Organic Photochemistry. VII. The Photosensitized and Thermal Cycloaddition Reactions of 1,3-Butadiene, Isoprene, and Cyclopentadiene to α-Acetoxyacrylonitrile. 1,2 *vs.* 1,4 Addition as a Function of Sensitizer Triplet Energy in Cross-Addition Reactions[1,2]

Wendell L. Dilling, Roger D. Kroening, and J. C. Little

Contribution from the Edgar C. Britton Research Laboratory,
The Dow Chemical Company, Midland, Michigan 48640.
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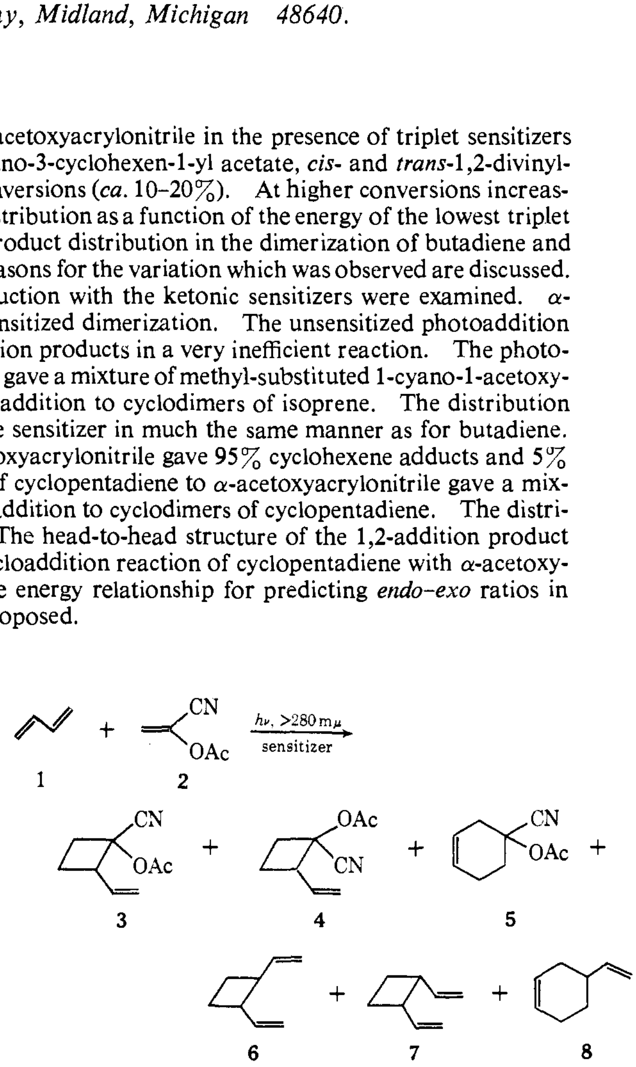
Abstract: Ultraviolet irradiation of 1,3-butadiene and α-acetoxyacrylonitrile in the presence of triplet sensitizers gave *cis-* and *trans*-1-cyano-2-vinylcyclobutyl acetate, 1-cyano-3-cyclohexen-1-yl acetate, *cis-* and *trans*-1,2-divinylcyclobutane, and 4-vinylcyclohexene in high yield at low conversions (*ca.* 10–20%). At higher conversions increasing amounts of a copolymer were formed. The product distribution as a function of the energy of the lowest triplet state of the sensitizer was found in general to parallel the product distribution in the dimerization of butadiene and isoprene studied by Hammond and coworkers. Possible reasons for the variation which was observed are discussed. Side reactions such as oxetane formation and pinacol reduction with the ketonic sensitizers were examined. α-Acetoxyacrylonitrile underwent a rather inefficient photosensitized dimerization. The unsensitized photoaddition of 1,3-butadiene and α-acetoxyacrylonitrile gave cycloaddition products in a very inefficient reaction. The photosensitized cycloaddition of isoprene to α-acetoxyacrylonitrile gave a mixture of methyl-substituted 1-cyano-1-acetoxy-2-vinylcyclobutanes and 4-cyano-4-acetoxycyclohexenes in addition to cyclodimers of isoprene. The distribution of products was also dependent on the triplet energy of the sensitizer in much the same manner as for butadiene. The thermal cycloaddition reaction of isoprene with α-acetoxyacrylonitrile gave 95% cyclohexene adducts and 5% cyclobutane adducts. The photosensitized cycloaddition of cyclopentadiene to α-acetoxyacrylonitrile gave a mixture of cyanoacetoxybicyclo[2.2.1]- and -[3.2.0]heptenes in addition to cyclodimers of cyclopentadiene. The distribution of products was not dependent on the sensitizer. The head-to-head structure of the 1,2-addition product was established by an alternate synthesis. The thermal cycloaddition reaction of cyclopentadiene with α-acetoxyacrylonitrile gave only norbornene adducts. A linear free energy relationship for predicting *endo-exo* ratios in thermal cycloadditions of 1,1-disubstituted ethylenes is proposed.

The photochemical cycloaddition of conjugated dienes to other olefins to give cyclobutane derivatives and other cyclic products is a well-established type of reaction and has considerable synthetic utility.[1] We have examined in some detail the photosensitized cross-additions of 1,3-butadiene (**1**), isoprene (**18**), and cyclopentadiene (**32**) to α-acetoxyacrylonitrile (**2**). The photocycloaddition reaction of the olefins **1** and **2** was of particular interest in view of the fact that these two olefins undergo simultaneous 1,2- and 1,4-thermal cycloadditions.[3] Also, no photocycloadditions of α,β-unsaturated nitriles to dienes had been reported. It was hoped that a study of the photoaddition might aid in an understanding of the mechanism of the thermal reaction. The thermal cycloaddition reactions of the dienes **18** and **32** with **2** were also examined.

Results

1,3-Butadiene. Irradiation of an equimolar mixture of the diene **1** and α,β-unsaturated nitrile **2** with a triplet sensitizer gave a mixture of three cross-adducts **3–5** and three dimers of butadiene **6–8**. In addition to these six products, a few minor components were formed in some cases, and at higher conversions (>~20% depending on the sensitizer) a 1.3:1 copolymer of **1** and **2** was formed.



The cyclobutane cross-adducts **3** and **4** were identified by nmr spectral comparisons of a mixture of the two collected by preparative gc with an authentic mixture prepared by the thermal reaction of **1** and **2**.[3] The two cyclobutanes **3** and **4** were not separated, but the presence of both isomers was established by the observation of two acetyl methyl peaks at −2.07 and −2.05 ppm in the nmr spectrum of the isolated mixture. The cyclohexene cross-adduct **5** had retention times identical with that of authentic material[3] on three different gc columns as did the isomeric cyclobutanes **3** and **4**. The three dimers of butadiene **6–8** were prepared by the method of Hammond and coworkers,[4] and iden-

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[1] Part VI: W. L. Dilling, *Chem. Rev.*, **69**, 845 (1969).

[2] Preliminary accounts of this work have been reported in parts II–V of this series: (a) W. L. Dilling and J. C. Little, *J. Am. Chem. Soc.*, **89**, 2741 (1967); (b) W. L. Dilling, *ibid.*, **89**, 2742 (1967); (c) W. L. Dilling and R. D. Kroening, *Tetrahedron Lett.*, 5101 (1968); (d) W. L. Dilling and R. D. Kroening, *ibid.*, 5601 (1968).

[3] J. C. Little, *J. Am. Chem. Soc.*, 87, 4020 (1965).

tified by comparison of the nmr and infrared spectra with authentic materials or data in the literature. The *cis*-divinylcyclobutane **7** was analyzed and isolated as the thermal rearrangement product, 1,5-cyclooctadiene (**9**).[4c,5] This thermal isomerization presumably occurs

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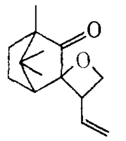
in the injection port of the gas chromatograph (temperature *ca.* 220°). We have not established that the divinyl compound **7** is the photoproduct in our reaction, but assume that it is based on Hammond's work.[4]

In most cases the sensitizers were recovered unchanged at the end of the reaction. One notable exception was camphorquinone. In addition to undergoing energy transfer this diketone reacted with the diene **1** to give an oxetane or oxetanes in both the presence and absence of the unsaturated nitrile **2**. The evidence indicated that the structure of the oxetane was **10** and/or closely related isomers. The gas chromatogram of the reaction mixtures containing **10** indicated



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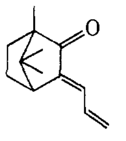

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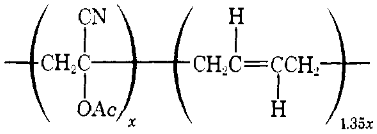
that several isomers may have been present. The spectral data obtained from the oxetane fraction isolated by preparative gc were in accord with structure **10** or a closely related isomer. The mass spectrum showed a molecular ion peak, *m/e* 220, and principal peaks at *m/e* 192 (M^+ − CO or C_2H_4), 166 (M^+ − C_4H_6), 138 (M^+ − C_4H_6 and CO or C_2H_4), 123 (M^+ − C_4H_6 and C_3H_7 or C_2H_3O), and 109 (M^+ − C_4H_6 and C_4H_9 or C_3H_5O). The infrared spectrum showed the presence of a vinyl group (3090 cm^{-1}, CH stretch; 1860, CH_2 wag overtone; 1650, C=C stretch; 1405, CH in plane deformation; 994, $-CH=CH_2$ twist; 923, CH_2 wag) and a five-membered ring ketone, 1750 cm^{-1}. Evidence for the *gem*-dimethyl group, doublet ~1380 cm^{-1}, and the oxetane ring, ~980 cm^{-1}, was also observed. In another preparation of the oxetanes, the product was pyrolyzed in the injection port of the gas chromatograph (*ca.* 220°). The product(s) collected were assigned the structure **11** or closely related isomers which would result from the loss of formaldehyde from the oxetane **10**.[6] The mass spectrum showed a molecular ion peak, *m/e* 190, and ion peaks for the losses of CH_3, *m/e* 175; CO or C_2H_4, *m/e* 162; C_3H_7 or CH_3CO, *m/e* 147; C_4H_9 or C_2H_5CO, 133; and C_5H_{10} or C_3H_6CO, *m/e* 120. The infrared spectrum indicated the presence of a vinyl group, and, moreover, a conjugated diene by the appearance of two C=C stretching absorption bands at 1650 and 1605 cm^{-1}. The carbonyl frequency of 1730 cm^{-1} was appropriate for this structure, and the pair of bands for the *gem*-dimethyl group was apparent. The nmr spectrum of **11** indicated the material was not pure dienone **11** but was entirely consistent with this as a major component. Multiplets appeared at -6.75 to -5.11 ppm for the vinylic protons, at -2.96 to -1.25 for the protons on secondary and tertiary carbon atoms, and at -1.25 to -0.68 for the methyl groups. The appearance of at least six methyl peaks indicated that more than one isomer was present since **11** should give only three unsplit methyl peaks. A doublet appeared at -2.83 ppm (J = 4.3 cps), probably due to the bridgehead proton. The absence of absorption in the -4.0 to -5.0 ppm region ruled out the presence of any oxetane.[6,7]

Material balances were determined for the reactions employing acetophenone, benzophenone, biacetyl, and benzil as sensitizers using *p*-bromotoluene as an internal standard (added at the end of the irradiation to avoid possible complications due to sensitization or quenching) for the gc analysis. In the acetophenone- and benzophenone-sensitized reactions (11 and 17% conversions of **1**, respectively), the butadiene was essentially all accounted for in the dimers and cross-adducts while in the biacetyl- and benzil-sensitized reactions (44 and 27% conversions of **1**, respectively) 20–40% of the diene **1** which disappeared was not accounted for. This material is undoubtedly in the polymer which was formed.

The polymer obtained in the benzophenone-sensitized reaction was insoluble in common solvents and had a composition of 1.0 part of nitrile **2** to 1.35 parts of diene **1** based on the elemental analysis. Mass spectral analysis of the copolymer at 150–300° showed the presence of 1–5% of benzophenone. The latter may have been incorporated into the polymer, and observed mass spectrometrically due to thermal degradation of the polymer, or the benzophenone may have been occluded in the polymer network. The infrared spectrum of the polymer showed bands for vinylic and aliphatic C–H stretch, 3052 (sh), 2940, 2860 cm^{-1}; C≡N stretch, ~2300; C=O stretch, 1755; C=C stretch, ~1675. A fairly intense band at 973 cm^{-1} was indicative of a *trans*-vinylene group.[8] A likely partial structure for this copolymer is **12**.



$$-\!\!\left(\mathrm{CH_2}\overset{\mathrm{CN}}{\underset{\mathrm{OAc}}{\mathrm{C}}}\right)_{x}\!\!-\!\!\left(\mathrm{CH_2}\overset{\mathrm{H}}{\mathrm{C}}=\underset{\mathrm{H}}{\mathrm{C}}\mathrm{CH_2}\right)_{1.35x}\!\!-$$

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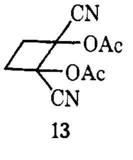
Irradiation of the nitrile **2** in the presence of acetophenone gave a very slow (compared with cross-addition) conversion to two dimeric products, tentatively assigned structures **13** and **14** on the basis of spectral and chromatographic data. The assignment of stereochemistry to the isomers **13** and **14** is tentative. This



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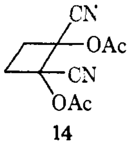

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(4) (a) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961); (b) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963); (c) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

(5) E. Vogel, *Ann.*, **615**, 1 (1958).

(6) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).

(7) J. S. Bradshaw, *J. Org. Chem.*, **31**, 237 (1966).

(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p 34.

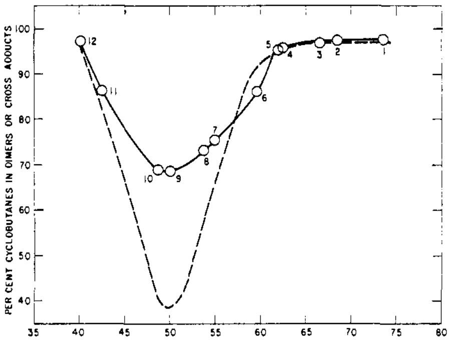

Figure 1. Butadiene-α-acetoxyacrylonitrile cross-adduct composition *vs.* triplet energy of sensitizer (solid line). Butadiene dimer composition (dashed line, Liu, Turro, and Hammond's data[4c]).

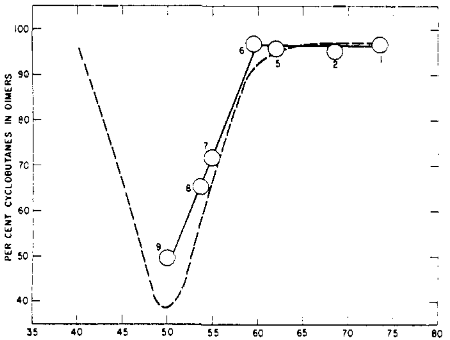

Figure 2. Butadiene dimer composition *vs.* triplet energy of sensitizer (solid line, this work; dashed line, Liu, Turro, and Hammond's data[4c]).

assignment is based on the relative chemical shifts of the acetoxy methyl protons, −2.23 ppm *cis* to cyano, −2.20 ppm *trans* to cyano. The above stereochemical assignment is in agreement with the expectation that the *trans* isomer **13** would predominate in the photodimerization reaction. The ratio of **13** to **14** was 57:43, respectively. The head-to-head nature of these dimers has not been established, but is assumed to be such by analogy to the photosensitized dimerization of acrylonitrile.[9] No more than trace amounts of these dimers **13** and **14** were formed in the cross-addition reactions.

The distribution of the cross-adducts and diene dimers is given in Table I. These data are plotted in Figures 1 and 2 for the cross-adducts and dimers, respectively. For comparison, the data of Hammond and coworkers[4c] are also plotted on each graph (dashed line).

Table I. Composition of Products from Photosensitized Cross-Addition of Butadiene and α-Acetoxyacrylonitrile

Sensitizer no.	Sensitizer[a]	E_T[b]	Distribution of cross-adducts and dimers, %[c]				
			3 + 4[d]	5	6	7	8
1	Acetophenone	73.6	34	0.7	56	7	2
2	Benzophenone	68.5	33	0.9	54	10	3
3	Triphenylene[e]	66.6	30	0.9	69	*f*	*g*
4	Anthraquinone[e,h]	62.4	60	3	31	6	*g*
5	Flavone	62.0	32	1.6	52	12	3
6	β-Naphthyl phenyl ketone	59.6	41	7	47	4	2
7	Biacetyl	54.9	38	12	28	7	14
8	Benzil	53.7	34	12	30	5	18
9	Camphorquinone	50.0	28	12	23	7	29
10	Pyrene[e]	48.7	38	17	34	11	*g*
11	Anthracene[e]	42.5	41	6	45	8	*g*
12	9,10-Dibromoanthracene[e]	40.2	45	1	44	10	*g*

[a] Sensitizer (1.0 mmole) in 5.0 mmoles of **1** and 5.0 mmoles of **2** irradiated through a Pyrex filter at *ca.* 30°. [b] Lowest triplet energy level in kilocalories per mole. See ref 4c and 10. [c] Determined by gas chromatography with each component corrected for thermal conductivity variation in detector. [d] The *cis* and *trans* isomers were not separated. [e] Saturated solution of sensitizer in an equimolar mixture of **1** and **2**. [f] Not determined due to low overall conversion. [g] Not determined due to interference by large excess of **2** and presence of small amount of **8** in the starting diene **1**. [h] A larger amount of polymer was formed in this reaction.

The relative amounts of the *cis* and *trans* isomers **3** and **4** were not determined except in the benzophenone-sensitized reaction. In this case two isomers were present in nearly equal concentrations, with the isomer having the lower field acetyl methyl resonance in the nmr predominating to a slight extent.

The relative yields with sensitizers numbered 3, 4, 10–12 were considerably lower than the others shown in Table I. An attempt to use naphthalene, E_T = 60.9 kcal/mole,[10] as a sensitizer in this cross-addition was unsuccessful; no reaction was observed.[11]

The product distribution at various stages of conversion for five sensitizers is shown in Table II. It will be noted that the relative amount of cyclobutane cross-adducts **3** and **4** in the total cross-adducts **3–5** did not vary appreciably. However the relative amounts of total cross-adducts **3–5** to total dimers **6–8** did vary at higher conversions.

The effect of changing the ratio of the diene **1** and the olefin **2** was determined for one sensitizer, acetophenone. The product distribution shown in Table III indicates, as expected, that increasing the amount of **2** increased the amount of cross-adducts **3–5** relative to the dimers **6–8**.

A brief study of solvent effects on this reaction indicated that the major effect was to decrease greatly the efficiency of the addition. Irradiation of **1** and **2** with acetophenone in ether solution for 2 days gave only a 3–4% conversion of the nitrile **2** to the cross-adducts, primarily the cyclobutanes **3** and **4**. Irradiation of the two olefins in acetonitrile and dimethyl sulfoxide solutions with acetophenone as the sensitizer gave the results shown in Table IV. The isomer distributions for the latter two reactions were not appreciably different from that obtained when no solvent was used. In an attempted large-scale run using benzophenone as the sensitizer in ether solution, irradiation for 5 days gave a 5–10% conversion to the cross-adducts, primarily **3** and **4**. Further irradiation failed to increase the cross-adduct concentration, and gave only additional polymer.

The cross-adducts **3–5** were relatively stable under the reaction conditions (no solvent) using benzophenone as the sensitizer. No indication of increased polymeriza-

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[9] (a) J. Runge and R. Kache, British Patent 1,068,230 (1967); *Chem. Abstr.*, **67**, 73215 (1967); (b) S. Hosaka and S. Wakamatsu, *Tetrahedron Lett.*, 219 (1968); (c) R. S. H. Liu and D. M. Gale, *J. Am. Chem. Soc.*, **90**, 1897 (1968); (d) J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968); see also (e) M. Herberhold and G. S. Hammond, *Ber. Bunsenges Phys. Chem.*, 72, 309 (1968).

