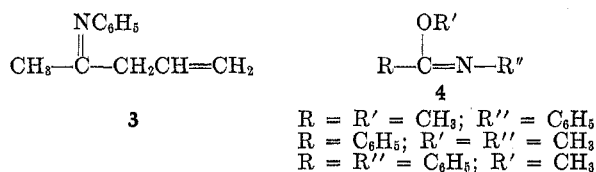


the limited and formal analogy between imine and carbon-carbon double-bond photochemistry, for those cases which involve a chromophore which contains the excited imine, is not so unreasonable as it might appear.

The *meso* isomers of **2a** and **2c** are unambiguously assigned on the basis of the above chemical conversions. Assignments of *meso* and *dl* stereochemistries for **2b** rest on the assumption that the resonances of the benzyl proton in the *meso* isomer will appear downfield from those of the *dl* isomer. Such a difference is observed in the mixture from **2c** and in analogous glycols.<sup>30</sup> The *meso* structure of **2d** is provisional and follows from its preparation by aluminum reduction of the imine, a reaction which appears to give *meso* products.<sup>3,8</sup> Small energy differences due to steric effects and hydrogen bonding in the transition states for radical coupling leading to the *meso* and *dl* products could account for the different stereochemistries,<sup>31</sup> but a contribution from photochemical equilibration has not been ruled out.

Intramolecular photocyclization between a carbonyl group and a carbon-carbon double bond has been observed with 5-hexen-2-ones.<sup>6b</sup> The corresponding



(30) J. Wiemann, G. Dana, S. Thuan, and M. Brami, *C. R. Acad. Sci., Ser. C*, **258**, 3724 (1964).

(31) J. H. Stocker and R. M. Jenevein, *J. Org. Chem.*, **34**, 2807 (1969).

anil **3** was prepared and irradiated in hexane, benzene, and alcohol. In each case starting anil or polymeric products were observed. Imidates also appear to be stable to some photolyses.<sup>32</sup> Photolyses of the imidates **4** in hexane, benzene, or ethanol give polymeric products or starting material. Attempts to sensitize the photo-reaction with benzaldehyde in ethanol give only hydrobenzoin<sup>33</sup> and 1-phenyl-1,2-propanediol.<sup>34</sup>

**Registry No.**—**1a**, 25630-14-2; **1b**, 25558-09-2; **1c**, 25558-10-5; **1d**, 25558-11-6; **1e**, 25558-12-7; **1f**, 25558-13-8; **2a** (*meso*), 25558-54-7; **2b** (*dl*), 25558-39-8; **2b** (*meso*), 25558-55-8; **2c** (*dl*), 25558-57-0; **2c** (*meso*), 25558-56-9; **2c** (*meso*) (picrate), 25630-15-3; **2d** (*meso*), 25558-58-1; **2e**, 25558-14-9; **2f**, 25558-15-0; **3**, 25558-16-1; 5-(*N*-phenyl)amino-1-hexene, 25558-17-2; *meso*-1,2-diamino-1,2-diphenylethane, 951-87-1; *meso*-*N,N'*-bis(3-aminopropyl)-1,2-diamino-1,2-diphenylethane, 2558-60-5; *meso*-*N,N'*-bis(3-aminopropyl)-1,2-diamino-1,2-diphenylethane (tetrabenzamide), 25557-86-2.

**Acknowledgment.**—We are grateful to the Public Health Service (GM-12595) and the Alfred P. Sloan Foundation for support and to the National Science Foundation for an NDEA fellowship to Charles Robert Payet.

(32) L. A. Paquette and G. R. Krow, *J. Amer. Chem. Soc.*, **90**, 7149 (1968); L. A. Paquette and J. R. Malpass, *ibid.*, **90**, 7151 (1968).

(33) G. Ciamician and P. Silber, *Chem. Ber.*, **34**, 1530 (1911).

(34) H. Göth, P. Cerutti, and H. Schmid, *Helv. Chim. Acta*, **48**, 1395 (1965).

## Photocyclizations of 5-Vinylnorbornenes

R. R. SAUERS AND K. W. KELLY

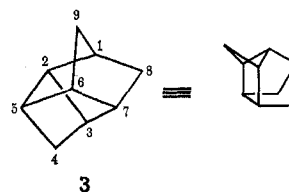
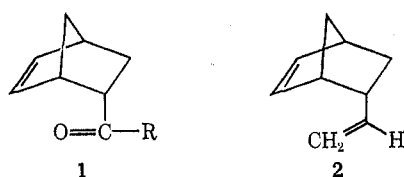
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Received April 3, 1970

Acetone-sensitized photocyclization of 5-vinylnorbornene (**2**) has been shown to produce tetracyclo[4.2.1.0<sup>2,5</sup>.0<sup>3,7</sup>]nonane (**3**). Ketone **12** has been prepared by an intramolecular thermal cycloaddition of ketene **11**. The chlorides **18c** and **18t** undergo rapid *cis-trans* interconversion in competition with cyclization to form **20**.

