The value of 0.65 derived above for m is the ratio between the calculated and observed substituent effects. It differs from unity, in part, because of the inappropriateness of transferring the Tanford parameterization, developed for proton dissociation, to silver cation dissociation. By trial and error it is found that, if the Tanford depths, d, are replaced by 1.5 Å for charges and 2.0 Å for dipoles, m becomes 1.0 with $\sigma_m = 0.13$. The 0.5-Å increase is consistent with the larger ionic radius of a silver cation.[30] The increased depths constitute a new cavity model, one designed specifically for treating silver–olefin complexation. It should be employed cautiously, however, because of the limited data set that went into its construction. In this calculation it was assumed that the formal 1+ charge of silver was localized on the silver cation.

The argentation constants of substituted styrenes in water measured by Fueno and coworkers were well correlated by a Hammett $\rho\sigma$ equation which yielded a $\rho = -0.766$. The substituent effects were interpreted qualitatively[6] and quantitatively[31] in terms of the variation in π density at the vinyl site induced by the substituent. It is noteworthy that application of the new cavity model described above leads to a calculated ρ of -1.1. Given that the styrene complexes are probably a blend of electrostatic (polarization) and resonance (charge transfer) effects the agreement is satisfactory and demonstrates once again that a major contribution to a substituent effect can be accounted for in terms of a simple electrostatic cavity model.

It is revealing to consider the argentation data for the substituted 1-alkenes. These constants, recorded in Table I, when plotted as a function of the appropriate σ^* values based on ethylene as the reference structure give a good fit with $\rho = -0.93$. A point for acrylaldehyde was included in the correlation by multiplying our measured value for crotonaldehyde by 2.0, the measured argentation ratio between 2-propen-1-ol and 2-buten-1-ol.[32] The conformational flexibility of the substituents of the 1-alkenes represents a formidable problem for cavity model calculations and they have not been attempted. However, the value of the modified cavity model can be seen by the good (surely fortuitous in part) agreement between the calculated log (K/K_0) of -1.75 for 1-hexene and allylammonium perchlorate compared to the observed value of -1.8.[33] If the allylammonium perchlorate constant is used to define the regression line for the argentation of the substituted 1-alkenes, then the flexible substituents tend to show larger than expected substituent effects just as with the bicyclic olefins.

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(30) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd revised ed, Pergamon Press, Elmsford, N. Y., 1961, p 875.

(31) T. Fueno, T. Okuyama, and J. Furukawa, *Bull. Chem. Soc. Jap.*, **39**, 2094 (1966).

(32) The correction factor was obtained from our measurements on allyl alcohol and crotyl alcohol and is consistent with other measurements[5] of the effect of methyl groups on argentation equilibria.

(33) F. R. Hartley and L. M. Venanzi, *J. Chem. Soc. A*, 335 (1967).

Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. III. The Synthesis and Degenerate Thermal Valence Isomerization of Pentacyclo[3.3.2.0^{2,4}.0^{3,7}.0^{6,8}]dec-9-ene[1]

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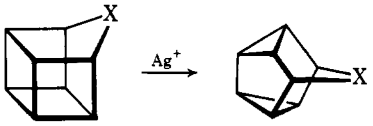
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received July 31, 1970*

Abstract: Exposure of *cis*-dimethyl pentacyclo[4.4.0.0^{2,5}.0^{3,10}.0^{4,7}]decane-8,9-dicarboxylate (**7**) to silver fluoroborate in an inert solvent results in skeletal isomerization *via* a $_\sigma2_a + {}_\sigma2_a$ electrocyclic mechanism to give the isomeric ester **8**. Hydrolysis of **8** and electrolytic decarboxylation afford pentacyclo[3.3.2.0^{2,4}.0^{3,7}.0^{6,8}]dec-9-ene (**3**). When the hydrolysis is performed in NaOD–D_2O and the deuterium labeled diacid is decarboxylated in analogous fashion, dideuteriohydrocarbon (**9**) is obtained. Gas phase pyrolysis of **9** in the 500° temperature range is seen to result in a highly specific degenerate rearrangement which effectively scrambles uniquely the vinyl and remote cyclopropyl protons. Mechanistic schemes are presented to account for this unprecedented behavior. At slightly higher temperatures, **3** gives rise to *cis*-9,10-dihydronaphthalene (**10**), together with further transformation products of this latter hydrocarbon. Interestingly, **9** affords **10** in which the deuterium label is completely scrambled. Mechanisms which accommodate the observed isotopic distribution are discussed.

