absence of ultraviolet light, the reaction does not proceed. However, at 300° in a sealed tube, P_2F_4 and C_2H_4 give material identical with that obtained in the photochemical reaction. Complete separation of the reaction mixture could be obtained by distillation through traps held at −63, −84, and −196°. Pure $F_2PCH_2CH_2PF_2$ (0.54 m*M*) was retained in the −84° trap only after no more condensable was recovered in the −196° trap. This required distillation periods from 12 to 20 hr. That the sample was pure was demonstrated by the mass spectrum (70 eV) which displayed the following peaks (all observed peaks are assignable to $P_2F_4C_2H_4$) (relative intensities and assignment in parentheses): 166 (15.3 $P_2F_4C_2H_4^+$), 147 (0.88 $FPCH_2CH_2PF_2^+$), 138 (6.32 $P_2F_4^+$ recombination), 97 (16.4 $F_2PCH_2CH_2^+$), 96 (0.70 $F_2PC_2H_3^+$), 83 (1.05 $F_2PCH_2^+$), 78 (1.2 $FPCH_2CH_2^+$), 77 (6.4 $FPC_2H_3^+$), 76 (0.35 $FPC_2H_2^+$), 75 (1.1 FPC_2H^+), 69 (100 PF_2^+), 59 (12.6 $PC_2H_4^+$), 58 (0.46 $PC_2H_3^+$), 57 (4.3 $PC_2H_2^+$), 56 (1.1 PC_2H^+), 55 (0.70 PC_2^+), 51 (4.18 PFH^+ recombination?), 50 (5.72 PF^+), 45 (0.49 PCH_2^+), 44 (0.70 PCH^+), 31 (1.5 P^+), 28 (7.2 $C_2H_4^+$), 27 (2.8 $C_2H_3^+$), 26 (6.0 $C_2H_2^+$).

The vapor density molecular weight also supports the assignment of the formula $P_2F_4C_2H_4$: exptl 171 (calcd 166). The compound is sufficiently stable to obtain vapor pressure data [T(°K), P(mm)]: 252.8, 6.9; 253, 7.85; 273.6, 25.0; 283.0, 41.45; 287.3, 51.75; 299.6, 90.6. The vapor pressure data follow the equation $\log P_{(\mathrm{mm})} = -1776/T + 7.891$. The infrared spectrum of gaseous $P_2F_4C_2H_4$ shows absorptions at 2955 (w), 2910 (m), 2800 (vw), 1645 (vw, br), 1410 (ms), 1197 (ms), 1175 (ms), 1072 (w), 1008 (w), 960 (w), 890 (w), 822 (vvs), 750 (ms), 737 (ms), 708 (s), 472 (m), 469 (ms), 425 (m), 399 (m), and 305–325 cm^{-1}. The infrared spectrum of solid $P_2F_4C_2H_4$ shows absorptions at 2912 (mw), 1420 (w), 1397 (s), 1199 (s), 1181 (s), 1084 (w), 1040 (vvw), 950 (mw), 793 (vvs), 770 (vvs), 720 (mw), 710 (s), 670 (mw), 470 (m), and 305–325 cm^{-1}.

Although analytical data were not obtained, unequivocal characterization of 1,2-bis(difluorophosphino)ethane was obtained from the nmr spectra obtained in the neat liquid.

The proton spectrum (60 MHz) (all spectra reported were run at ambient temperature) consists of a broad singlet centered at +1.6 ppm from TMS (external standard); splitting of the singlet by the other magnetically active nuclei is not distinguishable, and the results of decoupled spectrum will be reported in a succeeding paper.

The fluorine spectrum consists of a 1:1 doublet ($\delta_{\mathrm{CCl_3F}}$ +98.7 ppm) resulting from the splitting of the phosphorus nucleus directly attached to the fluorine (J_{PF} = 1168 Hz).

The phosphorus spectrum displays a sharp 1:2:1 triplet centered −234 ppm from OPA (external standard) corresponding to splitting by two equivalent fluorines directly attached to the phosphorus (J_{PF} = 1170 Hz). No additional splitting of the members of the triplet was discernible.

That $F_2PCH_2CH_2PF_2$ does display dibasic character is reflected by its reaction with diborane. When 0.072 m*M* of $P_2F_4C_2H_4$ and 0.159 m*M* of B_2H_6 were allowed to warm to room temperature together in a reaction vessel, a low volatile colorless liquid formed. Distillation through traps held at 0, −64, and −196° resulted in 0.087 m*M* B_2H_6 being recovered in the −196° trap. Since no volatile was recovered in the 0° trap, mass balance indicates that a 1:1 adduct ($P_2F_4C_2H_4 \cdot B_2H_6$) was recovered in the −64° trap.

