the σ complexes, present as metastable intermediates.[7,8] It is clearly important to delineate the conditions under which oxygen or carbon attack may be expected in the reaction of aryloxide ions with the nitroaromatic series.

Acknowledgments. The award by the National Research Council of Canada of a scholarship to J. G. K. W. is gratefully acknowledged.

(8) (a) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev., Chem. Soc.*, **22**, 123 (1968); (b) F. Pietra, *Quart. Rev., Chem. Soc.*, **23**, 504 (1969); (c) E. J. Fendler, D. M. Camaioni, and J. H. Fendler, *J. Org. Chem.*, **36**, 1544 (1971).

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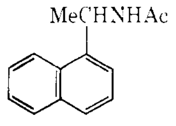
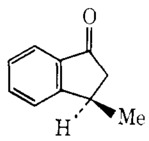
Asymmetric Induction during Transfer of Triplet Energy

Sir:

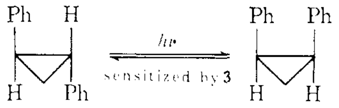
Asymmetric induction during energy transfer from an optically active sensitizer (**1**) to *trans*-1,2-diphenylcyclopropane (DPC) (**2**) has been described by Hammond and Cole.[1] They had initially supposed that it was a triplet–triplet energy transfer, in which the acceptor underwent a nonvertical transition. It is well known that the transfer of triplet excitation requires an effective collision between the donor and the acceptor and that its rate is slowed down in the case of nonvertical transition, so that steric effects can be expected to intervene. However, they showed later that this transfer of excitation took place from the singlet-state excited naphthalene (**1**).[2]



1



3



2t,t' **2**c

According to recent spectroscopic work,[3] *trans*-DPC has an unusually low-energy radical-like triplet at approximately 53 kcal/mol. Therefore, it was interesting to study the transfer from a triplet energy sensitizer, of triplet energy well above 53 kcal/mol, which should in theory take place at a diffusion-controlled rate, in order to see whether it could give rise to asymmetric induction.

We wish to report that the transfer of triplet energy from the optically active (*R*)-(−)-3-methyl-1-indanone (**3**)[4] to *trans*-DPC induces an asymmetry comparable to the one observed by Hammond.

A benzene solution containing 0.034 *M* **3**, $[\alpha]_D$ $-3.4°$ (neat),[5] and 0.10 *M* racemic **2**[6] was distributed in ten Pyrex tubes, each one containing 5 ml. These samples were degassed, sealed *in vacuo*, and irradiated through a Pyrex filter by means of a water-cooled 450-W medium-pressure mercury lamp (Hanovia) in a rotating turntable assembly. The tubes were opened periodically and analyzed by vapor chromatography. The optical rotations were determined with a Perkin-Elmer Model 141 polarimeter. The photostationary state, *cis*-DPC/*trans*-DPC = 77%, was approached either from *cis*- or *trans*-DPC by irradiating them in the presence of **3** (0.034 *M*).

The development of DPC optical activity as a function of time was determined by two methods. (1) The optical rotation of the irradiated solution was measured, the optical activity due to the sensitizer in the initial solution being taken in account. (2) The optical rotation of the mixture of *cis*- and *trans*-DPC was measured in solution after isolation by silica gel chromatography. The measured rotation was converted to *trans*-DPC specific rotation from chromatographic analysis.

The production of the cis isomer and the development of optical activity of *trans*-DPC are shown in Figures 1 and 2. The final optical rotation is +12.4°,[7] which corresponds to an asymmetric synthesis of 3% in (+)-(1*S*,2*S*)-*trans*-DPC.[8]

We have verified that the same optical activity, but of opposite sign, is developed by sensitizing the isomerization of *trans*-DPC by (*S*)-(+)-3-methyl-1-indanone.[9] In the case reported by Hammond and Cole,[1] the asymmetric induction was ~7%.