Recently, the unprecedented $[_\sigma2_a + {}_\sigma2_a]$ electrocyclic skeletal isomerization of homocubyl[3] and 1,1′-bishomocubyl systems[3,4] to pentacyclic derivatives of general structure **2** under unusually mild conditions (Ag^+, ambient temperature) was reported. Significantly, such metal ion catalyzed molecular rear-



1 **2**

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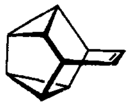
(1) For paper II of this series, note L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5765 (1970).

(2) National Institutes of Health Postdoctoral Fellow, 1969–1970.

(3) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970).

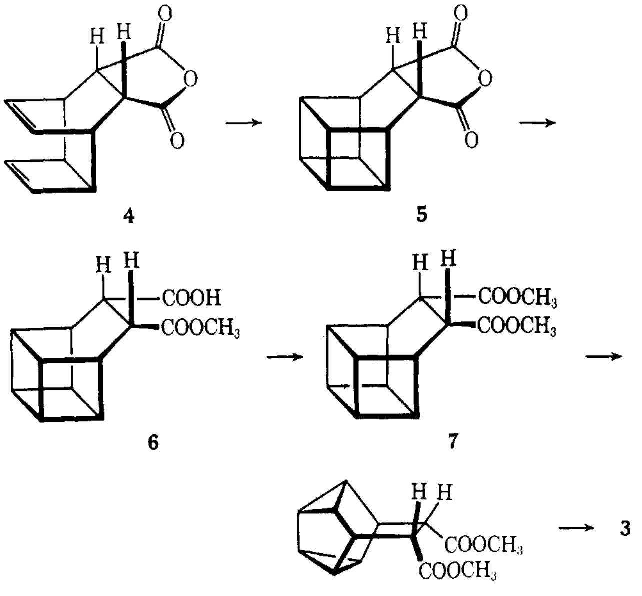
(4) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970).

rangements have revealed that silver(I) ions can complex with strained σ bonds (those endowed with enhanced p character) to an extent sufficient to permit the operation of otherwise thermally forbidden chemical transpositions.[5] More or less parallel with an expansive examination of the scope of silver(I) ion catalyzed reactions in this laboratory has been a companion general investigation of the physical and chemical properties of the rearrangement products.[6] In this paper, we wish to describe the synthesis of pentacyclo[3.3.2.$0^{2,4}$.$0^{3,7}$.$0^{6,8}$]dec-9-ene (**3**), for which we have proposed the name snoutene,[7] the remarkable degenerate thermal valence isomerization of this $(CH)_{10}$ hydrocarbon, and, lastly, its ultimate pyrolytic rearrangement under more forcing conditions.[8]



3

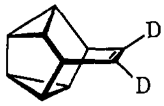
Synthesis. The synthetic scheme began by irradiation of acetone solutions of tricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene-9,10-dicarboxylic anhydride (**4**)[9] through Vycor optics with a 200-W Hanovia lamp source. The nmr spectrum of the resulting isomeric anhydride (**5**), of previously established structure,[10] displayed (in $CDCl_3$) two broad overlapping peaks at δ 3.18 and 3.28 and the absence of olefinic protons. Heating of **5** in methanol for several hours gave **6** as a viscous oil, direct further esterification of which with diazomethane afforded crystalline diester **7**.[11]



Addition of several crystals of silver fluoroborate to dilute deuteriochloroform solutions of **7** at nmr probe temperatures (~40°) resulted in rapid (<3 min) quantitative conversion to **8**. The proton resonance of **8** clearly shows the six-proton methoxyl singlet at δ 3.68, a broad singlet at 3.14 due to the two α-carbonyl protons, a broad multiplet centered at 2.7 attributable to the two bridgehead protons, and a complex absorption integrating for six protons in the 1.4–2.0 region resulting from the cyclopropyl hydrogens.