[10] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

[11] Similar results have been observed by L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

Table II. Dependence of Product Distribution on Extent of Conversion

Sensitizer no.	Sensitizer[a]	Time[b]	Distribution of cross-adducts and dimers, % 3 + 4	5	6	7	8	Cyclobutanes in cross-adducts, %	Cyclo butanes in dimers, %	Conversion, %	Sensitizer converted, %
1	Acetophenone	1	34	0.7	56	7	2	98	97	11 (**1**)[c]	
		4[d]	35	*e*	60	5	*f*			>47 (**1**)	
		24[g]	52	*e*	38	10	*f*				
2	Benzophenone	1	33	0.9	54	10	3	98	95	17 (**1**)	
		4[d]	31	*e*	59	10	*f*			>58 (**1**)	
		24[g]	96	*e*	2	2	*f*				
3	Triphenylene[h]	2	30	0.9	69	*i*	*f*	97		0.5 (**2**)[j]	
		4[g]	76	3	21	*i*	*f*	96			
7	Biacetyl	1	38	12	28	7	14	76	72	44 (**1**)	
		4[g]	36	11	34	8	*f*	77			
9	Camphorquinone	0.25	26	10	29	4	31	72[k]	52	1 (**2**)	5
		0.50	27	12	28	6	27	69	56	4 (**2**)	19
		1.0	28	12	23	7	29	69	50	9 (**2**)	29

[a] Sensitizer (1.0 mmole) in 5.0 mmoles of **1** and 5.0 mmoles of **2**. [b] Irradiation time in hours, Pyrex filter, *ca.* 30°. [c] Per cent of diene **1** converted to cross-adducts, dimers, or polymer. [d] A small amount of polymer was formed in the reaction. [e] Not determined due to lower sensitivity in analytical gc method. [f] Not determined due to interference by the presence of **2** and presence of a small amount of **8** in the starting diene **1**. [g] A large amount of polymer was formed in the reaction. [h] Saturated solution of sensitizer in equimolar mixture of **1** and **2**. [i] Not determined due to low overall conversion. [j] Per cent of olefin **2** converted to cross-adducts. [k] Least accurate of three runs due to low conversion.

Table III. Effect of Monomer Ratio on Product Distribution [Acetophenone (**15**) Sensitized][a]

Ratio of monomers 2/1	Distribution of cross-adducts and dimers, % 3 + 4	5	6	7	8	1 converted, %
0.1[b]	5	*c*	83	9	~3	6
1.0[d]	34	0.7	56	7	2	11
8[e]	88	1	11	*c*	*c*	12

[a] Irradiated for 1 hr through Pyrex filter at *ca.* 30°. [b] Molar ratio of reactants: 9.52:1.00:0.95 **1**:**2**:**15**. [c] Concentration too low to determine. [d] Molar ratio of reactants: 1.05:1.00:0.20 **1**:**2**:**15**. [e] Molar ratio of reactants: 1.00:8.17:0.80 **1**:**2**:**15**.

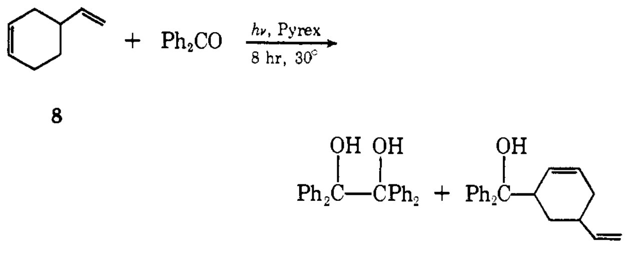
Table IV. Solvent Effect on Photoaddition of Butadiene and α-Acetoxyacrylonitrile [Acetophenone (**15**) Sensitized][a]

Solvent[b]	Distribution of cross-adducts and dimers, % 3–5	6–8	1 converted,[c] %
None	35	65	11
MeCN	37	63	1.7
Me_2SO	34	66	2.2

[a] Irradiated through Pyrex for 1 hr at *ca.* 30°. [b] 5 mmoles of **1**, 5 mmoles of **2**, and 1 mmole of **15** in 10 ml of solvent. [c] Determined by using *p*-bromotoluene as an internal standard.

tion was noted when an excess of these components was added before the irradiation. In contrast irradiation of diene **1**, olefin **2**, and benzophenone in the presence of 30 mole % (based on **1** or **2**) of vinylcyclohexene (**8**) markedly increased the rate of polymer formation although the olefin **8** was largely recovered. Cyclohexene caused only a slight increase in the amount of polymerization, but a new unidentified material was produced in quantities greater than any of the products **3**–**8**.

Vinylcyclohexene (**8**) and benzophenone when irradiated through Pyrex gave a mixture of products, the major of which were benzopinacol (**16**) and a material tentatively identified as the 1:1 adduct **17**, or a closely related isomer.[12] The structure of the adduct **17**, which was not isolated in a pure state, was based on spectral evidence. The mass spectrum showed a molecular ion peak at *m/e* 290 and an intense peak at *m/e* 272 ($M^+ - H_2O$). The infrared spectrum confirmed



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16, 32%

17, ~21%

the presence of a hydroxyl group, ν 3580, ~3500 cm^{-1}, and also exhibited bands consistent with the remainder of the structure: 3090 (vinyl CH stretch), 3070, 3035 (aromatic CH stretch), 2930 (aliphatic CH stretch), 1650, 1610, 1590 (vinyl and aromatic C=C stretch), 1000, 920 ($-CH=CH_2$ twist and wag), and 700 (phenyl CH out-of-plane deformation). The nmr spectrum showed the material to be a mixture but the appearance of signals at −7.8 to −6.9 ppm (11.1 H) for aromatic protons, −6.1 to −4.6 (3.4 H) for vinylic protons, and −3.8 to −0.9 (7.4 H) for protons on saturated carbon was consistent with the presence of **17**. This side reaction probably did not effect the isomer distribution shown in Table I since the conversion was rather low.

Addition of 2 mole % (based on **1** or **2**) of a known free-radical polymerization inhibitor, 4,6-dinitro-*o*-cresol, decreased markedly the rate of polymerization, but also greatly decreased the rate of cycloaddition. Using benzophenone as the sensitizer, this reaction gave only a 2% conversion of the nitrile **2** to the cross-adducts **3**–**5** in 4 hr in contrast to the >58% (Table II) conversion of diene **1** in the absence of the inhibitor.

Control reactions established the absence of any cycloaddition or polymerization reactions on irradiation of **1** and **2** through Pyrex in the absence of a sensitizer.

Direct irradiation of an equimolar mixture of the olefins **1** and **2** contained in quartz tubes with either a me-

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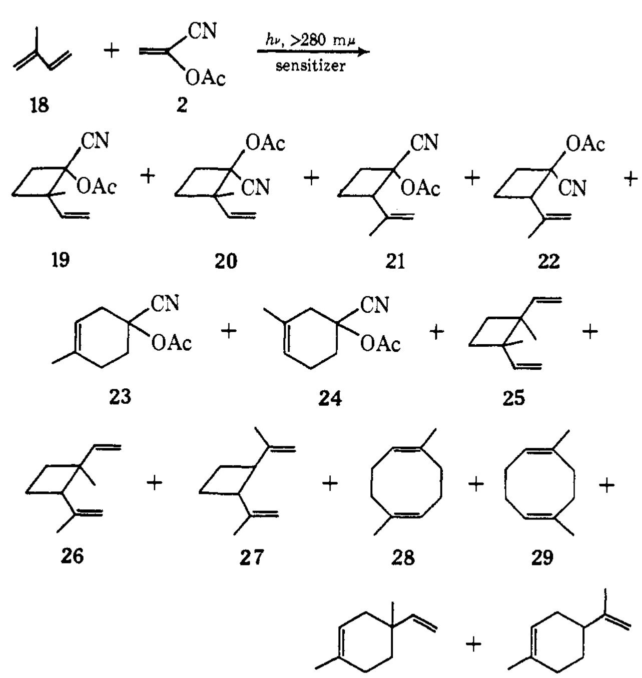
(12) Bradshaw[7] has reported a similar reaction with cyclohexene.

dium- or low-pressure mercury arc lamp (mainly 2537 Å) gave low conversions to the cyclobutane cross-adduct(s) **3** and/or **4** and the butadiene dimers **6** and **7** in addition to several unidentified compounds. One of these unknowns had a gc retention time only slightly different from the cross-adducts **3** and **4**. Also the proportion of polymer was greater in the direct irradiation than in the sensitized reaction. The conversions at 1 and 2 hr were *ca.* 0.5 and 1.4%, respectively. The proportion of cross-adducts to dimers was of the order of 1 : 1. Although the lower limit of detection was rather high, no cyclohexene cross-adduct was detected. Irradiation of the diene **1** alone through quartz gave largely polymeric material, possibly with a trace of dimer,[13] while the nitrile **2** under the same conditions gave only a small amount of polymer and *ca.* 2% conversion to five or six unidentified lower molecular weight components.

An attempt was made to observe the singlet–triplet absorption spectrum of the vinyl cyanide **2** by measuring the spectrum in methyl iodide solution in a 10-cm cell.[14] However, no absorption maxima or shoulders could be detected above the background due to methyl iodide.

Isoprene. Irradiation of an equimolar mixture of isoprene (**18**) and the olefin **2** in the presence of 20 mole % of a triplet sensitizer gave a mixture of six cross-adducts **19–24** and seven dimers of isoprene **25–31**. In addition several minor products were detected. The 13 cycloadducts **19–31** were the major products when the conversion was below *ca.* 30–40%. At higher conversions polymeric material was also formed as was observed in the photoaddition of butadiene to the olefin **2**.

The products were separated by preparative gc except for three pairs of isomers which were obtained only as mixtures of the two: **21** and **22**, **23** and **24**, and **28** and **29**. The structures of the products were established by spectroscopic methods and in some cases comparison with authentic samples (see Experimental Section).



The head-to-head nature of the cyclobutane cross-adducts **19–22** was not rigorously established, but was assigned by analogy with the products of addition of butadiene and cyclopentadiene (see below) to the olefin **2**. The stereochemistry of the two methyl, vinyl cross-adduct isomers **19** and **20** was assigned on the basis of the relative chemical shifts of the nonterminal vinyl protons, the tertiary methyl protons, and the acetoxy methyl protons. The nonterminal vinyl proton of the isomer assigned structure **20**, in which the vinyl group was *cis* to the cyano group, occurred at a lower field (−6.20 ppm) than in the isomer **19** (−5.91 ppm) in which the corresponding proton was on the vinyl group situated *trans* to the cyano group (and *cis* to the acetoxy group). The proton *cis* to the cyano group is expected to be deshielded since molecular models (Dreiding) indicate that this proton will be situated within the deshielding zone of the cyano group.[15] The proton on the vinyl group which is *cis* to the acetoxy group is predicted to be shielded by the alkyl C–O bond; thus the proton of isomer **19** should lie at higher field than that of isomer **20** in which this proton on the vinyl group is *trans* to the acetoxy group. The diamagnetic anisotropic effect of the acetoxy carbonyl group probably would be less important due to an averaging effect brought about by rotation about the alkyl C–O bond and the acyl C–O bond. Examination of molecular models with the acetoxy group in its predicted lowest energy conformations indicates that the nonterminal vinyl proton *cis* to the acetoxy group would be in the shielding region of the carbonyl group.[16] Thus the predicted effect of the acetoxy group, due both to the C–O bond and the carbonyl group, is one of shielding a proton on a *cis* substituent. Overall, the anisotropic effects of the cyano and acetoxy groups reinforce each other. In a similar manner the relative chemical shifts of the methyl groups on the tertiary ring carbon atoms support the above structure assignments. The methyl group which is *cis* to the cyano group and *trans* to the acetoxy group (isomer **19**) occurs at lower field (−1.48 ppm) than that of the isomer **20** (−1.23 ppm).[17] Finally, the chemical shifts of the acetoxy methyl groups corroborate these assignments. The anisotropic effect of the carbon–carbon double bond is such that a proton is shielded which lies above or below the plane of the four atoms attached to the double bond.[18] Molecular models of isomer **19** in which the acetoxy group is *cis* to the vinyl group indicate that on the average (in the predicted most stable conformations) the acetoxy

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(13) For the results of the unsensitized irradiation of butadiene see ref 1.

(14) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 57.

(15) (a) L. M. Jackman, *Fortschr. Chem. Org. Naturstoffe*, **23**, 335 (1965); (b) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 78.

(16) G. J. Karabatsos, G. C. Sonnichsen, N. Hsi, and D. J. Fenoglio, *J. Am. Chem. Soc.*, **89**, 5067 (1967).

(17) (a) H. Suginome, T. Tsuneno, and T. Masamune [*Tetrahedron Lett.*, 4605 (1967)] have reported the effect of neighboring C-6 cyano and acetoxy groups on the chemical shifts of the C-19 methyl protons of 3α,5α-cyclocholestane derivatives which are in agreement with the above arguments. Their data show that the *cis*-cyano group causes a greater deshielding of the C-19 methyl protons than does the *cis*-acetoxy group when compared with hydrogen. (b) P. D. Bartlett and K. E. Schueller [*J. Am. Chem. Soc.*, **90**, 6077 (1968)] have advanced similar arguments concerning the stereochemistry of some *cis*- and *trans*-1-cyano-2-methylcyclohexyl acetates.

(18) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 129.

Table V. Product Distribution from Photosensitized Cross-Addition of Isoprene and α-Acetoxyacrylonitrile

Sensitizer[a]	E_T[b]	Distribution of cross-adducts and dimers, %										Cyclobutanes in cross-adducts, %	Cyclobutanes + cyclooctadienes in dimers, %	Conversion,[d] %
		19	**20**	**21** + **22**[c]	**23** + **24**[c]	**25**	**26**	**27**	**28** + **29**[c]	**30**	**31**			
Acetophenone	73.6	9.0	7.5	10.2	2.3	19.9	22.0	6.4	20.6	2.1	0.5	92	96	3
		8.1	8.4	10.7	1.5	71[e]						95		40
Benzil	53.7	7.2	5.6	11.6	15.6	7.2	7.2	1.8	12.6	22.8	8.4	61	48	12
		7.8	5.7	10.3	17.2[f]	59[e]						58		36

[a] Sensitizer (1.0 mmole) in 5 mmoles of **18** and 5 mmoles of **2**. Irradiated at 0–5° through Pyrex filter. [b] Lowest triplet energy level in kilocalories per mole. See ref 4c and 10. [c] The presence of both isomers was established by nmr. [d] Based on diene **18**. [e] Total dimers **25**–**31**. [f] The ratio of **23**:**24** was *ca.* 2:1.

methyl group will be in the shielding zone of the vinyl group (δ −2.02 ppm *cis* to vinyl, δ −2.09 ppm *trans* to vinyl). The mixture of vinyl isomers **3** and **4** also shows the nonterminal vinyl protons at approximately the same positions, −6.12 and −5.91 ppm. Using the same arguments as outlined above, the −6.12 ppm proton is assigned to the *cis*-cyano isomer **4** and −5.91 ppm proton to the *cis*-acetoxy isomer **3**. In these isomers the chemical shifts of the acetoxy methyl groups differ by only 0.02 ppm compared with 0.07 ppm for the methyl, vinyl isomers **19** and **20**.

The mixture of isopropenyl isomers **21** and **22** showed essentially no differences in chemical shifts of any of the isopropenyl protons, possibly due to their being on the carbon atoms which are β to the cyclobutane ring. As observed for **3** and **4**, the chemical shifts for the acetoxy methyl groups differed by only 0.02 ppm. However the observation of two distinct peaks establishes the presence of both isomers. The similarity of the chemical shift differences for the acetoxy methyl groups of the vinyl isomers **3** and **4** and the isopropenyl isomers **21** and **22** suggests that the reason for the larger chemical shift difference in the methyl vinyl isomers **19** and **20** may be due to a conformational restriction brought about by the methyl groups on the cyclobutane ring.

The positions of the methyl groups in the cyclohexenes **23** and **24** have not been rigorously determined. The relative amounts of **23** and **24** in mixtures of the two was determined by measurement of the areas for the vinylic proton. Spectra recorded at both 60 and 100 Mc/sec established that the two multiplets at −5.5 and −5.2 ppm were due to different protons and not to coupling. The assignment of the −5.5-ppm multiplet to the 3-methyl isomer **24** and the −5.2-ppm multiplet to the 4-methyl isomer **23** is based largely on the relative distribution of these products in the thermal reaction. The isomer with the −5.2-ppm multiplet predominated and is assumed to be the 4-Me ("*para*") isomer by analogy with many other thermal Diels–Alder reactions of isoprene and other 2-substituted dienes.[19] One can rationalize, by the examination of molecular models, the chemical shifts of the vinylic protons of isomers **23** and **24** on the basis that the "*para*" proton of **24** would be more nearly in the deshielding region of the cyano group than would the "*meta*" proton of **23**. The cyano group would probably be in the pseudoaxial position in the more stable conformers of **23** and **24**.[20] It is somewhat surprising that the chemical shifts of the vinylic methyl groups of **23** and **24** are not separated significantly. However this may be a consequence of the methyl groups being further removed from the functional groups. Of significance to the argument that both isomers **23** and **24** are present is the slight difference in chemical shifts of the acetoxy methyl groups (Δδ 0.005 ppm). The difference in chemical shifts of the "*meta*" and "*para*" protons of the demethyl isomer **5** (Δδ 0.3 ppm) is nearly the same as that of the two methyl isomers **23** and **24**.

The dimers **25**–**31** were the same as those obtained by Hammond and coworkers[4c,21] in their study of the photosensitized dimerization of isoprene. Direct comparison of spectra and gc retention times were made on the dimers obtained in the cross-addition reaction with those obtained under the conditions described by Hammond and coworkers.[4b,c] Several discrepancies in chemical shifts of certain protons in the nmr spectra with those reported[4b] are noted in the Experimental Section.

Examination of the gas chromatogram of the reaction mixture from the cross-addition revealed two minor components which may have been the dimers **13** and **14**. These components were not formed in amounts exceeding 1% of the total cross-adducts **19**–**24**.

Several minor products were observed in the reactions involving benzil as the sensitizer; all had gc retention times greater than that of benzil, which suggested that they were higher molecular weight addition products as did their mass spectra.

In Table V are given the product distributions of cross-adducts and dimers in the cross-addition reactions for the two sensitizers at two different conversions. Our results for the dimerization of isoprene (**18**) in the absence of the nitrile **2** were nearly the same as those with the nitrile and those reported by Hammond and coworkers,[4c] 95% cyclobutanes and cyclooctadienes with acetophenone and 42% with benzil.[22] Control reactions established the absence of any thermal (dark) re-

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(19) A. S. Onishchenko, "Diene Synthesis," L. Mandel, Translator, Daniel Davey and Co., Inc., New York, N. Y., 1964, p 26.

(20) E. L. Eliel, *Angew. Chem. Intern. Ed. Engl.*, **4**, 761 (1965).

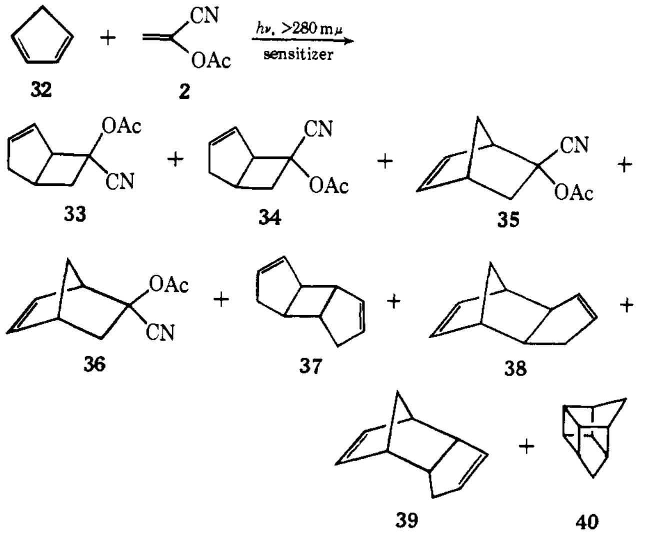
(21) G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963).

(22) Hammond and coworkers[4c] reported 92 and 45% cyclobutanes plus cyclooctadienes **25**–**29** for the acetophenone- and benzil-sensitized dimerizations, respectively, at 27–29°. Our reactions were run at 0–5°.

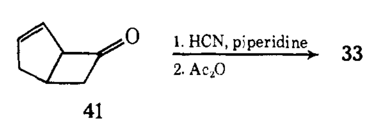
actions at the temperatures of the photosensitized reactions.

