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.

Acknowledgments.—We are indebted to J. Halpern for transmitting details of his work prior to publication, to E. C. Taylor for helpful suggestions, and to J. A. Berson, C. W. Jefford, and W. Kraus for supplying us with reference samples or spectra. This work was supported by grants from the National Science Foundation (GP 29078), the National Institutes of Health (GM-19134), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Hoffmann-La Roche Inc., Nutley, N. J.

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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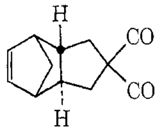
At temperatures near 200° 9-carbomethoxy-*trans*-5,6-trimethylene-2-norbornene undergoes a facile 1,3-sigmatropic rearrangement to give 9-carbomethoxy-*cis,anti,cis*-tricyclo[5.3.0.0^{2,6}]dec-3-ene in essentially quantitative yield. Pyrolysis of 9,9-dicarbo-*tert*-butoxy-*trans*-5,6-trimethylene-2-norbornene 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.



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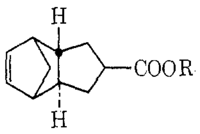
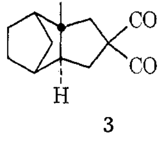


2a, R = CH_3
b, R = H



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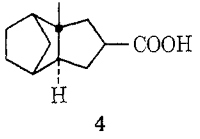

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The infrared spectrum of the rearranged ester (**5**) indicated a relatively unstrained olefinic linkage[3] ($\nu_{C=C}$ 1610 cm^{-1}) and a nonconjugated ester carbonyl group[4] ($\nu_{C=O}$ 1740 cm^{-1}). The structure of this compound was established 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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[1] (a) Grateful acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. (b) For part I of this series see ref 2. (c) W. B. King Visiting Professor, Department of Chemistry, Iowa State University, 1971–1972.

[2] G. B. Clemans, M. N. Essiet, and R. L. Tyson, *J. Org. Chem.*, **37**, 2312 (1972).

(3) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958).

(4) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, Chapter 5.

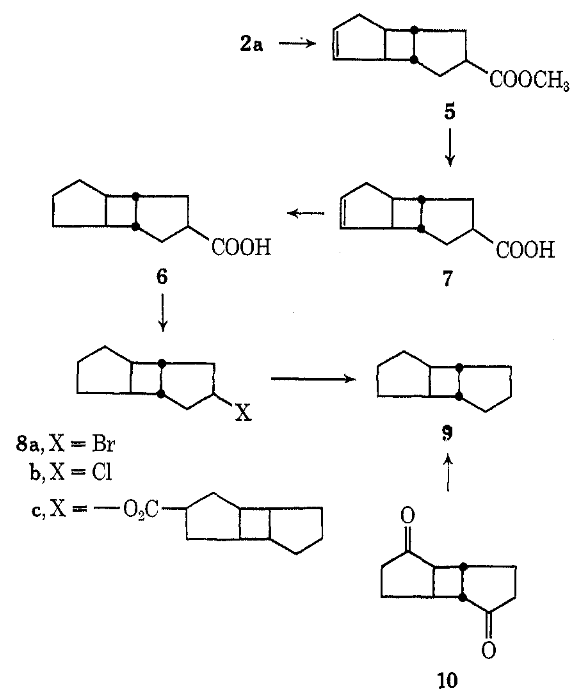
(5) J. Cason and D. M. Walba, *J. Org. Chem.*, **37**, 669 (1972).

(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).

(7) M. Freifelder, "Practical Catalytic Hydrogenation," Wiley, New York, N. Y., 1971, Chapter 20.

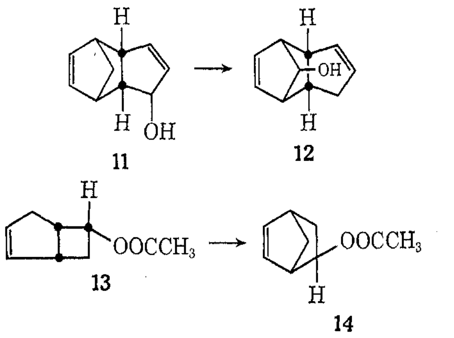
(8) P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344 (1962).

