Table II. Conversion of Olefins into the Corresponding Methylol Derivatives by the Hydroboration–Carbonylation Reaction

Olefin	Product	$T_{50\%}$, min	$T_{100\%}$, min	Yield,[a] %
Ethylene	1-Propanol	15	87	80
1-Butene	1-Pentanol	55	216	72
1-Octene	1-Nonanol	130	400	70
Cyclopentene	Cyclopentyl-methanol	56	230	69
Cyclohexene	Cyclohexyl-methanol	35	125	80
Norbornene	2-*exo*-Norbornyl-methanol[b]	100	350	85

[a] By glpc comparison with authentic samples. The yield is based on a theoretical production of 1 mole of alcohol from 1 mole of R_3B (**1**). [b] The absence of the *endo* isomer was indicated by nmr (<4%).

diborane (25 mmoles) in tetrahydrofuran, followed by stirring at room temperature for 0.5 hr. Then 1.09 g (50 mmoles) of lithium borohydride was added and the solution was heated to 45°. The system was flushed with carbon monoxide and reaction initiated by stirring the contents of the flask magnetically. After 6 hr, absorption of carbon monoxide ceased and a solution of 7 g of potassium hydroxide in 25 ml of absolute ethanol was added. The reaction mixture was heated to 70° for 1 hr to hydrolyze the intermediate. Then the flask was cooled in an ice–water bath and 22 ml of 30% hydrogen peroxide was added dropwise to oxidize the borinic acid, keeping the temperature at 30–35°. (It is purely a convenience to convert the organoboron intermediate to alcohols and boric acid.) The solution was stirred for 1 hr and then saturated with potassium carbonate. The supernatant liquid was analyzed by glpc, and a yield of 42.5 mmoles of *exo*-norbornylmethanol, 85%, was established.

In the present three communications[1,2] we have reported the use of hydroboration–carbonylation for the synthesis of trialkylcarbinols, dialkyl ketones, and monoalkylmethanols from the corresponding olefins. We have also found it possible to utilize this synthetic approach for the synthesis of cyclic and polycyclic derivatives and mixed ketones, as well as aldehydes and carboxylic acids. Finally, both hydroboration and carbonylation can tolerate a wide selection of functional groups. Consequently, it is now possible to synthesize many types of compounds, previously available only through Grignard syntheses, while utilizing building blocks containing reactive functional groups. We are actively exploring this new exciting development and will communicate additional developments shortly.

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Organic Photochemistry. II. The Photosensitized Cross-Addition of Butadiene to α-Acetoxyacrylonitrile[1]

Sir:

Although the photosensitized cross-addition of dienophiles to olefins is well-known,[2] the corresponding photosensitized addition of dienophiles to dienes is much less common. Examples of the latter reaction have been confined to the addition of dienes to α,β-unsaturated carbonyl compounds,[3] other dienes,[4] the haloethylenes,[5] and a simple olefin.[6] The photosensitized dimerization of the dienes themselves[4a,7] (the predominant reaction even in the presence of dienophiles[5,6]) may be regarded as a special case, but other examples are lacking, and the reaction has not yet been demonstrated to be general.[6]

The major products from these photosensitized diene–dienophile cross-additions are solely[3a,b,d] or predominantly[3c,4,5] cyclobutanes with the exception of the photosensitized addition of 1,3-cyclohexadiene to cyclopentene[6] (a poor dienophile[8]). When cyclohexenes are formed, they appear to be different (*e.g.*, *exo* rather than *endo* in the case of cyclic dienes[3c]) from the expected Diels–Alder (thermal) adducts. This fact, plus the observation of entirely different product ratios when the expected Diels–Alder adducts are formed, has led to the postulate that the photo- and thermal adducts result from quite different reaction paths.[3c,5,7b,h]

We now wish to report what appears to be the first photosensitized cycloaddition of an α,β-unsaturated nitrile to a simple diene to yield products *identical* with those formed in the thermal (Diels–Alder) reaction, albeit in different ratios.

