdot^+$), 327, 326, 193.

Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.82. Found: C, 80.10; H, 9.82.

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Registry No.—**9**, 15760-35-7; **10**, 41171-88-4; **11**, 41171-89-5; **12**, 875-72-9; **16**, 41163-74-0; **17**, 41163-75-1; **20**, 41171-91-9; **21**, 27174-68-1; **22**, 41171-93-1; **23**, 41171-94-2; **25**, 41171-95-3; **26**, 39750-93-1; **27**, 41171-97-5.

The Chemistry of the *trans*-Trimethylenenorbornene Ring System. II. Thermal Rearrangement to the *cis,anti,cis*-Tricyclo[5.3.0.0^{2,6}]decane System[1a,b]

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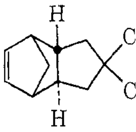
At temperatures near 200° 9-carbomethoxy-*trans*-5,6-trimethylene-2-norbornene undergoes a facile 1,3-sigmatropic rearrangement to give 9-carbomethoxy-*cis,anti,cis*-tricyclo[5.3.0.0^{2,6}]dec-3-ene in essentially quantitative yield. Pyrolysis of 9,9-dicarbo-*tert*-butoxy-*trans*-5,6-trimethylene-2-norbornene under similar conditions affords 9-carboxy-*cis,anti,cis*-tricyclo[5.3.0.0^{2,6}]dec-3-ene, whereas the corresponding saturated diester shows no rearrangement. The structures of these products are established by degradation to the parent hydrocarbon. The facility with which the rearrangement takes place is ascribed to the relief of internal strain. The specificity of the reaction and the marked stability of the reactants toward reverse Diels–Alder fragmentation are explained in terms of the orbital symmetry requirements of the system.

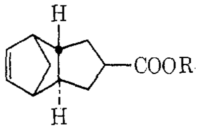
We recently reported the first successful synthesis[2] of the *trans*-5,6-trimethylene-2-norbornene ring system (**1**) and demonstrated that in structures of this type the rigid norbornene cage undergoes significant structural distortion in order to minimize the strain associated with the trans trimethylene bridge. As part of a general investigation of the chemistry of this new system, we herein describe its characteristic thermal behavior.

Results and Discussion

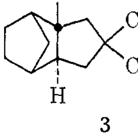
When a solution of the methyl ester **2a**[2] in decalin was heated at 220–230°, a facile stereospecific rearrangement occurred affording the isomeric ester **5** as the sole product. Saponification of this new ester then gave the carboxylic acid **7**, a product that could also be obtained in good yield by the pyrolysis of the di-*tert*-butyl ester **1**[2] under the same conditions. Similar treatment of the corresponding saturated diester **3**,[2] however, afforded only the unrearranged acid **4**.[2] The rearrangement of the methyl ester **2a** was shown to be irreversible by heating a 1.0 M solution of the ester **5** in Nujol at 225°. After 2 hr under these conditions, no change in the nmr spectrum of the reaction mixture was detected.



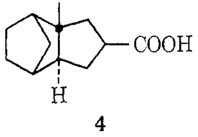
1



2a, R = CH_3
b, R = H



3



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The infrared spectrum of the rearranged ester (**5**) indicated a relatively unstrained olefinic linkage[3] ($\nu_{C=C}$ 1610 cm^{-1}) and a nonconjugated ester carbonyl group[4] ($\nu_{C=O}$ 1740 cm^{-1}). The structure of this compound was established by degradation to the parent hydrocarbon. The acid **7** readily absorbed 1 equiv of hydrogen to give the saturated acid **6**. Hunsdiecker decarboxylation[5] of **6** then afforded the bromide **8a**,[6] which on hydrogenolysis on palladium in the presence of potassium carbonate[7] yielded *cis,anti,cis*-tricyclo[5.3.0.0^{2,6}]decane (**9**). The infrared spectrum and gas chromatographic retention times of this product were identical with those of an authentic sample of **9** obtained by the Wolff–Kishner reduction of the diketone **10**.[8,9]

The thermal isomerization of the *trans*-trimethylenenorbornenes to derivatives of the tricyclo[5.3.0.0^{2,6}]decane system is unprecedented among the more familiar *endo,cis*- and *exo,cis*-trimethylenenorbornenes (dicyclopentadienes). The dicyclopentadienes have long

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[6] The bromide **8a** was accompanied by lesser amounts of the corresponding chloride **8b** and the ester **8c**. Analogous products have been observed in the decarboxylation of other carboxylic acids; see, for instance, F. W. Baker, H. D. Holz, and L. M. Stock, *J. Org. Chem.*, **28**, 514 (1963).

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[9] A sample of the diketone **10** was kindly supplied by Dr. P. E. Eaton. This material had mp 125–126° (lit.[8] 125–126.5°), ir (KBr) 1706 cm^{-1}.