

such a reaction in a nitrogen aromatic ketone. This also represents the first reported case of "photochemical cyclopropanol formation" in aryl alkyl ketones involving direct hydrogen abstraction.<sup>20</sup>

The anomalous photobehavior observed in the 4-butyrylpyrimidine (**2**) relative to the 2- and 5-butyrylpyrimidines (**1** and **3**) is not easily explained on the basis of present experimental information. However, 4-substituents are known<sup>23</sup> to affect the  $n, \pi^*$  absorption characteristics of pyrimidine to a greater extent than 2- and 5-substituents, and we do in fact observe a bathochromic shift in the  $n, \pi^*$  absorption band of 4-butyrylpyrimidine (**2**) relative to the 2- and 5-butyryl isomers, **1** and **3**. The unusual behavior may reflect, then, a closer proximity of the ring nitrogen and carbonyl  $n, \pi^*$  states in 4-pyrimidyl ketones and greater triplet interactions. There are two plausible mechanisms that can account for the solvent effect observed in the formation of cyclopropanol (**10**). The first involves a vibronically mixed<sup>3</sup> triplet state which undergoes hydrogen abstraction by both the excited carbonyl and ring nitrogen to form a normal 1,4-biradical and a 1,3-biradical. In nonpolar solvents formation of the 1,4-biradical is favored and leads primarily to type II products. In polar solvents the 1,3-biradical is favored and leads to a predominance of cyclopropanol product. Alternatively, the solvent effect could be rationalized in terms of two lowest lying nonequivalent  $n, \pi^*$  excited triplet states existing in thermal equilibrium.<sup>2</sup> If greater charge separation is associated with the nitrogen  $n, \pi^*$  state than with the corresponding carbonyl  $n, \pi^*$  state, the nitrogen  $n, \pi^*$  triplets would predominate in polar solvents and reaction in such solvents would lead primarily to cyclopropanol. Our present data do not allow distinguishing between either mechanism, and the observed solvent effect is being investigated further.

The reactions of the butyrylpyrimidines, **1**, **2**, and **3**, were quenched using 1,3-pentadiene and triplet lifetimes were determined from linear Stern-Volmer plots. A summary of the triplet reactivities and reaction quantum yields is shown in Table I. Although the quantum

**Table I.** Quantum Yields and Photoreactivity of Butyrylpyrimidines in Type II Photoelimination<sup>a</sup>

Ketone	$\Phi_{II}$	$\Phi_{\text{-ketone}}$	Slope ( $k_{qr}$ , $M^{-1}$ )	$10^8$ ( $1/\tau$ ), $\text{sec}^{-1}$
(3) 5-Pyrimidyl	0.34	0.42	90	0.55
(1) 2-Pyrimidyl	0.09	0.23	47.5	1.03
(2) 4-Pyrimidyl	0.13, 0.18 <sup>b</sup>	0.36	30 <sup>c</sup>	1.67 <sup>c</sup>

<sup>a</sup> In benzene solvent (originally 0.05 M in ketone). <sup>b</sup> Cyclopropanol formation. <sup>c</sup> In 50% benzene-*tert*-butyl alcohol.

efficiencies for reaction of the butyrylpyrimidines **1**, **2**, and **3** are found to be comparable to those reported<sup>7</sup> for related phenyl and pyridyl ketone systems, the triplet reactivities of ketones **1**, **2**, and **3** are enhanced. The magnitudes of the observed rate enhancements toward type II elimination, however, are in line with

(20) Other reports of photochemical cyclopropanol formation in aryl alkyl ketones appear to involve electron-transfer processes.<sup>21,22</sup>  
 (21) H. J. Roth and M. H. El Raie, *Tetrahedron Lett.*, 2445 (1970).  
 (22) A. Padwa and R. Gruber, *J. Amer. Chem. Soc.*, **92**, 107 (1970).  
 (23) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, p 182.

what might be expected for diaza ring substitution,<sup>7</sup> and the increased reactivities appear to result from the added inductive effect of two ring nitrogen atoms on the electrophilic  $n, \pi^*$  triplet state.<sup>2</sup>

Work designed to further elucidate the role of aza substitution on the photoreactivity of pyrimidyl alkyl ketones is in progress. We are also engaged in the synthesis of a number of the related aza aromatic ketone systems and will begin studying their photochemistry shortly.

