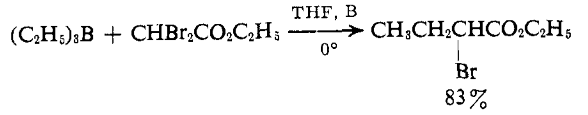
The reaction works equally well for the monoalkylation of ethyl dibromoacetate to produce ethyl α-bromobutyrate (eq 2). By utilizing 2 moles of base and 2



$$(C_2H_5)_3B + CHBr_2CO_2C_2H_5 \xrightarrow[0°]{THF,\ B} CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCO_2C_2H_5 \quad (2)$$

83%

moles of triethylborane, dialkylation was achieved (eq 3).

$$2(C_2H_5)_3B + CHBr_2CO_2C_2H_5 \xrightarrow[25°]{THF,\ 2B} (C_2H_5)_2CHCO_2C_2H_5 \quad (3)$$

66%

In these reactions we evidently utilize satisfactorily only one of the three alkyl groups on boron. This is a major disadvantage when one wishes to homologate a reaction intermediate in high yield. Fortunately, use of the B-alkyl-9-borabicyclo[3.3.1]nonanes (B-R-9-BBN) circumvents this difficulty in the procedures previously reported.[7,8] However, when we attempted to use B-ethyl-9-BBN to alkylate ethyl bromoacetate with potassium 2,6-di-*t*-butylphenoxide in THF, the yield dropped to 0!

Since the bromo ester had disappeared from the reaction mixture, the reaction must be taking another course. We considered the possibility that the reaction involved a migration in the intermediate of the cyclooctyl–boron bond, rather than the desired ethyl–boron bond, as observed in the reaction of B-*n*-butyl-9-BBN with ethyl diazoacetate.[8,9] However, examination of the reaction mixture, following oxidation with alkaline hydrogen peroxide, revealed the absence of ethyl *cis*-5-hydroxycyclooctylacetate, the product formed in such a migration of the cyclooctyl–boron bond.[8]

We then concluded that the difficulty must lie in the slow protonolysis of the rearranged boron intermediate, so that it is capable of reacting competitively with freshly formed α-bromo carbanions. We are exploring this question. Fortunately, the presence in the reaction mixture of *t*-butyl alcohol overcame the difficulty, whatever it may be.

Our final procedure involves making a 1 *M* solution of the organoborane in THF by the usual methods, adding an equimolar quantity of 2,6-di-*t*-butylphenol, followed by addition of a 1 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol. The reaction mixture is thus roughly 50:50 in THF and *t*-butyl alcohol. To this reaction mixture at 25° is added the bromo ester. With this procedure, both the trialkylboranes and the 9-alkyl-9-BBN reagents react satisfactorily.

The experimental results are summarized in Table I.

Perhaps the most unexpected feature about this development is the great speed and ease with which potassium 2,6-di-*t*-butylphenoxide is capable of bringing about these reactions. Certainly, the low pK_a value of the phenol, 11.7,[6] would not lead one to anticipate that it would be so effective in removing a proton from the α position of the α-halo ketones, nitriles, and esters (pK_a values[5] of the parent structures 20, 25, 24, respectively). Potassium *t*-butoxide is a far stronger base in tetrahydrofuran and dimethyl sulfoxide than in *t*-butyl alcohol. Presumably, this is due to the fact that the activity of the anion is not reduced by strong solvation. Perhaps the bulky substituents in 2,6-di-*t*-butylphenol serve a similar function in separating both the cation and solvent from the charged oxygen atom, so that the base is more effective in removing an active methylene hydrogen than one would predict from its pK_a value. Combined with the large steric requirements that prevent it from coordinating with trialkylboranes, it is evident that it must be considered an ideal base for the reactions under consideration.

Table I. α Alkylation of Ethyl Bromoacetate and Dibromoacetate with Organoboranes under the Influence of Potassium 2,6-Di-*t*-butylphenoxide[a]

Organoborane, R_3B or B-R-9-BBN	Bromo ester	Product	Yield,[b] %
Triethyl	Br	Ethyl butyrate	95
B-Ethyl	Br	Ethyl butyrate	70
B-Isobutyl	Br	Ethyl isovalerate	56
Tricyclopentyl	Br	Ethyl cyclopentylacetate	75
B-Cyclopentyl	Br	Ethyl cyclopentylacetate	57
Triethyl	Br_2	Ethyl α-bromobutyrate	96
B-Ethyl	Br_2	Ethyl α-bromobutyrate	83
B-Isobutyl	Br_2	Ethyl α-bromoisovalerate	81
Tricyclopentyl	Br_2	Ethyl α-bromocyclopentylacetate	76
B-Cyclopentyl	Br_2	Ethyl α-bromocyclopentylacetate	78

[a] Reaction was carried out in a 50:50 THF–*t*-butyl alcohol medium at 25°. [b] Yields by glpc analysis.