Irradiation of an equimolar mixture of butadiene (**1**) and α-acetoxyacrylonitrile (**2**) in the presence of 0.2 mole of a sensitizer through 7740 Pyrex glass (λ >280 mμ)[9] with a 450-w medium-pressure Hanovia mercury arc lamp at *ca.* 30° gave the three cross-adducts **3–5** (in yields of 30–50% of the total dimeric products, depending on the sensitizer[10]), previously observed from the thermal reaction,[11] along with the three butadiene dimers **6–8**.[7i,12] The products were identified

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(1) Part I: W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

(2) (a) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963); (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 194; (c) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 536.

(3) (a) G. O. Schenck, W. Hartmann, S.-P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962); (b) G. O. Schenck, W. Hartmann, and R. Steinmetz, *ibid.*, **96**, 498 (1963); (c) G. O. Schenck, J. Kuhls, and C. H. Krauch, *Z. Naturforsch.*, **20b**, 635 (1965); *Ann.*, **693**, 20 (1966); (d) H.-D. Scharf and F. Korte, *Chem. Ber.*, **99**, 1299 (1966).

(4) (a) R. S.-H. Liu, Ph.D. Thesis, California Institute of Technology, 1965; (b) G. Sartori, V. Turba, A. Valvassori, and M. Riva, *Tetrahedron Letters*, 211, 4777 (1966).

(5) N. J. Turro and P. D. Bartlett, *J. Org. Chem.*, 30, 1849 (1965).

(6) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1892 (1964).

(7) (a) G. S. Hammond, N. J. Turro, and A. Fischer, *ibid.*, **83**, 4674 (1961); (b) N. J. Turro and G. S. Hammond, *ibid.*, **84**, 2841 (1962); (c) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, **71**, 781 (1962); (d) D. J. Trecker, R. L. Brandon, and J. P. Henry, *Chem. Ind.* (London), 652 (1963); (e) G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963); (f) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963); (g) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964); (h) G. O. Schenck, S.-P. Mannsfeld, G. Schomburg, and C. H. Krauch, *Z. Naturforsch.*, **19b**, 18 (1964); (i) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965); (j) R. B. Cundall and P. A. Griffiths, *Trans. Faraday Soc.*, **61**, 1968 (1965); (k) J. E. Baldwin and J. P. Nelson, *J. Org. Chem.*, **31**, 336 (1966).

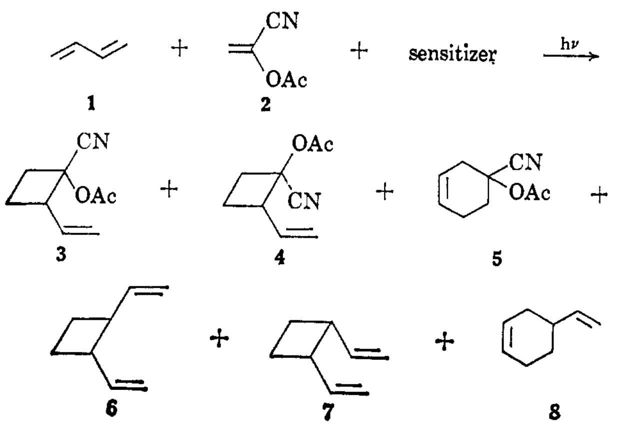
(8) (a) A. S. Onishchenko, "Diene Synthesis," L. Mandel, Translator, Daniel Davey & Co., Inc., New York, N. Y., 1964, p 278; (b) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67**, 723 (1945).

(9) Reference 2c, p 742.

(10) W. L. Dilling, *J. Am. Chem. Soc.*, **89**, 2742 (1967).

(11) J. C. Little, *ibid.*, **87**, 4020 (1965).

(12) At butadiene conversions greater than *ca.* 20%, depending on the sensitizer, a copolymer of **1** and **2** was also formed. The products of the reaction, **3–8**, were relatively stable under the reaction conditions



by comparison of their gas chromatographic retention times with those of authentic materials.[7f,11] Also the nmr and infrared spectra of samples isolated by preparative gas chromatography were compared with the spectra of authentic materials.[13]

The product distributions for various sensitizers are reported in the accompanying communication.[10] For the present discussion, let it suffice to say that the cyclohexene **5** constituted 2–31% of the total cross-adducts **3**–**5**, while the thermal reaction of **1** and **2** at 125–190° gave 77–91% **5**. 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.[11,14]