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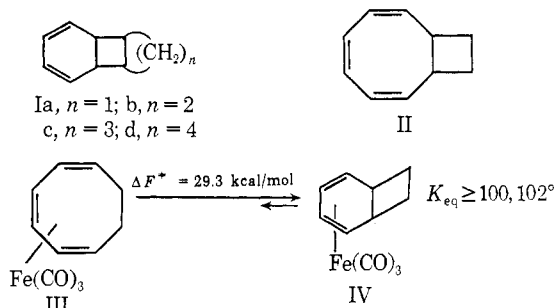
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### Selective Trapping of Dienes by Benzylideneacetoneiron Tricarbonyl. Synthesis and Thermal Rearrangement of Tricyclo[4.4.0.0<sup>2,5</sup>]deca-7,9-diene and Tricyclo[4.3.0.0<sup>7,9</sup>]nona-2,4-diene

Sir:

Binding transition metals to a polyolefin capable of tautomerism can have a substantial effect upon both the position of tautomeric equilibrium and the rates of interconversion of the tautomers. Cotton<sup>1</sup> has recently reported the isolation of stable iron tricarbonyl complexes of Ib–Id by reaction of the olefinic ligands with diiron nonacarbonyl. The isolation of the complex of Ib is of particular interest in that in the free ligand system the triene tautomer, II, is substantially favored at equilibrium over the tricyclic diene tautomer, Ib.

We have recently reported the ring closure of cyclooctatrieneiron tricarbonyl (III) to bicyclo[4.2.0]octadieneiron tricarbonyl (IV) ( $\Delta F^\ddagger = 29.3$  kcal/mol, 102°)



and a lower limit to the equilibrium ratio of IV/III of 100 at 102°. This represents a substantial shift in the equilibrium toward the bicyclic diene tautomer relative to the free ligand system in which the equilibrium ratio of 1,3,5-cyclooctatriene to bicyclo[4.2.0]octadiene is 85:15 at 100°. The origin of this shift was ascribed to distortion of the preferred tub conformation of cyclo-

(1) (a) F. A. Cotton and G. Deganello, *J. Amer. Chem. Soc.*, **90**, 1444 (1968); (b) *J. Organometal. Chem.*, **38**, 147 (1972); (c) *J. Amer. Chem. Soc.*, **95**, 396 (1973).

(2) M. Brookhart, N. M. Lippman, and E. J. Reardon, *J. Organometal. Chem.*, **54**, 247 (1973).

(3) (a) A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **74**, 4867 (1952); (b) R. Huisgen, F. Mietsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Publ.*, No. **19**, 3 (1965).

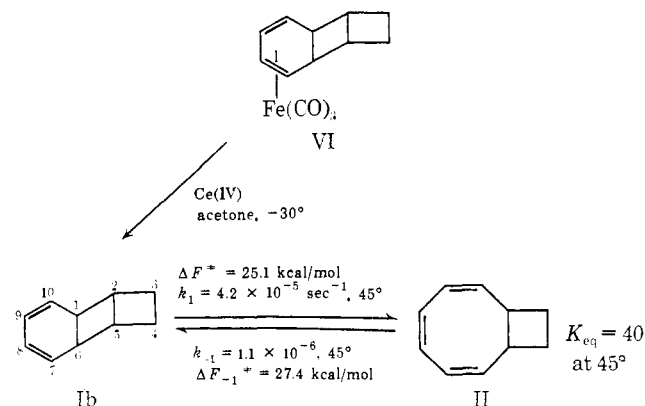
octatriene into an energetically unfavorable conformation in III in which C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> of the bound diene unit must be approximately coplanar.

We wish to report that benzylideneacetoneiron tricarbonyl<sup>4</sup> (BDAFe(CO)<sub>3</sub>) functions as a remarkably selective reagent in efficiency trapping as iron tricarbonyl complexes low concentrations of the diene tautomers present in equilibrium with the corresponding cyclooctatriene derivatives. These reactions represent useful synthetic routes not only to the iron tricarbonyl complexes of the dienes but also to the free diene tautomers. The utility of such reactions is illustrated below with two systems, bicyclo[4.2.0]deca-7,9-diene (II) and bicyclo[6.1.0]nonatriene (V).

