

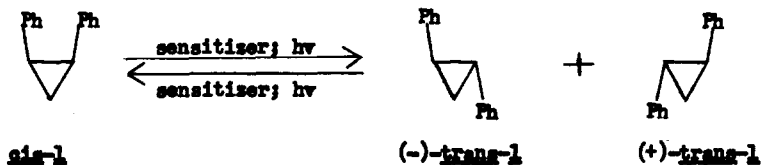
AN ATTEMPT TO INFLUENCE THE DECAY MODES OF 1,2-DIPHENYLCYCLOPROPANE EXCITED STATES
WITH OPTICALLY ACTIVE SOLVENTS

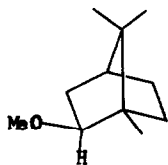
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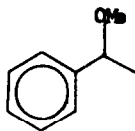
Methods for inducing optical activity photochemically in achiral or racemic molecules has been the subject of intense interest recently.² Numerous approaches, including preferential excitation of one enantiomer of a racemic mixture with circularly polarised light,³ photocycloaddition of two achiral molecules in a mixed single crystal,⁴ photoreduction of an achiral molecule in the presence of an optically active hydrogen donor,⁵ transient chirality of achiral molecules via hydrogen bonding to an optically active solvent,⁶ and partial photoresolution of an inorganic salt via selective intervention of an optically active counter ion,⁷ have been employed. In each of these cases, the means of resolution depends on an extremely intimate interaction between the molecule to be resolved and the resolving agent. Recently, Hammond and Cole,^{8a} Kagan and coworkers,^{8b} and we^{8c} induced optical activity in trans-1,2-diphenylcyclopropane (trans-1), methyl *p*-tolylsulfoxide, and penta-2,3-diene, respectively, with optically active photosensitizers. Since the mechanism in each of these cases probably involves an exciplex, the interaction between the resolving agent and the isomerizing molecule is very strong here, also. As a means of determining if less specific interactions can lead to photoresolutions, we have examined the effects of solvation, using optically active solvents (2, 3, and 4), on the decay modes of the excited states of 1.

It is known⁹ that ketone triplets of at least 58 kcal/mole can sensitise the cis,trans isomerisation of 1 and Becker *et al.*¹⁰ estimate the triplet state of trans-1 to be 53 kcal/mole above the ground state. Thus, acetone ($E_t = 78$ kcal/mole), the triplet sensitizer chosen for this work, should transfer energy to cis- and trans-1 at diffusion controlled rates (1, 2, $k_0 = k_d = k_1$; eqns. 2-4). In the absence of an optically active solvent, β and $1-\beta$ must be equal (eqn. 5). When the solvent is optically active, there may be a preference for the formation of one enantiomer of trans-1 ($\beta \neq 1-\beta$) if the solvating molecules are sufficiently close to and ordered around the triplets of 1 when they decay to the ground state.

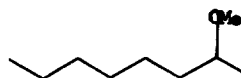




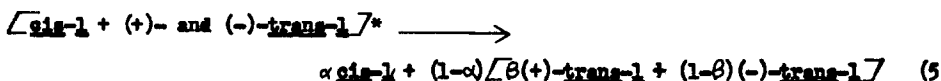
isobornyl methyl ether
(-)-2



methyl 1-(1-phenylethyl) ether
(+)- and (-)-3



methyl 2-octyl ether
(+)-4



Solutions of cis-1 or trans-1 (10^{-2} M), acetone (ca. $3 \cdot 10^{-2}$ M), and a drop of tetradecane in one of the optically active solvents were degassed (3 freeze-pump-thaw cycles at $3 \cdot 10^{-4}$ torr) and sealed in pyrex tubes. Irradiations with a 125 W phosphor coated low pressure mercury lamp were continued for 7-10 days at room temperature. Analyses of the absolute concentrations of cis-1 and trans-1 were conducted by glpc¹² and the trans isomer was isolated by preparative glpc¹² and distilled pot-to-pot in vacuo. Contrary to the conclusions of Becker *et al.*¹⁰ we noted that the triplets of 1 are extremely well behaved: after irradiation of ca. 10 mg in 0.5 ml of solvent for 10 days, the maximum quantity of 1 destroyed in any of our runs was 24%. ORD spectra of the isolated trans-1 ($5 \cdot 12 \cdot 10^{-4}$ M in cyclohexane) in the regions 250-300nm and 580-600 nm showed no rotations (1, 2, $\beta = 1-\beta$). We estimate from the spectrum of authentic (-)-(1R;2R)-1¹¹ that our trans samples are less than 2.3% optically active.¹³

It can be seen from Table 1 that the cis/trans photostationary state of 1 is slightly solvent dependant: the saturated ethers give lower cis/trans ratios than the aromatic ethers and acetonitrile. Since the energy of π, π^* triplet states are known to be affected only slightly by solvent changes¹⁴ and since $(\text{cis/trans})_{\text{pss}} = \alpha/(1-\alpha)$ under the reaction conditions, we conclude that the differences are derived from changes in the decay modes.

