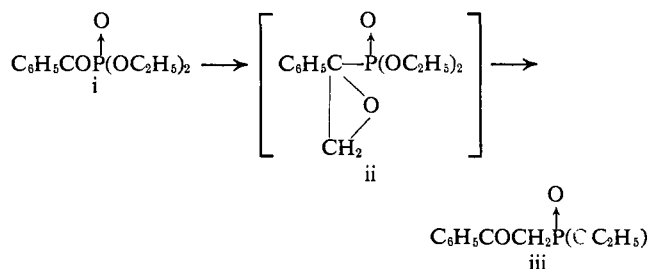and **1f** to **2e** and **2f** was achieved by treatment with boron trifluoride etherate at room temperature; rearrangements were complete in 10 min. In every instance only the carbonyl compound was isolated which necessarily involved migration of the phosphonate function; no evidence for the presence of the products of hydrogen migration, $RR'CHCOP(O)(OR'')_2$, was obtained.[6]

The preferential migration of the phosphono substituent observed in this study indicates that the group possesses a previously unrecognized high migratory aptitude.[8] The most closely related cases are those involving preferential migration of benzoyl[9] and chloride[10] substituents. Further studies of the mechanism and stereochemistry of this rearrangement and of rearrangements of phosphorus substituents in other systems are in progress.

(6) Arbuzov, et al.,[7] recently reported that the reaction of diethyl benzoylphosphonate (i) with diazomethane failed to yield the anticipated epoxide (ii); the product isolated by distillation of the reaction mixture was diethyl phenacylphosphonate (iii). It is quite probable that this reaction also represents a case of phosphonate migration similar to that cited above.

$$C_6H_5COP(OC_2H_5)_2 \longrightarrow \left[\begin{array}{c} O \\ C_6H_5C-P(OC_2H_5)_2 \\ O \\ CH_2 \end{array} \right] \longrightarrow$$

i

ii

$$C_6H_5COCH_2P(O C_2H_5)$$

iii

(7) B. A. Arbuzov, V. S. Vinogradova, N. A. Polezhaeva, and A. K. Shamsutdinova, *Bull. Acad. Sci. USSR*, 604 (1963).

(8) For a review of the rearrangement of epoxides, see R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(9) H. O. House, *J. Am. Chem. Soc.*, **76**, 1235 (1954); H. O. House and D. J. Reif, *ibid.*, **79**, 6491 (1957).

(10) R. N. McDonald and P. A. Schwab, *ibid.*, **85**, 4004 (1963); *J. Org. Chem.*, **29**, 2459 (1964).

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Stereospecificity and Solvent Control of Lumiproduct Formation vs. Fragmentation in Dienone Photochemistry[1,2]

Sir:

Recently, we postulated and provided evidence for a primary process, termed the radical fragmentation route, in the photochemistry of cross-conjugated cyclohexadienones.[3] That this reaction competes directly with the often-observed route to (so-called) lumiproduct[4] and that both reactions seem to proceed *via* a common triplet excited state is indicated by the following observations.

(1) Part VII of a series on the photochemistry of unsaturated ketones in solution. Part VI: D. I. Schuster and C. J. Polowczyk, *J. Am. Chem. Soc.*, **88**, 1722 (1966).

(2) Supported in part by a grant from the U. S. Army Research Office (Durham), No. DA-ARO(D)-31-124-G425.

(3) D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, **87**, 2515 (1965).

(4) For recent reviews, see (a) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962); (b) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (c) O. L. Chapman, *ibid.*, **1**, 323 (1963); (d) H. E. Zimmerman, *Tetrahedron Suppl.*, **2**, 393 (1963); (e) P. J. Kropp, *J. Am. Chem. Soc.*, **86**, 4053 (1964).

Irradiation (n → π^* band) of dienone I in a variety of solvents gives, in addition to *p*-cresol (II),[3] a new