Reaction of BDAFe(CO)<sub>3</sub> with II (1.5:1.0 mol ratio) under nitrogen in benzene at 65° for 48 hr followed by chromatography on alumina yields the tricyclic diene complex, VI, as the sole product (82% isolated yield), identical with that reported by Cotton.<sup>1b</sup> Reaction of VI with ceric ammonium nitrate in acetone at -30° yields, after flash distillation at 0°, pure tricyclo[4.4.-0.0<sup>2,5</sup>]deca-7,9-diene (Ib) (84%). The 100-MHz pmr spectrum in CS<sub>2</sub> (internal TMS standard) exhibits signals at δ 2.0–2.6 (m, H<sub>3</sub>, H<sub>4</sub>), 2.8–3.0 (m, H<sub>2</sub>, H<sub>5</sub>), 3.12 (br s, H<sub>1</sub>, H<sub>6</sub>), and 5.30–5.70 (m, H<sub>7</sub>, H<sub>8</sub>, H<sub>9</sub>, H<sub>10</sub>), while the <sup>13</sup>C{<sup>1</sup>H} spectrum run at -20° in CS<sub>2</sub> exhibits singlets at δ<sub>c</sub> 29.4 (C<sub>3</sub>, C<sub>4</sub>), 40.3 (C<sub>2</sub>, C<sub>5</sub> or C<sub>1</sub>, C<sub>6</sub>), 50.2 (C<sub>1</sub>, C<sub>6</sub> or C<sub>2</sub>, C<sub>5</sub>), 121.6 (C<sub>7</sub>, C<sub>10</sub> or C<sub>8</sub>, C<sub>9</sub>), and 126.3 (C<sub>8</sub>, C<sub>9</sub> or C<sub>7</sub>, C<sub>10</sub>). The tricyclic diene, Ib, undergoes clean first-order thermal electrocyclic ring opening to II at 45°,  $k = 4.2 \times 10^{-5} \text{ sec}^{-1}$ ,  $\Delta F^\ddagger = 25.1 \text{ kcal/mol}$ . The equilibrium ratio of II/Ib was determined as 40 using <sup>13</sup>C nmr,<sup>5</sup> and thus  $k_{-1}$  can be calculated as  $1.1 \times 10^{-6} \text{ sec}^{-1}$  at 45°.<sup>7</sup>

The kinetic and thermodynamic parameters are summarized below in Scheme I.

Scheme I



Reaction of bicyclo[6.1.0]nonatriene (V) with BDAFe(CO)<sub>3</sub> (1:3.5 mol ratio) in benzene at 55° for 48 hr followed by chromatography on alumina gave three mononuclear complexes, the tricyclic diene complex,

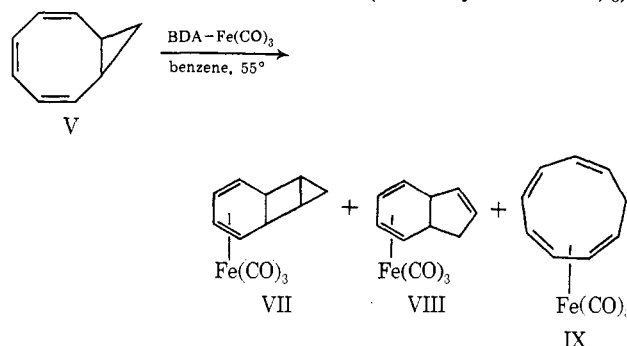
(4) J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Organometal. Chem.*, **39**, 329 (1972).

(5) Two methods, the gated decoupling technique and the use of the paramagnetic relaxation reagent tris(acetylacetonato) chromium(III)<sup>6</sup> (0.03 M), were used to obtain accurate <sup>13</sup>C integrals. Both techniques gave the same result.

(6) (a) O. A. Gansow, A. R. Burke, and G. N. LaMar, *J. Chem. Soc., Chem. Commun.*, 456 (1972); (b) G. C. Levy and R. A. Komoroski, *J. Amer. Chem. Soc.*, **96**, 678 (1974).

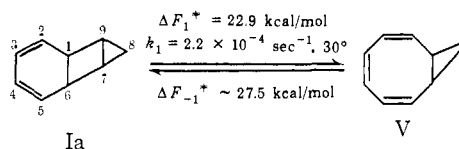
(7) Judging qualitatively from the variation of yields of VI with time and temperature, the rate of formation of VI is approximately equal to the rate of formation of Ib from II which indicates trapping of Ib by BDAFe(CO)<sub>3</sub> competes effectively with reopening of Ib to II.