Concurrently with our recent studies of photocyclizations of 5-acylnorbornenes (**1**)<sup>1</sup> we initiated a similar investigation of the isoelectronic system 5-vinylnorbornene (**2**).<sup>2</sup> Our interest in this molecule was de-

“crossed *vs.* parallel” addition.<sup>3</sup> By analogy with 5-acylnorbornene cyclization, the expected product should be tetracyclo[4.2.1.0<sup>2,5</sup>.0<sup>3,7</sup>]nonane (**3**); however, sim-



rived from the synthetic potential of the cyclization and from certain photochemical aspects in the realm of 1,5-diene systems.

The first major question we sought to answer concerned the regioselectivity of the cyclization, *i.e.*

(1) R. R. Sauer, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 79 (1969).

(2) R. R. Sauer and W. L. Schinski, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 112.

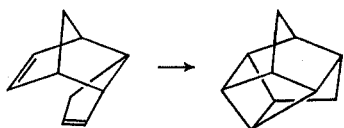
ple examples of this type of behavior are absent from the literature.<sup>4</sup> Furthermore, the double bonds of the constrained analog dicyclopentadiene undergo parallel cycloaddition.<sup>5</sup> Although crossed addition is probably

(3) R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967).

(4) Simple  $\gamma,\delta$ -unsaturated ketones usually give mixtures of the two product types on irradiation. For a recent summary see W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966). Comparable examples of simple 1,5-diene cyclizations are available only in the gas phase.<sup>3</sup>

(5) G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963).

structurally impossible in this system, it is clear that the parallel mode of addition between the double bonds



of 2 should be feasible. In any event, novel tetracyclic ring systems could be anticipated from cyclization of 2.

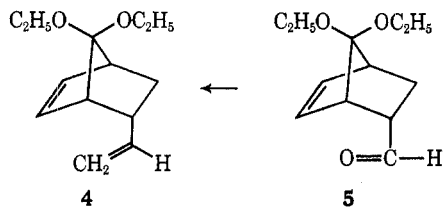
The notable absence of solution-phase photocyclizations of simple 1,5-dienes in the literature undoubtedly is a consequence of the expected inefficiency of vertical energy transfer to simple olefins.<sup>6</sup> In this context, the 5-vinylnorbornene system appeared to be a useful substrate for the study of the behavior of simple 1,5-dienes since triplet energy transfer to norbornene double bonds is well-documented for a variety of sensitizers.<sup>7</sup> Additionally, the ready availability of a variety of substituents on the vinyl group would allow for further elaboration of the details of these cyclizations.

In these initial studies we wish to report on some of the more chemical aspects of sensitized cyclizations of 2 and some of its derivatives.

### Results

Irradiation of dilute solutions of commercially available 5-vinylnorbornene (2)<sup>8</sup> in benzene-acetone with Corex-filtered light led to the production of one major and several minor photoproducts. The infrared and nmr spectra of the major product revealed no evidence of unsaturation in agreement with the presumed tetracyclic structure of this material. Owing to the simplicity of the nmr spectrum we were biased toward structure 3 for the major photoproduct. The next experiments were designed with the objective of introducing a substituent into the tetracyclic system which could serve as a site for future manipulations. In this way, it was hoped to provide suitable degradation products to establish the structures of the photoproducts and also to provide intermediates for the synthesis of other molecules of interest.

For these purposes, it was decided to attempt to introduce a carbonyl function at C<sub>9</sub>. For convenience, we chose to utilize the ketal 4 in the cyclization step since it appeared readily available from the known<sup>9</sup> aldehyde 5. Thus, reaction of 5 with methylenetri-



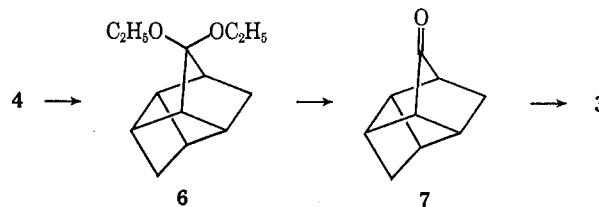
(6) For a recent discussion, see J. Saltiel, K. R. Neuberger, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 3658 (1969), and N. C. Yang, J. I. Cohen, and A. Shani, *ibid.*, **90**, 3264 (1968).

(7) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

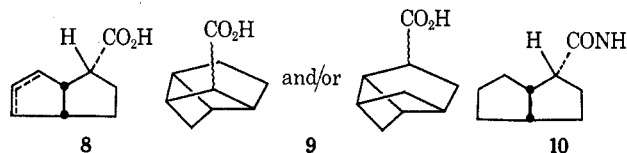
(8) This material was purchased from Columbia Chemicals Co., Inc., Columbia, S. C., and was shown to be a 50:50 mixture of the *exo* and *endo* isomers.

(9) The aldehyde 5 was reported by P. E. Eaton and R. A. Hudson, *J. Amer. Chem. Soc.*, **87**, 2769 (1965). Attempts to induce 1,3-butadiene to react with cyclopentadienone diethyl ketal did not produce significant yields of adduct: K. Kelly, unpublished observations.