The kinetics of the photosensitized isomerization of optically active *trans*-DPC have been studied by Matzke[10] using various triplet sensitizers. By analogy with his results in the case where acetophenone is the sensitizer, a possible mechanistic scheme can be written

$$\mathrm{S} \xrightarrow{h\nu} \mathrm{S}^{*1} \longrightarrow \mathrm{S}^{*3}$$

$$\mathrm{S}^{*3} \xrightarrow{k_d} \mathrm{S}$$

$$\mathrm{S}^{*3} + t\text{-DPC} \xrightarrow{k_{qt}} \mathrm{T}^* + \mathrm{S}$$

$$\mathrm{S}^{*3} + t'\text{-DPC} \xrightarrow{k_{qt'}} \mathrm{T}^* + \mathrm{S}$$

$$\mathrm{S}^{*3} + c\text{-DPC} \xrightarrow{k_{qc}} \mathrm{T}^* + \mathrm{S}$$

$$\mathrm{T}^* \xrightarrow{k_c} c\text{-DPC}$$

$$\mathrm{T}^* \xrightarrow{k_t} t\text{-DPC}$$

$$\mathrm{T}^* \xrightarrow{k_{t'}} t'\text{-DPC}$$

In this scheme *t* and *t'* represent both enantiomers of *trans*-DPC, *c* the cis isomer, and T* is a free triplet

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(1) G. S. Hammond and R. S. Cole, *J. Amer. Chem. Soc.*, **87**, 3256 (1965).

(2) S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 2957 (1968).

(3) R. S. Becker, L. Edwards, R. Bost, M. Elam, and G. Griffin, *J. Amer. Chem. Soc.*, **94**, 6584 (1972).

(4) The triplet energy of 3-methyl-1-indanone is not known but 1-indanone has a lowest triplet at ≃76 kcal/mol in solution (W. A. Case and D. R. Kearns, *J. Chem. Phys.*, **52**, 2175 (1970)); this energy is not expected to vary to a great extent by methyl substitution in position 3.

(5) A. M. Weidler and G. Bergson, *Acta Chem. Scand.*, **18**, 1484 (1964); J. Almy and D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 4459 (1969).

(6) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

(7) The correction taking in account the optical purity of our sample of indanone (83%)[5] would not change significantly the value of the asymmetric induction (3.5% *vs.* 3%).

(8) T. Aratani, Y. Nakanisi, and H. Nozaki, *Tetrahedron*, **26**, 1675 (1970).

(9) *trans*-DPC with optical purity in the range of 1% was also obtained when optically active 3-methyl- and 4-methyltetralone are used as chiral sensitizers: private communication from H. B. Kagan, G. Balavoine, and S. Jugé, to be submitted for publication.

(10) T. A. Matzke, Ph.D. Thesis, The University of Texas at Austin, 1971.

