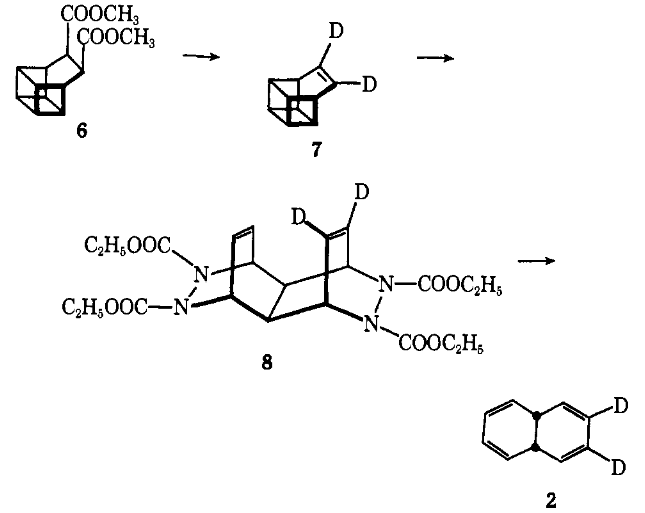
The synthesis of **2** began with the preparation of 9,10-dideuteriobasketene (**7**). This was achieved by heating *cis*-dimethyl ester **6** in CH_3OD containing sodium methoxide, hydrolysis of the resulting labeled *trans*-diester in $NaOD-D_2O$, and subsequent electrolytic bisdecarboxylation of the diacid as previously described.[18] The deuterium content of **7** was >98% d_2 by nmr analysis. Cycloaddition of diethyl azodicarboxylate to **7** gave **8** by analogy to the recent work of Shen.[19] The deuterium labeling pattern in **8** was clearly evident from its nmr spectrum: δ 5.8–6.5 (m, 2, olefinic), 4.5–5.1 (m, 4, C*H*N), 4.23 (q, 8, OCH_2), 2.93 (br s, 2, methine), and 1.25 (t, 12, CH_3). Hydrolysis–decarboxylation of **8** under a carefully deoxygenated nitrogen atmosphere and subsequent oxidation of the corresponding hydrazine afforded **2** with the high isotopic purity discussed above.



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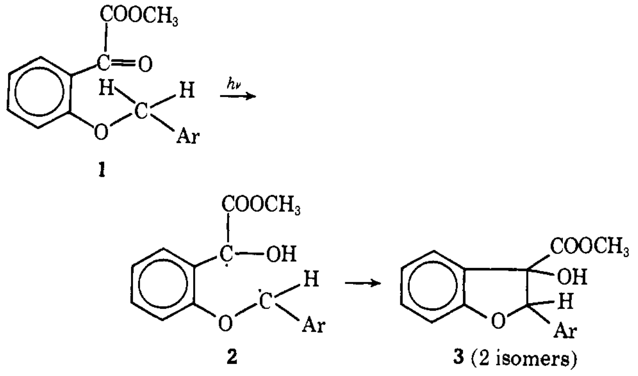
Heavy-Atom Effects on the Stereochemistry of Photoabstraction–Cyclization in a Carbonyl System[1]

Sir:

The effects of halogen substituents and halogen-containing solvents (heavy-atom effect) on the spectroscopic behavior of aromatic compounds are well documented and have been attributed to enhanced rates of S–T transitions.[2] The effect has also been observed on the photoreactivity of acenaphthalene.[3] On the other hand, theoretical arguments have been advanced against the importance of the heavy-atom effect on carbonyl systems,[4] and experimental evidence tends to support this prediction.[5] Herein, we report a heavy-atom effect on the stereochemistry of the photocyclization of methyl *o*-benzyloxyphenylglyoxylate (**1a**).