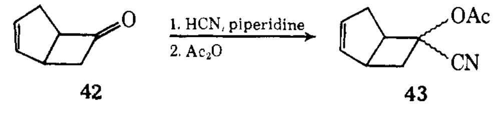
The thermal (Diels–Alder) reaction of equimolar amounts of the olefins **18** and **2** at 150° without a solvent gave all six cross-adducts in the following proportions: **23**, 63%; **24**, 32%; **19**, 2.1%; **20**, 1.7%; **21** + **22**, 1.2%.

Cyclopentadiene. Irradiation of cyclopentadiene (**32**) with an equimolar amount of the olefin **2** and 20 mole % of acetophenone gave four cross-adducts **33**–**36** and four dimers **37**–**40**. Use of benzil as the sensitizer also gave the same products with the exception of the saturated dimer **40,** which was not found.



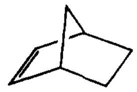
Each of the eight products was isolated by preparative gc. The cross-adducts **33**–**36** were identified by spectroscopic means (see Experimental Section), independent synthesis, and comparison with authentic samples in some cases. The two norbornene derivatives **35** and **36** were obtained *via* the thermal Diels–Alder reaction of the olefins **32** and **2**.[23a] One of the bicyclo[3.2.0]heptene isomers **33** was synthesized independently, thus establishing the position of the double bond. Treatment of the ketone **41**[23b] with hydrogen cyanide and piperidine and acetylation of the resulting cyanohydrin gave a single cyanohydrin acetate **33** identical with one of the products from the photoaddition reaction. One of the isomeric cyanohydrin acetates **43** was synthesized according to the procedure of Roberts and Gorham[24] by using the isomeric ketone **42**.[25] Only one isomer was isolated from the product mixture. A small shoulder on the gc peak of **43** was observed; no other evidence for the other stereoisomer of **43** was found. Careful examination of the crude reaction mixture from the irradiation of the olefins **32** and **2** showed no detectable amount of the cyanohydrin acetate **43**.

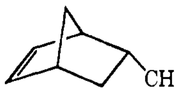




The stereochemical assignments for the bicyclo[3.2.0]heptene isomers **33** and **34** are based on the relative chemical shifts of the tertiary allylic protons, the vinylic protons, and the acetoxy methyl protons. The tertiary allylic protons in these isomers are on the cyclobutane ring rather than on carbon atoms α to the cyclobutane ring as are the methyl protons in the isoprene adducts **19** and **20** discussed above. It appears that in these cases the proton *cis* to the cyano group is shielded by the cyano group with respect to the proton which is *trans* (see discussion of norbornene derivatives below). It also appears that the *cis*-alkyl C–O bond of the acetoxy group has a larger shielding effect than the cyano group (see below). Thus the compound assigned as the *trans*-acetoxy isomer **34** has this tertiary proton (*cis* to acetoxy) at higher field (−3.49 ppm) than the corresponding proton (*cis* to cyano) of the *trans*-cyano isomer **33** (−3.97 ppm). One of the vinylic protons in isomer **33** is shifted upfield (−5.54 ppm) compared with the other proton (−5.94 ppm) which has nearly the same chemical shift as the two vinylic protons in isomer **34**. We attribute this upfield shift of one of the protons, probably the one nearer the acetoxy group, to the shielding effect of the *cis*-acetoxy group of **33**. The acetoxy methyl resonance appears at a higher field (−2.05 ppm) in the *cis*-acetoxy derivative **33** (*trans* −2.12 ppm). In this case there is less ambiguity about the conformation of the double bond since it is part of the fused ring system. The double bond isomer **43**, believed to have the *cis*-acetoxy configuration (see below), has its acetoxy methyl resonance at −2.09 ppm, *i.e.*, this methyl group is not as highly shielded as the *cis*-acetoxy isomer **33**. This is probably due to the double bond being further removed from the acetoxy group in isomer **43** than it is in isomer **33**. We would expect the stereoisomer of **43** to have its acetoxy methyl resonance at *ca.* −2.12 ppm.

The stereochemical assignments for the norbornene derivatives **35** and **36** were made by comparison of their nmr spectra with those of several model compounds **44**–**54**. The chemical shift data for the norbornene de-


44



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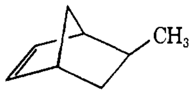

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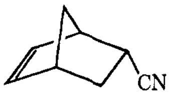

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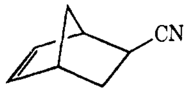

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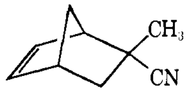

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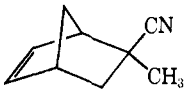

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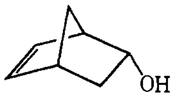

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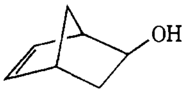

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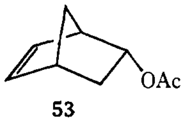

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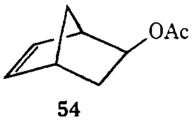

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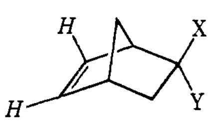
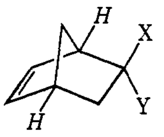
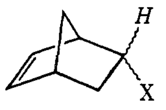
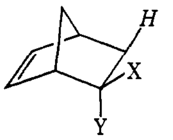
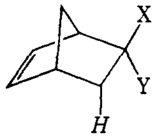
(23) (a) This reaction was originally reported by P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, **78**, 2473 (1956); (b) D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Lett.*, 1911 (1963).

(24) J. D. Roberts and W. F. Gorham, *J. Am. Chem. Soc.*, **74**, 2278 (1952).

(25) B. T. Brooks and G. Wilbert, *ibid.*, **63**, 870 (1941).

Table VI. Nmr Chemical Shifts of Bicyclo[2.2.1]hept-2-ene Derivatives[a]

Compound						CH_3
44[b]	−5.93	−2.83		−1.57	−0.94	
45[c]	−6.09, −5.88	−2.66	−2.4 to −0.9[d,e]	−2.4 to −0.9[d,f]	−0.43	−0.79
46[g]	−6.05, −5.91	−2.76, −2.36	−1.6 to −0.9[d]	−1.6 to −0.9[d]	−1.6 to −0.9[d]	−1.08
47	−6.34, −6.16	−3.20, −2.99	−2.83	−2.13	−1.20[h]	
48	−6.14, −6.01	−3.18, −3.03	−2.18	−1.93	−1.50[h]	
49	−6.28	−2.95, −2.79		−1.7 or −1.5	−1.7 or −1.5	−1.52
50	−6.25, −6.00	−3.0		−2.28	−1.5	−1.20
51[h]	−6.27, −5.98	−2.90, −2.73	−4.35	−1.97	−0.80	
52[h]	−6.08, −5.92	−2.72	−3.78	−1.72	−1.25	
53	−6.26, −5.89	−3.10, −2.80	−5.17	−2.10	−1.5 to −1.3	−1.87
54	−6.20, −5.95	−2.84	−4.57	−1.8 to −1.3[d]	−1.8 to −1.3[d]	−1.96
35	−6.40, −5.91	−3.64, −3.01		−2.52	−1.8 to −1.4[d]	−1.99
36	−6.47, −6.13	−3.31, −2.97		−2.1 to −1.9[d]	−2.1 to −1.9[d]	−2.07

[a] All spectra taken in CCl_4 solution (10–20%) unless otherwise specified. Chemical shifts in parts per million from internal Me_4Si. [b] Data from ref 26. [c] Spectrum taken on neat liquid. [d] Actual chemical shift is somewhere within stated range. [e] A chemical shift of −2.02 ppm in $CDCl_3$ solution was reported in ref 27. [f] A chemical shift of −1.84 ppm in $CDCl_3$ solution was reported in ref 27. [g] Spectrum taken in 50% CCl_4 solution. [h] Data from ref 28.

rivatives are presented in Table VI.[26–28] Even though unambiguous assignments for the vinylic protons were not made, the differences in the chemical shifts for these two protons provided useful information. The chemical shift differences ($\Delta\delta$) for the vinylic protons are listed in Table VII. The difference in the chemical shifts ($\Delta\delta$) for the vinylic protons are larger for the *endo* isomers (monosubstituted) in all cases in Table VII.

Table VII. Chemical Shift Differences of Vinylic Protons of Norbornene Derivatives

Compd	$\Delta\delta$ *endo*-X	$\Delta\delta$ *exo*-X	$\Delta(\Delta\delta)$[a]
45, 46	0.21	0.14	0.07
47, 48	0.18	0.13	0.05
53, 54	0.37	0.25	0.12
49, 50	0.25 (*endo*-Me)	0[b] (*exo*-Me)	
35, 36	0.49 (*endo*-OAc)	0.34 (*exo*-OAc)	

[a] $\Delta(\Delta\delta) = \lvert\Delta\delta_{endo\text{-X}} - \Delta\delta_{exo\text{-X}}\rvert$ ppm. [b] <0.05 ppm.

Several other groups have observed the same phenomenon with similar derivatives.[29] This is as expected since the *endo*-functional group would probably exert a greater influence on the vinylic protons than the *exo*-functional group due to its proximity in the *endo* position. The difference in chemical shift differences [$\Delta(\Delta\delta)$] is a measure of the difference in effects of a group in the *endo* and *exo* positions. This effect is greatest for the acetoxy group (0.12 ppm), next greatest for the methyl group, and least for the cyano group. Thus when two substituents are present on the same carbon atom one may expect the group with the larger $\Delta(\Delta\delta)$ value to have the dominant effect. This is true for the methyl, cyano compounds **49** and **50** where the *endo*-methyl derivative has the larger effect; the $\Delta\delta$ is larger for the *endo*-methyl-*exo*-cyano compound **50**. Applying the same arguments to the acetoxy, cyano derivatives **35** and **36** one obtains the assignments as indicated. The acetoxy group has the larger $\Delta\delta$, thus causing the *endo*-acetoxy-*exo*-cyano derivative **35** to have the larger $\Delta\delta$. The same conclusions would have been reached by looking only at the magnitude of $\Delta\delta$ for the *endo* isomers. The order is the same as above: OAc > Me > CN.

The same type of analysis of chemical shift differences made for the vinylic protons above can be applied to the bridgehead protons even though absolute assignments were not made. The chemical shift differences ($\Delta\delta$) for the bridgehead protons are given in Table VIII. The methyl group produces a larger $\Delta(\Delta\delta)$ (0.40 ppm) than does the cyano group (0.06 ppm). The *exo*-methyl group leads to a larger $\Delta\delta$ than the *endo*-methyl. Thus one predicts that in the methyl, cyano isomers **49** and **50** the methyl group should have the dominant effect and the *exo*-methyl isomer **49** should have the larger $\Delta\delta$; such is the case. In a like manner, the acetoxy group also produces a larger $\Delta(\Delta\delta)$ than the cyano group. In the acetoxy, cyano isomers **35** and **36**, the acetoxy group should have the dominant effect. The *endo*-acetoxy group leads to the larger $\Delta\delta$. The isomer **35** ($\Delta\delta$ = 0.63) is thus assigned the *endo*-acetoxy, *exo*-

Table VIII. Chemical Shift Differences of Bridgehead Protons of Norbornene Derivatives

Compd	$\Delta\delta$ *endo*-X	$\Delta\delta$ *exo*-X	$\Delta(\Delta\delta)$[a]
45, 46	0[b]	0.40	0.40
47, 48	0.21	0.15	0.06
53, 54	0.30	0[b]	0.30
49, 50	0[b] (*endo*-Me)	0.16 (*exo*-Me)	
35, 36	0.63 (*endo*-OAc)	0.34 (*exo*-OAc)	

[a] $\Delta(\Delta\delta) = \lvert\Delta\delta_{endo\text{-X}} - \Delta\delta_{exo\text{-X}}\rvert$ ppm. [b] <0.1 ppm.

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(26) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, 9 (1966).

(27) E. Pretsch, H. Immer, C. Pascual, K. Schaffner, and W. Simon, *Helv. Chim. Acta*, 50, 105 (1967).

(28) J. C. Davis, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, 87, 3900 (1965).

(29) (a) J. Paasivirta, *Suomen Kemistilehti*, B36, 76 (1963); (b) R. V. Moen and H. S. Makowski, presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstracts of Papers No. Q-9.

cyano stereochemictry, in agreement with the conclusion reached above.

The observation[30] that *endo* protons of the norbornene nucleus are shielded with respect to the *exo* protons by the double bond is born out in the compounds listed in Table VI. This shielding effect of the double bond on *endo* protons also is evident from an examination of the data in Tables IX and X. Of more interest for our purposes were the diamagnetic anisotropic and inductive effects of various functional groups on *cis*- and *trans*-vicinal protons. The conformationally rigid norbornene nucleus is a well-suited system for such observations since one can predict with a fair degree of accuracy the spacial arrangement of the atoms. The pertinent data for the *exo* protons are given in Table IX. Both the *endo*- and *exo*-cyano groups deshield the vicinal *exo* proton with respect to the unsubstituted compound **44**, probably due to an inductive effect. The *exo* proton is shielded by the *exo*-(*cis*) cyano group with respect to the *endo*-(*trans*) cyano group. Examination of molecular models of the isomeric nitriles **47** and **48** and magnetic anisotropy calculations employing the McConnell equation[31] for both the $C\equiv N$ and the C–C bonds of the nitrile group reveal that the cyano group shields the vicinal *cis* proton more than the vicinal *trans* proton.[28] The *exo* proton of the *endo*-acetoxy isomer **53** is deshielded with respect to the unsubstituted compound **44**, probably by an inductive effect. The corresponding proton of the *exo* isomer **54** also may be deshielded. The *cis*-acetoxy group exerts a larger anisotropic shielding effect on this proton (compared with the *endo* isomer **53**) than does the *cis*-cyano group (>0.3 *vs.* 0.2 ppm). The much higher field (−1.7 or −1.5 ppm) of the *exo* proton *cis* to the methyl group in **49** compared with the isomer **50** (−2.28 ppm) probably is due to the high shielding effect of the C–C bond (see discussion below on the *endo*-methyl compound **45**). The deshielding of the *exo* proton of **50** with respect to the *exo*-cyano isomer **48** (−2.28 *vs.* −1.93 ppm) is probably due at least in part to an anisotropic deshielding effect of the C–C bond of the methyl group. The isomer assigned the *exo*-acetoxy configuration **36** shows the vicinal *exo* proton at a higher field (>−2.1 ppm) than in the isomer **35** (−2.52 ppm) due to the greater shielding effect of the *cis*-acetoxy group compared with the *cis*-cyano group. The relative chemical shifts of the isomers parallel those of the methyl, cyano isomers **49** and **50** and also the methacrylic acid Diels–Alder adducts of cyclopentadiene reported by Fraser.[30a]

Table IX. Chemical Shifts of Vicinal *exo* Protons of Norbornene Derivatives

endo series		*exo* series		
Compd	δ	Compd	δ	Δδ
44	−1.57			
47	−2.13	**48**	−1.93	0.20
51	−1.97	**52**	−1.72	0.25
53	−2.10	**54**	>−1.8	>0.3
49	−1.7 or −1.5	**50**	−2.28	0.6 or 0.8
36	>−2.1	**35**	−2.52	>0.4

Table X. Chemical Shifts of Vicinal *endo* Protons of Norbornene Derivatives

endo series		*exo* series		
Compd	δ	Compd	δ	Δδ
44	−0.94			
45	−0.43	**46**	<−1.09	>0.5
47	−1.20	**48**	−1.50	0.30
49	−1.7 or −1.5	**50**	−1.05	0.4 or 0.6
51	−0.80	**52**	−1.25	0.45
36	<−1.9	**35**	>−1.8	>0.1

An analogous set of comparisons can be made for the vicinal *endo* protons; the pertinent data are given in Table X. The *endo*-methyl group of **45** causes a considerable (0.5 ppm) shielding of the vicinal *endo* proton compared with the unsubstituted compound **44**. The cyano group of both the *endo*-**47** and *exo*-**48** isomers deshields the vicinal *endo* proton, and, as in the case of the vicinal *exo* proton discussed above, the *cis*-cyano group has a shielding effect with respect to the *trans*-cyano group. The Δδ values for the two cases are about the same: 0.20 ppm for the vicinal *exo* proton, 0.30 ppm for the vicinal *endo* proton. The high shielding effect of a *cis*-methyl group (compared with the *cis*-cyano group) is also evident in the *endo*-methyl isomer **50**. The *exo*-cyano group deshields this proton compared with the *exo*-hydrogen atom of the *endo*-methyl isomer **45** (0.62 ppm) while the *endo*-methyl group shields this proton compared with the *endo*-hydrogen atom of the *exo*-cyano isomer **48** (0.45 ppm). The *endo*-acetoxy group of **35** shields the vicinal *endo* proton more than the *endo*-cyano group of **36** does (>0.1 ppm); this is also in accord with the structural assignments for these two isomers.

The *endo*-acetoxy methyl resonances occur at higher fields than those of the *exo*-acetoxy methyls (Table VI) for both pairs of isomers **53**, **54** (Δδ 0.09 ppm) and **35**, **36** (Δδ 0.08 ppm). This effect also is due presumably to shielding of the *endo*-acetoxy methyl group by the norbornene double bond. This phenomenon has been observed previously for the monosubstituted isomers **53** and **54**.[29b] These observations also support the structural assignments of **35** and **36**.

A similar effect of the double bond on the *endo*- and *exo*-methyl proton resonances also is evident from an examination of these chemical shifts of compounds **45**, **46**, **49**, and **50** in Table VI. The chemical shift differences are nearly the same for the two pairs of isomers: Δδ 0.29 ppm for **45** and **46**, 0.32 ppm for **49** and **50**. These data are the principal pieces of evidence for the stereochemical assignments of these isomers. A similar effect was observed for the cyclopentadiene–methacrylic acid Diels–Alder adducts.[30a]

All four dimers **37–40** were identified by comparison of gc retention times and spectra of authentic materials.[4b,32]

There were no appreciable differences in the distributions of cross-adducts **33–36** for the two sensitizers in parallel runs. Approximately equal amounts of the four cross-adducts **33–36** were formed when the thermal

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(30) (a) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962); (b) P. Laszlo and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964); (c) E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, 42, 1245 (1964).

(31) (a) H. M. McConnell, *J. Chem. Phys.*, 27, 226 (1957); (b) ref 18, p 113.

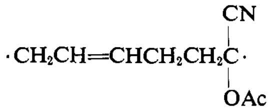
(32) (a) E. T. McBee, W. L. Dilling, and H. P. Braendlin, *J. Org. Chem.*, 27 2704 (1962); (b) W. L. Dilling, H. P. Braendlin, and E. T. McBee, *Tetrahedron*, 23, 1211 (1967).

reaction between **32** and **2** was minimized. The thermal reaction occurred slowly at 0–5°, the temperature of the photoreactions, and some variation in product distribution was observed in various runs. The 1,4 adducts **35** and **36** were stable to the reaction conditions with both sensitizers. The ratio of cross-adducts **33–36** to dimers **37–40** was *ca.* 2–3 : 1. The distribution of dimers **37–40** was not determined in the cross-addition reactions. In sensitized runs with the diene **32** alone approximately equal amounts of each dimer **37–39** were formed using either sensitizer as reported by Turro and Hammond.[33] The caged dimer **40** was formed at the expense of *endo*-dicyclopentadiene (**39**).

The thermal cycloaddition of cyclopentadiene (**32**) and the unsaturated nitrile **2** at 150° without solvent gave only 1,4-addition products in a ratio of 75% *endo*-acetoxy **35** and 25% *endo*-cyano **36**. At 0° the ratio was 76:24 as it was in benzene solution at 130°. It is estimated that 2% (relative to total cross-adducts) of the cyclobutanes **33** and **34** could have been detected.

Discussion

1,3-Butadiene. The cross-adducts formed in the photosensitized reaction are those expected from the intermediate formation of the more stable diradical **55**


$$\cdot CH_2CH{=}CHCH_2CH_2\overset{CN}{\underset{OAc}{C}}\cdot$$

55

$\cdot CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2\cdot$

56

followed by either 1,4- or 1,6-ring closure.