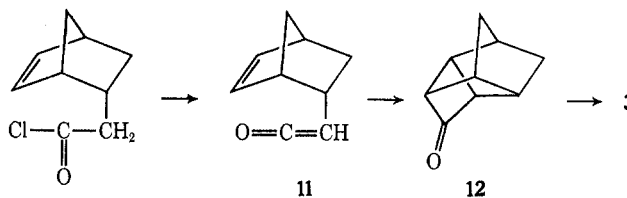
phenylphosphorane gave 4 in 78% yield. Photocyclization of the latter produced a tetracyclic ketal whose structure was correlated with that of 3 *via* hydrolysis to a ketone ( $\lambda_{C=O}$  5.67  $\mu$ ) which gave 3 on Wolff-Kishner reduction. The structures assigned to the ketal and ketone were those of 6 and 7, respectively, on



the basis of the outcome of base-catalyzed cleavage experiments. Thus, under the very mild conditions developed by Gassman and Zalar<sup>10</sup> ketone 7 was transformed into a mixture of unsaturated bicyclic and tricyclic acids. The major component of this mixture was shown to be a *cis*-bicyclo[3.3.0]octene-*endo*-2-carboxylic acid (8) by its conversion to the known<sup>11</sup> *cis*-bicyclo[3.3.0]octane-2-*endo*-carboxamide (10). No attempts were made to define the structure of the tricyclic components (presumably 9 and isomers) owing to the low yields of these.



Although this experiment would appear to establish satisfactorily the basic structures of the tetracyclic systems in question, a more direct correlation was sought.<sup>12</sup> Ketone 12 appeared to be better suited to this type of degradation procedure owing to the expected stability of the product and the presence of the symmetry plane. A viable synthesis of 12 was developed which utilized *in situ* generation and cycloaddition of ketene 11.<sup>13</sup> Not only could 12 be converted into hydrocarbon 3 (*via* the thioketal and Raney nickel desulfurization), but also the base-catalyzed



cleavage reaction<sup>10</sup> proceeded cleanly with the formation of a new tricyclic acid in good yield. The latter was shown to be tricyclo[3.3.0.0<sup>3,7</sup>]octane-2-carboxylic acid (13) by thermal decarboxylation of the *t*-butyl

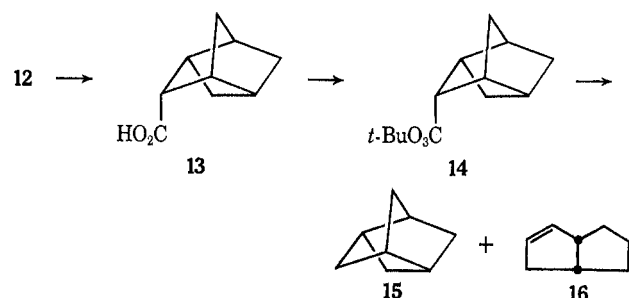
(10) P. G. Gassman and F. V. Zalar, *ibid.*, **88**, 2252 (1966).

(11) A. C. Cope and M. Brown, *ibid.*, **80**, 2859 (1958). We are indebted to Professor A. Nickon for a sample of this material.

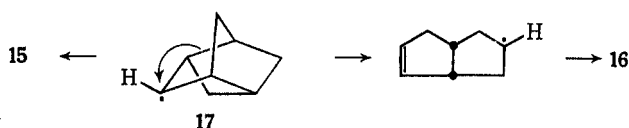
(12) The mechanism by which 8 is formed from 7 must involve addition of hydroxide ion to the carbonyl group followed by two ring openings. The second cleavage presumably involves ring opening of a cyclobutylcarbinyl anion. Precedent for this general type of reaction has been furnished with Grignard reagents. For a discussion and references, see E. A. Hill, R. J. Theissen, and K. Taucher, *J. Org. Chem.*, **34**, 3061 (1969).

(13) P. Yates and A. G. Fallis, *Tetrahedron Lett.*, 2493 (1968).

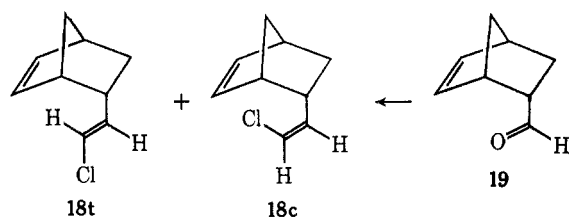
perester (14). This sequence produced the known<sup>14</sup> hydrocarbon tricyclo[3.3.0.0<sup>3,7</sup>]octane (15) and, surprisingly, an almost equal amount of bicyclo[3.3.0]octene-2 (16). Apparently, the intermediate free rad-