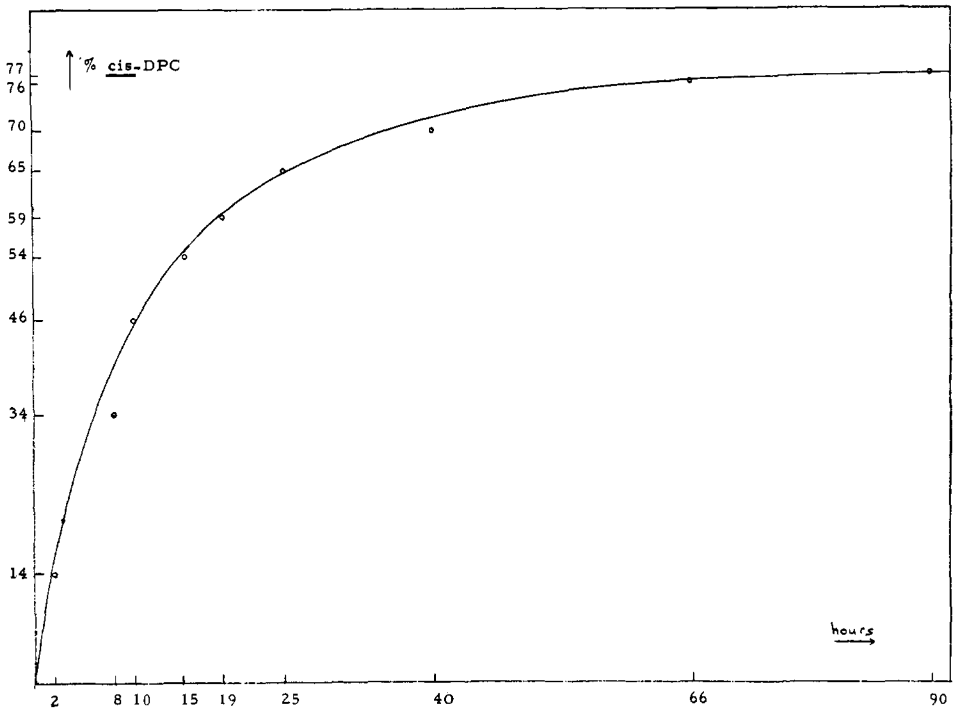

Figure 1. Production of the *cis*-DPC as a function of time.

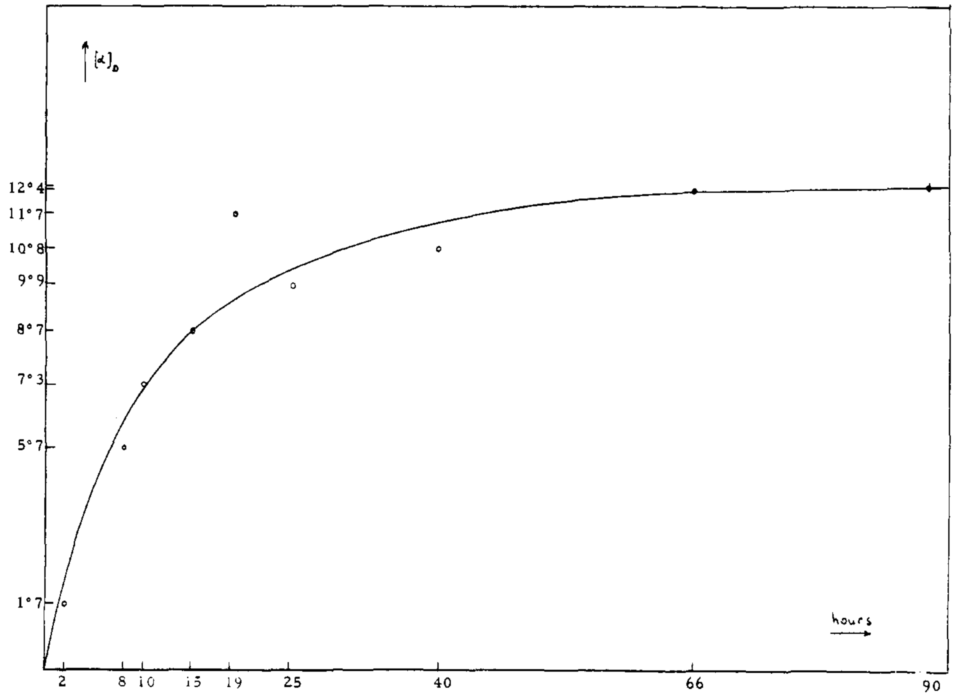

Figure 2. Development of optical activity as a function of time.

diradical intermediate which may be symmetrical or represents a set of rapidly equilibrating structures. On this basis $k_t = k_{t'}$; the development of optical activity is due to a kinetic photoresolution operating before the decay of T*.[11] From the value of the optical rotation at the photostationary state, we can calculate the ratio $kqt/kqt' = 1.06$.

Like Hammond and Cole,[1] we do not retain a mechanism of excitation transfer involving covalent bonding between sensitizer and substrate, since we have not observed the formation of adducts.[12] However, the

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(11) A. Horeau and A. Nouaille, *Tetrahedron Lett.*, 3953 (1966). J. D. Morrison and H. S. Mosher "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, pp 30–35.