Examination of Tables I and II reveals that in general the dimers **6–8** predominated over the cross-adducts **3–5** by a factor of 1–2 at low conversions. At higher conversions, as expected, the relative amounts of cross-adducts increased due to a larger mole fraction of the nitrile **2** (Tables II and III), which arose from the more rapid depletion of the diene **1** in the early stages of the reaction. If one makes the reasonable assumption that the relative amounts of the dimers and cross-adducts are a reflection of the stabilities of the two intermediates then it would appear that the triplet diallylic diradical **56** is slightly more stable than the triplet allylic acetoxycyano diradical **55**. Data in the literature indicate that a vinyl group is slightly better able to stabilize an adjacent radical than is a combination of a cyano and an acetoxy group.[34]

In general our results on the relative amounts of cyclobutanes **3** and **4** and cyclohexene **5** formed with sensitizers of different triplet energies (Figure 1) parallel quite closely those for the diene dimerization as determined by Hammond and coworkers.[4c] The major difference is the depth of the minimum in the cyclobutane/cyclohexene ratio in the 50-kcal/mole region. The breaking point at *ca.* 60 kcal/mole can be explained, as in the case of dimerization,[1,4a] by the *s-trans-* and *s-cis-*butadienes' having their lowest triplet energy levels at 59.6 kcal/mole[35] and *ca.* 53 kcal/mole, respectively.[4c] The increase in the relative amount of cyclobutanes with sensitizers having triplet energies lower than 50 kcal/mole could be due to "nonvertical" excitation as has been proposed for the butadiene and isoprene dimerizations,[4c] or alternatively to energy transfer from T_2 of the anthracene derivatives.[9c,36]

These explanations are based on the assumption that the reaction proceeded primarily *via* the butadiene **1** triplets rather than the α-acetoxyacrylonitrile **2** triplet. Evidence in support of this proposal is the very small (if any) amounts of cyanoolefin dimers **13** and **14** formed in the cross-addition reaction. Energy transfer to the cyanoolefin **2** is apparently rather inefficient or alternatively the lifetime of triplet **2** is quite short as evidenced by the low efficiency of photodimerization of **2** when compared with the diene. When the same lamp and apparatus were used only a 5% conversion of **2** to the dimers **13** and **14** occurred in 43 hr while a 10% conversion of **2** occurred in 5 hr in the cross-addition reaction with isoprene.

We attribute the difference in the relative amounts of cyclobutanes formed in the cross-addition and the dimerization in the 50-kcal/mole region of Figure 1 primarily to a difference in selectivity of ring closure of the *s-cis*-**1**–**2** triplet adduct **57** and the *s-cis*-**1**–**1** adduct **58** (Scheme I). The reaction of the diene triplets with ground-state *s-cis*-**1** has been neglected in the proposed reaction scheme since the *s-cis* form is present to a much smaller extent than the *s-trans*-**1**.[4c,37] This omission has no appreciable effect in the argument which follows. If the reasonable assumptions are made that the same relative amounts of *cis* and *trans* triplets are produced for any one sensitizer whether the olefin **2** is present or not, and that the reactivities of the two isomeric triplets with **2** (and with **1**) are the same,[38] then the difference in product distribution must reflect the difference in selectivity of ring closure of intermediates **57** and **58**. Thus the cross-intermediate **57** closed to a four-membered ring to a greater extent than did the dimer intermediate **58**. It has been shown from experiments on the termination reaction of free-radical copolymerizations that cross-termination between unlike radicals is favored over termination between like radicals, often to a rather large extent.[39] Thus the coupling of unlike radicals such as the ring closure of **57** (with electron spins paired) probably is faster and therefore less selective than the coupling of like radicals as in **58** (with spins paired). Since the intermediates **57** and **58** can exist in a large number of conformations ranging from cyclic to extended, at the moment of spin inversion the diradicals may be at least partially in the extended conformation (Scheme II). The triplet diradicals probably are most stable in the extended conformation due to electron–electron repulsion.[40] If the ring closure of **57** is more rapid than **58**, then a larger proportion of the cyclobutanes **3** and **4** would be expected. By virtue of its selectivity **58** has a greater chance to reach a confor-

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[33] N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, **84**, 2841 (1962).

[34] (a) C. Walling, *J. Phys. Chem.*, **64**, 166 (1960); (b) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 513, 516; (c) M. Hunt, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 5074 (1965).

[35] (a) D. F. Evans, *ibid.*, 1735 (1960); (b) R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.*, **87**, 4230 (1965).

[36] R. S. H. Liu and J. R. Edman, *ibid.*, **91**, 1492 (1969).

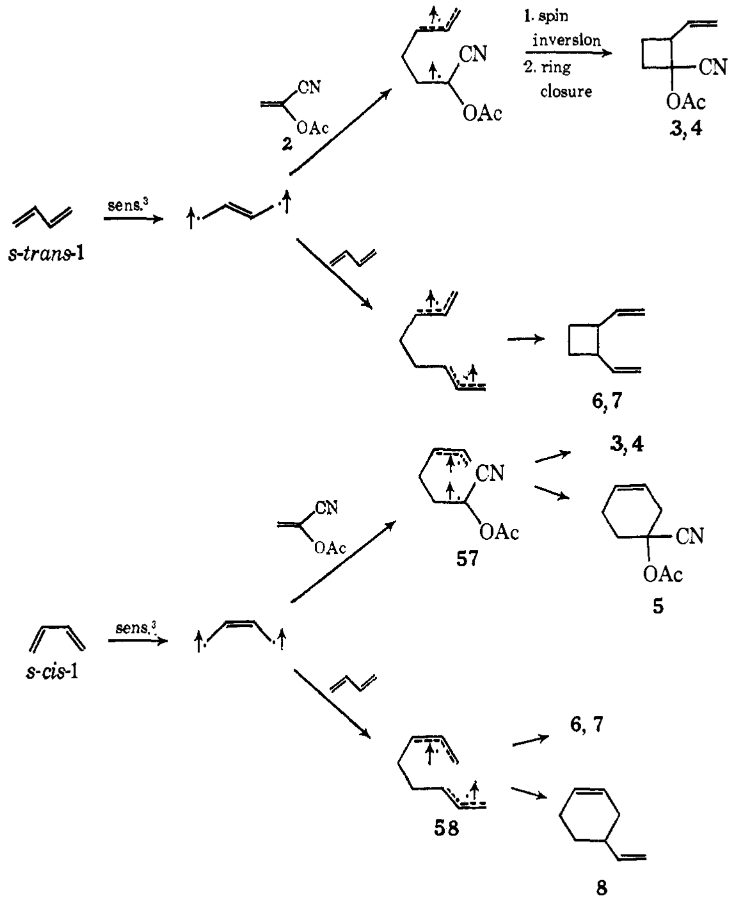
[37] (a) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946); (b) W. B. Smith and J. L. Massingill, *J. Am. Chem. Soc.*, **83**, 4301 (1961).

[38] The latter assumption may not be necessary. With sensitizers having triplet energies of 50–55 kcal/mole the amounts of *cis* triplets formed are probably much greater than the amounts of *trans* triplets based on the triplet energies of the species involved. Thus **57** and **58** may be the only significant diradicals involved.

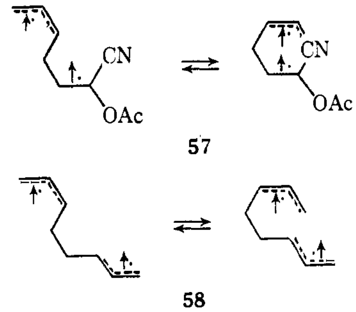
[39] Reference 34b, p 146.

[40] J. Saltiel, *Survey Progr. Chem.*, **2**, 255 (1964).

Scheme I



Scheme II



mation which will lead to the more stable product, namely the cyclohexene **8**.[41,42]

Pertinent to the above arguments is the report by Hammond and DeBoer concerning the thermal rearrangement of optically active *trans*-1,2-divinylcyclobutane to 4-vinylcyclohexene.[43] The cyclohexene formed had a trace of optical activity which indicated that the rate of ring closure of the intermediate diradical was of the same order of magnitude as the rates of rotation about single bonds in the intermediate **58** (with the electron spins not designated but presumably paired). These results indicate that the rates of ring closure and rotation of short chain diradicals such as **57** and **58** are in approximately the correct ratio to allow the above explanation to be valid. If the rates of ring closure were much faster than the rates of rotation then one should get mainly cyclobutanes from either intermediate **57** or **58**, while if the rates of ring closure were much slower than the rates of rotation the principal products from either diradical should be mainly the cyclohexenes. Benson[44] has also discussed these types of reactions, pointing out that the coupling of the diradical **58** (presumably the singlet) to the cyclohexene **8** has an apparent activation energy of 1.8 kcal/mole. Differences in lifetimes of the diradicals **57** and **58** with respect to intersystem crossing could also affect the cyclobutane–cyclohexene ratio. The crossed triplet diradical **57** could undergo intersystem crossing more rapidly due to the heteroatom functional groups.[45]

Although not studied in detail, our results indicated that there was no appreciable solvent effect except that the efficiency of the reaction was greatly reduced (Table IV). This reduced efficiency was probably due to deactivation of the sensitizers or excited butadiene by collision with the solvent molecules. In addition the process of dilution of the monomers lowers the rate of bimolecular addition required to form dimers and cross-adducts.[46]

Since the sensitizer did react with the diene **1** in the case of camphorquinone it was important to establish

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(41) "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956: (a) W. G. Dauben and K. S. Pitzer, p 38; (b) F. H. Westheimer, p 533.

(42) Heat of combustion data on the cyclobutanes **3** and **4** (*ca.* 1:1 mixture) and the cyclohexene **5** establishes that the cyclohexene is thermodynamically more stable than the cyclobutanes: $\Delta H^{\circ}_{c\,298.15}$ = −1177.01 ± 0.02 kcal/mole for **3**, **4** and −1153.13 ± 0.03 kcal/mole for **5**.

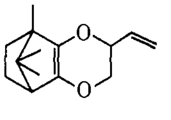
(43) G. S. Hammond and C. D. DeBoer, *J. Am. Chem. Soc.*, 86, 899 (1964).

(44) S. W. Benson, *J. Chem. Phys.*, 46, 4920 (1967).

(45) Reference 14, p 86.

(46) N. J. Turro and P. D. Bartlett [*J. Org. Chem.*, 30, 1849 (1965)] found no appreciable solvent effect in the photosensitized cycloaddition of dienes to 1,1-dichloro-2,2-difluoroethylene.

that this reaction did not affect the cyclobutane–cyclohexene ratio of cross-adducts. That there was no appreciable effect is borne out by the data in Table II. The oxetane product **10** (or isomer) of this reaction probably has a triplet energy in the neighborhood of 65–70 kcal/mole,[47] and might have been expected to alter the product distribution from that found at 50 kcal/mole. Hammond and coworkers[4c] did not report that this diketone underwent any photoreaction in the presence of butadiene (**1**) although several other sensitizers did undergo reaction (duroquinone and benzoquinone). The position of the vinyl group in **10** was assigned on the basis of the formation of more stable allylic radical intermediate.[48] The spectral data obtained for this product(s) appear to rule out the isomeric dioxene **59** and dihydropyran **60** as structures for the major adducts. We cannot rule out the presence of small amounts of **59** and **60** in the reaction mixture since several unidentified peaks appeared in the gas chromatogram with retention times close to that of the oxetane **10**.



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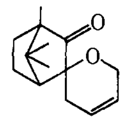


60

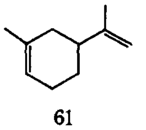
The photosensitized dimerization of α-acetoxyacrylonitrile has an analogy in the recently reported photosensitized dimerization of acrylonitrile.[9]

The composition of the copolymer, 1.35 parts of diene **1** to 1.0 part of nitrile **2** ($m_1/m_2 = 1.35$), is in fair agreement with that calculated (1.18) for a normal free-radical copolymerization of these two monomers by the Q–e scheme.[49]

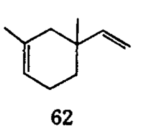
The unsensitized reactions probably involve the excited singlets of either the olefin **2** or the diene **1**. However, it is possible that the low yields of dimers and cross-adducts result from reactions of the triplet state (or a combination of singlet and triplet reactions) which is very inefficiently formed from the excited singlet of either **1** or **2**. The formation of polymer as the principal product is analogous to the polymer formed in the direct irradiation of the diene **1** in concentrated solutions.[50] The minor unidentified component with a gc retention time slightly greater than that of **3** and **4** may be a 1,3-substituted cyclobutane. This product would be analogous to the 1,3-divinylcyclobutane formed in the direct irradiation of butadiene alone.[1]

The entirely different product distributions in the photosensitized and thermal dimerizations of cyclopentadiene have been interpreted as evidence that the thermal reaction does not involve the triplet state.[33] The different product distributions from the photosensitized and thermal[3] cycloadditions of **1** and **2** could also be interpreted as evidence that the thermal reaction does not involve a triplet diradical. However this difference does not indicate that the thermal reaction does not involve a spin-paired intermediate as also pointed out by Turro and Hammond for the cyclopentadiene reaction.[33] The triplet diradical must cross over to the singlet before bond formation can occur. However, by the time this crossover occurs the ultimate product has already been determined as far as the *s-trans* diene giving cyclobutanes and the *s-cis* diene giving cyclohexenes is concerned. We interpret the fact that the cyclohexene **5** is formed at all in the sensitized cross-addition to indicate that the cyclohexene can arise *via* a two-step reaction.[3,51]

Isoprene. All of the cross-adducts can be rationalized as arising from the more stable triplet diradical intermediates analogous to **18**. Similarly all of the dimers **25–31** result from the more stable diallylic diradicals.[4b] Of significance is the absence of "*meta*" cyclohexene derivatives **61** and **62** from the isoprene dimers while the "*meta*" cross-adduct cyclohexene **24** is formed, although in smaller amount than the "*para*" cyclohexene **23**. The reason for this difference is not evident.



61



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A mechanism similar to that outlined above for the cross-addition of butadiene to the nitrile **2** is probably operative in the reaction with isoprene (**18**). The involvement of stereoisomeric isoprene triplets accounts for the variation in the product distribution as discussed for the diene dimerization[4c] and cross-addition. This explanation assumes that the conformational equilibrium of isoprene at near room temperature is greatly (>90%) in favor of the *s-trans* conformer. A Raman spectroscopic study indicated that the *s-cis* conformation was favored at room temperature,[52] but the bulk of the available spectroscopic[53] and other data[4c,21,53d,54] favor the *s-trans* conformation at room temperature as does the evidence for butadiene.[4c,37,55]

It is of interest to compare the results of the cross-addition and dimerization of both butadiene and isoprene. The pertinent data are listed in Table XI. The increased amount of cyclobutanes (58%) from the cross-addition of isoprene (**18**) and the olefin **2** with benzil sensitization, as compared with the dimerization of isoprene (45%), is in accord with the proposal of differing ring-closure rates of the crossed and dimer diradicals. The differences between the relative amounts of cyclobutane derivatives formed in the case of butadiene and isoprene with acetophenone sensitization (98% *vs.* 95%, 97% *vs.* 92%) are probably largely due to the difference in equilibrium constants between

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(47) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

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

(49) (a) T. Alfrey, Jr., J. J. Bohrer, and H. Mark, "Copolymerization," Interscience Publishers, New York, N. Y., 1952, p 64; (b) G. E. Ham, "Copolymerization," Interscience Publishers, New York, N. Y., 1964, pp 695, 847, 854.

(50) R. Srinivasan and F. I. Sonntag, *J. Am. Chem. Soc.*, **87**, 3778 (1965).

(51) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

(52) V. N. Nikitin and T. V. Yakovleva, *Zhur. Fiz. Khim.*, **28**, 697 (1954); *Chem. Abstr.*, **49** 5966 (1955).

(53) (a) N. Sheppard and D. M. Simpson, *Quart. Rev.* (London), **6**, 1 (1952); (b) G. J. Szasz and N. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953); (c) M. I. Batuev, A. S. Onishchenko, A. D. Matveeva, and N. I. Aronova, *Dokl. Akad. Nauk SSSR*, 132, 581 (1960); *Chem. Abstr.*, **54**, 22006 (1960); (d) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, **83**, 2885 (1961); (e) A. A. Bother-By and D. Jung, *ibid.*, **90**, 2342 (1968), and references cited therein.

(54) (a) J. Gresser, A. Rajbenbach, and M. Szwarc, *ibid.*, **82**, 5820 (1960); (b) A. J. Fry, R. S. H. Liu, and G. S. Hammond, *ibid.*, **88**, 4781 (1966); (c) M. H. Lehr, *Survey Progr. Chem.*, **3**, 222 (1966).

(55) (a) C. M. Richards and J. R. Nielsen, *J. Opt. Soc. Am.*, **40**, 438 (1950); (b) E. B. Reznikova, V. I. Tulin, and V. M. Tatevskii, *Opt. Spectrosc., USSR*, **13**, 200 (1962).

Table XI. Comparison of Product Distributions from Cross-Addition and Dimerization of Butadiene and Isoprene with α-Acetoxyacrylonitrile

Products	Sensitizer	—Distribution, %— Cyclobutanes + cyclooctadienes	Cyclohexenes
Butadiene Cross-adducts	PhCOMe	98	2
	$(PhCO)_2$	73	27
Butadiene Dimers[a]	PhCOMe	97	3
	$(PhCO)_2$	55	45
Isoprene Cross-adducts	PhCOMe	95	5
	$(PhCO)_2$	58	42
Isoprene Dimers[a]	PhCOMe	92	8
	$(PhCO)_2$	45	55

[a] Data from ref 4c.

s-cis and *s-trans* conformers. Also a portion of the differences observed with benzil sensitization (73% *vs.* 58%, 55% *vs.* 45%) is probably due to the same factor.

The 97:3 distribution of butadiene dimers with acetophenone is nearly equal to the best estimates (96:4)[37] of the *s-trans*:*s-cis* conformational equilibrium for butadiene. We would like to suggest that the 92:8 distribution for isoprene may be a reasonably accurate distribution of *s-trans-s-cis* isoprene conformers.

Another interesting aspect of the effect of sensitizer triplet energy was the ratio of cross-adducts to dimers. The pertinent data are summarized in Table XII. The data with other sensitizers (Table I) for the butadiene reactions confirm the trends noted in Table XII that the lower energy sensitizer gives a larger proportion of cross-adducts than the higher energy sensitizer.[56] Examination of all the product distribution data reveals that this increase in total cross-adducts with the lower energy sensitizers is due mainly to an increase in the amount of cyclohexene derivatives, with the amount of the cyclobutanes remaining more nearly constant. The reason for this apparent greater preference of the *cis*-diene triplets for cross-addition as compared with the *trans*-diene triplets is not clear. One argument which could be advanced is that the lower energy of the *cis* triplet (*ca.* 7 kcal/mole) leads to a greater selectivity in the addition step due possibly to a polar contribution in the transition state much like that proposed above for the ring-closure. The higher energy *trans* triplet may attack either the diene or cyanoolefin **2** in a less selective fashion; there is a statistical factor of 2 favoring addition to the diene since there are two equivalent positions for attack while the cyanoolefin has only one.

Table XII. Variation of Cross-Adduct–Diene Dimer Distributions with Sensitizer for Butadiene and Isoprene with α-Acetoxyacrylonitrile[a]

Diene	Sensitizer	—Distribution, %— Total cross-adducts	Total diene dimers
Butadiene	PhCOMe	35	65
	$(PhCO)_2$	46	54
Isoprene	PhCOMe	29	71
	$(PhCO)_2$	40	60

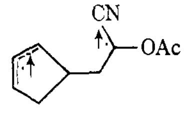
[a] Molar ratio of diene to nitrile **2** was 1:1. Conversions were less than 15% based on diene to ensure no large charge in relative concentrations.

The stabilization (hyperconjugative and/or inductive) of the allylic radical by the methyl group at the terminus of the allylic system is evident by comparing the relative amounts of methyl vinyl products with isopropenyl products (Table V). In all cases the methyl vinyl products predominated over the isopropenyl products. It would be of interest to know the total relative amounts of methyl vinyl radical *vs.* total isopropenyl radical products produced in these reactions. Unfortunately it is impossible to determine from which precursors the 1,6-dimethylcyclooctadiene **29** came.