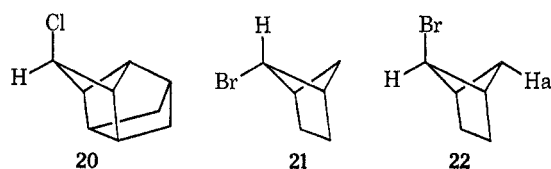
ical in this reaction (17) undergoes cleavage in competition with chain transfer.<sup>15</sup>



The final phase of the experimental work dealt with the synthesis and photocyclizations of 1-chloro-2-(5-norbornenyl)ethylenes **18c** and **18t**. The initial experiments utilized the *cis-trans* mixture obtained on treatment of aldehyde **19** with chloromethylenetri-



phenylphosphorane. The major product obtained on acetone-sensitized photocyclization was assigned structure **20** on the basis of spectral data and the fact that reductive dechlorination produced **3**. The configuration of the chlorine substituent is supported by the nmr spectrum owing to the appearance of a sharp singlet at  $\delta$  3.76. The 5-bromobicyclo[2.1.1]hexanes **21** and **22**



serve as models for this analysis.<sup>16</sup> Thus, the downfield proton in **21** appears as a multiplet owing to coupling by the two vicinal protons. The geometrical relationships in **22** are such that the only observable coupling is to H<sub>a</sub>. The similar geometry about C<sub>4</sub> in **20** coupled with the absence of a proton in the W configuration leads to the prediction of a singlet for the proton in question in agreement with the observed spectrum.

(14) P. K. Freeman, V. N. M. Rao, and G. E. Bigam, *Chem. Commun.*, 511 (1965).

(15) Free-radical chlorination of **15** reportedly leads only to the tricyclic chloride; chain transfer would be expected to be relatively more rapid in this case (private communication from P. K. Freeman).

(16) For a detailed discussion, see K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Amer. Chem. Soc.*, **84**, 1594 (1962).

Lastly, samples of the *cis* and *trans* isomers were isolated by preparative gas chromatography and subjected to irradiation in the presence of acetone. Samples were removed at 4 and 21 hr and analyzed (Table I) for

TABLE I  
SENSITIZED IRRADIATIONS OF **18t** AND **18c**

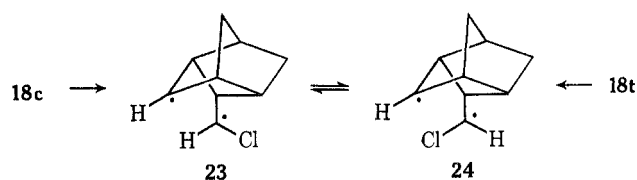
Conversion, %	% yield			Time, hr
	<b>18c</b>	<b>18t</b>	<b>20</b>	
0	0	100	0	0
19	9	81	3	4
60	18	40	7.5	21
0	100	0	0	0
9	91	7.5	0	4
47	53	19	1	21

total disappearance of starting material, percentage of geometrical isomerization, and percentage of product **20** formed.

### Discussion

The formation of tetracyclo[4.2.1.0<sup>2,5</sup>.0<sup>3,7</sup>]nonane systems on sensitized irradiation of 5-vinylnorbornenes has been demonstrated for several derivatives. These results reinforce the empirical rules developed for cyclizations of simple 1,5-dienes in the gas phase<sup>3</sup> and for more complex systems in solution.<sup>17</sup> In addition, the results found on photocyclization of the *cis* and *trans* chlorides provide data of mechanistic significance. This data may be summarized as follows: (a) both chlorides produced the same tetracyclic product, *i.e.*, **20**; (b) the *trans* isomer **18t** cyclized considerably faster than the *cis* isomer **18c**; (c) both chlorides underwent geometrical isomerization at about the same rates which in turn were considerably faster than cyclization.

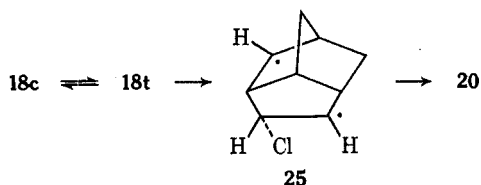
The formation of similar products from geometrically isomeric starting materials has been noted previously and has been attributed to rotational equilibration of intermediate diradicals.<sup>17</sup> In the present context, this argument requires the intermediacy of species **23** and **24** which must equilibrate faster than they cyclize.



It is difficult to rationalize the difference in rates of formation of **20** from **18t** and **18c** if **23** and **24** are necessary intermediates since the rates of formation of the latter would not be expected to be very different. Also, severe distortion of the norbornyl ring must accompany formation of **23** or **24**, an energetically costly process.

(17) R. S. H. Liu and G. S. Hammond, *ibid.*, **89**, 4936 (1967); R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *Tetrahedron*, **19**, 1995 (1963); R. C. Cookson, *Pure Appl. Chem.*, **9**, 575 (1964); J. D. White and D. N. Gupta, *Tetrahedron*, **25**, 3331 (1969); G. Büchi and I. M. Goldman, *J. Amer. Chem. Soc.*, **79**, 4741 (1957); F. T. Bond, H. L. Jones, and L. Scerbo, *Tetrahedron Lett.*, 4685 (1965); J. L. Charlton, P. DeMayo, and L. Skattebøl, *ibid.*, 4679 (1965); J. L. Courtney and S. McDonald, *Aust. J. Chem.*, **22**, 2411 (1969); J. K. Crandall and C. F. Meyer, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, ORGN 99.