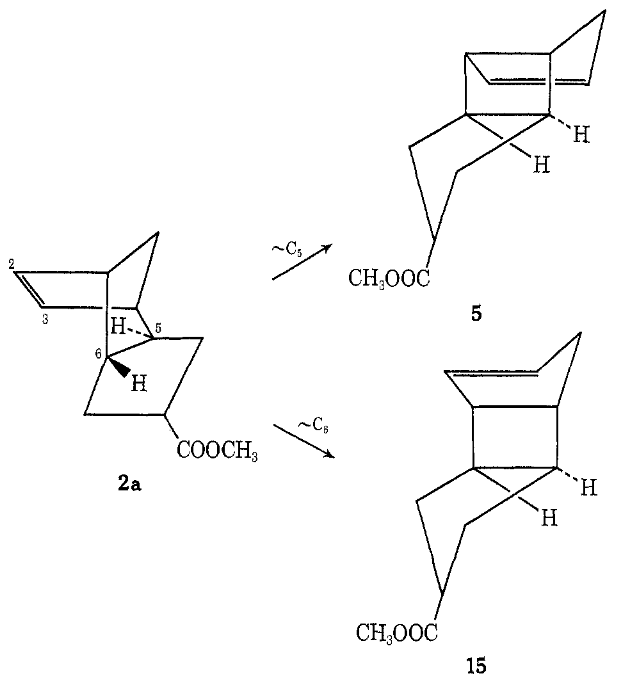
(9) A sample of the diketone **10** was kindly supplied by Dr. P. E. Eaton. This material had mp 125–126° (lit.[8] 125–126.5°), ir (KBr) 1706 cm^{-1}.



been known[10] to undergo thermal fragmentation by a reverse Diels–Alder process. Woodward and Katz observed that the dicyclopentadienol **11** thermally rearranged to the isomeric alcohol **12**,[11] and other workers have reported[12] similar rearrangements of related dicyclopentadienes.

The isomerization of **2a** is essentially the reverse of the 1,3-sigmatropic rearrangement of the bicycloheptene **13** to the norbornene **14** reported by Berson.[13] In contrast to this latter transformation, however, the rearrangement of **2a** is considerably faster and is unaccompanied by side reactions.[14] Examination of the structure of **2a** reveals that both C$_5$ and C$_6$ are correctly positioned to undergo 1,3-sigmatropic migration (to give **5** and **15**, respectively) and that both processes are constrained to a suprafacial geometry[15,16] by the cage system. In either case the symmetry-required[15] inversion of the migrating center would relieve the strain imparted by the trans ring junction by yielding either the cis,anti,cis (**5**) or cis,syn,cis (**15**) product. Nonetheless, the observation that **5** is the sole product of the reaction clearly shows that the rearrangement is specific for migration of C$_5$.





In traversing the reaction coordinate leading to **5**, clockwise rotation about the 5,6 bond not only permits the required[15] bonding interaction between the back lobe of the orbital of the migrating atom (C$_5$) and the orbital of the migration terminus (C$_2$), but also results in a continuous release of the strain of the trans trimethylene bridge as the inversion of C$_5$ progresses. In the alternative migration of C$_6$ to C$_3$, however, a counterclockwise rotation is forced by the trimethylene bridge which requires either a symmetry-forbidden rearrangement with retention or a severe uncoupling of the interacting orbitals to allow inversion of configuration of C$_6$. As a result, neither process can compete effectively with the concerted migration of C$_5$ to afford the product **5**.[17]

The stability of the *trans*-trimethylenenorbornenes toward reverse Diels–Alder fragmentation is quite striking since such a process, common among both the dicyclopentadienes and norbornenes, would appear potentially to be very effective in relieving strain. In fact, however, the symmetry-allowed pathway $(-[{}_{4}\pi_s + {}_{2}\pi_s])$[15] for the fragmentation of **2a** leads to the highly strained *trans*-cyclopentene **17**, and thus this route is rendered energetically inaccessible to the system.

The unique thermal properties of the compounds reported here compared to those of the dicyclopentadienes are thus seen to be a direct result of the trans

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(10) (a) For an excellent review of early studies of the dicyclopentadienes see G. T. Youngblood, Ph.D. Dissertation, Duke University, Durham, N. C., 1957; (b) M. Rosenblum, *J. Amer. Chem. Soc.*, **79**, 3179 (1957).

(11) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(12) D. L. Allara, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1964, and references cited therein.

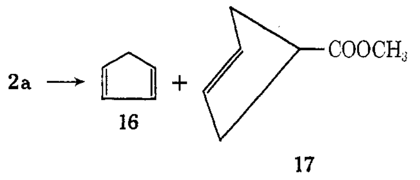
(13) J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972), and references cited therein.