Another interesting contrast in product distribution was the cross-adduct–diene dimer ratio for the two dienes. The relevant data are included in Table XII. The isoprene dimers predominated over the isoprene cross-adducts by a wider margin (71:29) for acetophenone, 60:40 for benzil) than the butadiene dimers predominated over the butadiene cross-adducts (65:35 for acetophenone, 54:46 for benzil). This is as expected since the diradical leading to the isoprene dimers is stabilized by two methyl groups while the diradical leading to the cross-adducts is stabilized by only one methyl group.

The thermal cycloaddition of isoprene (**18**) with α-acetoxyacrylonitrile (**2**) is another of the relatively few known examples of simultaneous thermal 1,2 and 1,4 cycloadditions.[3,17b,57] The 95:5 ratio of cyclohexene cross-adducts to cyclobutane cross-adducts indicates more of a preference for 1,4 addition in this system than in the butadiene–α-acetoxyacrylontrile system which has been studied in greater detail.[3] Consideration of only the conformational equilibria of the two dienes leads to a prediction of greater amounts of 1,4 addition from isoprene as was observed. As in the photoreactions discussed above, the cross-addition products from isoprene which would result from the more stable methyl allyl radical predominated. Further discussion of the significance of these thermal reactions must await a more detailed study (solvents effects, etc.).

Cyclopentadiene. All products of the cross-addition **33–36** can be explained as arising from the expected most stable intermediate diradical **63**. Since only two



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cyclobutyl derivatives were formed in the photoreaction we assume that **34** is the epimer of **33**, not of **43**. The bicyclo[3.2.0]heptenes **33** and **34** both were assumed to have *cis*-fused 5,4-ring systems. The alternate synthesis of the *trans*-cyano isomer **33** establishes the *cis*-ring fusion for this isomer. No unusual instability of the *trans*-acetoxy isomer **34** was noted and would indicate a *cis*-5,4-ring fusion. However, we cannot state unequivocally that this isomer has the *cis*-ring fusion. Until recently no products with a *trans*-fused 5,4-ring system had been prepared by a photocycloaddition reaction. However Scharf[58] has reported such a reaction.

The nondependence of the product distribution on the sensitizer triplet energy for the cyclic diene **32** is in agreement with the explanation offered for the variation in products with acyclic dienes,[4c,21] since the cyclic diene cannot assume the *s-trans* conformation.

The saturated dimer **40** probably arises *via* a secondary reaction of *endo*-dicyclopentadiene (**39**). This product **40** was detected only after extended periods of irradiation when the concentration of the diene **39** had risen to an appreciable level. We had shown previously that acetophenone does sensitize this reaction[59] in a manner similar to that of acetone reported by Schenck and Steinmetz.[60] One other long retention time product, probably an adduct of benzil and either of the olefins **32** or **2**, was detected by gc, but was not identified.

The formation of only one isomer (or predominantly one) in the reaction of each ketone **41** and **42** with hydrogen cyanide and piperidine followed by acetylation may be reasonably explained by assuming kinetically controlled additions in each case by attack of cyanide ion from the less hindered *exo* side of the [3.2.0] system. Under ordinary circumstances one would expect to get a mixture of cyanohydrins (thermodynamic control) from either ketone **41** or **42** by the reversibility of the addition step.[61] It is proposed that the reverse reaction is not favorable for these cyclobutanones since an sp^3-hybridized carbonyl carbon atom would be greatly favored over an sp^2 configuration due to angle strain.[62]

The thermal cycloaddition reaction of **32** and **2** has been reported previously but no stereochemical assignments were made.[23a] The absence of the cyclobutyl products **33** and **34** in the thermal cycloaddition proves that this reaction does not occur *via* a triplet diradical intermediate. However, a singlet diradical could be an intermediate, or the reaction could be concerted. The absence of 1,2-addition products is not unexpected since the diene **32** is locked in the *s-cis* conformation.

The *endo–exo* ratio of the cross-adducts, 75% *endo*-acetoxy **35**, 25% *exo*-acetoxy **36**, is intermediate between those reported for the addition of cyclopentadiene **32** to vinyl acetate[63] and acrylonitrile.[64] Since the acetoxy group has a greater preference for the *endo* orientation (81:19, 200°) than does the cyano group (60:40, ∼25–100°) one might predict that the major product from α-acetoxyacrylonitrile (**2**) should have the acetoxy group *endo* as observed. A quantitative estimate of the product distribution expected for this reaction can be made (eq 1 and 2) by assuming a linear free energy relationship for each of the substituents (OAc, CN) on the ethylene and kinetic control in all of the reactions, where $k_{endo\text{-X},\,exo\text{-Y}}$, $k_{endo\text{-X}}$, $k_{exo\text{-Y}}$, and k_E

$$\log k_{endo\text{-X},\,exo\text{-Y}} = \log k_{endo\text{-X}} + \log k_{exo\text{-Y}} + \log \frac{2}{k_\mathrm{E}} \quad (1)$$

$$\log k_{endo\text{-Y},\,exo\text{-X}} = \log k_{endo\text{-Y}} + \log k_{exo\text{-X}} + \log \frac{2}{k_\mathrm{E}} \quad (2)$$

are the rate constants for the formation of the disubstituted *endo*-X, *exo*-Y adduct, the monosubstituted *endo*-X and *exo*-Y adducts, and the unsubstituted ethylene adduct, respectively, etc. Using the product distributions cited above for the monosubstituted olefins, one calculates an isomer distribution of 74% *endo*-acetoxy **35** and 26% *endo*-cyano **36** in excellent agreement with the experimental results.

Examination of the literature[65] reveals few cases where this linear free energy relationship can be tested. Examples are the additions of methacrylic acid, isopropenyl acetate, α-chloroacrylonitrile, and methyl α-chloroacrylate to cyclopentadiene. The relevant data for these reactions in addition to those given above are as follows: propylene → 77% *endo*,[66] acrylic acid → 75% *endo*,[67] methacrylic acid → 65% *endo*-methyl,[68] isopropenyl acetate → 91.5% *endo*-acetoxy,[69] vinyl chloride → 55% *endo*,[56] α-chloroacrylonitrile → 80.5% *endo*-chlorine,[70] methyl acrylate → 76% *endo*,[71] methyl α-chloroacrylate → 64% *endo*-chlorine.[70] The calculated isomer distributions using eq 1 and 2 are 53% *endo*-methyl from methacrylic acid, 56% *endo*-acetoxy from isopropenyl acetate, 45% *endo*-chlorine from α-chloroacrylonitrile, and 28% *endo*-chlorine from methyl α-chloroacrylate. Thus the predominant isomers are predicted correctly in the first two examples, but quantitative correlation is poor. The calculated ratios for the last two examples do not even predict the correct major isomer. Possible sources of error are nonkinetic control, a large temperature dependence of the isomer ratios, and poor accuracy in the isomer ratios. For a linear free energy relationship of this type to be valid the electronic and steric interactions between the two substituents on ethylene should be minimal. These conditions are probably met reasonably well for nonbulky groups since these are cross-conjugated systems. Further examination of these relationships may provide added insight into factors which control the orientation in Diels–Alder reactions.

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Experimental Section

General. Melting points were taken in capillary tubes and were corrected. Boiling points were uncorrected. Elemental microanalyses were determined by Mr. L. E. Swim and coworkers. Infrared spectra were obtained by Mr. F. L. Beman and coworkers with a Perkin-Elmer 337 grating infrared spectrophotometer. The ultraviolet absorption spectra were obtained by Mr. Beman and coworkers with a Perkin-Elmer 202 ultraviolet-visible spectrophotometer. The nmr spectra were obtained by Mr. Beman and coworkers with a Varian A-60 analytical spectrometer operating at 60 Mc/sec; 100 Mc/sec spectra were obtained by Dr. J. P. Heeschen and coworkers using a Varian Model HA-100 high-resolution spectrometer. The chemical shifts are reported as δ[72] in parts per million from tetramethylsilane which was used as an internal reference. Mass spectral analyses were carried out by Mrs. M. L. Dilling and coworkers with a magnetically scanning 90° sector spectrometer using an electron ionizing voltage of 75 eV. The inlet temperature was 200° unless otherwise specified. High-resolution mass spectra were obtained by Dr. L. A. Shadoff with a Consolidated Electrodynamics Corp. Model 21-110B spectrometer. Analytical and preparative gc was carried out with both a F & M Model 500 temperature programmed gas chromatograph and a F & M Model 810 research chromatograph. The following gc columns were used: A, 10 ft × 0.25 in. 20% silicone rubber on 60–80 mesh Chromosorb W; B, 10 ft × 0.25 in. 20% Apiezon L on 60–80 mesh Chromosorb WAW; C, 20 ft × $^3/_8$ in. 20% Apiezon L on 60–80 mesh Chromosorb WAW; D, 10 ft × 0.25 in. 20% oxydipropionitrile on 60–80 mesh Chromosorb WAW; E, 2 m × 0.75 in 20% Union Carbide W98 (silicone rubber) on 60–80 mesh DMCS 775; F, 10 ft × 0.25 in. 20% E20,000 + 10% $AgBF_4$ on 30–60 mesh Chromosorb P; G, 10 ft × 0.25 in. 20% LAC 728-diethylene glycol succinate on 60–80 mesh Chromosorb WAW; H, 10 ft × 0.25 in. 5% Bentone 34 + 5% LAC 446 on 30–60 mesh Chromosorb WAW-DMCS (silanized). Helium was used as the carrier gas at a flow rate of *ca.* 40 ml/min unless otherwise specified.

Most of the irradiation experiments were carried out in sealed Pyrex pressure ampoules (5 mm i.d., 9 mm o.d. × 20 cm) or quartz tubes (7 mm i.d., 9 mm o.d. × 24 cm) attached to the lamp well. Reactants were degassed by three or four freeze–pump–thaw cycles at 10^{-4} mm pressure. Some reactions were carried out in non-sealed systems under purified nitrogen. The radiation source was a 450-W Hanovia medium-pressure mercury arc lamp, Type 679A.

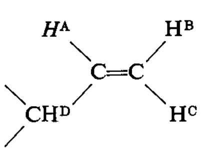
In the reactions involving butadiene after the irradiation was completed, the tubes were cooled to −78° and opened in a drybox. The weight loss on warming to room temperature was assumed to be unreacted butadiene. The remaining solution was analyzed directly by gc on columns A and B after the addition of an internal standard (p-$BrC_6H_4CH_3$) where appropriate. Column A was operated by temperature programming from 50 to 100° at a rate of 11°/min, followed by isothermal operation at 100° until a total of 16 min had elapsed, and finally temperature programming to 350° at a rate of 11°/min; retention times (minutes) were **1**, 2.2; biacetyl, 3.8; **6**, 7.2; **2**, 8.6; **8**, 9.2; **7** (**9**), 13.4; acetophenone, 19.2; p-$BrC_8H_4CH_3$, 19.8; **3**, **4**, 23.8; **5**, 25.6, camphorquinone, 26.1; benzophenone, 30.5; benzil, 32.6; anthracene, 34.1; pyrene, 37.5; β-naphthyl phenyl ketone, 38.0; flavone, 39.0; triphenylene, 40.5. Column B was operated isothermally at 180°; retention times (minutes) were **1**, 1.6; biacetyl, 1.9; **2**, 3.1; **6**, 3.5; **8**, 5.4; **7** (**9**), 8.5; acetophenone, 13.0; **3**, **4**, 13.2; p-$BrC_6H_4CH_3$, 14.8; **5**, 21.1. Acetic acid was eliminated from the acetate **2** on gc analysis. Varying the injection port temperature from 160 to 260° resulted in a large increase in the size of the peak due to acetic acid. An injection port temperature of *ca.* 220° was used to minimize the decomposition of **2** and still vaporize the higher boiling sensitizers. The ratio of **3** and **4** to **5** was usually in excellent agreement by analysis on the two gc columns. The relative distributions of products in these reactions are more accurate than the absolute amounts.

Butadiene (1). Two batches of Dow plant grade material were used without further purification. Gc analysis on column A at 30 and 100° of one batch showed the presence *ca.* 0.9 wt % of the dimer **8** and two very minor components with retention times (t_R) less than that of **1**. The other batch contained *ca.* 0.08% **8**. Corrections were made where necessary for the presence of the dimer **8** in **1** in the product distribution studies.

α-Acetoxyacrylonitrile (2). This material was synthesized by the procedure of Nowak.[73] One batch, bp 78° (25 mm), had a purity of 100.0% (gc column B, 150°) while another, bp 57–58° (10 mm), contained 1–2% of an impurity believed to be $CH_3C(CN)_2OAc$. Some reactions were run using **2** which contained *ca.* 0.1% hydroquinone and some without the inhibitor; no appreciable difference was observed.

Sensitizers. These compounds were purified by distillation, recrystallization, vacuum sublimation, or zone refining. Purity was checked by spectroscopic methods.

Photosensitized Cross-Addition of Butadiene (1) and α-Acetoxyacrylonitrile (2). a. Benzophenone Sensitized. The cyclobutane derivatives **3** and **4** present in the liquid portion of the benzophenone-sensitized reaction mixture (4 hr, Table II, entry 5) were collected as one fraction by preparative gc on column A at 150° (isothermal). The infrared spectrum was identical with that of an authentic mixture (*ca.* 50:50 **3** and **4**); $\nu_{max}^{CCl_4}$ 3100 (m) and 3015 (m) (=CH), 3000 (m), 2970 (m), 2935 (w), and 2890 (w) (CH), 2255 (w, C≡N), 1765 (s, C=O), 1650 (w, C=C), 1375 cm^{-1} (m); $\nu_{max}^{CS_2}$ 1220 (s, CO), 1149 (m), 1122 (m), 1108 (m), 1013 (m), 989 (m), and 927 cm^{-1} (m) (–CH=CH_2); obtained *via* the thermal reaction of **1** and **2**[3] except for an additional weak maximum at 1725 cm^{-1}. The relative intensities of the two bands at 1122 and 1108 cm^{-1} were reversed, possibly due to a different ratio of **3** to **4**. The nmr spectrum was essentially the same as that of the authentic material (CCl_4): two overlapping eight-line multiplets centered at −6.12 (H^A) and −5.91 ($H^{A'}$) (1.0 H total

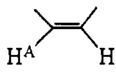


J_{AB} = 10.5 cps, J_{AC} = 16.5 cps, J_{AD} = 6.0 cps; $J_{A'B'}$ = 11.9 cps, $J_{A'C'}$ = 16.7 cps, $J_{A'D'}$ = 6.9 cps), two overlapping doublets centered at −5.20 (H^B) and −5.15 (H^C) showing further ill-defined splitting (1.9 H total, J_{AB} = ~10 cps, J_{AC} = ~17 cps), a broad multiplet at −3.8 to −2.9 centered at −3.3 (1.0 H, H^D), and two singlets at −2.07 ($COCH_3$) and −2.05 ($COCH_3{}'$) superimposed on a broad multiplet at −2.9 to −1.7 ppm (–CH_2–) (7.1 H total). The relative intensities of the two methyl resonances at −2.07 and −2.05 ppm indicated approximately equal quantities of each. The mass spectrum of an authentic sample of **3** and **4** follows: *m/e* 27 (HCN^+), 39 ($C_3H_3^+$), 43 (CH_3CO^+, base peak), 54 ($C_4H_6^+$, second most intense), 68 ($C_5H_8^+$), 77–79 ($C_6H_{5-7}^+$), 96 ($C_6H_{10}N^+$), 104–105 ($M^+ - CH_3CO_2H_{1-2}$), 122–123 ($M^+ - CH_{2-3}CO$), 137 ($M^+ - C_2H_4$), no M^+ detected.

The white polymer (0.24 g) which had precipitated from the reaction mixture was washed well with acetone, then pentane, and air dried. This polymer decomposed above 180° without completely melting and was insoluble in the common organic solvents. The infrared spectrum exhibited maxima at 3052 (sh), 2940, 2860, ~2300, 1755, ~1675, and 1440 cm^{-1} (mulls). Mass spectrometric analysis of the polymer using an inlet temperature of 150–300° indicated the presence of 1–5% of benzophenone in addition to an intense peak at *m/e* 43 (CH_3CO^+). At 250–300° some acetic acid was observed. Assuming *ca.* 1% of benzophenone to be present, the combustion analyses indicated a ratio of 1.00:1.35 for **2** and **1**.

Anal. Calcd for $C_5H_5NO_2 \cdot 1.35C_4H_6 \cdot 0.01C_{13}H_{10}O$: C, 68.0; H, 7.1; N, 7.5. Found: C, 67.7, 68.0; H, 6.9, 7.0; N, 7.5.

b. Biacetyl Sensitized. The components of the biacetyl-sensitized reaction mixture (1 hr, Table II, entry 9) attributed to the cyclohexene cross-adduct **5** and the cyclobutane cross-adducts **3** and **4** had gc retention times identical with those of the authentic materials, prepared by the thermal reaction, on both columns A and B. In addition the retention times were also identical with those of the authentic materials on a 10 ft × 0.25 in. column of Carbowax 20M on 80 mesh Fluoropak at 200° and 46 ml of He/min flow rate (**3**, **4**, t_R 9.4 min; **5**, t_R 15.7 min). Spectral data for **5** are given as follows: $\nu_{max}^{CCl_4}$ 3050 (m, =CH), 2975 (w), 2950 (m), 2920 (m), and 2860 (w) (C-H), no detectable C≡N stretching band in 2500–2000-cm^{-1} region, 1765 (s, C=O), 1670 (w, C=C), 1450 (m), 1375 cm^{-1} (m); $\nu_{max}^{CS_2}$ 1250 (m), 1228 (s, CO), 1217 (s), 1066 (m), 1048 (m), 665 cm^{-1} (m, *cis* olefinic hydrogens); nmr spectrum (CCl_4) a multiplet at −5.9 to −5.3 appearing as two unsymmetrical doublets centered



at −5.8 and −5.5 [1.8 H, J_{AB} = ~12 cps), a multiplet at −3.1 to −2.5 with major absorption at −3.05, −2.77, and −2.58 (1.9 H, two

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[72] Reference 18, p 46.

[73] R. M. Nowak, *J. Org. Chem.*, 28, 1182 (1963).

of secondary protons), a multiplet at −2.5 to −2.1 (4.0 H, remaining four secondary protons), and a singlet at −2.07 ppm (3.2 H, $COCH_3$); mass spectrum (150 and 200°); *m/e* 43 (CH_3CO^+, second most intense ion peak), 78 ($M^+ - HCN, CH_3CO_2H$; $C_6H_6^+$, fourth most intense), 104 ($M^+ - CH_3CO_2H_2$, third most intense), 105 ($M^+ - CH_3CO_2H$, base peak), 122–123 ($M^+ - CH_{2-3}$ CO), 139 ($M^+ -$ CN), 147 ($M^+ - H_2O$), no M^+ detected.

c. ***dl*-Camphorquinone Sensitized.** The cross-adduct **10** and/or isomer from the 1-hr reaction (Table II, last entry) was isolated by preparative gc (10 ft × 0.25 in. 10% 410 gum rubber on 60–80 mesh Chromo P, 190° isothermal, 40 ml of He/min, t_R 13–16 min). The chromatogram showed at least three overlapping peaks. The infrared spectrum of the light yellow liquid showed major maxima at ($\nu_{max}^{CCl_4}$) 3090 (w), 2965 (s), 2890 (s), 1860 (w), 1750 (vs), 1650 (m), 1490 (m), 1460 (m), 1440 (m), 1405 (m), 1385 (m, sh), 1380 (m), 1335 cm^{-1} (w); $\nu_{max}^{CS_2}$ 1215 (w), 1150 (w), 1102 (w), 1052 (m), 1021 (m), 1003 (s), 994 (s), 980 (m, sh), 939 (m), 923 (s), ∼800 (w), 755 (w), 707 cm^{-1} (w).

Photosensitized Dimerization of Butadiene (1). a. Biacetyl Sensitized. The dimerization of butadiene (**1**) using biacetyl was carried out according to the procedure of Hammond and coworkers.[4b] The three dimers were collected from the gc effluent (column A, 120° isothermal, injection port temperature 270–300°). The first component collected had an infrared spectrum which was in essential agreement with that reported by Reed for **6**.[57d] The nmr spectrum was essentially the same as that reported by Hammond and coworkers.[4b] The second and third components were identified as the cyclohexene **8** and cyclooctadiene **9** by comparison of their infrared and nmr spectra with those of authentic samples. The retention times were also the same as those authentic materials on columns A and B.

