generate a carbonium ion. A scheme which accommodates the experimental observations is illustrated using **2**. Probable prior equilibrium steps (which may be responsible for the observed rate differences) are omitted for simplification. According to this mechanism, after the initial diaxial opening of the epoxide by LiBr,[7] product is controlled by the simultaneous rearrangement and expulsion of equatorial bromide since only this conformation has the necessary transoid geometry for reaction. Lithium perchlorate, on the other hand, specifically cleaves the tertiary C–O bond in **2** to give the carbonium ion shown, with subsequent product formation dependent on migratory aptitudes ($H > CH_2$) and perhaps subtle conformational effects.

In the absence of a tertiary center, the carbonium ion mechanism may not hold for the $LiClO_4$ catalyzed reaction. Thus, no cyclohexanone was observed in the reaction of **1** with $LiClO_4$, with or without phosphine oxide. Volatile product material balances were poor in these instances, and it appears that the epoxide may be polymerized under these conditions.

The product control offered by this simple change in reactants promises to be of considerable synthetic utility.[8]

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under these conditions.[6] In our work, we find LiI to be more reactive than LiBr, while LiCl is not sufficiently solubilized by phosphine oxide to allow comparison with the present results.

(6) J. K. Heeren, T. C. Flood, and R. H. Cunningham, *Chem. Commun.*, 9, P18 (1967), and references cited therein.

(7) The reverse reaction is very rapid; when cyclohexene bromohydrin is treated with butyllithium in benzene, epoxide is formed instantaneously.

(8) Support by the National Science Foundation (GP-6043) is gratefully acknowledged.

(9) Alfred P. Sloan Fellow, 1967–1969.

(10) NASA Predoctoral Trainee.

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Reactivity of the n,π* Singlet State of 2-Hexanone

Sir:

Recent efforts from several laboratories to probe the behavior of the n,π* singlet excited state of simple aliphatic carbonyl compounds have led to several interesting but somewhat conflicting conclusions.[1–6] A specifically interesting aspect of the photochemistry of 2-hexanone is that its photochemical reactions take place from both its n,π* singlet and its n,π* triplet states,[7,8] and one may thus compare the relative reactivities of these two excited states under proper experimental conditions. Although there has been considerable interest in the chemical reactivity of the n,π* triplet state of aliphatic carbonyl compounds, little information is available about the chemical reactivity of the n,π* singlet state of these compounds. The current communication deals with the reactivity of the n,π* singlet state of 2-hexanone.

Biacetyl exhibits its lowest singlet absorption at 360–460 mμ, which overlaps well with the fluorescence spectrum of simple aliphatic carbonyl compounds and simple aromatic hydrocarbons[9] and a phosphorescence emission at 510 mμ, which is well below the n,π* triplet level of both of these groups of compounds;[10] it has been used successfully as an energy acceptor from singlet excited states and triplet excited states of these compounds in vapor phase as well as in solution.[5,6,9–14] DuBois and coworkers reported that aliphatic carbonyl compounds and aromatic hydrocarbons sensitize the fluorescence of biacetyl and that the fluorescence of these compounds is quenched by biacetyl at the rate of diffusion-controlled processes.[15] The lifetimes of singlet excited states of energy donors obtained by this method of energy transfer were verified by those measured directly from fluorescence.[15,16]

The current investigation deals with the application of biacetyl as a singlet energy acceptor from 2-hexanone. In order to examine the behavior of the singlet excited state of 2-hexanone, the investigation would have to be carried out under such conditions that the triplet-state energy transfer from 2-hexanone to biacetyl will not interfere with the investigation. 1,3-Pentadiene will not accept energy from the excited singlet state of either 2-hexanone or biacetyl, yet at moderate concentration (0.5 *M*) 1,3-pentadiene will quench essentially all the triplet excited state of 2-hexanone.[7,8] The solutions used contained 1.00 *M* 2-hexanone and 0.50 *M cis*-1,3-pentadiene in hexane and various concentrations of biacetyl (0.01–0.25 *M*). The irradiations were carried out using monochromatic light at 3130 Å in an apparatus previously described.[8] The quantum yields were determined with the aid of a 2-hexanone secondary actinometer. Under current experimental conditions, the extent of biacetyl decomposition is relatively insignificant (<5%). The formation of both acetone and propylene from the type II process was followed by vpc analysis at 155° with a 20-ft Carbowax 20M (30%) on Chromosorb P column and a He flow rate of 140 cc/min. In calculating the quantum yields of these reactions, corrections were made for the absorption of light by biacetyl (ϵ_{3130} 3.3 *vs.* ϵ_{3130} 3.5 for 2-hexanone) and by acetone formed as well as for the small amount of biacetyl decomposed.