(14) The rate of isomerization of **2a** was estimated by carrying out the reaction in an nmr sample tube and noting the changes in the nmr spectrum of the reaction mixture with time at 225°. In this way the half-life of **2a** (1.0 *M* in decalin) was found to be about 20 min under these conditions. Only a 5% conversion was observed for **13** (0.6 *M* in decalin) after 1 hr at 300°. The isomerization of **13** was complicated by Diels–Alder fragmentation–recombination of the product (**14**) under the reaction conditions: J. A. Berson and J. W. Patton, *J. Amer. Chem. Soc.*, **84**, 3406 (1962).

(15) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1971.

(16) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5503 (1967).

(17) The possibility that the migration of C$_6$ occurs by way of a radical process rather than the sigmatropic pathway proposed here is rendered extremely unlikely by the previously noted specificity of the reaction. Further, the intermediate diradical in such a pathway would be expected[16] to close preferentially to the *endo,cis*-dicyclopentadiene isomeric with **2a** rather than to **5**.



geometry of the trimethylene bridge. Other aspects of the chemistry of the *trans*-trimethylenenorbornene ring system will be reported in the future.

Experimental Section

General.—Infrared spectra were obtained using a Perkin-Elmer Model 337 recording spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer. Chemical shifts (δ) are reported downfield relative to tetramethylsilane as internal reference in the indicated solvents, and coupling constants (J) are reported in hertz. Mass spectra were obtained with a Varian MAT CH-4 spectrometer. Gas chromatographic analyses were carried out using either a Hewlett-Packard Model 700 or a Gow-Mac Model 69-500 gas chromatrograph. In both cases a 6-ft column of 5% Carbowax on Chromosorb P was used at the indicated temperatures. All melting points and boiling points are uncorrected. Microanalyses are by M-H-W Laboratories, Garden City, Mich.

Thermal Rearrangements.—All pyrolyses were carried out by the same general procedure of which the following is representative. A solution of 338 mg (1.0 mmol) of the di-*tert*-butyl ester **1** in 5 ml of diphenyl ether (Nujol and decalin were used as solvents in some runs) was heated at 210–230° under an atmosphere of dry nitrogen for 6.0 hr. The solution was then cooled, taken up in ether, and extracted with two 5-ml portions of 10% sodium hydroxide and with 5 ml of water. The combined aqueous extracts were washed once with ether and were acidified with 4 ml of concentrated hydrochloric acid. The precipitate was taken up with three 30-ml portions of ether, and the combined ether layers were washed once with saturated brine, dried ($MgSO_4$), and concentrated to yield the acid **7** in essentially quantitative crude yield as a pale yellow oil that crystallized on cooling. Recrystallization of this material from light petroleum followed by sublimation at reduced pressure afforded the pure product as white needles: mp[18] 83–86°; ir (KBr) 3300–2800 (OH), 3044 (vinyl H), 1690 (C=O), 1609 cm^{-1} (C=C); nmr ($CDCl_3$) δ 11.4 (s, 1, COOH), 5.77 (m, 2, vinyl H); mass spectrum (16 eV) *m/e* (rel intensity), 178 (18), 133 (2), 132 (2), 113 (2), 112 (5), 66 (100).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.31; H, 7.87.

Treatment of the saturated di-*tert*-butyl ester **3** under similar conditions gave the unrearranged acid **4** in 92% yield as a white solid, mp 46–48°. The infrared spectrum of this material was identical with that of the same compound reported earlier[2] and showed no depression of melting point on admixture with an authentic sample.

The isomerization of the methyl ester **2a** was carried out similarly except that decalin was used as solvent. The product was not isolated as such, but was saponified in aqueous sodium hydroxide yielding the acid **7**, identical in melting point and mass spectrum with the same product obtained above.

9-Carbomethoxy-*cis,anti,cis*-tricyclo[5.3.0.0^{2,6}]dec-3-ene (5).—The carboxylic acid **7** was esterified by the same procedure reported earlier[2] for the esterification of the acid **2b**. The product (**5**) was obtained after distillation at reduced pressure as a colorless oil: ir (neat) 3038 (vinyl H), 1734 (C=O), and 1609 cm^{-1} (C=C); nmr (CCl_4) δ 5.73 (m, vinyl H), 3.67, 3.65 (s, methoxyl H).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.27; H, 8.61.