I   III   IV
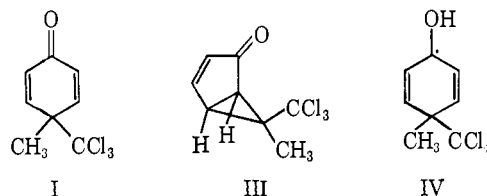
ketone III which was isolated by repeated column chromatography from reactions in hexane. More conveniently, III was isolated by precipitation of polymer from the crude benzene photolysate upon addition of hexane, followed by recrystallization and vacuum sublimation of the residue, to give a white solid, mp 62–64°. Elemental analysis and mass spectroscopy gave a molecular formula of $C_8H_7Cl_3O$, while the mass spectrum indicated fragments from loss of from one to three chlorines along with loss of CO. A fragment of mass 144, corresponding to $C_3H_3Cl_3$, established that the methyl and trichloromethyl groups were attached to the same carbon. The chromophore is established by the ultraviolet spectrum ($\lambda_{max}^{dioxane}$ 226 mμ (ϵ 7200) and 334 mμ (ϵ 29)) and infrared peaks at 1740, 1585, 1040, and 690 cm^{-1}. The nmr spectrum (parts per million relative to tetramethylsilane) shows a singlet (3 H) at 2.01, a doublet ($J = 6$ cps) at 3.15 (1 H), a symmetrical eight-line spectrum ($J = 6$, $J' = 4$, $J'' = 1.5$ cps) at 4.00 (1 H), a pair of doublets ($J'' = 1.5$, $J''' = 6$ cps) at 6.40 (1 H), and another pair of doublets ($J' = 4$, $J''' = 6$ cps) at 7.66 (1 H). The chemical shifts and magnitude of the coupling constants[5] are consistent with the proposed structure III. One equivalent of hydrogen was rapidly taken up over Pd–C to give a saturated ketone (no vinyl H in nmr; no infrared peaks at 1585 and 690 cm^{-1}) with a carbonyl band at 1755 cm^{-1}. The unusual high-frequency carbonyl band in III (bicyclo[3.1.0]hex-3-en-2-ones usually absorb at 1700–1710 cm^{-1})[4] is attributable to dipole interactions between the carbonyl and neighboring CCl$_3$ groups, requiring the stereochemistry shown in III. It is significant that the nmr spectrum of the crude benzene photolysate was identical in detail with that of purified III except for two broad peaks attributed to the polymer. The epimer of III would be expected to have much different nmr and infrared spectra and, if formed, would easily have been detected and should have survived the mild isolation procedure.

III is stable to further photolysis in benzene, while in ether it leads to a new photoketone; no cresols are formed in these reactions.

The formation of only one isomer of the lumiproduct is unexpected, and the generality of this observation remains to be shown. In this case, 3,5-bond formation from the excited state Ia would be expected to favor formation of Ib over Ib' so as to minimize nonbonded and dipolar interactions with the CCl$_3$ group. Concerted rearrangement by pivoting around the 5–6 bond, perhaps after electron demotion to the zwitterion,[4] would account for formation of III with the observed stereochemistry. The other alternative, that III

(5) O. L. Chapman, *ibid.*, **85**, 2014 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963); G. V. Smith and H. Kreloff, *ibid.*, **85**, 2016 (1963).

is formed exclusively by a nonpivot bond-shift mechanism[4b] via Ib', seems much less reasonable.[6]
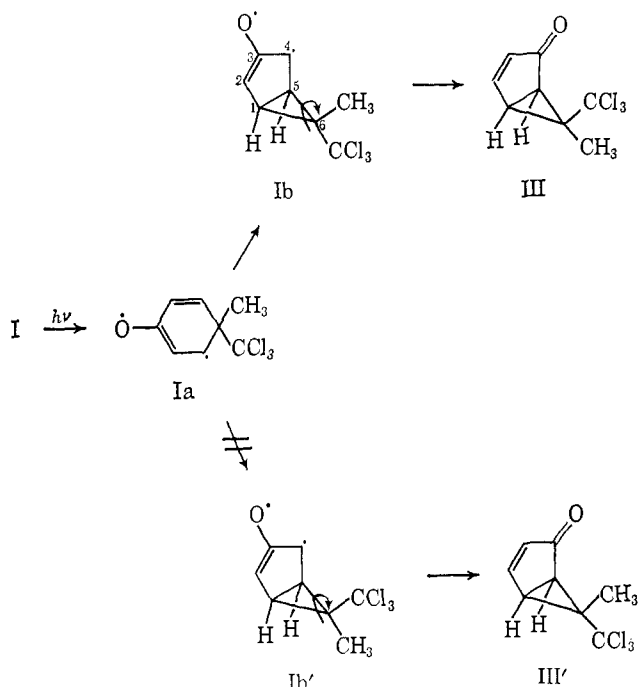
A summary of photolyses of I in a variety of solvents is given in Table I. The yields of I, II, and III are determined by quantitative gas–liquid partition chromatography, calibrated with known mixtures. Higher yields of p-cresol (II) are associated with solvents which are good hydrogen donors (ethyl ether, dioxane, cyclohexane, isopropyl alcohol). The formation of III and absence of II was noted from photolyses of I in toluene and carbon tetrachloride, as well as in benzene. A possible explanation is that radical fragmentation follows hydrogen abstraction, i.e.

$$Ia \xrightarrow{RH} IV \longrightarrow II + CCl_3 \cdot$$
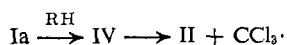
In the absence of a good hydrogen donor, Ia instead reacts by 3,5-bond formation to give Ib and ultimately III.[7]

The results in Table I also indicate that both reactions are sensitized by benzophenone (30-fold excess; 95% of incident light absorbed by benzophenone) and both are approximately equally quenched by piperylene.[8] Thus, a triplet state with E_T = 60–70 kcal/mole[9] is implicated as a reactive intermediate in the formation of II and III, respectively. Moreover, it is consistent with the entire set of results to suggest that there is only one triplet state involved, which we picture as Ia. The fact that the rate of reaction of I is about the same in the direct as well as the sensitized photolyses indicates that singlet–triplet intersystem crossing in excited I is a relatively efficient process.