For preparative purposes, it was found convenient to reflux acetone solutions of **7** in the presence of catalytic amounts of $AgBF_4$ for 2 hr. The new highly crystalline ester was saponified and the derived diacid was electrolytically decarboxylated[12,13] to give snoutene (**3**), a highly volatile crystalline substance, in 17% yield. The nmr spectrum of this previously unrecognized $(CH)_{10}$ isomer[3,4,14] consists of multiplets, each of area 2, at δ 6.33 (vinyl), 3.15 (allyl), and 2.12 (remote cyclopropyl), together with a multiplet of area 4 centered at 1.55 resulting from the remaining cyclopropyl protons. The structure of **3** follows not only from the highly symmetrical nmr spectrum, but also from the analogous conversion of homocubane to pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane,[3] a hydrocarbon which has been synthesized unequivocally in a number of alternative fashions. In addition, the structural assignment to **3** has been confirmed independently by X-ray structure analysis of the 3-nitro-4-chlorobenzoate of the derived alcohol (available from **3** by hydroboration).[4]

With the establishment of the structure of **3**, attention was directed to the preparation of the d_2 analog **9**. To this end, **8** was hydrolyzed with a solution of sodium deuterioxide in D_2O. Subsequent electrolysis as above gave the unsaturated pentacyclic hydrocarbon with 63%



9

Table I. Hydrogen Atom Distribution in Dideuteriosnoutene (**9**) (60 MHz, $CDCl_3$ Solutions)

		Hydrogen atom distribution[a]		
		Prior to thermal rearrangement	After thermal rearrangement	
Chemical shift, δ	Assignment		Run A (530°)	Run B (500°)
1.55	Proximate cyclopropyl	4.00	4.00	4.00
2.12	Remote cyclopropyl	2.00	1.44	1.68
3.15	Allyl	2.00	2.00	2.02
6.33	Vinyl	0.74	1.24	0.99

[a] The area of the proximate cyclopropyl protons was used as an internal standard throughout; the validity of this approach is readily established by the invariant nature of the *total* hydrogen content of the degenerate thermal rearrangement products.

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(5) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **91**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(6) See ref 1 for an earlier illustration of this point.

(7) This name is derived from the medieval English word "snoute" and pertains to the structural similarity of this molecule with the anterior prolongation of the head of various animals such as the crocodile. The authors have submitted the name "snoutane" for the parent hydrocarbon to the appropriate authorities for approval and have received same (Dec 8, 1970).

(8) Summaries of the known interconversions of $(CH)_{10}$ hydrocarbons have recently appeared: (a) J. C. Stowell, Seminar in Organic Chemistry, The Ohio State University, April 7, 1970, copies of which are available from the authors; (b) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970).

(9) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948).

(10) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966).

(11) W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966).

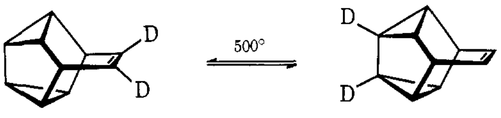
(12) P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *ibid.*, 5117 (1968).

(13) H. H. Westberg and H. J. Dauben, Jr., *ibid.*, 5123 (1968).

(14) R. Furstoss and J.-M. Lehn, *Bull. Soc. Chim. Fr.*, 2497 (1966).

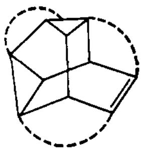
deuterium (d_2) substitution at the vinyl positions (Table I).