We have not yet explored its utility as a basic catalyst for other types of reactions, such as Darzen's condensation and the Michael addition. However, it is evident that its unusual characteristics also offer promise in such applications.

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[7] H. C. Brown and M. M. Rogić, *J. Am. Chem. Soc.*, **91**, 2146 (1969).

[8] H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969).

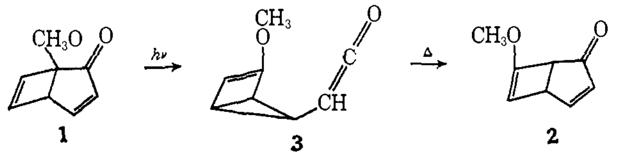
[9] J. Hooz and S. Linke, *ibid.*, **90**, 5936, 6891 (1968).

[10] Visiting scholar on funds provided by the Mitsui Petrochemical Industries, Ltd., Tokyo, Japan.

Photochemistry of Bicyclic Dienones. A Homoelectrocyclic Reaction[1]

Sir:

The photoisomerization of 1-methoxybicyclo[3.2.0]hepta-3,6-dienone (**1**) to 7-methoxybicyclo[3.2.0]hepta-3,6-dienone (**2**) has been shown to proceed *via* a ketene intermediate (**3**). Attempts to trap the intermediate have been unsuccessful because of the facile thermal isomerization of the ketene.[2] In a search for analogous reactions in which the intermediate ketenes might be



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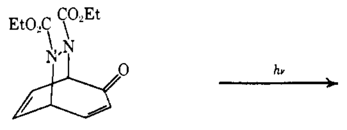
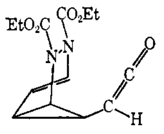
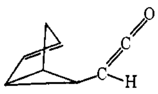
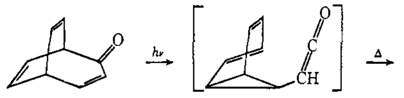
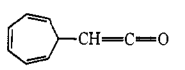
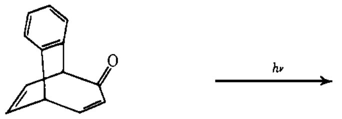
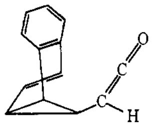
[1] Photochemical Transformations. XXXV.

[2] O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968).

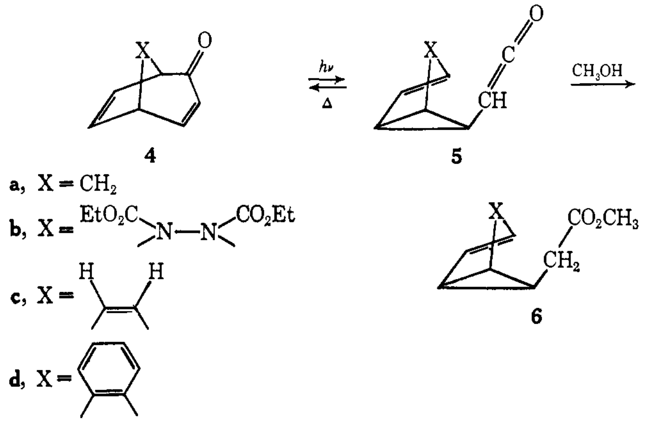
Table I. Summary of Irradiations

Method of generation	Ketene	$\nu_{C=C=O}$, cm$^{-1\,a}$	RCH=C=O, δ, ppm^{b}	% yield of ester
		2120	2.88	>90
		2112	2.62	100
		2116	3.33	>90 (methyl 7-cycloheptatrienyl acetate)
		2117	2.50	70

[a] Neat film at −190°. [b] Chemical shifts were determined in dideuteriodichloromethane at −80° relative to internal tetramethylsilane.

more amenable to detailed study, we turned to derivatives of **1** in which the zero-atom bridge has been replaced by one- and two-atom bridges. These experiments have led to a general reaction which can be viewed as a homoelectrocyclic reaction.[3]