a, Ar = C_6H_5
b, Ar = C_6H_4-*p*-CH_3
c, Ar = C_6H_4-*p*-Cl

A mechanistic study on the phototransformation **1a** → **3a** has demonstrated the intermediacy of a reactive n,π^* triplet which undergoes intramolecular H abstraction from the benzyloxy carbon.[6] Both the quantum yields of product formation and the stereoselectivity were found to be significantly lower in the polar solvents acetonitrile and *tert*-butyl alcohol relative to benzene and *n*-hexane.[6,7] However, as indicated in Table I, the stereochemical results in chloroform, bromoform, and, to a lesser extent, bromobenzene provide a striking con-

Table I. Solvent and Substituent Effects on the Phototransformation **1** → **3**

Compd	Solvent	Cis/trans[a] (temp, °C)	ϕ_{+3}[b]	$1/\tau$,[c] 10^7 sec^{-1}
1a	$(Me)_3COH$	1.0 (35)[d]	0.47	1.3
	MeCN	2.2 (35)[d]	0.56	3.7
	C_6H_6	6.7 (35)	0.89	4.3
	C_6H_6[e,f]	14.6 (0)		
	C_6H_5Br[e]	17.7 (0)		
	$CHCl_3$	28.2 (0)	0.65	
	$CHBr_3$[e]	90.0 (0)	0.65	
1b	C_6H_6[e,f]	16.0 (0)	0.69	3.5
1c	C_6H_6[e,f]	21.2 (0)	0.78	2.1
1a-d_1	MeCN	2.1 (35)	0.52	
	C_6H_6	7.2 (35)	0.86	
1a-d_2	MeCN	1.9 (35)	0.41	
	C_6H_6	7.4 (35)	0.81	

[a] Ratio of isomers **3** with respect to the geometric relationship of the 2-phenyl and 3-hydroxyl groups; estimated error ±5%. [b] Quantum yields for formation of **3** at 35° and 366 nm by ferrioxalate actinometry; 0.06 *M* **1**; conversions, <15%; estimated error, ±8%. [c] Reciprocal lifetimes obtained from slopes ($k_q\tau$) of Stern–Volmer quenching plots utilizing literature values for k_q (see ref 6). These values correspond to maximum rates for hydrogen abstraction. Minimum rates may be obtained by multiplying these values by ϕ_{+3}. [d] Little or no temperature effect on the isomer ratios in these solvents. [e] Contained 20% by volume of cyclohexane for melting point depression. [f] The same ratios were obtained in *n*-hexane.

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trast to this trend. The solvent effects are complemented by enhanced stereoselectivity of the chloro analog **1c**.

Since the presence of heavy atoms is manifested in the stereoselectivity of photocyclization, the effect may be attributed to an enhanced rate of intersystem crossing in the conversion of the reactive n,π^* triplet carbonyl to cyclized products. In this event, it follows that facile intersystem crossing allows a highly stereoselective formation of the *cis*-2-phenyl-3-hydroxy isomer and, furthermore, that the loss of this specificity occurs in competition with the crossing process. These conclusions are particularly pertinent to the nature of solvent effects on the stereochemical course of this process. Whereas the previous results might have been explicable solely in terms of solvation of a biradical intermediate and the cyclization thereof, the high order of stereoselectivity in the polar heavy atom solvents is inconsistent with this possibility. Rather, in the event that a biradical intermediate is involved, the results indicate that stereochemical control is established in its formation, which clearly implicates a favored geometry for abstraction. Thus, both the stereochemistry of abstraction and cyclization are important considerations. These factors have been discussed previously[7] with reference to this system as well as the analogous case of *o*-benzyloxybenzaldehyde.[8]

The loss of specificity may well occur by solvent-dependent rotational relaxation of an intermediate triplet biradical in competition with intersystem crossing and cyclization. A similar argument has been advanced to explain a heavy atom effect on the quantum yield of sensitized photodimerization of coumarin.[9] In this view, the low order of stereoselectivity in polar solvents and the temperature effect in nonpolar media may reflect an enhanced rate of rotational equilibration of the triplet biradical or a diminished rate of intersystem crossing in its conversion to cyclized products.