The Degenerate Snoutene Rearrangement. Snoutene is a $(CH)_{10}$ hydrocarbon of appreciable thermal stability. For example, heating a solution of the dideuterio analog **9** in carbon tetrachloride solution at 150° for 3 hr in a sealed nmr tube gave no evidence of spectral alterations. When **9** was subjected to gas phase pyrolysis (500°, contact time ~1 sec), 86% of the starting material could be recovered; *cis*-9,10-dihydronaphthalene (**10**) was also produced (14% yield). Leaving aside for the moment a discussion of the formation of **10**, it is highly significant to note that the dideuteriosnoutene recovered from such thermal treatment unquestionably had undergone an exceedingly specific degenerate rearrangement (**9a** ⇄ **9b**). At 500°, the recovered hydrocarbon possessed the hydrogen atom distribution shown in Table I (run B); the result of such thermal activation was that the protium contents of the proximate cyclopropyl and allyl carbons remained unaffected, whereas the deuterium label distributed between the vinyl and remote cyclopropyl sites differed significantly from the original values. At 500°, the extent of isotope scrambling was in the order of 45%. An increase in temperature to 530° gave rise to 84% scrambling of the deuterium label (run A, Table I).



9a **9b**

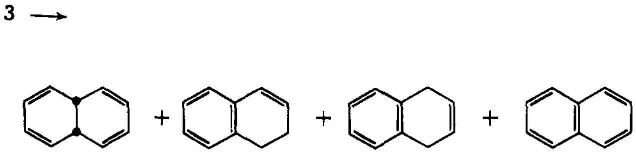
Clearly, the remarkable degenerate thermal valence isomerization of snoutene comprises the uncatalyzed cleavage of the two "edge" cyclopropyl bonds in conjunction with bond reorganization involving conversion of the original π bond to a σ bond and concomitant generation of a new unsaturated linkage. It is entirely possible that the geometry inherent in the snoutene molecule is a favored arrangement which permits the operation of a concerted symmetry-allowed $[_{\sigma}2_s + {}_{\sigma}2_a + {}_{\pi}2_a]$ process. The consequence of holding a double bond proximate to two strained three-membered rings in the fashion dictated by the rigid structural nature of snoutene could realistically permit antarafacial bonding to the existing π linkage by the two rupturing cyclopropyl bonds. A further interesting point which emerges is that opening of the two cyclopropyl bonds in opposite modes (one suprafacial and one antarafacial) permits reclosure to the new snoutene structure with minimal geometrical readjustment (*cf.* **11**).



11

In the above discussion, we wish only to point out that a reasonable concerted pathway is available to snoutene for the degenerate valence tautomerism. A nonconcerted homolytic pathway is, of course, also capable of operation. If free-radical intermediates were involved, however, one might expect that the large amount of vibrational energy present at the moment of homolytic bond fission would be best dissipated by passage to structures less strained than snoutene rather than by the remarkable return to starting material.[15]

The Pyrolytic Rearrangement. Gas phase pyrolysis of snoutene at 530° afforded not only recovered starting material (51%), but a mixture of four additional hydrocarbon products. These were separated by preparative scale gas chromatography and identified as *cis*-9,10-dihydronaphthalene (**10**, 32%), 1,2-dihydronaphthalene (**12**, 4%), 1,4-dihydronaphthalene (**13**, 8%), and naphthalene (**14**, 5%). Characterization in each instance was achieved by spectral comparisons with authentic samples. As one would expect, an increase in the pyrolysis temperature to 580° resulted in diminution of the amounts of isolatable snoutene (8%) and **10** (5%); on the other hand, the quantities of **12** (32%), **13** (36%), and **14** (18%) were all seen to increase. These observations are in agreement with the fact that independent pyrolysis of *cis*-9,10-dihydronaphthalene (**10**) gives rise to these aromatic hydrocarbons.[16]