Irradiation of the compounds **4a–d** gives in each case a ketene which can be observed by infrared (−190°) and nmr (−80°) spectroscopy. The ketenes absorb at shorter wavelength than the bicyclic dienones, and essentially complete conversion to the ketenes can be achieved at −80° in Pyrex. On addition of methanol, the methyl esters are formed in high yield. The methyl esters **5a,d** were identified by comparison with authentic samples synthesized by unambiguous methods. Characterization of **5b** rests on molecular composition and spectroscopic evidence.[4] Compound **4c** gives methyl 7-cycloheptatrienylacetate on irradiation in methanol.[5] The dihydroindenone reported by Goldstein and Odell[5] may be formed by a thermal reaction of the ketene or it may be a minor photoproduct. It seems reasonable to postulate 7-*endo*-norcaradienylketene (**6c**) as an initial intermediate which isomerizes to 7-cycloheptatrienylketene. In the irradiation of **4c** at −80°, we have observed only 7-cycloheptatrienylketene. The postulate of the norcaradieneketene is quite plausible in view of the ketenes **6a,b,d** and the earlier experiments,[5] but it must isomerize rapidly to 7-cycloheptatrienylketene at −80° if it is formed.



4

5

6

The nmr spectra of ketenes **6a,b,d** are quite similar to the spectra of the corresponding bicyclic esters. The nmr spectrum of 7-cycloheptatrienylketene shows a methine proton (δ 2.35, m, 1 H), RCH=C=O (δ 3.33, d, J = 9 Hz, 1 H), and six olefinic protons (δ 5.25, m, 2 H; 6.2, m, 2 H; 6.75, m, 2 H).

Irradiation of **4d** in methanol at room temperature[6] gives a mixture of *endo* and *exo* esters (**7** and **8**). At

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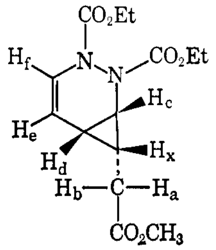
(3) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(4) Parent ion *m/e* 312; ν_{max} 1730 (broad), 1635, 740 cm^{-1}; nmr (C_4Cl_6 at 120°) δ 6.78 (q, H$_f$, J = 1.5, 7.5 Hz), 5.17 (o, H$_e$, J = 1.0, 3.5, 7.5 Hz), 4.1 (m, 4 H, OCH$_2$), 3.52 (s, OCH$_3$), 3.31 (t, H$_c$, J = 7.5 Hz), 2.32 and 1.98 (AM part of AMX spectrum, H$_a$ and H$_b$, J_{ab} = 17, J_{ax} = 9, J_{bx} = 5 Hz), 1.7–1.3 (m, H$_d$ and H$_x$), and 1.15 (m, 6 H, CH$_3$). The

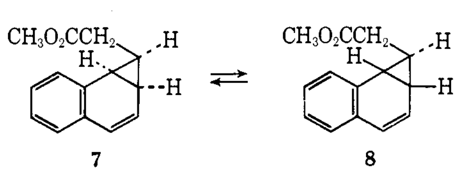


nmr spectrum is temperature dependent because of the conformational mobility of the heterocyclic system and the amide rotation. The spectrum is sharp and well resolved at 120°.

(5) M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967). For related work see E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, *Helv. Chim. Acta*, **50**, 297 (1967); T. H. Kinstle and P. D. Carpenter, *Tetrahedron Letters*, in press.

(6) This process has been studied independently by Professor A. S. Kende: A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *J. Amer. Chem. Soc.*, **91**, 6858 (1969); J. Ciabattoni, J. E. Crowley, and A. S. Kende, *ibid.*, **89**, 2778 (1967). We are indebted to Professor Kende for informing us of his results prior to publication.

−80° only one ketene (**6d**) is formed, and addition of methanol at −80° gives only the *endo* ester **7**. The *endo* ester equilibrates with the *exo* ester at room temperature (*endo*:*exo* 35:65). The activation parameters for the *endo* to *exo* ester isomerization are $\Delta H^{\ddagger} = 22.1$ kcal/mole, $\Delta S^{\ddagger} = -6.5$ eu. The rate constant, k, for the isomerization at 25° is 5.10×10^{-6} sec^{-1}. These values compare favorably with those reported for benzonorcaradiene.[7]



7

8

Photoisomerization of **4d** to a labile dihydronaphthalenone at room temperature has been reported.[6] This photoisomerization is a minor competitor with ketene **6d** formation at low temperatures. Experiments at −190° show that the dihydronaphthalene and the ketene **6d** are both primary photoproducts.

In the absence of nucleophiles, the major thermal reactions of the ketenes **6a,b,d** are recyclization to **4a,b,d** and dimerization.

The photoisomerization of bicyclic dienones described above is apparently general and gives high yields of products in a stereospecific manner. It provides an attractive route to novel heterocyclic systems and to all *cis*-cyclopropane derivatives.

Acknowledgment. This research was supported by grants from the National Science Foundation (GP-10164), the National Institute of General Medical Sciences (GM-14305), and the Mobil Foundation. The 100-MHz nmr spectrometer was purchased with funds provided by the National Science Foundation (GP-6966).

