complex in aqueous solution does not react with N_2 to give the dinitrogen compound, whereas $[Ru(NH_3)_5H_2O]^{2+}$ does react with N_2 to yield the mononitrogen compound.[4]

The dinitrogen and the aquonitrogen complexes were prepared by mixing at 0° an aqueous solution (2 ml, 0.000038 mole) of *cis*-$[Ru(en)_2N_2N_3]PF_6$ with a freshly prepared solution (5 ml, 0.000038 mole) of HNO_2. Immediate vigorous gas evolution occurred, and the solution color changed from red-brown to pale yellow. An ice-cold solution (4 ml, 0.00012 mole) of $NaB(C_6H_5)_4$ was then added at various times (Figure 1) to identical reaction mixtures. An immediate yellow precipitate was formed which was rapidly collected in a suction filter. It was washed with a 50:50 water–methanol mixture and sucked until dry (15 min). Its ir spectrum in a Nujol mull was then determined.

The product obtained after a reaction time of 90 sec was entirely the aquonitrogen salt. It was collected on a suction filter, washed with water, and dried. It was stored in a desiccator in a refrigerator.

Anal. Calcd for $[Ru(en)_2H_2ON_2][B(C_6H_5)_4]_2$: C, 68.9; H, 6.5; N, 9.3. Found: C, 68.0; H, 6.6; N, 9.1. The molar conductivity at 25° of a 10^{-3} *M* solution of the salt in dry dimethyl sulfoxide was 35 ohm^{-1} cm^2 $mole^{-1}$, which is consistent with the 2:1 electrolyte formulation. The product was diamagnetic confirming the absence of any Ru(III). Its ir spectrum showed a single strong band in the N–N stretch region at 2130 cm^{-1} and also supported the presence of coordinated water (bands at 1610 and 3500 cm^{-1}). In addition its uv spectrum had a sharp band at 220 mμ (ϵ ~13,000). This corresponds with the band at 221 mμ (ϵ 16,000) reported[5] for $[Ru(NH_3)_5N_2]^{2+}$.

The starting compound, *cis*-$[Ru(en)_2N_2N_3]PF_6$, for this investigation was prepared by reaction scheme 2. The

$$\begin{tikzcd} cis\text{-}[Ru(en)_2Cl_2]^+ \arrow[r, "Ag^+", "H_2O"'] & cis\text{-}[Ru(en)_2(H_2O)_2]^{3+} \arrow[d, "PF_6^- \mid N_3^-"] \\ cis\text{-}[Ru(en)_2N_2N_3]PF_6 & cis\text{-}[Ru(en)_2(N_3)_2]PF_6 \arrow[l, "65°", "30\ min"'] \end{tikzcd} \qquad (2)$$

dichloro complex was prepared by the method described earlier.[6] The azidonitrogen complex was obtained by the solid-state decomposition of the diazido compound. These two compounds have been characterized by means of elemental analyses, evolution of N_2 by Ce(IV) oxidation, conductivity, magnetic susceptibility, ir and uv spectra, and optical activity. Details of the syntheses of these and related compounds will be published later.

Acknowledgment. We wish to thank Dr. T. Studer, who initiated our studies on metal–nitrogen complexes, for his helpful experiments and discussions. This research was supported in part by grants from the National Institutes of Health and the National Science Foundation.

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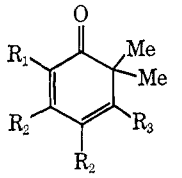
A New General Photochemical Reaction of 2,4-Cyclohexadienones

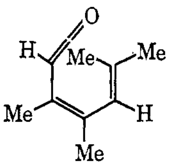
Sir:

Recently we showed that hexamethyl-2,4-cyclohexadienone forms a ketene efficiently from an unspecified singlet excited state.[1] We now have evidence that this well-known photochemical reaction of 2,4-cyclohexadienones[2] arises from the dienone n,π* singlet state. In addition we wish to describe a method for reversing the energies of the n,π* and π,π* states and a new general type of isomerization of these compounds which occurs from the first π,π* singlet state of the dienone.