It is interesting to compare our results with those of Givens and Cottle¹⁵ for direct (254 nm) irradiations of 1. From their photostationary states, they calculate $\alpha/(1-\alpha)$ to be 0.38 for acetonitrile and 0.52 for dioxane. Thus, the singlets and triplets of 1 decay quite differently and do not exhibit the same solvent dependence.

Since direct irradiation of 1 leads to a complex mixture of products,¹⁶ singlet isomerizations were sensitized with naphthalene.¹⁷ Samples of cis-1 or trans-1 (10^{-2} M) and naphthalene (0.55 M) in solvents 2 and 4 were prepared as before and sealed in pyrex tubes. Glpc analyses,¹² conducted after 14 days of irradiation with a 450 W medium pressure mercury lamp,

Table 1.^a

solvent	$[\alpha]_D^{24.5}$ (cyclo- hexane)	<u>cis</u> -1 ^b		<u>trans</u> -1 ^b		irradiation time (days)
		cis/trans	% destroyed	cis/trans	% destroyed	
(-)-2	-80.7°	0.915	1.1	0.808	1.8	7
		2.23 ^d	2	0.291 ^d	8	14
(+)-3	+141.5°	1.01	26	0.992	22	10
(-)-3	-134.5°	0.983	7.5	1.06	13	10
(+) -4	+8.25°	0.874	14	0.852	8	10
		3.83 ^d	2	0.418 ^d	14	14
dioxane ^c		0.935 (0.52) ^e		0.931 (0.52) ^e		7
acetonitrile ^c		1.16 (0.38) ^e		1.16 (0.38) ^e		7

- a) all isomerizations sensitized by acetone except where noted; b) starting isomer; c) starting material 1 enriched in cis or trans as noted; d) naphthalene sensitization; e) $\alpha/(1-\alpha)$ as calculated in ref. 15 from direct irradiations of 1.

showed that a common photostationary state had not been established (see Table 1). After isolation as before,¹² the trans-1 samples were analyzed by ord. To the limit of our detection, all were racemic. Since at low conversions, trans-1, produced from the pure cis isomer, is formed in an enantiomeric ratio which should be more different from unity than $\theta/(1-\theta)$,¹⁸ it can be stated that solvents 2 and 4 have little effect on the ratio of enantiomers of trans-1 formed from the singlets of 1.

That α was changed by solvent but θ was not in both the singlet and triplet cases indicates that the solvation responsible for photoresolution is more specific than that for geometrical isomerization. This is not surprising since a photoresolution would require the optically active center of the solvent to be near the locus of isomerization in 1 whereas a change in the cis/trans ratio could occur with changes in any 1-solvent interaction. From these results, we estimate that to observe photoresolution, the critical distance between 1 and the resolving molecule can be approximately a single bond length^{8a} but must be less than the sum of their van der Waals radii.

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- (11) We thank Professors C. C. Wanzer and G. S. Hammond for samples of *cis*- and *trans*-**1** and optically active **1**.
- (12) Glpc analyses were performed with a 6'x1/8" 20% UC-W98 on 80/100 chromosorb W column at 170°. Preparative separations were accomplished with a 5'x1/4" 20% carbowax 400 on 42/60 firebrick column at 190°. No *cis-trans* interconversion of **1** occurred under these conditions.
- (13) We estimate that α_{260}^{27} 0.002° could have been detected easily. Extrapolation of this rotation to 589 nm using our spectrum of (-)-**1** and assuming $[\alpha]_{589}^{27}$ 418° as the specific rotation for optically pure **1** (see: T. Aratani, Y. Nakanishi, and H. Nozaki, *Tetrahedron Lett.*, 1809(1969)) gave the limit noted above.
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- (18) We assume, reasonably, that the major part of optical induction should occur during the decay of *cis*-**1***.