zation. Therefore the major singlet process involves benzo-vinyl interaction in contrast to the preferred vinyl-vinyl interaction in the triplet.

The preferred triplet vinyl-vinyl bonding seems to derive from the lower energy of the triplet species engendered in an endwise overlap. Vinyl-vinyl overlap gives a species approximating the electronics of triplet cisoid butadiene (E_T = 53.5 kcal/mole[9a]) while vinyl-benzo overlap leads to a styrene-like triplet (E_T = 61.8 kcal/mole[9b,c]).

Finally, it should be noted that the excited singlet vinyl-vinyl and vinyl-benzo cycloadditions are symmetry allowed.[10]

Acknowledgment. Support of this research by predoctoral National Institutes of Health fellowships to R. S. G. and R. M. P., by National Institutes of Health Grant GM 07487, and by the National Science Foundation is gratefully acknowledged.

(9) (a) D. F. Evans, *J. Chem. Soc.*, 1735 (1960), for cyclohexadiene; (b) D. F. Evans, *ibid.*, 1351 (1957); (c) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965), for *trans*-β-methylstyrene (59.8 kcal/mole).

(10) (a) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965); (b) H. E. Zimmerman, *ibid.*, **88**, 1564 (1966); (c) H. E. Zimmerman, *Science*, **153**, 837 (1966).

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The Lithium Salt Catalyzed Epoxide–Carbonyl Rearrangement

Sir:

We wish to report that epoxides undergo facile lithium salt catalyzed rearrangement to carbonyl compounds in benzene solution. A dual mechanism is proposed which accounts for the strong anion dependence of both product distribution and reaction rate.

Lithium bromide is effectively insoluble in benzene, but the addition of 1 mole of tri-*n*-butylphosphine oxide/mole of salt leads to a soluble complex which may be used to effect epoxide rearrangement.[1] The electrophilic aspect of this reaction is evident from the marked rate depression observed on addition of a small amount of THF or the use of monoglyme in place of benzene as solvent. However, cyclohexene oxide reacts more rapidly than its 1-methyl or 1,2-dimethyl analog, as shown by the data in Table I. Product yields were excellent in all instances.[3] Rate constants were obtained by following loss of epoxide (vpc).

Table I. Rearrangement by LiBr·$Bu_3P \rightarrow O$ (0.71 *M*) in Benzene at 80°

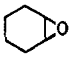
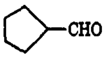
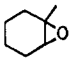
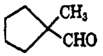
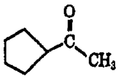
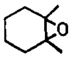
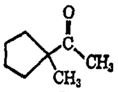
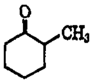
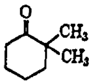
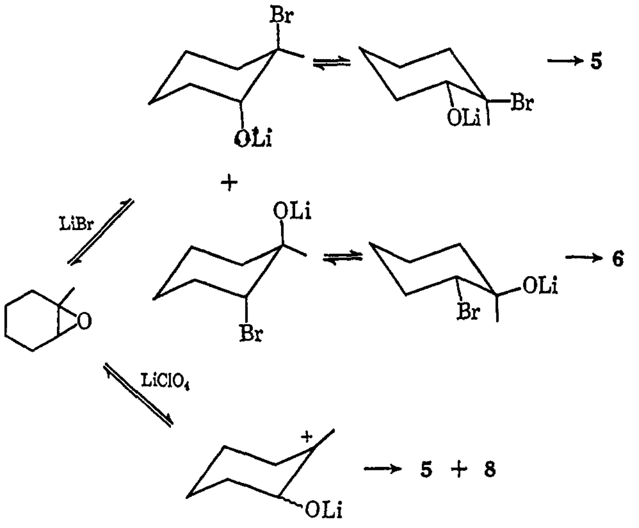
Reactant	10^4k, sec^{-1}	Products
 **1**	2.85	 **4**
 **2**	1.0	 **5**,70% +  **6**,30%
 **3**	0.05	 **7**

Table II. Rearrangement by $LiClO_4 \cdot Bu_3P \rightarrow O$ (0.71 *M*) in Benzene at 80°

Reactant	10^4k, sec^{-1}	Products
1	0.01	**4** (low yield)
2	Too fast (> 30)	**5**,20% +  **8**,80%
3	8.8	**7**,90% +  **9**,10%

Lithium perchlorate is also insoluble in benzene, but again can be solubilized by tri-*n*-butylphosphine oxide. Interestingly, both the rates and the products obtained with this reagent (Table II) differ greatly from those obtained with LiBr. Thus the rate of rearrangement of the secondary,secondary epoxide **1** falls off sharply, while both **2** and **3**, containing tertiary centers, react more rapidly. Increasing the proportion of phosphine oxide to $LiClO_4$ causes a large rate decrease, and, in fact, the fastest reactions observed to date are those of **2** and **3** with "insoluble" $LiClO_4$ alone.[4] The product ratios under these conditions remain as shown in Table II.



We suggest that the lithium halide catalyzed reaction occurs through the intermediacy of the halohydrin salt,[5] while the lithium perchlorate catalyst serves to

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[1] Other dipolar materials also exert this solubilizing influence, *e.g.*, hexamethylphosphoramide and the ylide tri-*n*-butylcarboethoxymethylenephosphorane. The mechanism described here is responsible for the ylide–epoxide reaction we have recently reported;[2] details will be presented in the full paper.

[2] R. M. Gerkin and B. Rickborn, *J. Am. Chem. Soc.*, **89**, 5850 (1967).

[3] The aldehyde **4** is partially lost in the course of reaction, possibly *via* aldol condensation (**5** is stable). When run in the presence of ylide,[1] the unsaturated ester[2] is obtained in ~90% yield.

[4] Quite clearly the epoxides exert a considerable solubilizing influence on this salt; when epoxide is added to a refluxing mixture of benzene and $LiClO_4$ (on the bottom of the flask), a ring of the salt appears almost immediately at the surface of the boiling liquid. Under these conditions, the reactions of **2** and **3** are complete in less than 5 min.

[5] A similar intermediate has been proposed for the reaction of **1** with methyllithium in the presence of lithium iodide (in ether).[6] Lithium bromide apparently does not compete well with the methyllithium

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]

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

(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).

(3) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(4) M. A. El-Sayed, *Accounts Chem. Res.*, **1**, 15 (1968).

(5) F. Wilkinson and J. T. DuBois, *J. Chem. Phys.*, **39**, 377 (1963).

(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).

(8) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(9) J. T. DuBois and M. Cox, *J. Chem. Phys.*, **38**, 2536 (1963).

(10) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(11) J. T. DuBois and F. Wilkinson, *J. Chem. Phys.*, **38**, 2541 (1963).

(12) H. Ishikawa and W. A. Noyes, Jr., *ibid.*, **37**, 583 (1962).

(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).