(7) E. Vogel, D. Wendisch, and W. Roth, *Angew. Chem. Intern. Ed. Engl.*, 3, 443 (1964).

(8) National Institutes of Health Postdoctoral Fellow, 1968–1969.

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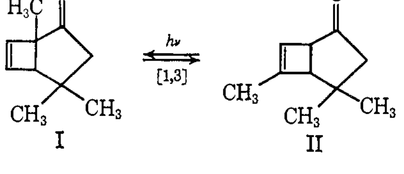
Competitive [1,3] *vs.* [3,3] Sigmatropic Photorearrangements in Bicyclo[3.2.2]nonatrienones

Sir:

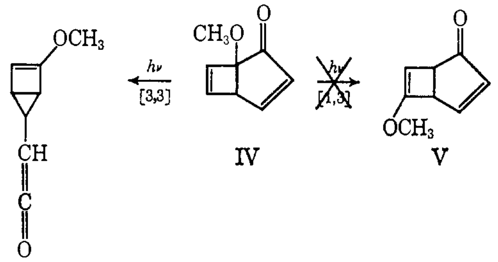
Absorption of light by β,γ-unsaturated ketones leads characteristically to [1,3] sigmatropic[1] shifts exemplified by the photoequilibrium between ketones I and II discovered by Büchi and Burgess.[2] Where the β,γ-enone system is further extended by α′,β′ unsaturation, as is the case for phototropolone methyl ether (IV), there is observed a different photochemical pathway leading to the ketene III by what is formally a [3,3] sigmatropic rearrangement.[3]



I

II

While the ketone IV reportedly shows no propensity for the alternative [1,3] sigmatropic shift to produce V, we now describe a related class of compounds for which both [1,3] and [3,3] photorearrangements may be detected and products derived from either pathway made to predominate depending on reaction conditions.

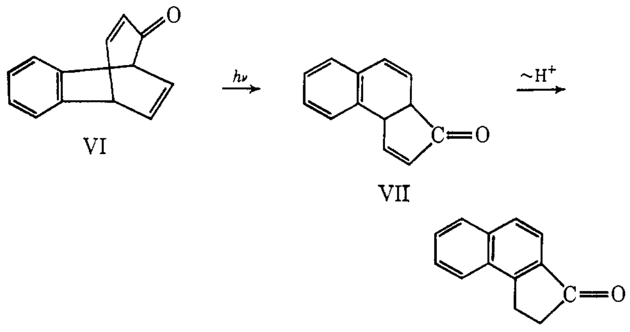


III

IV

V

An earlier communication has noted the facile photoisomerization of the tropone–benzyne adduct VI in acetonitrile to the labile dihydronaphthalene ketone VII which is rapidly and irreversibly converted by weak bases to the prototropic rearrangement product VIII.[4]



VI

VII

VIII

We have recently observed that in aqueous solvents the photochemistry of ketone VI takes a new course to give, besides traces of VII, predominantly an acidic product from which a single crystalline $C_{13}H_{12}O_2$ carboxylic acid,[5] mp 92–93°, may be obtained by careful manipulations. The ultraviolet spectrum of this photoacid closely resembles that of the benzonorcaradiene acid IXa,[6] and the nmr spectrum also parallels that of IXa except for an additional two-proton doublet (J = 7 Hz) at δ 2.53. Together with the mass spectrum[7] (major peaks at m/e 200, 155, 141, 128) these data point to the structure Xa for the photoacid, and this assignment has been confirmed by its synthesis in good yield from the acid IXa through the crystalline diazo ketone IXb, mp 108–110°, using a photochemical Wolff rearrangement.[8]

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(1) For nomenclature and notation, see R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 2511 (1965).

(2) G. Büchi and E. M. Burgess, *ibid.*, 82, 4333 (1960).

(3) O. L. Chapman and J. D. Lassila, *ibid.*, 90, 2449 (1968).

(4) J. Ciabattoni, J. E. Crowley, and A. S. Kende, *ibid.*, **89**, 2778 (1967).

(5) All new compounds have been characterized by ir, nmr, and satisfactory analytical data.

(6) R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961).

(7) Mass spectra were taken on a Perkin-Elmer-Hitachi RMU6E instrument; we are indebted to the National Science Foundation for a grant toward purchase of this spectrometer.

(8) L. Horner, E. Spietschka, and A. Gross, *Ann.*, 573, 17 (1951). Acid Xa could also be obtained in poor yield through a conventional silver oxide catalyzed decomposition of diazo ketone IXb in methanol followed by hydrolysis.