We believe that the data is better rationalized in terms of the intermediacy of diradical **25**. Clearly, the



formation of **25** requires relatively little distortion of the ring system. In addition, the incursion of a large steric effect on the relative ease of formation of a new bond between the ends of the diene systems now seems eminently reasonable provided that the geometrical integrity of the isomers is maintained at the onset of cyclization. In other words, it is the partitioning of the planar triplets between addition and relaxation to twisted states which governs the relative importance of isomerization and cyclization.<sup>18</sup> The fact that 5-vinylnorbornene could be induced to cyclize on sensitization with acetophenone ( $E_T = 73.6$  kcal/mol<sup>19</sup>) is best rationalized in terms of initial energy transfer to the norbornene double bond ( $E_T \sim 72$  kcal/mol)<sup>7</sup> as opposed to the vinyl group ( $E_T \sim 82$  kcal/mol<sup>20</sup>).

The alternate possibility suggested by White and Gupta<sup>17</sup> that initial exiplex formation precedes cyclization would not be inconsistent with our results. Since a close association between the two olefinic centers would be expected, it would not be unlikely that the *trans* chloride would be considerably more reactive than the *cis* isomer.

In any event, it would appear that the nonplanar chloroethylene triplets are not the immediate precursors of the cyclized product.<sup>21,22</sup>

### Experimental Section

Elemental analyses were determined by Micro-Tech Laboratories, Skokie, Ill. Infrared spectral data was obtained from a Perkin-Elmer Model 137 spectrometer on thin films or as noted. Nuclear magnetic resonance spectra were obtained from a Varian Model A-60 spectrometer in carbon tetrachloride with tetramethylsilane as internal standard. Gas chromatograms were determined on an Aerograph A90P (analytical and preparative) and a Barber-Coleman Model 5000 chromatograph (capillary) on the following columns: (A) 15-ft 5% Carbowax 20M, (B) 12-ft 2% Carbowax 20M, (C) 12-ft 10% Apiezon L, (D) 150-ft Apiezon L, and (E) 150-ft Castorwax. Melting points were determined on a Mel-Temp apparatus and were uncorrected.

**Photocyclization of 2. A. Acetone Sensitization.**—A deoxygenated solution of 2.00 g of **2** in a mixture of 2 ml of acetone and 300 ml of benzene was irradiated with the light from a 450-W medium pressure immersion lamp equipped with a Corex filter. Only traces of **2** remained after 22 hr. Analysis by gc (D, 80°) indicated one major component and ~8% minor constituents. The solvents were removed by slow distillation at atmospheric pressure to yield a residue which was distilled at 65–69° (28.5 mm), yield 0.70 g. A pure sample of tetracyclo[4.2.1.0<sup>2,5</sup>.0<sup>3,7</sup>]nonane (**3**), mp 63.5–64.5°, was obtained by preparative gc (C, 140°): nmr  $\delta$  2.30 (m, 5), 1.96 (s, 1), 1.44 (m, 5), 1.09 (d,  $J = 8$  cps, 1).

(18) The  $S_0 \rightarrow T_1$  transition energy for a vinyl chloride group is unknown. For *trans*-dichloroethylene, estimates range from 72 to 60 kcal/mol; cf. G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944), and Z. R. Grabowski and A. Bylina, *Trans. Faraday Soc.*, **60**, 1131 (1964).

(19) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(20) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(21) It is necessary to assume that energy transfer to the isomeric chloroethylenes does not produce noninterconverting diastereomeric twisted triplet states.

(22) For a relevant discussion with diene triplet states, see P. A. Leermakers, J.-P. Montillier, and R. D. Raub, *Mol. Photochem.*, **1**, 57 (1969).

*Anal.* Calcd for C<sub>9</sub>H<sub>12</sub>: C, 89.92; H, 10.07. Found: C, 89.78; H, 10.21.

**B. Acetophenone Sensitization.**—A solution of 10 g of **2** and 10 g of acetophenone in 1200 ml of benzene was irradiated by the above procedure for 33 hr. The benzene was evaporated and the residue was distilled. A 4.0-g fraction was collected which had bp 40–83° (18 mm). Analysis by gc revealed two components in nearly equal amounts and two minor components (<2%). The two major components were collected by gc and shown to be starting material and **3**.