The mass spectrum of the low volatile fraction supports the formulation as the borane adduct since peaks were obtained which can be assigned to the $F_2PCH_2CH_2PF_2$ part of the molecule as well as those peaks requiring attachment of boron: *m/e* 193 ($P_2F_4C_2{}^{11}B_2H_9^+$, $P_2F_4C_2{}^{10}B^{11}BH_{10}^+$, $P_2F_4C_2{}^{10}B_2H_8^+$, relative intensity compared to PF_2 as 100 equals 2.5), 45 ($P^{11}BH_3^+$, 8.4), and 44 ($P^{11}BH_2^+$, $P^{10}BH_3^+$, 3.5).

Further evidence for the existence of the adduct is obtained from its nmr spectra.

The proton spectrum consists of a broad 1:1:1:1 quartet centered 0.6 ppm downfield from TMS, J_{BH} = 97 Hz. The methylene protons may be assigned to an unresolved multiplet centered 2.4 ppm downfield from TMS. The fluorine spectrum (ambient temperature) shows a 1:1 doublet (J_{PF} = 1170 Hz) with a chemical shift of +89.3 from $CFCl_3$. The phosphorus spectrum consists of a broadened (compared to $P_2F_4C_2H_4$) 1:2:1 triplet (J_{PF} = 1160 Hz) centered −264 ppm from OPA. The observed splitting is rationalized in the same way as $P_2F_4C_2H_4$, the broadness of the peaks resulting from the expected quadrupolar relaxation by the coordinated boron nucleus, thereby showing that the BH_3 is coordinated to both the PF_2 sites.

The infrared spectrum of solid $P_2F_4C_2H_4 \cdot B_2H_6$ (the peaks in the gas-phase spectrum were very weak because of the low volatility of the sample) shows absorptions at 2975 (w), 2965 (mw), 2919 (m), 2600 (vvw, br), 2422 (s, sh), 2417 (s), 2360 (w), 2230 (vw, br), 1403 (m), 1263 (w), 1250 (w), 1218 (m), 1203 (mw), 1138 (m), 1128 (m), 1100 (mw, br), 1061 (m), 910 (s), 895 (vs), 882 (vvs, sh), 870 (vvs), 786 (vs), 594 (ms), 430 (m), 410 (m), 400 (m), and 360 (s) cm^{-1}.

The sites of BH_3 attachment are also supported by ir evidence since it has been observed that shifts in the PF stretching motions to higher frequencies occur upon coordinate bond formation by the phosphine or by an increase in oxidation state.[2,3] Thus, the increase from ν_{PF} 793 and 770 cm^{-1} to ν_{PF} 895 and 870 cm^{-1} for the solid and ν_{PF} 822 to ν_{PF} 892 cm^{-1} in the gas support that both PF_2 groups have been coordinated.

Acknowledgments. The support of the U. S. Army Research Office—Durham and the Utah State University Research Council is gratefully acknowledged. We are also indebted to Mike Thomas at the University of Utah for some of the ^{19}F and ^{31}P nmr spectra.

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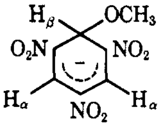
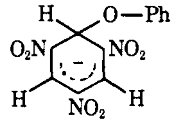
σ Complex Formation Involving Ambident Phenoxide Ion

Sir:

We wish to report on the unusual interaction between phenoxide ion and 1,3,5-trinitrobenzene (TNB) in dimethyl sulfoxide–methanol medium. Since TNB is known to react with methoxide ion to yield the σ-complex **1**,[1] one would have expected that reaction with phenoxide ion would yield the structurally analogous complex **2**. Literature reports do not allow conclusive interpretation to be made concerning structural aspects of the interaction of phenoxide ion with TNB.[2] The intriguing suggestion has been put forward by Tronov, *et al.*,[2b] on the basis of colorimetric studies of phenoxide ion with dinitrobenzene, that bond formation occurs between the phenoxy oxygen and the nitrogen of a nitro group. We have obtained definitive evidence of bonding between the para carbon of the phenoxide moiety and one of the unsubstituted carbon atoms of TNB, in accord with the ambident nature of the phenoxide ion.[3]