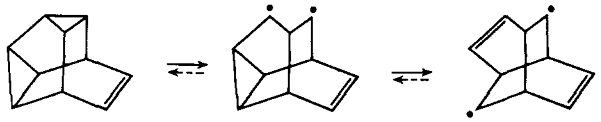


10 **12** **13** **14**

Since **10** appeared to be the major, if not the unique, source of the other pyrolysis products, it became of interest to examine the mechanism of the snoutene to *cis*-9,10-dihydronaphthalene interconversion. Two mechanisms seemed especially reasonable, and these are outlined in Chart I. Mechanism a is based on sequential homolytic fission of two "edge" cyclopropyl bonds, followed by rupture of one of the two σ bonds symmetrically disposed between the two radical sites in **15**. In this pathway, deuterium labeling of snoutene as in **9** would lead to 1,2-dideuterio **10**.

Mechanism b would result in a different prediction for the placement of the deuterium label in **10**. Thus, partial relief of strain could perhaps be attained by retrodgrade (4 + 2) cycloaddition in **3** to give **16**, in the manner established for the closely related basketene molecule.[17] Disrotatory ring opening of the norcaradiene segment of **16** would give tropilidine **17** with the potential to progress to **10** by means of an intermolecular Diels–Alder reaction and Cope rearrangement of the resulting adduct (**18**) to afford **19**, a molecule well recognized to be related thermally to *cis*-9,10-dihydronaph-

(15) In more explicit terms, these remarks relate to diradical intermediate i (see also Chart I) and to the question of its innate capability to return to snoutene (dotted arrows). We do recognize that in strainless diradical i the p orbitals at the free-radical centers are twisted approximately 30° out of planarity (molecular models) with respect to the σ bonds which must rupture to afford **10**.



i

(16) W. von E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **88**, 2078 (1966), and J. C. Stowell, unpublished observations.

(17) H. H. Westberg, E. N. Cain, and S. Masamune, *J. Amer. Chem. Soc.*, **91**, 7512 (1969).

Chart I. Possible Mechanisms for Snoutene to *cis*-9,10-Dihydronaphthalene Interconversion

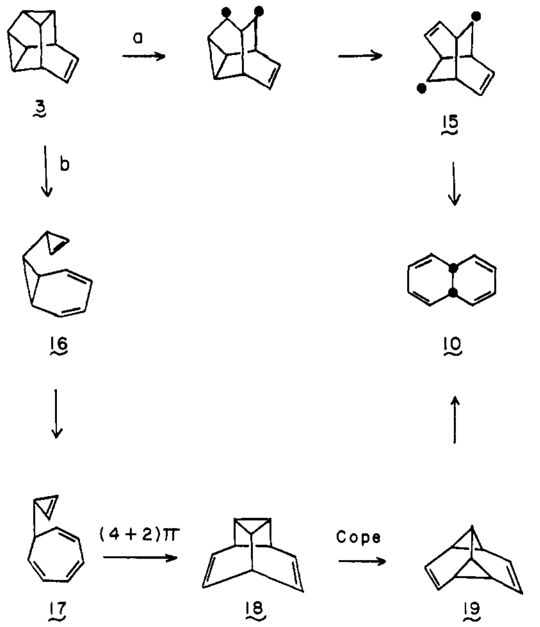
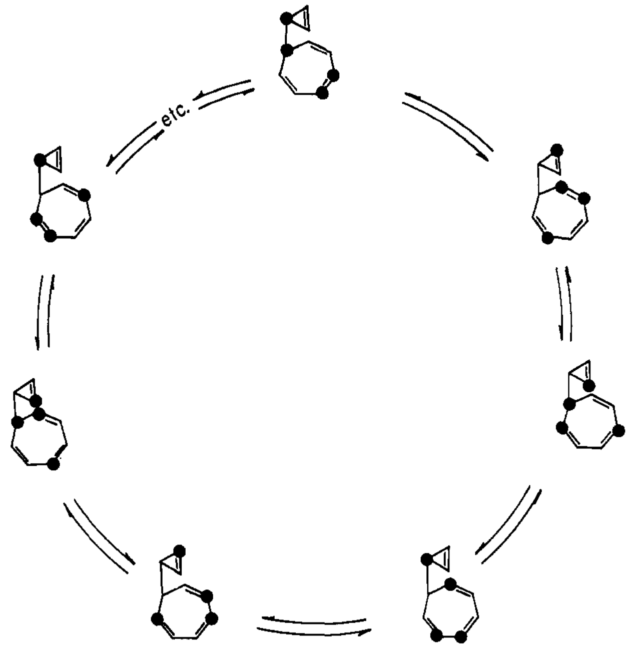