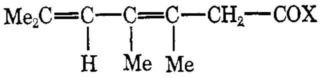
The uv spectrum of dienone **1a**[3] shows well-separated π,π* and n,π* bands at 302 and 354 mμ, respectively, in hexane. The latter was characterized by its low extinction coefficient (ϵ 130), blue shift in polar solvents, and vibrational spacing of approximately 1200 cm^{-1}.[4] Selective excitation of the n,π* band resulted in the efficient formation of ketene **2**, which was detected by ir at −100° (ν_{max} 2100 cm^{-1}), and was readily trapped as the amide **3a** with dimethylamine or the ester **3b**[3] with ethanol. The combined results from the hexamethyldienone and dienone **1a** suggest that the photochemical cleavage of the 1,6 bond in 2,4-cyclohexadienones can occur efficiently (but not necessarily exclusively) from the n,π* singlet state.



1a, $R_1 = R_3 = H; R_2 = Me$
b, $R_1 = Me; R_2 = R_3 = H$
c, $R_1 = H; R_2 = R_3 = Me$
d, $R_1 = R_2 = R_3 = H$



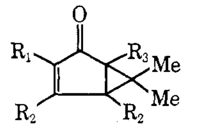
2



$$Me_2C{=}\underset{H}{C}{-}\underset{Me}{C}{=}\underset{Me}{C}{-}CH_2{-}COX$$

3a, $X = NMe_2$
b, $X = OEt$

Although dienone **1a** is photochemically inert in nonnucleophilic solvents,[3] we have observed that in trifluoroethanol it was smoothly converted to a product which did not arise by trapping of the ketene **2** by the solvent. The product was identified as the isomeric bicyclic ketone **4a** on the basis of its elemental analysis, infrared ($\nu_{C=O}$ 1692 cm^{-1}), nmr (τ 8.51 (1 H, s), 8.59 (3 H, s), 8.76 (3 H, s), 8.86 (3 H, s), 4.55 (1 H, q, *J* =



4a, $R_1 = R_3 = H; R_2 = Me$
b, $R_1 = Me; R_2 = R_3 = H$
c, $R_1 = H; R_2 = R_3 = Me$

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[1] J. Griffiths and H. Hart, *J. Am. Chem. Soc.*, **90**, 3297 (1968).

[2] (a) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960). (b) For a review see G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, **4**, 211 (1965).

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1.5 Hz), 8.04 (3 H, d, J = 1.5 Hz), and uv ($\lambda_{\max}^{\mathrm{MeOH}}$ 228, 260, and 320 mμ (ϵ 5950, 3080, and 500)). The photochemical formation of **4a** is unusual as it cannot be detected in any other solvent thus far investigated.

Addition of 40% by volume of trifluoroethanol to a solution of the ketene **2** in 2-methyltetrahydrofuran at −125° gave no trace of the photoisomer after the mixture was allowed to attain room temperature. *Thus the photoisomerization of the dienone* **1a** *to* **4a** *in trifluoroethanol does not involve the intermediacy of the ketene.*

Trifluoroethanol exerts a pronounced effect on the uv spectrum of dienone **1a**. The π,π^* maximum suffers a bathochromic shift from 302 mμ in hexane to 318 mμ and completely obscures the n,π^* band. Thus in trifluoroethanol the π,π^* state is lower in energy than the n,π^* state, and the observed photochemical reaction of the dienone, which is most likely to occur from the lowest excited state,[5] will not be ketene formation. Photoisomerization could then arise from either the π,π^* singlet, π,π^* triplet, or n,π^* triplet states.

A test for this hypothesis was suggested by the recent work of Leermakers, *et al.*,[6] on the effect of silica gel adsorption on the uv spectra of organic molecules. The marked bathochromic π,π^* shifts and hypsochromic n,π^* shifts previously noted were also evident in the 2,4-cyclohexadienones (see Table I). The uv spectrum of the tetramethyl dienone **1a** on silica gel shows complete obscuring of the n,π^* band by the π,π^* band (Figure 1). Accordingly, irradiation[7] of **1a** in a benzene–cyclohexane–silica gel slurry resulted in its smooth conversion to the isomer **4a**.[8] It was readily shown that the action of silica gel on the ketene **2** did not give rise to **4a**.

Table I. Solvent Effects on the π,π^* Band of 2,4-Cyclohexadienones

	$\lambda_{\max}$, mμ			
Dienone	C_6H_{12}[a]	CF_3-CH_2OH	C_6H_{12}[a]–silica gel	Yield[b] of **4**, %
1a	302	318	330	54
1b	300	310	317	60
1c	312	340	350	60
1d	293	293	309	0

[a] Cyclohexane. [b] Based on reacted starting material, from irradiation in a benzene–cyclohexane–silica gel slurry to about 80% conversion.