***cis,anti,cis*-Tricyclo[5.3.0.0^{2,6}]decane-4-carboxylic Acid (6).**—A solution of 415 mg (2.33 mmol) of rearranged acid **7** in 20 ml of ethyl acetate was hydrogenated at atmospheric pressure and room temperature over 30% palladium-on-carbon catalyst. A total of 56 ml of hydrogen was absorbed (theoretical = 52 ml). The catalyst was removed by filtration through Celite, and the solvent was evaporated to afford the crude acid **6** in essentially quantitative yield. This material was recrystallized from light petroleum to give the pure product as white needles: mp[18] 93–110°; ir (KBr) 3300–2500 (OH), 1690 cm^{-1} (C=O); nmr (CCl_4) δ 13.4 (s, 1, COOH), 3.0 (m, 1, α-H); mass spectrum (70 eV) *m/e* (rel intensity) 180 (25), 135 (47), 134 (100), 68 (25), 67 (73).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.46; H, 8.77.

4-Bromo-*cis,anti,cis*-tricyclo[5.3.0.0^{2,6}]decane (8a).—This compound was prepared by an adaptation of the procedure of Cason and Wilba.[5] A stirred mixture of 362 mg (2.0 mmol) of the saturated acid **6**, 284 mg (1.31 mmol) of red mecuric oxide, and 20 ml of carbon tetrachloride was heated until 10 ml of solvent had distilled. Distillation was continued, and a solution of 136 μl (2.5 mmol) of bromine in 10 ml of carbon tetrachloride was added over a period of 1.2 hr. When addition was complete, an additional 5 ml of solvent was distilled, and the final volume of the reaction mixture had been reduced to about 5 ml. This mixture was diluted with 50 ml of ether and was filtered through Celite. The filtrate was washed with two 5-ml portions of 5% aqueous sodium hydroxide and with 5 ml of water. The resulting ether solution was dried ($MgSO_4$) and concentrated to afford the crude product as a pale yellow oil.

Preliminary separation of the product mixture was achieved by chromatography on a dry 1.5 × 10 cm column of alumina. A mixture of the bromide **8a** and the chloride **8b**[6] (198 mg) was eluted with 100 ml of pentane, and the ester **8c**[6] (187 mg) was subsequently eluted with 100 ml of ether. The halide mixture was further fractionated by preparative gas chromatography at 185°. The chloride **8b** was eluted first and was collected as a colorless oil: ir (CCl_4) 2930, 2845, 1265 cm^{-1}; positive Beilstein test for halogen.[19] The bromide **8a** was eluted later and was likewise collected as a colorless oil: ir (CCl_4) 2920, 2845, 1230, 1180 cm^{-1}; positive Beilstein test for halogen.[19]

The ester **8c**[6] was similarly purified and was obtained as a colorless oil: ir (CCl_4) 1730 cm^{-1}.

***cis,anti,cis*-Tricyclo[5.3.0.0^{2,6}]decane (9).**[7]—A 51-mg sample of the halide mixture (**8a** and **8b**) obtained above was dissolved in 20 ml of methanol, and 66 mg of potassium carbonate and 38 mg of 30% palladium on carbon were added. The mixture was then subjected to hydrogen at atmospheric pressure and room temperature for 24 hr. The reaction mixture was filtered through Celite and concentrated. The residue was taken up in pentane, filtered, and concentrated to yield a pale yellow oil. Gas chromatographic analysis of this product at 140° indicated that the bromide **8a** had reacted completely, but that some of the chloride (**8b**) remained. The hydrocarbon **9** appeared at considerably shorter retention time than either **8a** or **8b** and was collected as a colorless oil: ir (CCl_4) 2920, 2830, 1465, 1450 cm^{-1}. The infrared spectrum of this product was identical with that of the same compound obtained below by the reduction of the diketone **10**. Further, the two samples had identical retention times on two different columns on gas chromatographic analysis.

Wolff-Kishner Reduction of the Ketone 10.—The diketone **10** was converted into the hydrocarbon **9** by the procedure of Eaton.[8] The product was purified by gas chromatography at 140° and was obtained as a colorless oil.

Acknowledgment.—The author is indebted to the Department of Chemistry of Iowa State University for partial support of this work.

Registry No.—**1**, 41163-81-9; **2a**, 41265-37-6; **3**, 41163-82-0; **4**, 40252-86-6; **5** epimer a, 41163-83-1; **5** epimer b, 41163-84-2; **6** epimer a, 41163-85-3; **6** epimer b, 41163-86-4; **7** epimer a, 41163-87-5; **7** epimer b, 41163-88-6; **8a** epimer a, 41163-89-7; **8a** epimer b, 41163-90-0; **8b** epimer a, 41163-91-1; **8b** epimer b, 41163-92-2; **8c**, 41172-07-0; **9**, 36444-30-1; **10**, 2065-43-2.

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[18] Since the compounds in this series are obtained as mixtures of epimers, sharp melting points are often not observed.

[19] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd ed, Interscience, New York, N. Y., 1958, p 177.