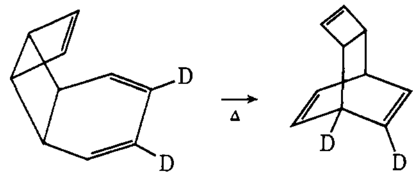
Chart II. The Sequential Degenerate Cope Rearrangements in 7-(2-Cyclopropen-1-yl)-1,3,5-cycloheptatriene (**17**)[a]



● *denotes deuterium*

[a] The more facile degenerate rearrangement of 9,10-dideuteriosnoutene would ultimately lead to **17** with deuterium substitution as indicated in the uppermost structure. The additional labeling of the cyclopropenyl hydrogens affords the opportunity for generation of 21 equivalent structures.

thalene.[18-20] In addition, it was deemed not unreasonable to assume that **17** would be capable of Cope rearrangement, a phenomenon expected by analogy to the behavior of **20**. Interestingly, however, a [3,3]sigmatropic shift in **17** would lead only to a molecule identical with the starting structure and thus this rearrangement would be entirely degenerate. Continued repetition of the process would effectively average the seven carbon atoms of the tropilidine ring and the three atoms of the cyclopropene system, it being evident that such a succession of rotational operations results in retention of the structural integrity of the two carbocyclic moieties involved. The degenerate behavior of labeled **17** is shown in Chart II. The combination of Charts I and II in conjunction with the established degenerate behavior of snoutene suggests that, should this hydrocarbon undergo thermally induced bond reorganization by mechanism b, the deuterium label in **10** would be extensively scrambled.



20 **21**

Pyrolysis of **9** at 530° was found to give rise to a limiting product distribution containing 32% **10**. Isolation of this hydrocarbon and examination of its nmr spectrum revealed that the ratio of hydrogen distribution was 4:4:2 within experimental error, that is, that complete scrambling of the deuterium label had resulted. Such an observation would appear to support the view that snoutene rearranges chiefly by mechanism b. However, at the present time it is unknown whether *cis*-9,10-dihydronaphthalene is capable in its own right of undergoing a degenerate rearrangement.[21] If this phenomenon were operative, scrambling of the deuterium at a much later stage of the rearrangement would be entirely possible. Mechanism a could therefore be uniquely operative, but the functioning of this homolytic pathway would be masked. A final solution of this mechanistic question may reside in knowledge of the thermal behavior of specifically labeled *cis*-9,10-dihydronaphthalene under conditions which are not self-immolating.[21]

In any event, the position of snoutene on the $(CH)_{10}$ energy surface is now established. One of the sources of fascination with this molecule is its propensity for degenerate rearrangement, a property shared only by two other $(CH)_{10}$ congeners, bullvalene and bicyclo[4.2.2]decatetraene.