When the irradiation of 2-hexanone was carried out in the presence of 0.5 *M cis*-1,3-pentadiene, the part of the reaction due to the n,π* triplet state was practically all quenched, and the remaining reaction may be taken as entirely due to the n,π* singlet state (ϕ_{s_0}). Further addition of pentadiene has little or no effect on the reaction, yet addition of biacetyl causes a steady decrease of the quantum yield. By plotting the ratio of

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(1) G. W. Robinson and V. E. DiGiorgio, *Can. J. Chem.*, **36**, 31 (1958).

(2) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2503 (1967).

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(6) J. T. DuBois and B. Stevens in "Luminescence of Organic and Inorganic Materials," H. P. Kallman and G. M. Spruch, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p 115.

(7) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966).

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(13) H. Ishikawa and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **84**, 1502 (1962).

(14) J. T. DuBois and R. L. Van Hemert, *J. Chem. Phys.*, **40**, 923 (1964).

(15) For a review of this process, see F. Wilkinson, *Advan. Photochem.*, **3**, 253 (1965).

(16) T. V. Ivanova, P. I. Kudriashov, and B. Ya. Sveshinikov, *Dokl. Akad. Nauk SSSR*, **138**, 572 (1961).

ϕ_{s_0} and the quantum yield of the type II process due to the n,π^* singlet state in the presence of biacetyl (ϕ_s) against the biacetyl concentration, linear Stern–Volmer plots were obtained for both acetone and propylene in three individual runs with an average slope of 7.3 ± 0.5 l. mol^{-1} and an average intercept of 1.00 ± 0.04.

From the familiar expressions that $\phi_{s_0}/\phi_s = 1 + k_{q_s}[Q]\tau_s$ and $\phi_{t_0}/\phi_t = 1 + k_{q_t}[Q]\tau_t$, where ϕ_0 is the quantum yield of the type II process at zero quencher concentration, ϕ is the quantum yield of the type II process at various quencher concentrations, k_q is the quenching constant, τ is the mean lifetime of the excited state, k is the first-order rate constant for the type II process, and the subscripts s and t denote the respective terms for the singlet and the triplet states, the slopes of these plots obtained are $k_{q_s}\tau_s$ for the singlet excited state and $k_{q_t}\tau_t$ for the triplet state. The experimental slope for the Stern–Volmer plot of the triplet-state reaction of 2-hexanone has been reported to be 10;[7] therefore, $k_{q_s}\tau_s = 7.3$ and $k_{q_t}\tau_t = 10$.

ϕ_{s_0} and ϕ_{t_0} have been determined to be 0.097 and 0.15,[6] and are defined as $k_s\tau_s$ and $k_t\tau_t\phi_{isc}$, respectively, where ϕ_{isc} is the quantum yield of intersystem crossing from the singlet to the triplet state. We obtain

$$k_s = \frac{\phi_{s_0}}{\tau_s} = \frac{0.097k_{q_s}}{7.3} = \frac{k_{q_s}}{75}$$

and

$$k_t = \frac{\phi_{t_0}}{\tau_t\phi_{isc}} = \frac{0.15k_{q_t}}{10\phi_{isc}} = \frac{k_{q_t}}{67\phi_{isc}}$$

Since ϕ_{isc} is relatively high for aliphatic ketones[8] and the k_q's are likely to be similar for both excited states, our data indicate that the chemical reactivities of the n,π^* singlet and the n,π^* triplet states of 2-hexanone for the type II process are of the same order of magnitude. Assuming k_{q_s} and k_{q_t} are of the order of 10^{10} l. mol^{-1} sec^{-1}, k_s and k_t are then of the order of 10^8 sec^{-1}.

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[18] National Science Foundation Trainee, 1966–1968.