The excited state involved in the formation of **4a** almost certainly is not the n,π^* triplet state, as the boron trifluoride complex of the dienone is also readily converted to **4a** on irradiation. In this instance n,π^* states cannot be involved, but π,π^* states similar to those in the free dienone will be available.[9] Quenching and sensitizing studies in trifluoroethanol were complicated by the sensitivity of the reaction to solvent effects. However, dienone solutions 2 M in piperylene were photoisomerized faster than solutions containing the same proportion of diethyl ether. Benzophenone exhibited only a rate-retarding effect. On silica gel, where solvent effects were less important, no detectable quenching in 2 M piperylene occurred.[10] These results, though not conclusive, suggest that the photoisomerization proceeds from the first π,π^* singlet state of the dienone.

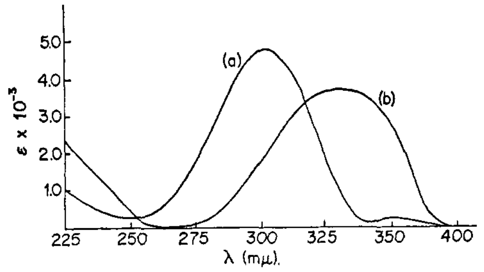

Figure 1. Ultraviolet absorption spectra of **1a** in (a) cyclohexane and (b) cyclohexane–silica gel.

The generality of this photoreaction was confirmed by investigation of the trimethyl-[11] and pentamethyldienones[12] **1b** and **1c**. These dienones, which had previously been shown to give only ketene-derived products on irradiation,[2a,12] were readily photoisomerized in trifluoroethanol or on silica gel to the corresponding bicyclic ketones **4b** and **4c**, respectively. Both dienones showed the marked uv band shifts necessary for the occurrence of this reaction. However, dienone **1d**[13] appeared to be exceptional, as it was inert to irradiation under these conditions, except for the formation of small amounts of an ester in trifluoroethanol and an acid[2a] on silica gel. Clearly ketene formation is the predominant reaction, and in agreement with theory the uv spectrum of the dienone showed that in trifluoroethanol and on silica gel the π,π^* band was insufficiently displaced and broadened for inversion of the π,π^* and n,π^* levels.

Other functionality may be present. Irradiation of 2,4,6-trimethyl-6-acetoxy-2,4-cyclohexadienone adsorbed on silica gel gave a bicyclo[3.1.0]hexenone with the expected structure.

This novel, π,π^* photoisomerization reaction of 2,4-cyclohexadienones resembles the few known photochemical rearrangements of the related methylenecyclohexadienes,[14] and presumably similar excited states are involved. The reaction provides a new general route to bicyclo[3.1.0]hex-2-enones, complementary to the well-known photoisomerization of 2,5-cyclohexadienones.[15] The major requirement is that the dienone can be sufficiently perturbed by medium

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(7) All irradiations were carried out with a uranium glass filter (short-wavelength cut-off at about 360 mμ).

(8) Prolonged irradiation resulted in the photoisomerization of the ketone **4a** to 3,4,4,5-tetramethyl-2,5-cyclohexadienone. This reaction, which also occurred in trifluoroethanol, was very rapid if a Pyrex filter was employed.

(9) Boron trifluoride does not react with the ketene **2** to form **4a**.

(10) Quenching of triplet states of molecules adsorbed on silica gel by piperylene has been shown to proceed without difficulty: L. D. Weis, B. W. Bowen, and P. A. Leermakers, *J. Am. Chem. Soc.*, **88**, 3176 (1966).

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effects to bring about inversion of the n,π^* and first π,π^* singlet states.