Experimental Section

Pentacyclo[4.4.0.0^{2,5}.0^{3,10}.0^{4,8}]decane-8,9-dicarboxylic Anhydride (5). A solution of 10.0 g of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic anhydride (4)[9] in 350 ml of acetone was irradiated under nitrogen at 23° with a 200-W Hanovia mercury lamp through Vycor for 15 hr. The solvent was removed on a rotary evaporator to give a viscous oil which was subjected to 0.3 mm pressure to remove diacetone alcohol. Chromatography of the residue on a column of silica gel (3 × 35 cm) and elution with carbon tetrachloride–chloroform (1:1) gave 4.52 g (45%) of **5** as a white solid, mp 100–124°, in the first three 100-ml fractions. Recrystallization of a sample from carbon tetrachloride gave crystals melting at 124–135° (lit.[10] mp 126–130°).

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(18) M. Jones, Jr., and B. Fairless, *Tetrahedron Lett.*, 4881 (1968).

(19) W. Grimme, H. J. Riebel, and E. Vogel, *Angew. Chem.*, **80**, 803 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 823 (1968).

(20) R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970).

(21) In this regard, *cis*-9,10-dihydronaphthalene with deuterium distributed at C-9,10 (0.6 D) and at C-2,3,6,7 (1.2 D) does not appear to scramble at 410°.[22] This problem is presently under active investigation.

***cis*-Dimethyl Pentacyclo[4.4.0.0^{2,5}.0^{3,10}.0^{4,7}]decane-1,9-dicarboxylate (7).** A solution of 4.52 g (22.3 mmol) of **5** in 40 ml of methanol was heated at reflux for 6 hr. Evaporation of the solvent gave **6** as a viscous oil. This material was directly dissolved in ether and treated with diazomethane. Evaporation gave a semisolid mixture which was recrystallized three times from hexane to afford 2.12 g (38%) of **7** as white crystals, mp 78–82°. Two more recrystallizations from hexane gave crystals melting at 80–82° (lit.[11] mp 81–82°).

***cis*-Dimethyl Pentacyclo[3.3.2.0^{2,4}.0^{3,7}.0^{6,8}]decane-9,10-dicarboxylate (8).** A solution of 2.08 g of **7** and 150 mg of silver fluoroborate in 10 ml of acetone was heated at reflux for 2 hr. The cooled solution was passed through a short column of alumina to remove the silver salt; elution with acetone yielded 2.03 g (97%) of **8** as white needles, mp 95–101°. Recrystallization of this solid from hexane gave crystals melting at 101–103° (lit.[14] mp 102°).

Pentacyclo[3.3.2.0^{2,4}.0^{3,7}.0^{6,8}]dec-9-ene. Snoutene (3). Diester **8** (2.00 g, 8.06 mmol) and sodium hydroxide (1.2 g, 30 mmol) were heated at reflux in 50 ml of water until the solid dissolved (*ca.* 2 hr). The solution was cooled and acidified with sulfuric acid. The resulting precipitate was filtered, washed with water, and dried to give 1.37 g (77%) of crude diacid (mixture of cis and trans isomers), mp 210–224°.

This diacid (1.36 g) and 1.4 ml of triethylamine were dissolved in 10 ml of water and added to 90 ml of pyridine in a water-jacketed electrolysis cell equipped with platinum electrodes. The electrolysis was allowed to proceed for 10 hr at 10–23°; initial current 0.5 A, final current 0.1 A. The dark solution was diluted with 250 ml of water and extracted with five 7-ml portions of pentane. The combined pentane extracts were washed with dilute hydrochloric acid, dried, and evaporated through a Vigreux column. The residue was sublimed at room temperature and 20 mm (Dry Ice condenser) to give 133 mg (16.5%) of white crystals, mp 61–62° (lit.[14] mp 61–62°).

9,10-Dideuteriosnoutene (9). Diester **8** was hydrolyzed as above, except that NaOD in D_2O was employed. Electrolysis in the predescribed fashion gave **9** with 63% deuteration at the vinyl positions (consult Chart I).