VII, the known dihydroindeneiron tricarbonyl complex,<sup>8</sup> VIII, and the *cis*<sup>4</sup>-cyclononatetraeneiron tricarbonyl complex,<sup>8</sup> IX, in a *ca.* 10:5:1 ratio<sup>9</sup> (overall yield *ca.* 50%).



The 100-MHz pmr spectrum of VII in C<sub>6</sub>D<sub>6</sub> (internal C<sub>6</sub>D<sub>5</sub>H standard) exhibits signals at δ 0.59 (dt, H<sub>8a</sub>, J<sub>8a,8b</sub> = 4.6 Hz, J<sub>8a,7</sub> = J<sub>8a,9</sub> = 1.4 Hz), 0.76–0.96 (m, H<sub>8b</sub>) 1.14–1.30 (m, H<sub>7</sub>, H<sub>9</sub>), 1.84–2.02 (m, H<sub>1</sub>, H<sub>6</sub>), 2.90–3.12 (m, H<sub>2</sub>, H<sub>5</sub>), and 5.05 (dd, H<sub>3</sub>, H<sub>4</sub>) while the <sup>13</sup>C{<sup>1</sup>H} spectrum in C<sub>6</sub>D<sub>6</sub> showed singlets at δ<sub>c</sub> 21.5 (C<sub>8</sub>), 24.0 (C<sub>7</sub>, C<sub>9</sub>), 43.4 (C<sub>1</sub>, C<sub>6</sub>), 66.4 (C<sub>2</sub>, C<sub>5</sub>), 86.8 (C<sub>3</sub>, C<sub>4</sub>), and 212.8 (carbonyls).

Cleavage of VII with ceric ammonium nitrate in acetone at -20° yields the free tricyclo[4.3.0.0<sup>7,9</sup>]nona-2,4-diene (Ia) which exhibits pmr signals (100 MHz, CDCl<sub>3</sub>) at δ 0.27–0.53 (m, H<sub>8a</sub>, H<sub>8b</sub>), 1.65–1.79 (m, H<sub>7</sub>, H<sub>9</sub>), 2.47–2.59 (m, H<sub>1</sub>, H<sub>6</sub>), and 5.37–5.83 (m, H<sub>2</sub>, H<sub>3</sub>, H<sub>4</sub>, H<sub>5</sub>). The diene Ia undergoes first-order thermal isomerization to bicyclo[6.1.0]nonatriene (V) at 30°,  $k = 2.15 \times 10^{-4} \text{ sec}^{-1}$ ,  $\Delta F^\ddagger = 22.9 \text{ kcal/mol}$ . The free energy of activation for closure of V



can be estimated<sup>10</sup> to be *ca.* 27.5 kcal/mol which coupled with the measured  $\Delta F^\ddagger$  of 22.9 kcal/mol for opening indicates an equilibrium ratio of V/Ia of *ca.* 4500 at 50°. Such a ratio reveals the remarkable selectivity of BDAFe(CO)<sub>3</sub> for reaction only with tautomer Ia in which the diene moiety is planar.<sup>12</sup>

It is interesting to contrast the very selective reaction of BDAFe(CO)<sub>3</sub> with II and V to reactions with iron

(8) (a) E. J. Reardon and M. S. Brookhart, *J. Amer. Chem. Soc.*, **95**, 4311 (1973); (b) G. Deganello, H. Maltz, and J. Kozarich, *J. Organometal. Chem.*, **60**, 323 (1973).

(9) At lower BDAFe(CO)<sub>3</sub>:V ratios a decrease in the yield of VII is observed, along with decreased trapping of *cis*-cyclononatetraene, an intermediate in the thermal rearrangement of V to *cis*-8,9-dihydroindene.

(10) The free energies of activation for the closure of cyclooctatriene derivatives are remarkably similar, for example, 1,3,5-cyclooctatriene<sup>9b</sup> (26.9 kcal/mol, 45°C), triene II (27.4 kcal/mol, this work) and cyclooctatetraene<sup>9b</sup> (27.7 kcal/mol, 45°C). We would expect  $\Delta F^\ddagger$  for V to lie between the values for II and cyclooctatetraene, i.e., *ca.* 27.5 kcal/mol. The ring closure of V must be somewhat faster than dihydroindene formation since VII is formed in greater yields than VIII; therefore, the known  $\Delta F^\ddagger$  of 28 kcal/mol for formation of dihydroindene sets an upper limit to the  $\Delta F^\ddagger$  for closure of V.<sup>11</sup>

(11) A. G. Anastassiou and R. C. Griffith, *Chem. Commun.*, 1301 (1971).