**5-Vinylnorbornen-7-one Diethyl Ketal (4).**—A slurry of 1.93 g (0.080 mol) of sodium hydride in 35 ml of dimethyl sulfoxide (DMSO) was stirred and heated at 70–75° until the mixture became homogeneous. A solution of 28.67 g (0.083 mol) of methyltriphenylphosphonium bromide in 70 ml of DMSO was added to the above solution. After 10 min, a solution of 13.8 g (0.066 mol) aldehyde **5** in 25 ml of DMSO was added slowly. The temperature of the reaction mixture was kept between 35 and 40° by means of an ice bath. The resulting mixture was allowed to cool to 25° over 1 hr at which time it was poured into 1 l. of an ice-water mixture. The reaction product was extracted into a total of 300 ml of pentane in several stages. After drying and evaporative removal of the solvent, an oil was obtained which on distillation at 58.3° (0.3 mm) yielded 10.64 g (78%) of **4**: nmr  $\delta$  5.95–5.00 (m, 5), 3.37 (m, 4), 2.08 (m, 1), and 1.10 (m, 7); ir 7.67 (s), 7.82 (s), 8.09 (s), 8.92 (s), 9.30 (s), 10.98 (s), 11.48, 12.05, 12.80, 13.45, 13.62, 13.90, and 14.30  $\mu$ .

*Anal.* Calcd for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>: C, 74.96; H, 9.68. Found: C, 74.64; H, 9.82.

**Tetracyclo[4.2.1.0<sup>2,5</sup>.0<sup>3,7</sup>]nonan-8-one Diethyl Ketal (6).**—A solution of 1.5 g of **4** in 600 ml of benzene which contained 1.5 ml of acetone was irradiated for 20 hr under the above conditions. Only a trace of starting material could be detected by gc (A, 150°); one major and one minor peak were seen. Evaporation of the solvent and distillation of the residue gave 1.0 g (66%) of **6**: bp 74–75° (0.3 mm); nmr  $\delta$  3.50 (m, 4), 2.48 (s, 4), 2.80–1.30 (m, 4), 1.15 (m, 6); ir 8.80 (s), 8.91 (s), 9.24 (s), 9.44 (s), 10.14, and 11.38  $\mu$ .

*Anal.* Calcd for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>: C, 74.96; H, 9.68. Found: C, 75.18; H, 9.79.

**Tetracyclo[4.2.1.0<sup>2,5</sup>.0<sup>3,7</sup>]nonan-8-one (7).**—A solution of 3.34 g (0.016 mol) of **6** in 33 ml of ether was stirred vigorously with 33 ml of 1 N hydrochloric acid for 3.5 hr. The ether layer was separated, dried and distilled to yield 1.72 g (80%) of **7**: bp 42° (0.5 mm); nmr  $\delta$  2.95–2.35 (m, 4), 2.30–1.97 (m, 2), 1.97–1.66 (m, 3), 1.50–1.05 (m, 1); ir 5.67, 8.84, 11.90, 12.62, 13.21, and 13.61  $\mu$ .

*Anal.* Calcd for C<sub>9</sub>H<sub>10</sub>O: C, 80.56; H, 7.51. Found: C, 80.76; H, 7.80.

**Wolff-Kishner Reduction of 7.**—A solution of 0.30 g (2.29 mmol) of **7** and 0.30 g (6.0 mmol) of hydrazine hydrate in 3 ml of abs ethanol was heated at reflux for 6 hr. After standing overnight at 25° the reaction mixture was diluted with water and the product was extracted into chloroform. The crude hydrazone was dissolved in 2 ml of DMSO and added over 2 hr to a solution of excess potassium *t*-butoxide in 2 ml of DMSO. After standing for 0.5 hr, the mixture was poured into ice-water and the product was extracted into pentane. Evaporation of the solvent followed by sublimation of the residue gave 0.147 g (58%) of **3**: ir identical with that of above material.

**Cleavage of 7 with Base.**<sup>10</sup>—A slurry of 10.65 g (0.095 mol) of potassium *t*-butoxide and 30 ml of dry ether was cooled in an ice bath in a nitrogen atmosphere. With vigorous stirring, 0.51 g of water was added from a syringe through a rubber septum. The ice bath was removed and 1.65 g (0.012 mol) of ketone **7** was added. After stirring for 2 hr at 25°, the reaction mixture was poured onto ice. The aqueous phase was extracted with ether followed by acidification with hydrochloric acid. On extraction with ether there was obtained 1.42 g (75%) of crude acidic product. A small amount (0.37 g) of crystalline material was separated from the oily acids by trituration with pentane. The two acid fractions were separately converted to methyl esters by conversion to acid chlorides (thionyl chloride in benzene) followed by reaction with methanol in benzene-triethylamine. The esters prepared from the noncrystalline fraction were resolved into four components on gc (A, 175°) in the relative proportions 15:30:51:4. On preparative gc the major component and the first two peaks could be collected. The major component proved to be identical with the ester prepared from the crystalline acid: nmr  $\delta$  5.45 (m, 2), 3.59 (s, 3), 3.4–1.1 (m, 9); ir 3.27, 5.75

(s), 8.50 (s), 9.58, 9.72, 10.75, and 14.00 (s)  $\mu$ . The structure assigned to this ester is that of methyl *endo*,*cis*-bicyclo[3.3.0]oct-2-ene-6-carboxylate or its isomer **8**.