(6) The pivoting mechanism postulated for Ib → III is in contrast to the more complex route required in cases (e.g., α-santonin → lumisantonin) for which a pivot mechanism is stereochemically prohibited.[4b] We are assuming at this time that only one mechanism, pivot or nonpivot, operates exclusively in a given system.

(7) It is also possible that radical fragmentation occurs in benzene and the other poor hydrogen donor solvents, but leads exclusively to the observed polymer.

(8) The quenching may be due to chemical reaction with, as well as triplet energy transfer to, piperylene.

(9) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. C. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, J. Am. Chem. Soc., 86, 3197 (1964).

Table I. Products of 20-Min Irradiation of Dienone I[a]

Solvent	Sensitizer or quencher	—% yields—		
		I	II	III
Ethyl ether	None	11	65	0
Ethyl ether	Benzophenone (0.47 M)	2	68	0
Ethyl ether	Piperylene (1.6 M)	72	15	0
Benzene	None	34	0	31
Benzene	Benzophenone (0.47 M)	24	0	32
Benzene	Piperylene (1.6 M)	84	0	5
Cyclohexane	None	22	30	2
Isooctane	None	26	13	15
Isooctane[b]	Piperylene (1.6 M)	86	1	0

[a] Irradiation with a 450-w high-pressure mercury arc surrounded by a Pyrex filter in a quartz immersion well. Solutions of 0.01 mole of I + sensitizer or quencher diluted to a total volume of 640 ml. Yields determined by quantitative gas–liquid partition chromatography; estimated error ±2%. [b] Irradiation time 45 min.

Yet another pathway is available for photolysis of I in methanol or aqueous dioxane, as shown independently by other workers,[10] with further relevance to the characterization of the reactive intermediates in these systems. Our experiments in methanol will be reported shortly.
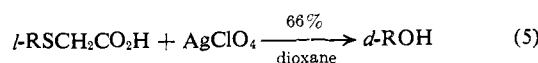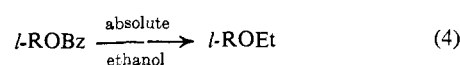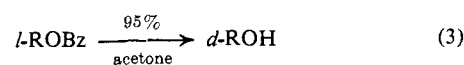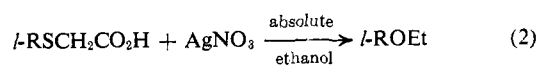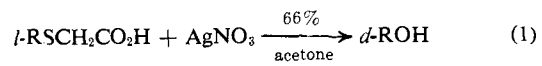
(10) J. King and D. Leaver, Chem. Commun., 539 (1965).

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Stereochemistry of Nucleophilic Substitution of Optically Active Trityl Derivatives. Carbonium Ion Asymmetry Due to Restricted Rotation

Sir:

We demonstrated earlier that the two stereospecific nucleophilic substitution reactions (1 and 2) of l-phenylbiphenyl-α-naphthylmethylthioglycolic acid[1] (l-RSCH₂CO₂H) take the same stereochemical course, and evidence suggested that the reactions proceed with net retention of configuration.[2] We now report the first

$$l\text{-RSCH}_2\text{CO}_2\text{H} + \text{AgNO}_3 \xrightarrow[\text{acetone}]{66\%} d\text{-ROH} \tag{1}$$

$$l\text{-RSCH}_2\text{CO}_2\text{H} + \text{AgNO}_3 \xrightarrow[\text{ethanol}]{\text{absolute}} l\text{-ROEt} \tag{2}$$

$$l\text{-ROBz} \xrightarrow[\text{acetone}]{95\%} d\text{-ROH} \tag{3}$$

$$l\text{-ROBz} \xrightarrow[\text{ethanol}]{\text{absolute}} l\text{-ROEt} \tag{4}$$

$$l\text{-RSCH}_2\text{CO}_2\text{H} + \text{AgClO}_4 \xrightarrow[\text{dioxane}]{66\%} d\text{-ROH} \tag{5}$$

stereochemical study of the solvolysis of an optically active trityl benzoate, l-phenylbiphenyl-α-naphthylmethyl benzoate[3] (l-ROBz), an example of a nucleophilic substitution reaction (3) that occurs with high net retention of configuration (Table I). Evidence is presented that the observed stereospecificity results from solvent capture of a free, asymmetric carbonium

(1) E. S. Wallis and F. H. Adams, J. Am. Chem. Soc., 55, 3838 (1933).
(2) B. L. Murr, ibid., 85, 2866 (1963).
(3) Prepared by the method of W. von E. Doering, K. Okamoto, and H. Krauch, ibid., 82, 3579 (1960). Thus l-ROBz, l-ROEt, and d-ROH are correlated.