1



2

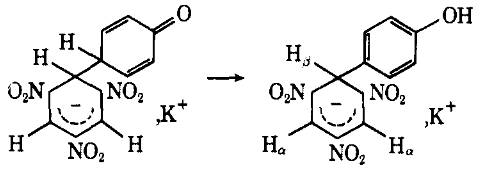
TNB reacts with potassium phenoxide in Me$_2$SO–MeOH (80:20, v/v) to give, as the first product, the methoxide adduct **1**. Evidently **1** is produced as a result of solvolysis of PhOK and the highly favorable rate and equilibrium processes in formation of **1** from TNB and methoxide ion.[4] An nmr spectrum taken immediately on preparation of a solution of TNB (0.4 *M*) and PhOK (0.8 *M*) in Me$_2$SO–MeOH (80:20, v/v) at 45° showed the characteristic absorptions of **1**: H$_\alpha$ 8.69 ppm (doublet, J = 1.2 Hz); H$_\beta$ 6.37 ppm (poorly resolved triplet). The OCH$_3$ signal is obscured by the solvent peak, while a complex signal pattern is observed centered around 6.9 ppm arising from the phenoxy aromatic protons. However, in time, the advent of some new process becomes apparent, since the signals at 8.69 and 6.37 ppm gradually decrease in intensity as signals at 8.54 (singlet) and at 5.72 ppm (singlet) increase in intensity. The latter signal is partially obscured by the OH absorption; however, this overlap is eliminated when the reaction is carried out with phenol (0.3 *M*) initially present, as a result of a low-field shift of the combined phenol–methanol OH signal. The spectral changes become complete after 6 hr at 45°.

Although the nmr evidence appeared to be indicative of the formation of an aryloxy σ complex, one feature alerted our attention. Thus, the chemical-shift difference between the H$_\alpha$ and H$_\beta$ protons, which was 2.32 ppm for the initial complex **1**, increased to 2.82 ppm in the newly produced complex. Such a change would have been surprising if bonding of phenoxide ion had occurred *via* the oxygen and raised the possibility of bonding *via* an atom of lesser electronegativity.

Further information was sought from uv–visible spectroscopy; the spectra were recorded at various times after 100-fold dilution, in a 0.1-mm cell. The initial spectrum with absorption maxima at 428 and 510 nm, characteristic of **1**, becomes replaced in time with a spectrum somewhat similar in overall character but the twin absorptions are shifted to longer wavelengths, that is to 468 and 570 nm (broad shoulder), respectively. These λ_{max} values are not typical of alkoxide σ complexes of TNB.[5] Even more definitive was the observation that the spectrum due to product (λ_{max} 468 and 570 nm) *was not destroyed on acidification.* The reversibility of alkoxide ion σ complexes of TNB is a characteristic property of such complexes. However, the observed nonreversibility in our system is paralleled by the report[6] that the complex formed between TNB and 2,6-dimethoxyphenylsilver, in which bonding occurs *via* carbon, is not decomposed in dilute acid.

Structural proof was obtained by isolation and nmr examination of the complex in the absence of interfering signals which prevail under the conditions (excess phenoxide and phenol) when the complex is formed in solution. The complex was obtained on reaction of TNB (9.0 g) with PhOK–MeOH (20 ml, 4.3 *M*) and PhOH (7.5 g) in Me$_2$SO (100 ml total volume), followed by acidification with H$_2$SO$_4$ (4.25 ml, 10 *N*) and workup, as a dark semicrystalline solid. Analysis corresponded to the monopotassium salt **3**. The nmr spectrum in Me$_2$SO-d_6 exhibited singlets at 8.44 and 5.62 ppm (2.1:1.0) assigned to H$_\alpha$ and H$_\beta$ of **3**. However, the most striking feature was the appearance of a quartet in the region corresponding to phenoxy protons (centered at 6.9 ppm, integral 4.2). This quartet is characteristic of an A$_2$B$_2$ spin system, typical for a para-disubstituted benzene, and provides conclusive evidence that attachment to the TNB ring occurs *via* the para carbon of phenoxide ion. Formation of complex **3** in these systems plausibly occurs by prior dissociation of **1** to free TNB, followed by reaction with phenoxide ion and subsequent rearomatization.

TNB + PhOK ⟶



3

In alkylation reactions, the ability of phenoxide ion to act as a carbon or oxygen nucleophile is known to be dependent on the nature of the electrophile, the solvent, etc.[3] It is noteworthy therefore that phenoxide ion displaces halogen from nitro-activated aryl halides to form the diphenyl ethers.[7] This shows that the oxygen of phenoxide ion can also act as the nucleophilic atom toward a nitroaromatic substrate. Moreover, it is believed that such substitution reactions proceed *via*

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(1) (a) K. L. Servis, *J. Amer. Chem. Soc.*, **89**, 1508 (1967); (b) M. R. Crampton and V. Gold, *J. Chem. Soc.*, 4293 (1964); (c) R. Foster and C. A. Fyfe, *Tetrahedron*, **21**, 3363 (1965).

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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.

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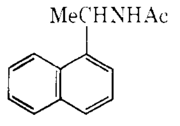
Asymmetric Induction during Transfer of Triplet Energy

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]



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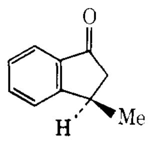

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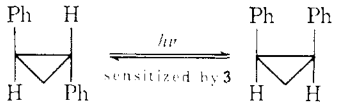

2*t,t′*   2*c*

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

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

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

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

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

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

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

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

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

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).

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[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.

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