In order to obtain evidence on the possible intermediacy of a biradical, irradiation of the mono- and dideuterated analogs **1a**-d_1 and -d_2, substituted at the benzyloxy carbon, was carried out in benzene and acetonitrile. Whereas the D:H ratio at the benzylic carbon of the cyclized products derived from **1a**-d_1 was found to be between 2 and 3:1 in both solvents, indicative of favored H abstraction, the quantum yields of product formation were found to be only slightly lower relative to the protiated parent (Table I). The quantum yields for **1a**-d_2 were somewhat lower still. Together, these results are indicative of an efficient abstraction process and serve as evidence against the importance of reverse hydrogen abstraction in this system, thereby neither implicating nor excluding the intermediacy of a biradical.[10]

In precluding the importance of inefficiency in abstraction and cyclization, the results do, however, support a recent study which correlates the low quantum yields in polar media with inefficient intersystem crossing in the population of the reactive triplet carbonyl.[11] Thus, the low quantum yields and the low order of stereoselectivity in polar solvents do not appear to be directly related. However, both effects are explicable in terms of reduced rates of intersystem crossing, the former in the formation of the reactive triplet carbonyl, the latter in its conversion to products. As such, both effects may reflect a reordering of energy levels in polar media.[12]

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Transition Metal Promoted Reductive Decyanation of Alkyl Nitriles

Sir:

In the hope that the reaction may find synthetic utility, we wish to describe the convenient, transition metal promoted reductive decyanation of alkyl nitriles to

$$\text{R—CN} \longrightarrow \text{R—H}$$

hydrocarbons. In representative cases, the transformation was carried out in 58–100% yields by the action of Fe(acac)$_3$–Na or, in lower yields, by means of "titanocene" ($C_{20}H_{20}Ti_2$), prepared and utilized *in situ*.[1]

Products and yields listed in Table I resulted from use of the following procedure. Under an argon atmosphere,[2] Fe(acac)$_3$ (10 mmol), organic cyanide (10 mmol), and sodium sand (20 mg-atoms) were stirred in 25 ml of

Table I. Reductive Cleavage of Nitriles (RCN) to Hydrocarbons by Fe(acac)$_3$–Na^0 (1:2)

Starting material, R =	Product	Yield, %
Methyl	Methane	98
n-Octyl	*n*-Octane	100
tert-Butyl	Isobutane	58
	Isobutylene	40
Cyclopentyl	Cyclopentane	77
Δ^3-Cyclohexenyl	Cyclohexene	80
Benzyl	Toluene	56
Δ^1-Cyclohexenylmethyl	1-Methylcyclohexene	43
Allyl	Propylene	40
Phenyl[a]	Benzene	46
1,1′-Dicyanobicyclohexyl	Bicyclohexyl	76

[a] Toluene solvent.

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(1) Formation of hydrocarbon by reductive cleavage of nitriles results from the action of Na or Li in liquid NH_3 or $C_2H_5NH_2$, or by electrolysis in $C_2H_5NH_2$. See: P. G. Arapakos, *J. Amer. Chem. Soc.*, **89**, 6794 (1967); P. G. Arapakos and M. K. Scott, *Tetrahedron Lett.*, 1975 (1968); and P. G. Arapakos, M. K. Scott, and F. E. Huber, Jr., *J. Amer. Chem. Soc.*, **91**, 2059 (1969). It is pertinent that, in contrast to the present findings, yields in the alkali metal–amine reductions were optimal with trityl, benzhydryl, benzyl, phenyl, and *tert*-alkyl cyanides, while in primary–secondary alkyl cases, the expected hydrocarbon products were generated in 35–49% and were accompanied by considerable amounts of organic amine and hydrocarbons resulting from carbon skeletal rearrangements. The entire body of results points to intrinsic mechanistic differences between the transition metal promoted and nontransition metal promoted processes, in keeping with the view of Arapakos and coworkers that ther system involves a stepwise, two (solvated) electron transfer to nitrile with formation of radical and carbanion, followed by protonation of the latter.

(2) In one octyl cyanide run, wherein the reactants were weighed, and the reaction started, in air, the yield fell from 100 to 71%.