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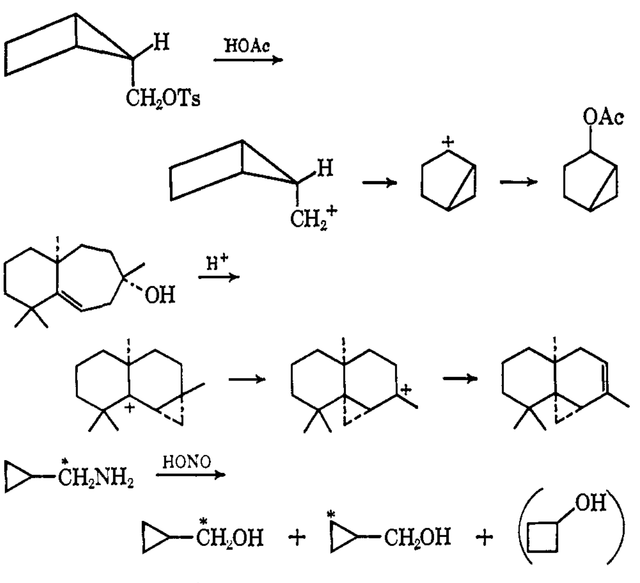
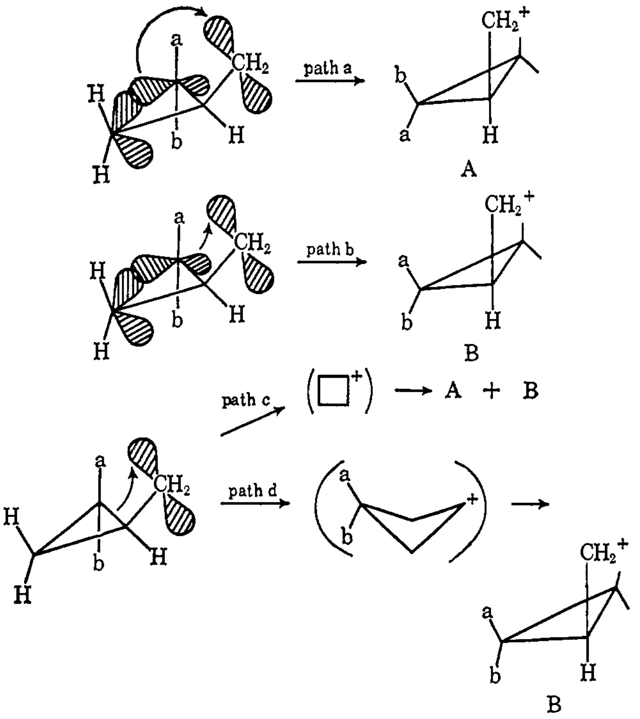
Stereochemistry of the Cyclopropylcarbinyl–Cyclopropylcarbinyl Rearrangement[1]

Sir:

The rearrangement of one cyclopropylcarbinyl ion to another occurs in the rearrangement of bicyclo[2.1.0]pentane-5-carbinyl derivatives to the bicyclo[3.1.0]hexyl-2 cation[2] in the rearrangement of widdrol to thujopsene[3] and in the label scrambling process of the cyclopropylcarbinyl ion itself.[4] Three courses are possible for the reaction. First, the 2,3 bond may be involved, leading to rotation of the methylene group in the process. Second, the back side of the orbital forming the 2,3 bond may be involved, leading to no rotation of the methylene group. Finally, the rearrangement may proceed *via* a cyclobutyl cation as an intermediate or an activated complex. Here, different stereochemical results would be obtained if the ring is planar or if it is puckered. In the first case, the relationship between location a and the carbinyl carbon is inverted, whereas in the second it is retained. In the third, a mixture of A and B should be obtained if the cyclobutane ring is planar, and B should be obtained if it is not.





The protolysis of bicyclobutanes occurs with retention of configuration leading to a cyclopropylcarbinyl ion.[5] When the reaction was carried out in acetic acid-

[1] This investigation was supported by Public Health Service Grant GM12800 from the National Institute of General Medical Service.

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[5] This has been observed by W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964), and by us in the reactions of tricyclo[4.1.0.0^{2,7}]octane and bicyclobutane. This is also the mode of reaction of cyclopropanes (*cf.* C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968)).