The relative amounts of the three dimers were **6**, 57%; **7** (as **9**), 9%; **8**, 34%. Hammond and coworkers[4b] reported the following relative amounts for the same reaction: **6**, 52%; **7**, 13%; **8**, 35%.

b. ***dl*-Camphorquinone Sensitized.** A solution of *dl*-camphorquinone (0.332 g, 2.00 mmoles) in 0.80 ml (−78°) of butadiene (0.01 mole) was irradiated through Pyrex for 20 hr at 12–14°. Gc analysis of the reaction mixture showed one major peak with shoulders and four minor peaks with retention times greater than that of the starting diketone. The major peak had the same retention time as that of **10** in the preceding reaction. The components **11** and isomers giving rise to the major peak (with shoulders) and the largest of the minor peaks were collected using column B (225° isothermal for 27 min, then programming at 11°/min to 300°, injection port 220°). The larger component was a yellow oil which showed the presence of at least two components by mass spectrometric analysis. The major peaks were at *m/e* 190, 175, 162, 147, 133, and 120, probably due to compound **11**. Minor peaks were present at *m/e* 192, 177, 164, 149, 135, and 122, indicating a compound with two more hydrogen atoms than **11**, or the presence of an oxygen atom in place of a CH_2 group. The infrared spectrum showed ($\nu_{max}^{CCl_4}$) 3100 (w), 2965 (s), 2940 (m), 2880 (m), 1860 (w), 1730 (vs), 1650 (s), 1605 (m), 1485 (m), 1465 (m), 1400 (m), 1385 (m), 1380 (m), 1345 cm^{-1} (m); $\nu_{max}^{CS_2}$ 1260 (m), 1110 (m), 1069 (s), 1020 (s), 1009 (m), 991 (m), 924 (s), 912 (m), 662 cm^{-1} (m). The nmr spectrum showed a broad multiplet at −6.75 to −5.11 ppm (relative area 3.0) for the vinyl protons, a multiplet at −2.96 to −1.25 (5.6) for the protons on secondary and tertiary carbon atoms, and a multiplet at −1.25 to −0.68 (9.4) for the methyl protons (individual singlets at −1.08, −0.97, −0.94, −0.85, −0.81, −0.78) indicating at least two sets of three methyl groups. No absorption was observed in the −5.0 to −4.0 ppm region indicating the absence of the –CHRO– group such as in oxetanes.[74]

The smaller component collected had a mass spectrum with significant peaks at *m/e* 234, 220, 218, 206, 204, and 192. The infrared spectrum showed significant absorption at ($\nu_{max}^{CCl_4}$) 3055 (w), 2970 (s), 2940 (m), 2885 (m), 1765 (s), 1670 (w), 1460 (m), 1405 (m), 1390 (m), 1385 (m), 1093 (s), 1005 (m), 658 cm^{-1} (m). This spectrum indicated that the camphor nucleus was probably present as did the nmr spectrum shich showed methyl peaks in to −1.1 to −0.7 ppm region. Weak absorption was also noted in the −4.9 to −4.3 ppm region possibly indicating the presence of an oxetane ring.

Photosensitized Dimerization of α-Acetoxyacrylonitrile (2). A degassed solution of acetophenone (0.120 g, 1.0 mmole) in the nitrile **2** (0.605 g, 5.5 mmoles) was irradiated for 19 hr at 0°. Gc analysis on column B (150° for 18 min, then programmed at 5.6°/min to 300°; *trans*-**13**, 29.2 min; *cis*-**14**, 35.9 min) showed *ca.* 5% conversion of the olefin **2** to the dimers **13** and **14** which were present in a ratio of 57:43, respectively (assuming equal thermal conductivities on a weight basis). The contents of the tube were degassed again, and the tube was resealed. Continued irradiation for 24 hr (total 43 hr) produced a light yellow viscous liquid with some polymer on the tube wall; gc analysis now showed *ca.* 13% conversion of the olefin **2** to the dimers **13** and **14** in a ratio of 56 ± 1:44 ± 1, respectively. Samples of each of the dimers **13** and **14** were isolated by preparative gc using the conditions described above for the analysis. The *trans* isomer **13** was a liquid, soluble in both CCl_4 and $CHCl_3$, while the *cis* isomer **14** was a solid, mp 143–144°, soluble in $CHCl_3$, but only very slightly soluble in CCl_4.

trans-1,2-Dicyano-1,2-diacetoxycyclobutane (**13**) had the following spectral properties: infrared spectrum $\nu_{max}^{CHCl_3}$ 2980 (w), 2950 (w), and 2870 (w) (CH), 2260 (w, C≡N), 1780 (s, C=O), 1440 (m), 1370 (m), ∼1170 (s), 1098 (m), 1035 (m), 1009 (m), 931 (m), 881 (m), 861 (m), 612 (w), 598 (m), 559 cm^{-1} (m); $\nu_{max}^{CCl_4}$ 1785 (s, C=O), 1208 cm^{-1} (s, CO); nmr spectrum [$(CD_3)_2SO$] an approximately 16-line multiplet at −3.0 to −2.3 (4.0 H) (–CH_2–) and a singlet at −2.23 ppm (6.0 H) ($COCH_3$); mass spectrum *m/e* 43 (CH_3CO^+, base peak), spectrum at *m/e* <111 was nearly identical with that of the monomer **2**, *m/e* 111 ($C_5H_5NO_2^+$, $M^+/2$, *ca.* 1% of *m/e* 43; *m/e* 111 is *ca.* 0.04% of *m/e* 43 in the spectrum of **2**), 138 ($M^+ - 2C_2H_2O$), 152 ($M^+ - HCN, CH_3CO$), 153 ($M^+ - CN, CH_3CO$), 162 ($M^+ - CH_3CO_2H$), 163 ($M^+ - CH_3CO_2$), 180 ($M^+ - C_2H_2O$), no M^+

cis-1,2-Dicyano-1,2-diacetoxycyclobutane (**14**) had the following spectral properties: infrared spectrum $\nu_{max}^{CHCl_3}$ 2990 (w), 2940 (w), and 2860 (w) (CH), 2260 (w, C≡N), 2210 (w), 1770 (s, C=O), 1380 (m), 1179 (s), 1149 (m), 1107 (m), 1040 (m), 1000 (m), 979 (m), 855 (m), 615 (m), 594 cm^{-1} (m); $\nu_{max}^{CCl_4}$ 1790 (C=O); nmr spectrum [$(CD_3)_2SO$] a doublet at −2.78 (3.9 H) (–CH_2–, J = 1.2 cps) and a singlet at −2.20 ppm (6.1 H) ($COCH_3$); mass spectrum *m/e* 43 (CH_3CO^+, base peak), spectrum at *m/e* <111 was nearly identical with that of the monomer **2**, *m/e* 111 ($C_5H_5NO_2^+$, $M^+/2$, *ca.* 1% of *m/e* 43), 138 ($M^+ - 2C_2H_2O$), 152 ($M^+ - HCN, CH_3CO$), 153 ($M^+ -- CN, CH_3CO$), 165 ($M^+ - CH_3CO, CH_2$), 180 ($M^+ -$ C_2H_2O), no M^+.

Irradiation of Benzophenone in 4-Vinylcyclohexene (8). A solution of benzophenone (0.189 g, 1.04 mmoles) in the cyclohexene **8** (0.870 g, 8.04 mmoles) was irradiated 8 hr at *ca.* 30° through Pyrex. During the irradiation 0.0501 g (26%) of white crystals precipitated. Recrystallization from benzene–heptane gave 0.0280 g of benzopinacol (**16**): mp 176–183°, mmp 176–189° with an authentic sample of **16**, mp 187–189° (lit.[75] mp 178–193°). The infrared and nmr spectra were identical with those of an authentic sample. The ultraviolet spectrum of pure **16** was $\lambda_{max}^{n\text{-hexane}}$ mμ (ε) 255 (sh) (811), 260.5 (969), 270 (sh) (580); λ_{max}^{MeOH} (ε), 248 (sh) (664), 254 (864), 259 (1003), 264 (sh) (820), 258 (sh) (586).

The liquid portion of the reaction mixture showed at least five new peaks on gc analysis. The largest component **17** was collected by preparative gc (column A, 250° isothermal): $\nu_{max}^{CCl_4}$ 3580 (m) and ∼3500 (w, sh) (OH), 3090 (m) and 3070 (s) (=CH), 3035 (s), 2930 (s), and 2730 (w) (CH), 1735 (s, C=O), 1670 (s) and 1650 (m) (C=C), 1610 (m), 1590 (m), 1500 (s), 1455 (s), 1330 (m), 1280 (s), 1170 (w), 1080 (m), 1035 (m), 1000 (m), 945 (w), 920 (s), 702 (s), 640 cm^{-1} (m). The yield of **17** (∼21%) was estimated from the gc curve.

Direct Irradiation of 1 and 2 through Quartz. Equimolar mixtures of **1** and **2** (5.0 mmoles each) were irradiated for 1–4 hr at 20°. Gc analysis of the reaction mixtures showed a new component (less than 5% of the **3**, **4** peak) with a retention time close to that of the cyclobutane cross-adducts **3** and **4** [column A, t_R 24.6 min; column B, t_R *ca.* 14.1 min (shoulder)].

Isoprene (18). Phillips Petroleum material was redistilled, bp 33.5°. Gc analysis (column B) indicated a purity of 99.8%.

Photosensitized Cross-Addition and Dimerization of Isoprene (18) and α-Acetoxyacrylonitrile (2). A solution of benzil (0.210 g, 1.00 mmole) and isoprene (**18**, 0.340 g, 4.99 mmoles) in the nitrile **2** (0.484 g, 4.36 mmoles) was degassed and irradiated at 0–5° for 4 hr. The solution contained a small amount of solid polymeric material. Analytical and preparative gc on the crude reaction

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(74) G. M. Barrow and S. Searles, *J. Am. Chem. Soc.*, **75**, 1175 (1953).

(75) (a) W. Thörner and T. Zincke, *Chem. Ber.*, **10**, 1473 (1877); (b) M. W. D. Cohen, *Rec. Trav. Chim.*, **38**, 72 (1919); (c) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **49**, 236 (1927); (d) W. E. Bachmann, *Org. Syn.*, **14**, 8 (1934).

mixture was carried out with column B (column temperature 150° for the first 25 min, then programmed at 5.6°/min to 300°, injection port temperature 235°). The product distribution is shown in Table V (last entry). The thermal conductivity factors for a mixture of the cyclohexene cross-adducts **23** and **24** and for limonene (**31**) were the same. Therefore all of the adducts **19–31** were assumed to have equal conductivities. The retention times (t_R, minutes) of the various components of this reaction mixture under the above conditions were as follows: **18**, 2.2; **2**, 6.0; **25**, 13.1; **26**, 15.9; **27**, 17.3; **30**, 20.4; **31**, 30.3; **28** and **29**, 36.4; **19**, 38.5; **20**, 40.0; **21** and **22**, 41.7; **23** and **24**, 46.9; benzil, 68.9. The two cyclobutanes **25** and **26** underwent rearrangement under these conditions.[43]

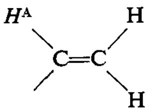
The first component collected by preparative gc was identified as *trans*-1,2-diisopropenylcyclobutane (**27**). The infrared and nmr spectra were in good agreement with those reported by Hammond and coworkers[4b] for **27**.

The second component collected by preparative gc was identified as 1,4-dimethyl-4-vinylcyclohexene (**30**). The infrared and nmr spectra agreed in general with those reported by Hammond and coworkers[4b] for **30** except for the chemical shift of the ring olefinic proton which appeared as a broad singlet with some fine structure at −5.4 to −5.2, centered at −5.29 ppm (CCl_4).

The third component was identified as limonene (1-methyl-4-isopropenylcyclohexene) (**31**) by comparison of its spectral properties and gc retention time with those of an authentic sample.

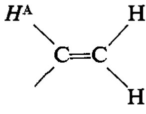
The fourth fraction collected was identified as a mixture of 1,5-dimethylcycloocta-1,5-diene (**28**) and 1,6-dimethylcycloocta-1,5-diene (**29**). In general the infrared and nmr spectra were in agreement with those reported by Hammond and coworkers[4b] for a mixture of **28** and **29**.[76]

The fifth component was identified as 1-cyano-*cis*-2-vinyl-*trans*-2-methylcyclobutyl acetate (**19**): $\nu_{\max}^{\mathrm{CCl_4}}$ 3100 (w) and 3020 (m, sh) (=CH), 2995 (m), 2975 (m), 2940 (m), and 2880 (w) (CH), 2250 (w, C≡N), 1765 (s, C=O), 1700 (w), 1650 (m, C=C), 1460 (m), 1450 (m, CH_3), 1425 (m), 1385 (m), 1375 cm^{-1} (s, CH_3); $\nu_{\max}^{\mathrm{CS_2}}$ 1270 (m), ~1225 (s, CO), 1184 (s), 1125 (s), 1096 (s), 1031 (s), 1008 (m, -CH=CH_2), 952 (m), 924 (s, -CH=CH_2) 891 (m), 761 (w), 731 (w), 680 (m), 608 (m), 569 cm^{-1} (m); nmr spectrum (CCl_4) a doublet of doublets with increasing intensity on going upfield centered at −5.91 (1.0 H



J_{AB} = 9.5 cps, J_{AC} = 18.0 cps), a doublet of doublets centered at −5.18 (H^B, J_{AB} ~ 11 cps, J_{BC} = 1.7 cps) overlapping with another doublet of doublets centered a −5.14 (H^C, J_{AC} ~ 16 cps, J_{BC} = 1.6 cps) (2.0 H total), a broad multiplet at −2.7 to −1.6 (-CH_2-) overlapping with a singlet at −2.02 (-COCH_3) (7.1 H total), and a singlet at −1.48 ppm (2.9 H, ⪢CCH_3). Significant ion peaks in the mass spectrum appeared at *m/e* 119 (M^+ − HOAc), 136 (M^+ − CH_3CO), and 138 (M^+ − HCN, CH_3).

The sixth component was identified as 1-cyano-*cis*-2-methyl-*trans*-2-vinylcyclobutyl acetate (**20**): $\nu_{\max}^{\mathrm{CCl_4}}$ 3100 (w) and 3020 (m) (=CH), 2980 (m), 2945 (m), and 2880 (m) (CH), 2250 (w, C≡N), 1765 (s, C=O), 1700 (w), 1650 (m, C=C), 1455 (m), 1450 (m, CH_3), 1425 (m), 1375 cm^{-1} (s, CH_3); $\nu_{\max}^{\mathrm{CS_2}}$ 1286 (m), 1269 (m), ~1225 (s, CO), 1185 (s), 1132 (s), 1098 (s), 1031 (s), 1011 (s) and 1000 (s) (-CH=CH_2), 957 (m), 922 (s, -CH=CH_2), 875 (m), 761 (w), 730 (w), 691 (m), 611 (m), 578 cm^{-1} (m); nmr spectrum (CCl_4) a doublet of doublets with increasing intensity on going upfield centered at −6.20 (1.0 H



J_{AB} = 10.8 cps, J_{AC} = 16.9 cps), a doublet of doublets centered at −5.18 (H^B, J_{AB} = 10.3 cps, J_{BC} = 1.1 cps) overlapping with another doublet of doublets centered at −5.05 (H^C, J_{AC} = 17.4 cps, J_{BC} = 1.2 cps) (1.9 H total), a broad multiplet at −2.7 to −1.4 (-CH_2-) overlapping with a singlet at −2.09 (-COCH_3) (7.3 H total), and a singlet at −1.23 ppm (2.8 H, ⪢CCH_3). The mass specrum was similar to that of the isomer **19** described above except that *m/e* 138 was not detected and an ion peak was observed at *m/e* 137 (M^+ − CH_2CO).

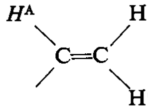
Collection of the seventh component afforded a mixture of 1-cyano-*cis*-2-isopropenylcyclobutyl acetate (**21**) and 1-cyano-*trans*-2-isopropenylcyclobutyl acetate (**22**): $\nu_{\max}^{\mathrm{CCl_4}}$ 3100 (w, =CH), 3005 (m), 2990 (m), 2970 (m), and 2930 (w) (CH), 2250 (w, C≡N), 1765 (s, C=O), 1660 (m, C=C), 1450 (m) and 1375 cm^{-1} (s) (CH_3); $\nu_{\max}^{\mathrm{CS_2}}$ 1276 (m), ~1220 (s, CO), 1199 (s), 1150 (m), 1115 (s), 1101 (s), 1041 (m), 1011 (s), 960 (w), 944 (w), 900 (s, >C=CH_2), 871 (m), 794 (w), 751 (w), 692 (w), 606 (w), 580 (w), 551 cm^{-1} (w); nmr spectrum (CCl_4) a broad singlet at −5.1 to −4.9 with maximum intensity at −5.00 showing fine structure (1.0 H, =C*H*), a broad singlet at −4.9 to −4.7 centered at −4.82 showing some fine structure (0.91 H, =C*H*), a broad multiplet at −3.6 to −1.9 (-CH_2-, ⪢C*H*) overlapping with two intense singlets at −2.07 and −2.05 (relative areas ~60:40, respectively, -COCH_3) (8.2 H total), and a broad singlet at −1.81 ppm with shoulders on each side separated by ~0.5 cps from the center (2.9 H, C=CCH_3). The mass spectrum was similar to that of the isomer **19** except that *m/e* 82 ($C_6H_{10}^+$), 136 (M^+ − CH_3CO), and 137 (M^+ − CH_2CO) were more intense. Also ion peaks were observed at *m/e* 124 (M^+ − C_2H_4, HCN), 150 (M^+ − C_2H_5), 151 (M^+ − C_2H_4), and 179 (M^+).

The eighth fraction collected was a mixture of 1-cyano-4-methylcyclohex-3-enyl acetate (**23**) and 1-cyano-3-methylcyclohex-3-enyl acetate (**24**): $\nu_{\max}^{\mathrm{neat}}$ 3030 (m, =CH), 2975 (s), 2940 (s), 2930 (s), and 2860 (s) (CH), 2250 (w, C≡N), 1760 (s, C=O), 1685 (m), 1660 (m, C=C), 1590 (w) 1450 (s) and 1380 (s) (CH_3), 1230 (s, CO), 1168 (m), 1070 (s), 1044 (s), 978 (m), 968 (m), 868 (m), 807 (m) (>C=CH-), 628 (m), 610 (m), 561 (m), 443 (m), 427 cm^{-1} (m); nmr spectrum (CCl_4, 100 Mc/sec) a broad peak showing fine structure at −5.5 to −5.4 centered at −5.45 (0.39 H, =C*H* of **24**), a broad singlet showing fine structure at −5.3 to −5.2 centered at −5.24 (0.66 H, =C*H* of **23**), two broad multiplets at −3.0 to −2.6 (0.94 H) and −2.6 to −1.9 with maximum intensity at −2.51, −2.21, and −2.17 (-CH_2-) overlapping with two singlets at −2.075 and −2.070 (-COCH_3) for **23** and **24**) (8.0 H total), and a doublet centered at −1.74 ppm (1.6 cps splitting) with a shoulder on each side (~1.5 cps on either side of the doublet branches) (3.0 H, C=CCH_3). The 60 Mc/sec nmr spectrum showed the two olefin protons of **24** and **23** at −5.46 and −5.24 ppm, respectively, in a 33:67 ratio. The gc retention time of this component mixture was the same as that observed for the major products **23** and **24** of the thermal reaction of **18** and **2**. The mass spectrum was similar to that of the isomer **19** with small differences in relative intensities.

One minor unknown component with t_R slightly less than that of benzil and three with t_R greater than benzil were collected. Spectral data indicated that these materials were adducts of benzil and the starting olefins **18** and **2**.

The two thermally unstable isoprene dimers **25** and **26** were isolated by preparative gc by direct on-column injection (column C, injection port temperature 80°, column temperature 125°, He flow rate 130 ml/min) of an acetophenone sensitized dimerization reaction mixture.