*Anal.* Calcd for  $C_{10}H_{14}O_2$ : C, 72.26; H, 8.94. Found: C, 72.44; H, 8.52.

The nmr of the mixture of the first two components showed no olefinic protons, two methyl peaks at  $\delta$  3.63 and 3.56 and complex absorption from  $\delta$  2.70 to 1.0. This data is consistent with what would be expected for a mixture of tricyclic esters **9**.

*Anal.* Calcd for  $C_{10}H_{14}O_2$ : C, 72.26; H, 8.94. Found: C, 72.59; H, 8.61.

*endo-cis*-Bicyclo[3.3.0]octane-2-carboxamide (**10**).—A solution of 0.35 g of the above crystalline acid in 20 ml of methanol was reduced at 40 psi of hydrogen in the presence of 5% palladium on carbon. After removal of the catalyst by filtration and evaporation of the methanol, the saturated acid was converted to the acid chloride (thionyl chloride) and the amide (ammonium hydroxide); mp 162–163.8° (lit. mp 162.4–163.3°) after crystallization from benzene; yield, 0.155 g (45%). The infrared spectrum ( $CHCl_3$ ) was virtually identical with that of an authentic sample of **10**<sup>11</sup> and was quite different from that of a sample of *exo-cis* isomer.<sup>23</sup>

Tetracyclo[4.2.1.0<sup>2,5</sup>.0<sup>3,7</sup>]nonan-4-one (**12**).—A solution of 22.21 g (0.146 mol) of 5-norbornene-2-acetic acid<sup>24</sup> in 250 ml of dry benzene was allowed to react with 23.2 g (0.196 mol) of thionyl chloride for 48 hr at 25°. Evaporation of the solvent followed by distillation of the residue yielded 17.34 g (70%) of acid chloride, bp 55–62° (0.1 mm). A solution of the latter in 50 ml of dry benzene was added over 2 hr to a solution of 10.35 g (0.10 mol) of triethylamine in 1 l. of refluxing benzene. The cooled mixture was poured onto ice-water and the benzene layer was washed successively with dilute aqueous hydrochloric acid and sodium bicarbonate solutions. The dried extracts were concentrated to yield a brown oil which gave 8.37 g (61%) of a white sublimate at 75° (10 mm): nmr  $\delta$  2.69 (d,  $J = 1.3$  cps, 3), 2.50 (s, 3), and 1.58 (s, 4); ir ( $CCl_4$ ) 5.57 (sh), 5.61 (s), 7.72, 7.93, 9.00, and 9.68  $\mu$ .

*Anal.* Calcd for  $C_9H_{10}O$ : C, 80.56; H, 7.51. Found: C, 80.36; H, 7.42.

Conversion of **12** to **3**.—A solution of 0.10 g of ketone **12** in 2 ml of ether was treated with 0.20 g of ethanedithiol and *ca.* 1 mg of boron trifluoride etherate. After 4 hr at 25° the solution was washed with aqueous sodium bicarbonate, dried and evaporated. The crude thioketal was dissolved in 5 ml of ethanol and treated with a small quantity of Raney nickel suspended in ethanol. The resulting mixture was heated at reflux for 4 hr after which time the nickel was removed by filtration. The filtrate was diluted with water and the product was extracted into pentane. Preparative gas chromatography of the concentrated extracts revealed one component whose ir spectrum was identical with that of **3**.

Tricyclo[3.3.0.0<sup>3,7</sup>]octane-2-carboxylic Acid (**13**).—The ketone (7.24 g, 0.054 mol) was cleaved as before with 47.2 g (0.42 mol) of potassium *t*-butoxide and 2.26 g of water. The acidic fraction obtained (6.37 g, 78%) had mp 99–100.5° after crystallization from hexane: nmr  $\delta$  11.98 (s, 1), 2.52–2.38 (s, 5), and 1.42 (s, 6); ir (Nujol) 5.86 (s), 7.76 (s) 10.44 (s), and 13.38  $\mu$ .

*Anal.* Calcd for  $C_9H_{12}O_2$ : C, 71.02; H, 7.95. Found: C, 71.08; H, 7.91.

Decarboxylation of **13**.<sup>25</sup>—The *t*-butyl perester of **13** was prepared by addition of 0.75 g (4.4 mmol) of the acid chloride (thionyl chloride, triethylamine) to 0.901 g (10.0 mmol) of *t*-butyl hydroperoxide in 5 ml of *p*-cymene. After 2 hr at 0°, the reaction was quenched by addition of ice water. The organic layer was washed with water, hydrochloric acid and aqueous sodium bicarbonate. The dried organic phase was placed in a 15-ml flask equipped with a short-path distillation head. On heating to 125–130° carbon dioxide evolution was observed. After 1 hr the temperature was raised and three fractions were collected: (a) bp <110°; (b) 110–174°; (c) 174–176°. Gc analysis (C, 168°) of these fractions revealed two volatile components in fraction b in the ratio of 57:43. The major component had an infrared spectrum which was identical with that of *cis*-bicyclo[3.3.0]oct-2-ene (**16**).<sup>26</sup> The second component and infrared and nmr spectra congruent with those of tricyclo[3.3.0.0<sup>3,7</sup>]octane (**15**).