(12) A referee argued that "the fact that no adducts are observed does not imply that no adduct of any kind could not have existed. For example, the excited state triplet of the phenylcyclopropanes has been shown to be essentially a diradical. Thus, this species could complex with the sensitizer but upon decay (radiative or internal conversion) of the triplet excited state of *trans*-DPC (in the case of this paper) to a singlet closed form, the complex would no longer be stable. This could well be a reasonable mechanism explaining the results yet no adduct would ever be seen." The authors agree with this comment. In their opinion, this report is intended to draw the attention on a remarkable phenomenon. They are well aware that further experiments are needed in order to learn more about the photophysical primary process taking place when the optical active sensitizer collides with DPC.

development of optical activity shows that in the transfer step there exists some kind of diastereoisomeric relationship between the systems constituted by one enantiomer of *trans*-DPC or the other and the sensitizer. This probably implies preferential orientation of sensitizer and substrate to allow maximum π overlap.[13] Although the absolute configurations of both are known, the extent of the induced asymmetry is too small to allow one to predict which enantiomer of *trans*-DPC is approached most easily by (*R*)-(−)-3-methyl-1-indanone.

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(13) P. J. Wagner, J. M. McGrath, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 6883 (1972); E. F. Ullman and N. Baumann, *ibid.*, **90**, 4158 (1968); C. C. Wamser and P. L. Chang, *ibid.*, **95**, 2044 (1973).

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Photochemistry of 1-Benzoyl-4-*p*-anisoylbutane. Reaction from Equilibrating Upper Triplets[1]

Sir:

The problem of energetically proximate excited states has aroused much interest, both spectroscopic[2] and chemical,[3] but remains puzzling. In the particular case of ketones with π,π^* lowest triplets, it is difficult to differentiate whether n,π^*-like chemical reactivity is induced by vibronic mixing with a nearby n,π^* state[4] or actually emanates from low equilibrium concentrations of the upper n,π^* triplet. We have already reported evidence for the latter possibility.[5] We now report unequivocal evidence for reaction from at least one and probably two upper triplets of a molecule with a π,π^* lowest triplet. Not only does this evidence provide further support for the hypothesis of efficient equilibration of triplet excitation within one chromophore, it clearly demonstrates chemical reaction *via* equilibration of excitation between two chromophores.

Upon uv irradiation in degassed benzene containing 0.5 *M* pyridine[6] 1-benzoyl-4-anisoylbutane (**1**) undergoes normal type II photoelimination[8] reactions from each end, producing acetophenone, *p*-methoxyphenyl allyl ketone, *p*-methoxyacetophenone, and phenyl allyl ketone. The former two are formed in equal yield, as are the latter two, with the overall yield of the former pair (type II from the benzoyl group) far surpassing that of the latter pair (type II from the anisoyl group). The benzoyl–anisoyl product ratio is independent of excitation wavelength (313 or 365 nm) and decreases with increasing temperature, as indicated in Table I.

Table I. Temperature Effect on Ratio of Products Obtained from **1**[a]

T, °C[b]	Acetophenone/ *p*-Methoxyacetophenone[c]
25	19.4[d]
30	18.4
90	11.5
116	9.5

[a] 0.01 *M* diketone, 0.5 *M* pyridine in degassed benzene, irradiated at 313 nm. [b] All the temperatures were controlled within ±0.5°. [c] Product ratios measured by vpc and corrected for different FID responses. [d] Same value obtained with 365-nm irradiation.

Four further products are formed in 5–6% total yield at all temperatures and are assumed to be the expected cyclobutanols.[9] The total quantum yield of products at 25° equals 0.21. Addition of various concentrations of 2,5-dimethyl-2,4-hexadiene results in quenching of both benzoyl and anisoyl reactions with almost the same efficiency, $k_q\tau$ values of 240 and 370 M^{-1} being measured.[10]

Like several other molecules in which two chromophores are separated by more than one methylene group,[11] **1** manifests no evidence for significant ground-state electronic interaction between the two aroyl groups, *i.e.*, the uv spectrum of **1** is nearly identical with the spectrum of an equimolar mixture of valerophenone and *p*-methoxyvalerophenone. The phosphorescence of **1** in an ethanol glass at 77°K is identical in both spectral shape and lifetime with that of *p*-methoxyvalerophenone (71 kcal 0–0 band, 0.4 sec lifetime), indicating that the lowest triplet of **1** is the π,π^* state of the anisoyl group. The second lowest triplet of **1** should be the n,π^* state of the benzoyl group, since we have shown that such states of simple phenyl alkyl ketones have an excitation energy of 72 kcal in solution.[12] Scheme I depicts our best estimate of the various triplet energy levels in **1** (in kilocalories).