The first component collected was identified as *trans*-1,2-dimethyl-1,2-divinylcyclobutane (**25**), t_R 31 min; nmr spectrum (CCl_4) a doublet of doublets with increasing intensity on going upfield centered at −5.86 (1.8 H)



J_{AB} = 11.2 cps, J_{AC} = 16.3 cps), a doublet of doublets centered at 4.94 (H^B, J_{AB} = 9.6 cps, J_{BC} = 2.0 cps) overlapping with another doublet of doublets centered at −4.86 (H^C, J_{AC} = 18.5 cps, J_{BC} = 2.0 cps) (3.9 H total, the highest field component of both H^B and H^C appeared as a doublet, 0.08 cps separation), a broad multiplet at −2.5 to ~−1.2 (4.9 H, -CH_2-), and a singlet at −1.06 ppm (5.4 H) (-CH_3). The infrared spectrum was consistent with that reported by Trecker and Henry[76] and by Hammond and coworkers[4b] except for the presence of a band at 683 cm^{-1} (14.65 μ) (CS_2) which the latter group did not report and the absence of a strong band near 13.7 μ (730 cm^{-1}) which they did report. The nmr spectrum was in agreement with that given by Trecker and Henry[76] except for the magnitude of the coupling constants, and with that reported by Hammond and coworkers[4b] (no solvent reported) except that all chemical shifts were *ca.* 0.2 ppm lower field than those reported.

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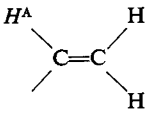
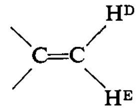
(76) See also D. J. Trecker and J. P. Henry, *J. Am. Chem. Soc.*, **86**, 902 (1964).

The second component collected was identified as *cis*-1-methyl-*trans*-1-vinyl-2-isopropenylcyclobutane (**26**): t_R 39 min; nmr spectrum (CCl_4) a doublet of doublets with increasing intensity on going upfield centered at −5.99 (1.0 H



J_{AB} = 17.5 cps, J_{AC} = 10.0 cps), a doublet of doublets centered at −4.90 (H^B, J_{AB} = 17.0 cps, J_{BC} = 1.5 cps) overlapping with another doublet of doublets centered at −4.84 (H^C, J_{AC} = 10.0 cps, J_{BC} = 1.5 cps) and a multiplet at −4.9 to −4.7



(H^D or H^E) (2.9 H total), a multiplet at −4.7 to −4.5 (centered at −4.62) (0.9 H, H^E or H^D), a series of three broad peaks at −2.9 to −2.5 (1.0 H, appearance of a triplet centered at −2.75, ~8 cps peak separation ($\geqslant CH$), a broad multiplet at −2.3 to −1.3 ($-CH_2-$) overlapping with a singlet at −1.57 with some (<1 cps) splitting ($=CCH_3$) (7.3 H total), and a singlet at −1.01 ppm (2.9 H, $\geqslant CCH_3$). The infrared spectrum was in agreement with that reported by Hammond and coworkers[4b] except for the presence of the band at 905 cm^{-1} (11.05 μ) (CS_2) which these authors do not report; this band is expected due to the presence of the vinyl group.[77] The nmr spectrum is also in agreement with that reported by Hammond and coworkers[4b] except that all chemical shifts are downfield *ca.* 0.2 ppm from the reported values.

Thermal Cycloaddition of Isoprene (18) and α-Acetoxyacrylonitrile (2). A degassed mixture of diene **18** (0.354 g, 5.20 mmoles), nitrile **2** (0.484 g, 4.36 mmoles), and 0.009 g of 2,4-dinitro-*o*-cresol was heated in a sealed tube at 150° for 3 hr. Gc analysis (column B) indicated a *ca.* 60% conversion of the diene **18** and a product distribution of **23** + **24**, 80%; **19**, 1.8%; **20**, 1.4%; **21** + **22**, 1.0%; **31**, 11%; **30**, 3.4%; **26**, 0.2%; **27**, 0.03%; and **28** + **29**, 1.1%. A sample of the cyclohexene mixture **23** and **24** was isolated by preparative gc (column B, 200°). Nmr analysis of this mixture indicated a product ratio of 34 parts **24** (−5.45 ppm) to 66 parts **23** (−5.24 ppm).

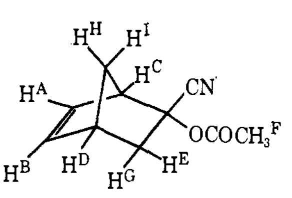
The total cross-addition products **19**–**24** were isolated in a larger scale reaction (73% yield), bp 123–126° (10 mm). The analytical sample had bp 115.4–115.5° (10 mm), $n^{25}D$ 1.4670.

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.42; H, 7.05; N, 7.87.

Cyclopentadiene (32). Cyclopentadiene was prepared fresh each time by pyrolysis of the dimer **39** and slow distillation through a 2-ft Vigreux column, bp 39°. The only impurity detected by mass spectroscopy was a small amount of dimer **39**.

Photosensitized Cross-Addition of Cyclopentadiene (32) and α-Acetoxyacrylonitrile (2). A degassed solution of the diene **32** (1.55 g, 23.4 mmoles), and acetophenone (0.50 g, 4.2 mmoles) in the nitrile **2** (2.20 g, 19.8 mmoles) was irradiated at 5° for 38 hr. The slightly viscous reaction mixture was distilled (150° pot temperature, 10 mm) to separate the cross-adducts and dimers from polymeric material. A crude separation of the four cross-adducts **33**–**36** from other materials (dimers, etc) was made by preparative gc on column C (column temperature 250°, He flow rate *ca.* 150 ml/min), retention time (t_R) 13–18 min. The thermal conductivity factors for a mixture of norbornene cross-adducts **35** and **36** and *endo*-dicyclopentadiene (**39**) were 0.87 and 0.84, respectively (weight basis, based on *p*-$BrC_6H_4CH_3$ as 1.00). The individual cross-adducts were analyzed and separated by preparative gc on the same column (column temperature 145°, He flow rate *ca.* 160 ml/min); t_R at peak maximum: **35**, 84.8 min; **33**, 92.2 min; **36**, 97.6 min; **34**, 103.8 min. Base line separation was not achieved. All cross-adducts **33**–**36** were liquids.

The first component eluted was identified as *exo*-2-cyanobicyclo[2.2.1]hept-5-en-*endo*-2-yl acetate (**35**): $\nu_{max}^{CCl_4}$ 3080 (w, =CH), 2990 (m), 2960 (m), and 2885 (w) (CH), 2250 (w, C≡N), 1760 (s, C=O), 1585 (w, C=C), 1450 (m), 1370 (s), 1340 cm^{-1} (s); $\nu_{max}^{CS_2}$ 1281 (w), 1270 (w), 1262 (w), 1236 (s, CO), 1201 (m), 1168 (m), 1129 (m), 1109 (w), 1098 (w), 1092 (w), 1055 (s), 1046 (s), 1001 (w), 961 (w), 913 (w), 897 (w), 859 (w), 782 (w), 745 (m), 720 (m, *cis* hydrogens), 713 (w), 615 (w), 569 cm^{-1} (w); nmr spectrum (CCl_4) a doublet of doublets centered at −6.40 (1.0 H, $H^{A\text{ or }B}$, J_{AB} =

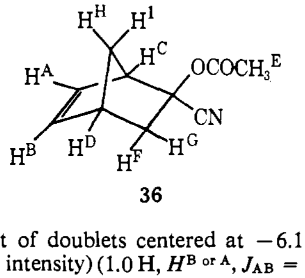


35

5.7 cps, $J_{AC\text{ or }BD}$ = 3.0 cps, additional poorly resolved splitting of 0.6 cps was observed, $J_{AD\text{ or }BC}$), a doublet of doublets centered at −5.91 (1.0 H, $H^{B\text{ or }A}$, J_{AB} = 5.7 cps, $J_{BD\text{ or }AC}$ = 3.0 cps), an eight-line multiplet at −3.7 to −3.5 centered at −3.64 (1.0 H, $H^{C\text{ or }D}$), an unresolved broad peak at −3.1 to −2.9 centered at −3.01 (1.0 H, $H^{D\text{ or }C}$), a doublet of doublets centered at −2.52 (1.0 H, H^E, J_{EG} = 13.0 cps, J_{DE} = 3.7 cps), a singlet at −1.99 (3.1 H, H^F), a multiplet at −1.8 to −1.5 (2.5 H) and a triplet centered at −1.39 ppm, J = 2.1 cps (0.5 H, H^G, H^H, H^I). The mass spectrum showed significant ion peaks at *m/e* 43 (CH_3CO^+) and 66 ($C_5H_6^+$) (base peak), 134 ($M^+ - CH_3CO$), 135 ($M^+ - CH_2CO$), and 177 (M^+). The infrared and nmr spectra of the mixture of acetates **35** and **36** obtained from the thermal (Diels–Alder) reaction of **32** and **2** (see below) were in agreement with those of the *endo*-acetate **35** and the *exo*-acetate **36** (see below) obtained photochemically. The gc retention time was identical with that of one of the adducts from the thermal reaction.

The second component collected was *trans*-6-cyanobicyclo[3.2.0]hept-3-en-*cis*-6-yl acetate (**33**): $\nu_{max}^{CCl_4}$ 3070 (m, =CH), 3000 (m), 2980 (m), 2955 (m), 2920 (m), and 2855 (m) (CH), 2250 (w, C≡N), 1765 (s, C=O), 1665 (w), 1620 (w, C=C), 1445 (m), 1435 (m), 1370 (s), 1355 (m), 1288 (w), 1240 (s), 1225 (s, CO), 1192 (s), 1169 (w), 1155 (m), 1119 (s), 1110 (s), 1083 (m), 1050 (m), 1021 (m), 1003 (w), 960 (w), 931 (m), 885 (m), 840 (w), 717 (m, *cis* hydrogens), 690 (w), 613 (w), 578 (w), 562 cm^{-1} (w); nmr spectrum (CCl_4) multiplets at −6.1 to −5.8 centered at −5.94 (1.0 H) and −5.7 to −5.3 centered at −5.54 (0.9 H) (=CH), a broad singlet at −4.2 to −3.8 centered at −3.97 (0.9 H) ($=CCH$), multiplets at −3.2 to −2.7 (1.8 H), −2.7 to −2.2 (1.9 H), and −1.8 to −1.5 (0.7 H) remaining secondary (4) and tertiary (1) protons, a singlet at −2.05 ppm (3.8 H) ($COCH_3$). The mass spectrum showed significant ion peaks at *m/e* 43.0185 (calcd for CH_3CO^+, 43.0184, base peak), 66.0478 (calcd for $C_5H_6^+$, 66.0470), 79 ($C_6H_7^+$), 134.0598 (calcd for $M^+ - CH_3CO$, C_8H_8NO, 134.0606), 135.0678 (calcd for $M^+ - CH_2CO$, C_8H_9NO, 135.0684), 177 (M^+). A weak metastable ion peak for the transition, *m/e* 177 ± 1 → *m/e* 134 was observed. The infrared, nmr, and mass spectra and gc retention time (column A) were identical with those of the sample prepared by the alternate ketone route described below.

The third component eluted was identified as *endo*-2-cyanobicyclo[2.2.1]hept-5-en-*exo*-2-yl acetate (**36**): $\nu_{max}^{CCl_4}$ 3080 (w, =CH), 2990 (m), 2955 (m), and 2885 (w) (CH), 2250 (w, C≡N), 1760 (s, C=O), 1660 (w), 1585 (w, C=C), 1440 (m), 1365 (s), 1335 (s), 1282 (w), 1261 (m), [1235 (s), 1224 (s)] (CO), 1204 (s), 1185 (m), 1133 (w), 1109 (w), 1080 (m), 1054 (m), 1040 (s), 1019 (m), 1005 (w), 967 (w), 944 (w), 930 (m), 888 (w), 868 (w), 829 (w), 724 (m, *cis* hydrogens), 696 (w), 613 (w), 573 cm^{-1} (w); nmr spectrum (CCl_4) a doublet of doublets centered at −6.47 (two high-field branches of greater intensity) (1.0 H, $H^{A\text{ or }B}$, J_{AB} = 5.7 cps, $J_{AC\text{ or }BD}$ =



36

2.8 cps), a doublet of doublets centered at −6.13 (two low-field branches of greater intensity) (1.0 H, $H^{B\text{ or }A}$, J_{AB} = 5.7 cps, $J_{BD\text{ or }AC}$ = 3.0 cps), a broad multiplet at −3.5 to −3.2 centered at −3.31 (1.0 H, $H^{C\text{ or }D}$), a broad singlet at −3.1 to −2.9 centered at −2.97 (1.1 H, $H^{D\text{ or }C}$), a singlet at −2.07 (H^E) overlapping with a multiplet at −2.2 to −1.9 centered at −2.02 (two protons from H^F, H^G, H^H, H^I) (5.0 H total), a broad singlet at −1.8 to −1.6 centered

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(77) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 147.

at −1.70 ppm (2.0 H, remaining two protons from H^F, H^G, H^H, H^I). The mass spectrum showed significant ion peaks at *m/e* 43 (CH_3CO^+) and 66 ($C_5H_8^+$) (most intense peaks in spectrum), 134 ($M^+ - CH_3CO$), 135 ($M^+ - CH_2CO$), 177 (M^+). The infrared and nmr spectra were in agreement with those of one of the thermal cross-adducts, as was the gc retention time.

The fourth component collected was *cis*-6-cyanobicyclo[3.2.0]-hept-3-en-*trans*-6-yl acetate (**34**): $\nu_{max}^{CCl_4}$ 3070 (m, =CH), 3000 (sh, m), 2980 (m), 2955 (m), 2920 (m), and 2855 (m) (CH), 2250 (w, C≡N), 1765 (s, C=O), 1665 (w), 1620 (w, C=C), 1450 (m), 1430 (m), 1370 (s), 1355 (m), 1305 (w), 1291 (w), 1263 (m), 1239 (s), 1219 (s, CO), 1156 (m), 1110 (s), 1076 (s), 1058 (m), 1020 (m), 1010 (m), 971 (m), 944 (w), 912 (w), 888 (w), 860 (w), 852 (w), 702 (w, *cis* hydrogens), 687 (w), 613 (w), 589 cm^{-1} (w); nmr spectrum (CCl_4) a multiplet at −6.2 to −5.8 centered at −5.97 (1.9 H, $=CH$), a broad multiplet at −3.7 to −3.2 centered at −3.49 (0.9 H, $=CCH$), a broad multiplet at −3.2 to −2.7 (1.0 H, $\geqslant CH$), a broad multiplet at −2.8 to −2.3 (2.9 H, three secondary protons), a singlet at −2.12 ($COCH_3$) overlapping with a multiplet at −2.3 to −1.5 ppm (remaining secondary proton) (4.2 H total). The mass spectrum showed significant ion peaks at *m/e* 43 (CH_3CO^+) and 66 ($C_5H_6^+$) (most intense peaks in spectrum), 134 ($M^+ - CH_3CO$), 135 ($M^+ - CH_2CO$), 177 (M^+).

Photosensitized Dimerization of Cyclopentadiene (32). A degassed solution of acetophenone (0.116 g, 0.97 mmole) in the diene **32** (0.330 g, 4.99 mmoles) was irradiated for 16 hr at 2–3°. The slightly viscous liquid was passed through a preparative gc (column C, column temperature 150°, isothermal) to separate the four dimers **37–40**, t_R 17–21 min, from other materials. The dimer fraction was separated into the individual components by preparative gc on column D (column temperature 70°); t_R at peak maximum: **40**, 25.3 min; **38**, 39.9 min; **37**, 44.3 min; **39**, 47.8 min. Base line separation was not achieved for the three latter components.

The first component eluted was identified as pentacyclo-[$5.3.0.0^{2,5}.0^{3,9}.0^{4,8}$]decane (**40**). The infrared, nmr, and mass spectra were identical with those of an authentic sample.[32b,78]

The second component collected was *exo*-dicyclopentadiene (**38**): $\nu_{max}^{CCl_4}$ 3055 (m, =CH), 2970 (s), 2950 (s), 2915 (s), and 2850 (m) (CH), 1630 (w, cyclopentenyl C=C), 1580 cm^{-1} (w, norbornenyl C=C); $\nu_{max}^{CS_2}$ 712 cm^{-1} (s, *cis* hydrogens); nmr spectrum (CCl_4) a triplet centered at −6.00 (1.9 H, bicycloheptenyl $=CH$, J = 1.6 cps), a multiplet at −5.8 to −5.3 with maxima at −5.62 and −5.54 (2.1 H, cyclopentenyl $=CH$), a multiplet at −2.8 to −1.6 with maxima at −2.56, −2.48, and −2.31 (6.1 H, $\geqslant CH$ and $=CCH_2$–), two unsymmetrical doublets of triplets centered at −1.49 and −1.27 ppm (2.0 H, bridge $-CH_2-$, J_{gem} = 8.6 cps, J_{vic} = 1.5 cps). The mass spectrum was quite similar to that of an authentic sample of *endo*-dicyclopentadiene (**39**).

The third component eluted was identified as *cis,trans,cis*-tricyclo[$5.3.0.0^{2,6}$]deca-3,9-diene (**37**): $\nu_{max}^{CCl_4}$ 3055 (s, =CH), 2950 (s), 2910 (s), and 2850 (s) (CH), 1615 cm^{-1} (w, C=C); $\nu_{max}^{CS_2}$ 765 (s), 708 cm^{-1} (s, *cis* hydrogens). The mass spectrum showed an intense ion peak at *m/e* 66 ($C_5H_6^+$, $M^+/2$). The nmr spectrum was in agreement with that reported by Hammond and coworkers.[4b]

The fourth component collected had infrared, nmr, and mass spectral properties identical with those of an authentic sample of *endo*-dicyclopentadiene (**39**).

Thermal Cycloaddition of Cyclopentadiene (32) and α-Acetoxyacrylonitrile (2). A solution of olefin **2** (52 ml, 56 g, 0.50 mole), diene **32** (44.0 g, 0.67 mole), and 0.5 g of 2,4-dinitro-*o*-cresol in 50 ml of redistilled benzene was heated in a steel bomb at 130° for 3 hr. After cooling, the benzene was removed from the dark, nonviscous reaction mixture under vacuum at 40°. Distillation of the residue gave 64.8 g (73%) of clear liquid acetates **35** and **36**, bp 123–125° (10 mm) [lit.[23a] bp 84–85° (1.5 mm)]. Bartlett and Tate[23a] list a cyanide band at 1560 cm^{-1} and a carbonyl band at 1736 cm^{-1} ($CHCl_3$); we find these bands at 2250 and 1760 cm^{-1} (CCl_4), respectively. Nmr analysis of the distilled material indicated a distribution of 74% *endo*-acetate **35** and 26% *endo*-cyano compound **36**. Gc analysis (column C, 150°) showed a distribution of 80% **35**, 20% **36** (the crude reaction mixture had a distribution of 76% **35**, 24% **36**); no cyclobutane cross-adducts **33** and **34** could be detected. It is estimated that *ca.* 2% of the latter would have been detected.

The reactions at 0 and 150° without solvent were run with equimolar quantities of **32** and **2**, degassed in Pyrex tubes.