(12) A referee has suggested that complexes VI and VII may not be formed by trapping dienes Ia and Ib but perhaps rather *via* an intermediate triene-Fe(CO)<sub>3</sub> or triene-Fe(CO)<sub>3</sub>-BDA complex which undergoes accelerated ring closure. Intermediacy of  $\eta^4$  1,3- and 1,5-bonded triene-Fe(CO)<sub>3</sub> complexes can be ruled out on the basis of their slow ring closures.<sup>8,13</sup> A  $\eta^2$  bound triene intermediate such as a triene-Fe(CO)<sub>3</sub>-BDA complex cannot be ruled out on the basis of available data; however, since ring closure requires a 1,2-iron shift in the  $\eta^2$  complex, we would not expect ring closure to be accelerated.<sup>2,8</sup> Data in footnote 7 suggest the diene tautomer is being trapped.

carbonyl reagents. Reaction of II thermally with  $\text{Fe}_2(\text{CO})_9$ <sup>1b</sup> or photolytically with  $\text{Fe}(\text{CO})_5$ <sup>13</sup> leads only to very small isolated yields of VI along with several other complexes, while reaction of V with  $\text{Fe}(\text{CO})_5$  photolytically or  $\text{Fe}_2(\text{CO})_9$  thermally leads chiefly to cyclononatetraeneiron tricarbonyl, complex VIII, bicyclo[6.1.0]nonatrieneiron tricarbonyl, and none of complex VII.<sup>8</sup> In view of these examples, it is clear  $\text{BDAFe}(\text{CO})_3$  complements the reactions of iron carbonyl reagents and may offer general synthetic utility for selectively trapping various types of dienes. We are currently exploring the utility of this reagent in other tautomeric systems as well as the reasons for its remarkable selectivity.

**Acknowledgment.** This work was supported in part by the National Science Foundation (Grant GP-29580) and by the Materials Research Center of UNC under Grant No. GH-33632 from the National Science Foundation.

(13) G. Scholes and M. Brookhart, unpublished results.

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### Gas Phase Pyrolysis of *trans*- and *cis*-1,2-Diethynylcyclobutane. A New Entry to the $\text{C}_8\text{H}_8$ Energy Surface

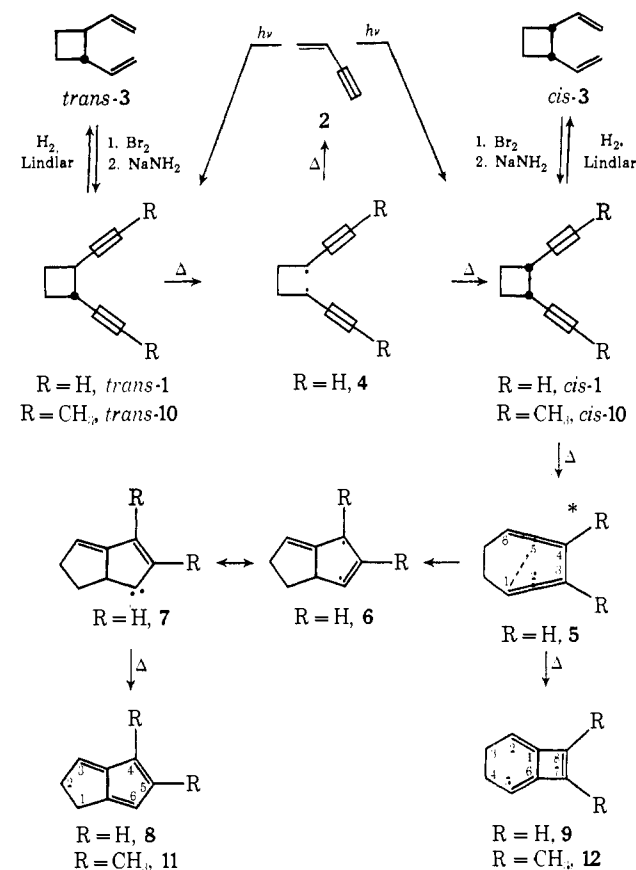
Sir:

Whereas thermal rearrangements of mono- and polyolefins have been extensively studied,<sup>1,2</sup> far less is known about the pyrolytic behavior of the corresponding alkynes.<sup>3</sup> Since their thermal isomerization reactions are expected to provide valuable preparative and mechanistic information, we have started a comprehensive study of the gas phase pyrolysis of acetylenes.<sup>4</sup> This communication reports the rearrangement of *trans*- and *cis*-1,2-diethynylcyclobutane (Scheme I, R = H, *trans*- and *cis*-1), the acetylenic pendants of the thoroughly investigated divinylcyclobutanes *trans*- and *cis*-3.<sup>1,2,5</sup> The isomeric bisalkynes are conveniently prepared in 84% yield by sensitized (Michler's ketone) photodimerization of vinylacetylene (2) using a 450-W Hannovia lamp (*trans*/*cis* ratio by glpc, 2.5:1). An alternative route, bromination of *trans*- and *cis*-3 followed by dehydrobromination with sodium amide, affords the same compounds in lower yield (*trans*-1, 18%; *cis*-1, 9.6%). The isomerically pure hydrocarbons were obtained by preparative gas chromatography (6 ft DEGS column, 65°), and their structures were established by spectroscopic and chemical means.

The nmr spectrum ( $\text{CDCl}_3$ , int TMS) of *trans*-1 shows three groups of protons at  $\delta$  3.25–2.85 (m, 2), 2.50 (d,  $J = 1.0$  Hz, 2), and 2.40–1.90 (m, 4) which are easily recognized as the tertiary, acetylenic and methylene

protons, respectively. In the *cis* isomer these signals are shifted to somewhat lower field: 3.45–3.05 (m, 2), 2.45–2.10 (m, 6). The ir ( $\text{CDCl}_3$ ) shows the expected bands at 3310 and 2120 ( $-\text{C}\equiv\text{C}-\text{H}$ ), 2958, 2878, and 1258 (cyclobutane ring) for *trans*-1, and at 3304, 2996, 2950, 2870, 2115, and 1250  $\text{cm}^{-1}$  for *cis*-1.<sup>6</sup> Their relative stereochemistry is established by Lindlar hydrogenation to *trans*- and *cis*-3 (Scheme I).

Scheme I



When *trans*-1 is pyrolyzed in a stream of nitrogen at 500° (contact time approximately 28 sec) three products are formed: vinylacetylene (2, 52% by nmr analysis), 1,2-dihydropentalene (8, 43%), and bicyclo[4.2.0]octa-1,5,7-triene (9, 4.5%). Hydrocarbon 8 was identified by spectral comparison with an authentic sample. The structure of the previously unknown  $\text{C}_8\text{H}_8$  isomer, 9, rests on the following spectral data: its nmr ( $\text{CCl}_4$ , int TMS) shows a pseudo-singlet at 6.80 ( $\text{H}_1, \text{H}_5$ ) a broad singlet at 5.18 ( $\text{H}_2, \text{H}_6$ ), and a pseudo-triplet at 2.30 ( $\text{H}_3, \text{H}_4$ ). In the ir ( $\text{CCl}_4$ ) the main absorption bands appear at 3100 and 3050 ( $\text{C}=\text{C}-\text{H}$ ), 2920, 2820, 1436, and 1336 ( $-\text{CH}_2$ ), and at 1665  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$ ).

Compound 9 (molecular weight 104 by mass spectral determination) is colorless after gas chromatographic separation (DEGS, 75°) and stable for a few hours at room temperature. Exposure to air causes rapid polymerization, and so far has prevented the determination of a quantitative uv spectrum. The qualitative spectrum (ethanol) with bands at 213 and 258 nm is in accordance with data for model compounds.<sup>7</sup> When

(1) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).  
 (2) M. R. Wilcott, R. L. Cargill, and A. B. Sears, *Progr. Phys. Org. Chem.*, **9**, 25 (1972).  
 (3) W. D. Huntsman, *Intra-Sci. Chem. Rep.*, **6**, 151 (1972).  
 (4) For Part V of this series see V. Dalacker and H. Hopf, *Tetrahedron Lett.*, 15 (1974).  
 (5) For new results on the thermal rearrangement of substituted divinylcyclobutanes, cf. J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 269 (1973).

(6) All new compounds had correct molecular weight (mass spectrum) and elemental analysis.

(7) 3,4-Bismethylenecyclobutene absorbs (isooctane) at 211.5 (10,000) and 248 nm (19,950).<sup>8</sup>

(8) A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc., London*, 332 (1961).