Thermal Rearrangement of Snoutene (3). The hydrocarbon (25 mg) was slowly sublimed into a quartz tube (28 cm × 16 mm) packed with quartz chips maintained at the desired temperature. The pressure in the system was maintained at 20 mm as a slow stream of dry nitrogen was passed through the system. The pyrolysis product (24 mg) was collected in a trap cooled in a Dry Ice-acetone bath. The mixture was analyzed by vpc (SF-96 at 110°) and separated by this technique.

At 530°, there was obtained in addition to recovered snoutene (51%), *cis*-9,10-dihydronaphthalene (32%),[22] 1,2-dihydronaphthalene (4%),[23] 1,4-dihydronaphthalene (8%),[24] and naphthalene (5%). At 580°, the ratio of these products was found to be 8:5:32:36:18.

Degenerate Thermal Rearrangement of 9,10-Dideuteriosnoutene (9). The hydrocarbon (82 mg, 63% d_2 at the vinyl positons) was pyrolyzed as above at 530° to afford 80 mg of a pale yellow liquid. Vpc analysis indicated the presence of snoutene (58%) in addition to the other products found earlier. The snoutene was collected and analyzed by nmr (see Table I). Repetition of the procedure at 500° gave 86% of recovered starting material with the deuterium label specifically scrambled (Chart I).

Acknowledgment. The authors wish to express their indebtedness to the Petroleum Research Fund, administered by the American Chemical Society, for their partial support of this work.

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(22) Authentic *cis*-9,10-dihydronaphthalene was prepared by pyrolysis of bicyclo[4.2.2]decatetraene.[18]

(23) H. Hock and S. Lang, *Chem. Ber.*, **75**, 313 (1942).

(24) We thank Dr. John F. Hansen for a sample of this hydrocarbon which was prepared according to the procedure of E. S. Cook and A. J. Hill, *J. Amer. Chem. Soc.*, **62**, 1995 (1940).

Photochemical Synthesis. The Addition of Aromatic Nitro Compounds to Alkenes[1,2]

J. L. Charlton, C. C. Liao, and P. de Mayo*

Contribution from the Department of Chemistry,
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Abstract: It is shown that the photochemical addition of aromatic nitro compounds to alkenes gives 1,3,2-dioxazolidines. Certain members of this group of substances have been obtained in pure crystalline form at low temperature, but decompose readily at room temperature. Evidence is provided that the addition proceeds through an n,π* triplet in a two-step electrophilic process. The mode of decomposition of the dioxazolidine derived from *m*-chloronitrobenzene and cyclohexene has been examined. It seems very probable that an intermediate nitrenium ion is involved. In the presence of diethylamine, however, hydrogen abstraction followed by cyclization occurs in preference.

The photocycloaddition of the carbonyl group to alkenes has been extensively studied,[3] but, in contrast, the parallel property of the aromatic nitro group has received little attention.[4] In 1956 Büchi and Ayer reported on the irradiation of nitrobenzene in cyclohexene and in 2-methyl-2-butene.[5] They recorded the formation of carbonyl products, azobenzene, and other substances, and rationalized this transformation on the basis of the formation of an intermediate 1,3,2-dioxazolidine (see Scheme I). Both previously and since, such dioxazolidine formation has been postulated, but in most cases the evidence, in comparison with the experiments reported by Büchi and Ayer, has been tenuous,[6] tentative, or has been questioned.[7] The intermediary addition of the nitro group to a Schiff[8] base and

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(1) Part XXXV in this series. A preliminary account of a part of the work here described has been reported: J. L. Charlton and P. de Mayo, *Can. J. Chem.*, **46**, 1041 (1968).

(2) Publication No. 17 from the Photochemistry Unit, Department of Chemistry, University of Western Ontario.

(3) See, for example, an excellent review by D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(4) For a review see H. A. Morrison in "The Chemistry of the Nitro and Nitroso Groups," Part 1, H. Feuer, Ed., Interscience, New York, N. Y., 1969, p 193.

(5) G. Büchi and D. E. Ayer, *J. Amer. Chem. Soc.*, **78**, 689 (1956).

(6) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955).

(7) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).