Bicyclo[3.2.0]hept-3-en-6-one (41). This compound was prepared by the procedure described by Schuster, Axelrod, and Auerbach,[23b] with a slight modification. A solution of bicyclo[2.2.1]-hept-5-en-2-one (**64**)[23a] (10.0 g) in *ca.* 800 ml of anhydrous ether was deoxygenated with a slow stream of purified nitrogen for 1 hr and irradiated in an immersion reactor with a 450-W Hanovia medium-pressure mercury arc lamp through a quartz well with a 9700 Corex filter at 0° for 3.5 hr. The ratio of product ketone **41** to starting ketone **64** was *ca.* 85:15 (gc analysis, column A). The total combined area of **41** and **64** was *ca.* 60% of original area of **64**. The odor of ketene was evident. The ether was removed, and the residue was taken up in a small amount of benzene. Preparative gc separation (column E) gave 2.0 g (20%) of the ketone **41** as a slightly yellow liquid. The spectral properties were in agreement with those reported.[23b]

Reaction of Ketone 41 with Hydrogen Cyanide and Acetic Anhydride. The ketone **41** (1.6 g, 15 mmoles) was added to anhydrous liquid hydrogen cyanide[79] (∼0.7 ml, ∼0.5 g, ∼18 mmoles). Piperidine (redistilled from sodium; 5 μl, 4 mg, 0.05 mmole) was added, and the solution was allowed to stand at 0° for 24 hr. Concentrated sulfuric acid (5 μl, 9 mg, 0.09 mmole) was added to neutralize the piperidine; anhydrous ether (1 ml), acetic anhydride (3.2 ml, 3.5 g, 34 mmoles), and acetyl chloride (0.1 ml, 0.11 g, 1.4 mmoles) were added. After standing at 0° for 24 hr and at room temperature for 10 days, the low-boiling materials were removed under vacuum, and the residue distilled at 3 mm (pot temperature to *ca.* 150°) to give 1.1 g of slightly yellow liquid. Gc analysis of this liquid (column F, 125° isothermal for 18 min, then programmed at 5.6°/min to 200°, ∼40 ml of He/min) showed 56% starting material, t_R 28.6 min, and 24% cyanohydrin acetate **33**, t_R 39.2 min. The remainder consisted of three minor components.

The acetate **33** was collected by preparative gc and identified by comparison of its spectra and gc (column B) retention time with those of the product from the photosensitized addition of the diene **32** to the cyanoacetate **2** described above. No evidence for the isomeric acetate **34** was detected.

Analysis of the crude distilled product by the gc method used with the photoaddition reaction above (column B) showed none of the isomer **34**. It is estimated that the presence of 5% (compared with **33**) of this material would have been detected.

Reaction of Bicyclo[3.2.0]hept-2-en-6-one (42) with Hydrogen Cyanide and Acetic Anhydride. According to the procedure of Roberts and Gorham[24] hydrogen cyanide (∼4 ml, ∼2.8 g, ∼0.1 mole), ketone **42**[25,80] (10.0 g, *ca.* 93 % pure, 0.86 mole), piperidine (30 μl, 26 mg, 0.30 mmole), sulfuric acid (30 μl, 0.055 g, 0.56 mmole), ether (6.5 ml), acetic anhydride (20 ml, 21.6 g, 0.21 mole), and acetyl chloride (0.65 ml, 0.72 g, 9.2 mmoles) (8 days at ∼25°) gave 7 ml of crude product. Distillation gave 2.4 g of liquid boiling at 90–100° (2 mm) [lit.[24] bp 106–110° (3 mm)]. Gc analysis (column F, 175°) showed two major components in a 44:56 ratio. The first component collected by preparative gc was mainly starting ketone as shown by spectral data.

The second component collected, t_R 35.6 min, was identified as the cyanohydrin acetate **43**: $\nu_{max}^{CCl_4}$ 3070 (m, =CH), 2985 (m), 2955 (m), and 2865 (m) (CH), 2250 (w, C≡N), 1760 (s, C=O), 1620 (w, C=C), 1450 (m), 1435 (m), 1375 (s), 1355 (m), 1297 (w), 1236 (s, CO), 1211 (s), 1150 (w), 1118 (m), 1109 (m), 1075 (m), 1068 (m), 1021 (m), 978 (w), 937 (w), 895 (w), 880 (w), 710 (m, *cis* hydrogens), 613 (w), 578 cm^{-1} (w); nmr spectrum (CCl_4) a singlet at −5.79 (1.9 H) ($\geqslant CH$), a broad multiplet at −3.7 to −2.5 (5.1 H, five of the six $\geqslant CH$ and $-CH_2-$ protons), and a singlet at −2.09 ($COCH_3$) superimposed on a multiplet at −2.3 to −1.9 ppm (1 of $-CH_2-$ protons); mass spectrum *m/e* 43 (CH_3CO^+, base peak), 66 ($C_5H_6^+$), 117 (M^+ − HOAc), 177 (M^+). The yield of acetate **43** was *ca.* 25% by gc analysis.

The retention time of the acetate **43** on column B at 175° was 25.0 min. Under the same conditions the retention times of the photoadducts **35**, **33**, **36**, and **34** were 22.5, 23.6, 25.0, and 26.1 min, respectively. The presence of **43** in the photoproduct mixture would not have been detected by gc. However, examination of the nmr spectra of the photoproducts **33–36** did not reveal the presence of any of the isomer **43**.

Bicyclo[2.2.1]hept-2-ene (44). Aldrich material, mp 45–47°, was used without further treatment; nmr spectrum (CCl_4) an

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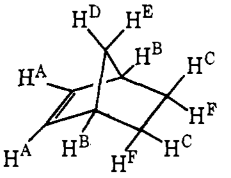
(78) W. L. Dilling and M. L. Dilling, *Tetrahedron*, 23, 1225 (1967).

(79) K. Ziegler, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 314.

(80) H. L. Dryden, Jr. and B. E. Burgert, *J. Am. Chem. Soc.*, 77, 5633 (1955).

apparent triplet centered at −5.95 (2.0 H, H^A, line separation 1.8 cps on each side), a seven-line multiplet centered at −2.83 (2.0 H, H^B, average separation between each line 1.7 cps), and a broad multiplet from −1.8 to −0.8 ppm (6.0 H, H^C, H^D, H^E, H^F) separated roughly into three groups of multiplets, −1.8 to −1.4 (1.9 H, H^C, centered at ∼−1.6), −1.4 to −1.2 (1.3 H, H^D, consisting mainly of a doublet of triplets centered at −1.34, J_{DE} = 8.0 cps, J_{BD} = 1.9 cps), and −1.2 to −0.8 ppm (2.8 H, H^E, H^F, centered at ∼−1.0 ppm) (lit.[27,29a,30b,81] nmr spectrum).



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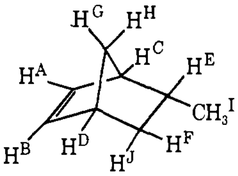
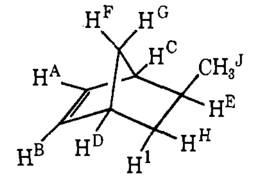
endo-**5-Methylbicyclo[2.2.1]hept-2-ene (45).** This material was obtained from Mr. J. R. Mann: nmr spectrum (neat) an unsymmetrical doublet of doublets centered at −6.09 (H^A, or H^B, J_{AB} = 5.8 cps, $J_{\text{AC or BD}}$ = 3.0 cps) and another unsymmetrical doublet of doublets centered at −5.88 (H^B or H^A, J_{AB} = 5.7 cps, $J_{\text{BD or AC}}$ = 2.8 cps) (2.1 H total), a broad peak centered at −2.66 (2.0 H, H^C, H^D), a broad multiplet at −2.4 to −0.9 (4.3 H, H^E, H^F, H^G, H^H), a doublet centered at −0.79 (2.7 H, CH_3^I, J_{EI} = 6.5 cps), and an eight-line multiplet centered at −0.43 ppm (0.8 H, H^J, $J_{FJ(\text{gem})}$ = 10.2 cps, $J_{EJ(\text{trans})}$ = 3.3 cps, J_{GJ} = 2.4 cps) (lit.[27,82] nmr spectrum).



45

exo-**5-Methylbicyclo[2.2.1]hept-2-ene (46).** This material was obtained from Mr. J. R. Mann: nmr spectrum (50%, CCl_4) two overlapping doublet of doublets centered at −6.05 (H^A or H^B, J_{AB} ∼ 5.8 cps, $J_{\text{AC or BD}}$ ∼ 2.5 cps) and −5.91 (H^B or H^A, J_{AB} ∼ 5.8 cps, $J_{\text{BD or AC}}$ ∼ 2.5 cps) (2.2 H total), a broad peak centered at −2.76 (1.3 H, H^C or H^D), a broad peak centered at −2.36 (1.0 H, H^D or H^C), a multiplet at −1.6 to −0.9 (H^E, H^F, H^G, H^H, H^I) overlapping with an unsymmetrical doublet centered at −1.08 ppm (CH_3^J, J_{EJ} = 5.4 cps) (7.6 H total).



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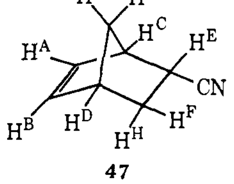
endo-**5-Cyanobicyclo[2.2.1]hept-2-ene (47).** Aldrich material was used without further purification: nmr spectrum (CCl_4) an unsymmetrical doublet of doublets centered at −6.34 (1.0 H, H^A or H^B, J_{AB} = 5.7 cps, $J_{\text{AC or BD}}$ = 2.9 cps), an unsymmetrical doublet of doublets centered at −6.16 (1.0 H, H^B or H^A, J_{AB} = 5.7 cps, $J_{\text{BD or AC}}$ = 2.8 cps), a multiplet centered at −3.20 (1.0 H, H^C or H^D), a multiplet centered at −2.99 (1.0 H, H^D or H^C, an eight-line multiplet centered at −2.83 (1.0 H, H^E, $J_{EF(cis)}$ = 9.2 cps, J_{CE} = 3.7 cps, J_{EH} = 3.7 cps), an eight-line multiplet centered at −2.13 (1.0 H, H^F, $J_{FH(gem)}$ = 11.4 cps, J_{EF} = 9.2 cps, J_{DF} = 3.5 cps), a pair of apparent quartets centered at −1.50 with a total coupling of 14.7 cps (1.1 H, H^G or H^I, $J_{GI(gem)}$ = 8.6 cps), and a multiplet at −1.4 to −1.1 ppm (1.9 H, H^H, H^I or H^G) (lit.[28,29a,81a,d] nmr spectrum)



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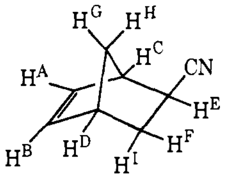
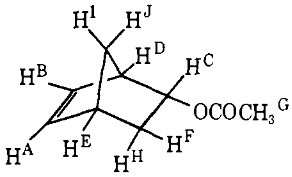
exo-**5-Cyanobicyclo[2.2.1]hept-2-ene (48).** Aldrich material was used without further purification: nmr spectrum (CCl_4) an unsymmetrical eight-line multiplet centered at −6.14 (H^A or H^B, J_{AB} = 5.7 cps, $J_{\text{AC or BD}}$ = 2.8 cps, $J_{\text{AD or BC}}$ = 0.9 cps) and another unsymmetrical eight-line multiplet centered at −6.01 (2.0 H total) (H^B or H^A, J_{AB} = 5.8 cps, $J_{\text{BD or AC}}$ = 2.9 cps, $J_{\text{BC or AD}}$ = 0.9 cps), a multiplet centered at −3.18 (1.0 H, H^C or H^D), a multiplet centered at −3.03 (1.0 H, H^D or H^C), an unsymmetrical doublet of doublets centered at −2.13 (H^E, $J_{EI(cis)}$ = 9.1 cps, $J_{EF(trans)}$ = 4.0 cps) and an eight-line multiplet centered at −1.93 (2.0 H total) (H^F, $J_{FI(gem)}$ = 11.9 cps, $J_{EF(trans)}$ = 4.0 cps, J_{DF} = 3.6 cps), and a series of peaks at −1.7 to −1.4 (100 Mc, 3.0 H, H^G, $H,^H$ H^I) (lit. [28,29a,81d] nmr spectrum).



48

endo- **(53) and** *exo*-**Bicyclo[2.2.1]hept-5-en-2-yl Acetate (54).** The mixture of isomers from Aldrich Chemical Co. was separated by preparative gc (column G, 150°): retention times at 175°: *exo*-**54**, 8.2 min; *endo*-**53**, 9.0 min. Base-line separation was not achieved. The following nmr spectral data (CCl_4) were obtained on the isolated isomers: *endo*-**53**: an unsymmetrical doublet of doublets centered at −6.26 (1.0 H, H^A or H^B, J_{AB} = 5.9 cps, $J_{\text{AE or BD}}$ = 3.1 cps), an unsymmetrical doublet of doublets centered at −5.89 (1.0 H, H^B or H^A, J_{AB} = 5.9 cps, $J_{\text{BD or AE}}$ = 2.9 cps), an eight-line multiplet centered at −5.17 (1.0 H, H^C, J_{CF} = 8.1 cps, $J_{CD,CH}$ = 3.5, 3.3 cps), a broad singlet at −3.10 (1.0 H, H^D or H^E), a broad singlet at −2.80 (1.0 H, H^E or H^D), an eight-line multiplet centered at −2.10 (1.0 H, H^F, J_{FH} = 12.4 cps, J_{CF} = 8.1 cps, J_{EF} = 3.6 cps), a singlet at −1.87 (3.0 H, $COCH_3^G$), a multiplet at −1.5 to −1.3 with maximum intensity at −1.38 (1.9 H, H^H, H^I, or H^J), and a doublet of triplets centered at −0.87 ppm (1.1 H, H^J or H^I, J_{IJ} = 12.5 cps, $J_{\text{DJ,EF or DI,EI}}$ = 3.0 cps) (lit.[29b,30c,81a,d] spectrum); *exo*-**54**: an unsymmetrical doublet of doublets centered at −6.20 (1.0 H, H^A or H^B, J_{AB} ∼ 5.5 cps, $J_{\text{AD or BE}}$ ∼ 2.4 cps), an unsymmetrical doublet of doublets centered at −5.95 (0.9 H, H^B or H^A, J_{AB} ∼ 5.5 cps, $J_{\text{BE or AD}}$ ∼ 3.0 cps), a doublet of doublets centered at −4.57 (1.0 H) (H^C, J_{CH} ∼ 7.1 cps, J_{CG} ∼ 2.4 cps), a broad singlet at −2.84 (2.0 H, H^D, H^E), a singlet at −1.96 (3.2 H, $COCH_3^F$), a multiplet at −1.8 to −1.3 including a



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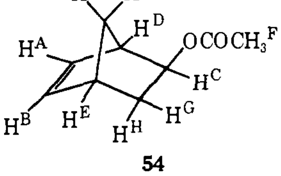

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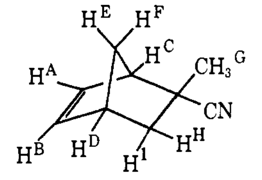
triplet centered at -1.44 ppm ($J_{DJ,EJ \text{ or } DI,EI} = 2.6$ cps) (4.0 H total H^{G}, H^{H}, H^{I}, H^{J}) (lit.[29b,30c,81d,83] nmr spectrum).

***endo*-5-Cyano-*exo*-5-methyl- (49) and *exo*-5-Cyano-*endo*-5-methylbicyclo[2.2.1]hept-2-ene (50).** The mixture of isomers from Eastman Kodak Co. was separated by preparative gc (column H, 140°, 60 ml of He/min); retention times *exo*-cyano **50**, 11.6 min; *endo*-cyano **49** 13.0 min. The following nmr spectral data (CCl_4) were obtained on the isolated isomers: *endo*-cyano-**49**, an apparent triplet centered at -6.28 (2.0 H, H^{A}, H^{B}, line separation 1.9 cps), a six-line multiplet centered at -2.95 (1.0 H, H^{C} or H^{D}, line separations 1.8 cps), a six-line multiplet centered at -2.79 (1.0 H, H^{D} or H^{C}, line separations 1.6 cps), a multiplet centered at -1.7 (2.2 H, two of the four protons, $H^{F,E,H,I}$), and a singlet at -1.52 ($CH_3{}^{G}$) overlapping with a multiplet centered at -1.5 ppm (two remaining protons from $H^{F,E,H,I}$) (4.8 H total); *exo*-cyano-**50**, an unsymmetrical doublet of doublets centered at -6.25 (1.0 H, H^{A} or H^{B}, $J_{AB} = 5.6$ cps, $J_{AC \text{ or } BD} = 3.0$ cps), an unsymmetrical doublet of doublets centered at -6.00 (0.9 H, H^{B} or H^{A}, $J_{AB} = 5.7$ cps, $J_{BD \text{ or } AC} = 3.0$ cps), a multiplet at -3.1 to -2.8 with maximum intensity at -3.01 (1.9 H, H^{C}, H^{D}), a doublet of doublets centered at -2.28 (H^{E}, $J_{EI} = 12.1$ cps, $J_{DE} = 3.7$ cps), a doublet of an apparent triplet centered at -1.81 (H^{F}, $J_{FG} = 8.8$ cps, $J_{CF,DF} = 1.3$ cps) and a doublet of an apparent quartet centered at -1.63 (H^{G}, $J_{FG} = 9.0$ cps, $J_{CG,DG,GI} = 2.0$ cps) (2.1 H total), and a singlet at -1.20 ($CH_3{}^{H}$) overlapping with a doublet of doublets centered at -1.05 ppm (H^{I}, $J_{EI} = 12.1$ cps, $J_{GI} = 2.4$ cps) (4.0 H total). Irradiation of the multiplet at -3.0 ppm caused the doublet of doublets centered at -2.28 ppm to collapse to a doublet, $J \sim 12.1$ cps. Irradiation at -2.3 ppm caused the doublet of doublets centered at -1.05 ppm to collapse to a narrow multiplet, *ca.* 4 cps wide at half-height.



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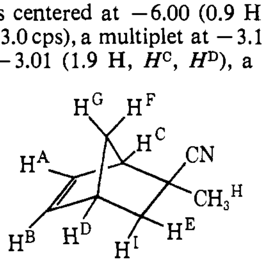

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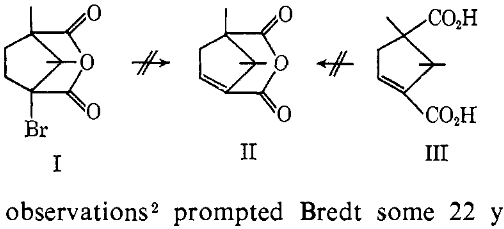
The Synthesis and Chemistry of Bicyclo[3.3.1]non-1-ene

James A. Marshall and Hermann Faubl

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received May 13, 1969

Abstract: Bicyclo[3.3.1]non-1-ene, a strained bicyclic olefin that violates Bredt's rule, was prepared *via* heterolytic β fragmentation of *endo*-2-methanesulfonoxybicyclo[3.3.1]nonane-1-carboxylic salts in dimethyl sulfoxide. The β-lactone, *exo*-2-hydroxybicyclo[3.3.1]nonane-1-carboxylic acid lactone, resulting from internal displacement of the mesylate grouping, was also isolated from this reaction mixture. Pyrolysis of the β-lactone above 260° constituted a second route to the strained bicyclononene. This olefin exhibited normal spectral properties but showed a high degree of reactivity in addition reactions. Acetic acid and methyllithium added to the double bond with the expected Markovnikov orientation. The epoxide and the 2,5-diphenylisobenzofuran adduct were readily prepared but a stable silver complex could not be isolated.

In 1902 J. Bredt and coworkers postulated that their inability to prepare the camphoric anhydride II either by dehydrobromination of α-bromocamphoric anhydride (I) or through cyclization of the unsaturated diacid III might be attributable to the instability of such unsaturated bicyclic structures.[1] These findings and related observations[2] prompted Bredt some 22 years later to suggest that double bonds at the bridgehead atoms of camphenes, pinenes, and similarly constituted bicyclic compounds would impose an unnatural spatial arrangement upon the involved atoms and these compounds would therefore suffer prohibitive strain.[3] Bredt's rule[4] was more precisely defined by the work of Prelog and coworkers[5] who found that bicyclo[*n*.3.1] systems with bridgehead double bonds could be prepared if *n* were greater than 4. In Fawcett's terminology,[4] these findings indicated that for bicyclo[*x*.*y*.*z*] systems in which $x \geq y \geq z$ $(z \neq 0)$, Bredt's rule fails to apply when *S*, the sum of *x*, *y*, and *z*, equals or exceeds 9.



I II III

Prelog's studies were carried out under conditions where double bond isomerization could be expected and his findings therefore apply only to systems at equilibrium. Conceivably, bridgehead olefins with *S* values less than 9 might be considered as feasible synthetic objectives if their synthesis could be carried out in

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[1] J. Bredt, J. Houben, and P. Levy, *Ber.*, **35**, 1286 (1902).

[2] P. Rabe, *Ann.*, **360**, 265 (1908).

[3] J. Bredt, H. Thouet, and J. Schmitz, *ibid.*, **437**, 1 (1924).

[4] For a review, see F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).

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