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A 1,3 Elimination Proceeding by Double Inversion

Sir:

There is relatively little evidence available concerning the stereochemistry of 1,3-elimination reactions to form C–C bonds in systems wherein the configuration at both C-1 and C-3 can be examined. The much more rapid reaction of *exo*- than *endo*-norborneneboronic acid with mercuric chloride to form nortricyclylmercuric chloride indicates an appreciable preference for inversion at each carbon center during the ring closure step.[1] On the other hand, in the base-initiated 1,3 elimination of *p*-toluenesulfonic acid from *exo*- and *endo*-norbornyl tosylates to form nortricyclene the 6-*endo* proton was lost somewhat more readily in each instance, indicating some preference for retention of configuration at C-6.[2] Base-catalyzed ring openings of cyclopropanols occur with inversion of configuration at the carbon atom being protonated, but acid-catalyzed ring openings occur with retention of configuration.[3] Ring opening of quadricycloheptane-2,3-dicarboxylic acid by bromine occurs with inversion at both carbon atoms of the cyclopropane ring.[4]

We wish to report that 1,3 elimination of bromine from *dl*- and *meso*-$PhCHBrSO_2CHBrPh$ (**1** and **2**, respectively) by the action of triphenylphosphine occurs in a highly stereoselective manner with inversion at C-1 and at C-3. Dimethylformamide (DMF) catalyzes stereoselective loss of hydrogen bromide from **1** and **2**; once again inversion of configuration occurs at C-1 and at C-3.

The two diastereoisomers of $PhCHBrSO_2CHBrPh$ were distinguished unambiguously by a three-dimensional, single-crystal X-ray analysis of **2**, which was shown to be the *meso* isomer. The space group is Pbca, with $a = 16.53$, $b = 12.81$, $c = 13.46$ Å, $Z = 8$; 1275 reflections were obtained by θ–2θ scan techniques on a Picker four-angle diffractometer. The structure has refined to a conventional R factor of 0.08, using 92 parameters; refinement continues. Bond lengths and angles are normal. One of the bromine atoms is *cis* to, and flanked by, the sulfonyl oxygen atoms.

Triphenylphosphine is assumed to initiate attack on bromine to form an ion pair, $[Ph_3PBr]^+$[carbanion]$^-$. In the presence of methanol protonation of the carbanion competes with intramolecular displacement, but the stereochemistry for the latter remains unchanged (Table I). α-Sulfonyl carbanions of this type are known to be asymmetric and to maintain configuration for appreciable periods of time.[5] In closely analogous systems there is evidence for a nearly planar, pyramidal carbanion which has an appreciable barrier for rotation, but not for inversion.[6] Furthermore, there is evidence that the carbanion is formed from a conformation in which the proton abstracted is *cis* to, and flanked by, the sulfonyl oxygen atoms.[6c] If it is assumed that the carbanion in the present instance is formed from a conformation in which the bromine atom being removed is *cis* to the two sulfonyl oxygen atoms, one arrives at the representation shown below.[7]

Table I. Products from 1,3 Eliminations from *dl*- and *meso*-$PhCHBrSO_2CHBrPh$ (**1** and **2**, respectively)

			PhCH=CHPh		PhCBr=CHPh		
Isomer	Solvent	Nucleophile	% *cis*[a]	% *trans*[a]	% *cis*[b]	% *trans*[b]	Yield, %
1	C_6H_6	Ph_3P	4	96			85–90
2	C_6H_6	Ph_3P	95	5			85–90
1	2% MeOH in C_6H_6	Ph_3P	7	93			90[c]
2	2% MeOH in C_6H_6	Ph_3P	96	4			90[c]
1	DMF	DMF	1[d]	2[d]	79	21	85–90[e]
2	DMF	DMF	2[d]	4[d]	9	91	85–90[e]

[a] Based on 100% PhCH=CHPh. [b] Based on 100% PhCBr=CHPh. [c] About 40% stilbenes and 60% reduction products. [d] Based on total yield [e] Consisting of 73–75% PhCBr=CHPh, 3–6% PhCH=CHPh, and 24–19% PhC≡CPh.

The transformation of carbanion conformation **3a** to **3b** involves rotation around the S–CHBrPh bond to provide the proper orientation of atoms for double inversion. Loss of sulfur dioxide from *cis* episulfone **4** (or from its *trans* isomer) has been shown to occur stereospecifically with retention of configuration in the absence of base.[12]

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(7) The stereochemical evidence could also be rationalized by a mechanism involving retention of configuration at each asymmetric center. There is abundant evidence to show, however, that 1,3-intramolecular displacements by nucleophiles, *e.g.*, $-O^-$,[8] $>S$,[9] $\geqslant N:$,[10] and $\geqslant C^-$,[11] involve inversion at the carbon atom holding the leaving group. Furthermore, 1,3-intramolecular displacements initiated by carbanions fail when a front-side attack is required.[11b–d] A double-retention mechanism appears, therefore, to be highly unlikely.

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