Experiments on the unsensitized (direct irradiation through quartz[15]) photoreaction of **1** and **2** indicated that of the cross-addition processes only 1,2 addition occurred, probably *via* the excited singlet state of the diene **1**.[16]

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employed in this study. The conversions were kept low to avoid complications due to possible further reactions of the products. Another side reaction was observed when camphorquinone was used as the sensitizer. This sensitizer undergoes a photoreaction with butadiene to give a product which we have tentatively identified as a vinyloxetane (possibly several isomers) arising from the addition of one carbonyl group of triplet camphorquinone to one butadiene double bond. We have measured the (**3** + **4**):**5** ratio at different stages of conversion and find no significant change.[10]

[13] The *cis*-divinylcyclobutane (**7**) was isolated as the thermal rearrangement product, 1,5-cyclooctadiene.[7f]

[14] See R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

[15] Reference 2c, p 748.

[16] For the results of the unsensitized irradiation of butadiene alone see (a) R. Srinivasan and F. I. Sonntag, *J. Am. Chem. Soc.*, **87**, 3778 (1965); (b) I. Haller and R. Srinivasan, *J. Chem. Phys.*, **40**, 1992 (1964); (c) P. A. Leermakers and G. F. Vesley, *J. Chem. Educ.*, **41**, 535 (1964); (d) ref 2b, p 216.

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Organic Photochemistry. III. 1,2 *vs.* 1,4 Addition as a Function of Sensitizer Triplet Energy in a Cross-Addition Reaction[1]

Sir:

In the preceding communication[1] we described the photosensitized cycloaddition of the diene **1** to the olefin **2**.[2] In this communication we report the effect of the sensitizer triplet energy on the product distribution.

The product distribution between the 1,2-divinylcyclobutanes and the 4-vinylcyclohexenes in the photosensitized dimerization of butadiene or isoprene has been shown to be dependent on the triplet energy of the sensitizer.[3] This dependence was attributed to the difference in the energy levels of the *cis*- and *trans*-diene triplets,[4] the *trans* forms giving mostly cyclobutanes and the *cis* forms giving relatively large amounts of cyclohexenes.

The product distributions for the cross-addition of **1** and **2** with various sensitizers are given in Table I. The relative amount of cyclobutanes **3** and **4** in the total cross-adducts **3**–**5** as a function of the sensitizer triplet energy is shown in Figure 1 along with the curve obtained by Hammond and co-workers[3c] for the dimerization of butadiene (**1**).

In general, our results on the cross-addition parallel quite closely those for the dimerization except for the depth of the minimum in the amount of cyclobutanes in the 50-kcal/mole region. The breaking point at *ca.* 60 kcal/mole can be explained, as in the case of dimerization,[3c] by the *s-trans*- and *s-cis*-butadienes having their lowest triplet energy levels at 59.6 kcal/mole[3c,5] and *ca.* 53 kcal/mole,[3b,c] respectively.[6] 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.[3c]

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 to a difference in selectivity of ring closure of the *s-cis*-**1**–**2** triplet adduct, a, and the *s-cis*-**1**–**1** adduct, b (Scheme I). 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 reactivity of the two isomeric triplets with **2** (and with **1**) are the same, then the difference in product distribution must reflect the difference in selectivity of ring closure of intermediates a and b. Thus the cross-intermediate, a, closed to a four-membered ring, **3** or **4**, to a greater extent than did the dimer intermediate, b. 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.[7] Thus the coupling of unlike radicals such as the ring closure of a (with electron spins paired) is probably faster and therefore less selective than the coupling of like radicals as in b (with spins paired). Since the intermediates a and b can exist in a

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[1] Part II: W. L. Dilling and J. C. Little, *J. Am. Chem. Soc.*, **89**, 2741 (1967).

[2] The numbering system in ref 1 is retained in this paper.

[3] (a) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961); (b) G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963); (c) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *ibid.*, **87**, 3406 (1965).

[4] For a theoretical explanation for this energy difference see (a) R. Hoffmann and R. A. Olofson, *ibid.*, **88**, 943 (1966); (b) ref 3c.

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

[6] These explanations are based on the assumption that the reaction proceeded *via* the butadiene triplets rather than the α-acetoxyacrylonitrile triplet.

[7] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 146.