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*cis,trans*-1-Chloro-2-(bicyclo[2.2.1]hept-2-en-5-yl)ethene (**18c**, **18t**).—A solution of 70 g (0.57 mol) of aldehyde **19**<sup>27</sup> (88% *endo*) in 200 ml of ether was added over 30 min to a suspension prepared from 1.0 mol of *n*-butyllithium, 262 g (1.0 mol) of triphenylphosphine and 99 g (1.0 mol) of methylene chloride in 400 ml of ether.<sup>28</sup> The temperature was maintained at –30° during the addition after which the reaction mixture was allowed to warm to 25° overnight. The resulting mixture was poured onto ice and filtered. The aqueous layer was extracted with ether and the combined extracts were washed with water and dried. The crude product obtained on evaporation of the extracts was triturated with pentane to remove triphenylphosphine oxide. Evaporation of the filtered pentane solution gave 42.14 g (48%) of an oil, bp 74–76° (6 mm). Gc analysis (A, 147°) revealed two main components in nearly equal amounts. Each peak had a small shoulder attributable to the corresponding *exo* isomer. The nmr spectra of the separated materials in both cases revealed clean quartets attributable to the protons on C<sub>2</sub> of the ethylenic moiety. In the spectrum of the component believed to consist of *exo* and *endo trans* isomers this quartet appeared at  $\sim\delta$  5.25 and showed two couplings, 13 cps (*trans*-HC=CH) and 9 cps (*vic*-CH-CH). In the mixture of *cis* isomers the quartet ( $\delta$  5.23) showed couplings of 9 cps (*cis*-HC=CH) and 7 cps (*vic*-HC-CH).

*Anal.* Calcd for  $C_9H_{11}Cl$ : C, 69.90; H, 7.17; Cl, 22.93. Found (*trans*): C, 69.74; H, 7.31; Cl, 22.85. Found (*cis*): C, 70.15; H, 7.37; Cl, 23.08.

4-Chlorotetracyclo[4.2.1.0<sup>2,5</sup>.0<sup>3,7</sup>]nonane (**20**).—A solution of 20.4 g of the mixture of *cis* and *trans* chlorides (**18c**, **18t**) in 5 l. of benzene and 25 ml of acetone was irradiated as before for 5 days. The solvents were removed *in vacuo* and the residue was distilled, bp 78–86° (8 mm), to yield 13.24 g of distillate. Gc analysis (E, 100°) showed two new materials in the amounts 11% and 27% (**20**) and considerable amounts of starting materials (~62%). Unsaturated materials were removed by addition of excess bromine in carbon tetrachloride followed by distillation. The only component to survive this treatment was **20**: yield 1.33 g; bp 85–86° (8 mm); nmr  $\delta$  3.76 (s, 1), 3.22 (s, 1), 2.6–2.0 (m, 5), and 1.50 (s, 4); ir 7.70, 7.79, 7.90, 8.14, 12.22, 13.00 (s), and 13.58  $\mu$ .

*Anal.* Calcd for  $C_9H_{11}Cl$ : C, 69.90; H, 7.17; Cl, 22.93. Found: C, 70.12; H, 7.11; Cl, 22.75.

Irradiations of **18c** and **18t**.—In separate test tubes were placed 65  $\mu$ l of the *cis* (*exo*, *endo*) and *trans* (*exo*, *endo*) chlorides, 100  $\mu$ l of acetone, and 4 ml of benzene. The tubes were suspended in the center of a Rayonet photochemical reactor and irradiated with the 3000-Å source. Five-microliter aliquots were removed at 4 and 21 hr and analyzed by gc (A, 147°). Since the conditions used did not resolve the *exo* and *endo* components, the percentages reported in Table I refer to the total changes in *cis* and *trans* chlorides normalized to the unirradiated solutions. The qualitative conclusions reached are not affected by the presence of the *exo* isomers.

Conversion of **20** to **3**.—To a suspension of 0.60 g (0.263 mg-atoms) of lithium dispersion (1% sodium) in 5 ml of ether was added 0.474 g (3.1 mmol) of **20**. The reaction mixture was stirred and heated at reflux for 2.5 hr. The reaction mixture was quenched with excess methanol and then washed with water. The ether layer was dried and concentrated. Preparative gc (C, 140°) gave 0.105 g (28%) of a single product whose nmr and ir spectra were identical with those of **3**.

Registry No.—**3**, 25557-71-5; **4**, 25554-54-5; **6**, 25557-72-6; **7**, 25557-73-7; **8** (2-ene methyl ester), 25554-55-6; **8** (1-ene methyl ester), 25554-56-7; **12**, 25557-74-8; **13**, 25679-33-8; **18c**, 25554-57-8; **18t**, 25554-58-9; **20**, 25630-08-4.

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