We chose compound **1** for this study because it has been shown that exothermic triplet energy transfer[11d] and charge transfer[13] between groups separated by four methylenes both proceed with a rate $\sim 3 \times 10^9$ sec^{-1}. This rate is appreciably faster than the 5×10^7 sec^{-1}

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(1) We are grateful to the National Science Foundation, Grant No. GP-19850, for support of this work.

(2) (a) N. C. Yang and S. L. Murov, *J. Chem. Phys.*, **45**, 4358 (1966); (b) A. A. Lamola, *ibid.*, 47, 4810 (1967); (c) R. M. Hochstrasser and C. Marzzacco, *ibid.*, **49**, 971 (1968); (d) W. A. Case and D. R. Kearns, *ibid.*, **52**, 2175 (1970); (e) R. M. Hochstrasser and C. A. Marzzacco in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 631; (f) Y. H. Li and E. C. Lim, *Chem. Phys. Lett.*, 7, 15 (1970); (g) A. M. Nishimura and D. S. Tinti, *ibid.*, **13**, 278 (1972); (h) T. H. Cheng and N. Hirota, *ibid.*, **14**, 415 (1972); (i) L. Goodman and M. Koyanagi, *Mol. Photochem.*, 4, 365 (1972); (j) M. E. Long and E. C. Lim, *Chem. Phys. Lett.*, **20**, 413 (1973).

(3) (a) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Amer. Chem. Soc.*, **89**, 5466 (1967); (b) R. D. Rauh and P. A. Leermakers, *ibid.*, 90, 2246 (1968); (c) P. J. Wagner, A. E. Kemppainen, and H. N. Schott, *ibid.*, 90, 5898 (1968); (d) J. N. Pitts, Jr., D. R. Bailey, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5902 (1968); (e) T. J. van Bergen and R. M. Kellogg, *ibid.*, **94**, 8451 (1972).

(4) (a) N. C. Yang and R. Dusenbery, *ibid.*, **90**, 5899 (1968); (b) C. D. DeBoer, W. G. Herkstroeter, A. P. Marchetti, A. G. Schultz, and R. G. Schlessinger, *ibid.*, **95**, 3963 (1973).

(5) P. J. Wagner, A. E. Kemppainen, and G. N. Schott, *ibid.*, **92**, 5280 (1970); **95**, 5604 (1973).

(6) The pyridine maximizes type II yields by suppressing reverse hydrogen transfer in the biradical intermediate,[7] thus ensuring that product ratios actually equal triplet rate ratios.

(7) P. J. Wagner, I. Kochevar, and A. E. Kemppainen, *J. Amer. Chem. Soc.*, 94, 7489 (1972).

(8) P. J. Wagner, *Accounts Chem. Res.*, 4, 168 (1971).

(9) (a) N. C. Yang and D. H. Yang, *J. Amer. Chem. Soc.*, **80**, 2913 (1958); (b) R. B. LaCount and C. E. Griffin, *Tetrahedron Lett.*, 1549 (1965); (c) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **94**, 3852 (1972); (d) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott, and R. G. Zepp, *ibid.*, **94**, 7506 (1972).

(10) $k_q\tau$ values for 1,4-dibenzoylbutane and 1,4-dianisoylbutane are 55 and 1000 M^{-1}, respectively. The observed quenching is triplet quenching; supposition of singlet quenching would demand an incredibly long singlet lifetime for **1** of at least 10^{-7} sec.

(11) (a) O. Schnepp and M. Levy, *J. Amer. Chem. Soc.*, **84**, 172 (1962); (b) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, **87**, 2322 (1965); (c) A. A. Lamola, *ibid.*, **92**, 5045 (1970); (d) D. O. Cowan and A. A. Baum, *ibid.*, **93**, 1153 (1971).

(12) P. J. Wagner, M. J. May, and A. Haug, *Chem. Phys. Lett.*, **13**, 545 (1972).

(13) P. J. Wagner, A. E. Kemppainen, and T. Jellinek, *J. Amer. Chem. Soc.*, **94**, 7512 (1972).