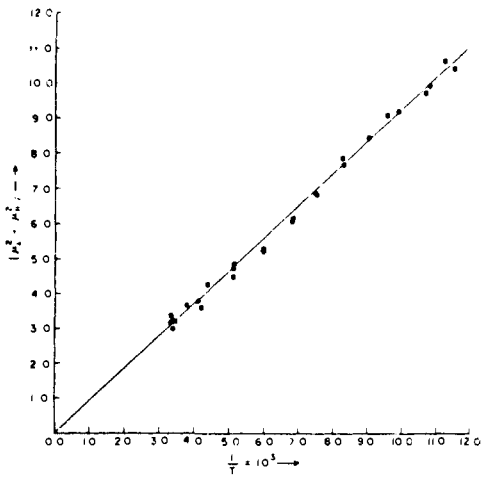

Figure 1. Temperature dependence of $(\mu_\perp^2 - \mu_\parallel^2)$ of TPPFeCl. The circles are experimental data, and the solid line is the theoretical plot for $D = 5.9$ cm^{-1}.

ported for TPPFeCl in the same solvent.[7] Large well-developed single crystals weighing up to 1–5 mg were grown from dichloromethane. The identity of the crystals was established by taking x-ray photographs and matching the unit cell constants and space group reported for TPPFeCl.[8] The unit cell constants matched, within the experimental errors, the reported values. The crystal anisotropies were measured by a null deflection method[9] using the equipment described earlier.[10] The overall error in the measurement is estimated to be not more than 2%. The single crystals of TPPFeCl belong to a tetragonal system, with the porphyrin skeletons of the different molecules so arranged in the unit cell that the Fe–Cl bond directions of all the molecules are parallel to the c axis of the crystal.[8] The crystal anisotropy is then the same as the molecular anisotropy $(K_\perp - K_\parallel)$; the parallel and perpendicular subscripts refer to the quantity parallel and perpendicular to the c axis of the crystal. The observed anisotropy must, however, be corrected for diamagnetic anisotropy due to the porphyrin skeleton, which is expected to be significant. The paramagnetic anisotropies were thus obtained by correcting the observed values by the diamagnetic anisotropy of nickel(II) tetraphenylporphyrin.[11] The corrected experimental anisotropies are plotted in Figure 1 in the form of $(\mu_\perp^2 - \mu_\parallel^2)$ vs. $1/T$. Here $(\mu_\perp^2 - \mu_\parallel^2) = 7.997(K_\perp - K_\parallel)_c T$; $(K_\perp - K_\parallel)_c$ is the experimentally measured corrected molecular anisotropy and μ_i, the principal magnetic moment.

The experimental results in Figure 1 show that $K_\perp > K_\parallel$, implying that D is positive.[1,12] Including the g anisotropy in eq 1, the principal magnetic moments μ_i are given by:

$$\mu_\parallel^2 = \frac{3g_\parallel^2[1 + 9e^{-x} + 25e^{-3x}]}{4[1 + e^{-x} + e^{-3x}]}$$

$$\mu_\perp^2 = \frac{3g_\perp^2[9 + (16 - 11e^{-x} - 5e^{-3x})/x]}{4[1 + e^{-x} + e^{-3x}]} \qquad (2)$$

where

$$x = 2D/kT$$

If $D/kT \ll 1$, which is generally true in the liquid nitrogen temperature range, eq 2 can be simplified and written as:

$$(\mu_\perp^2 - \mu_\parallel^2) = \frac{35}{4}(g_\perp^2 - g_\parallel^2) + (g_\perp^2 + 2g_\parallel^2)\frac{28D}{3kT} \qquad (3)$$

The intercept of the plot of $(\mu_\perp^2 - \mu_\parallel^2)$ vs. $1/T$ would give, according to eq 3 the g anisotropy. The experimental data so plotted in Figure 1 establish that the g anisotropy is almost zero in TPPFeCl. Thus taking $g_\perp = g_\parallel = 2$, the fit of the experimental data to eq 2 gives $D = 5.9 \pm 0.1$ cm^{-1}. In deducing this value, more stress was given in fitting the experimental data below 200 K, so that even large uncertainty in the diamagnetic anisotropy of TPPNi will not significantly affect the value.[13]

The value of the ZFS parameter for TPPFeCl, deduced from the measurements of paramagnetic anisotropy, is thus in disagreement with the values reported from the analysis of the low temperature average magnetic moment and isotropic proton shift studies. However, the present value, as expected, is very close to that of the analogous chlorohemin and protoporphyrin dimethyl ester ferric chloride. It is interesting to note that the analysis of average magnetic susceptibility data has also given an incorrect value of D for chlorohemin and an explanation of this discrepancy has earlier been given.[14]

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Modification of Chlorobenzene Photoreactivity through Exciplex Formation

Sir:

The photochemistry of aryl halides is believed to involve aryl radicals as reactive intermediates.[1] Most often, these radicals are proposed to arise through bond homolysis (eq 1), though in some cases there is evidence to suggest that electron transfer from a donor to the excited aryl halide can occur.[2,3] The resulting aryl halide radical anion then expels a halide ion[4] (eq 2).

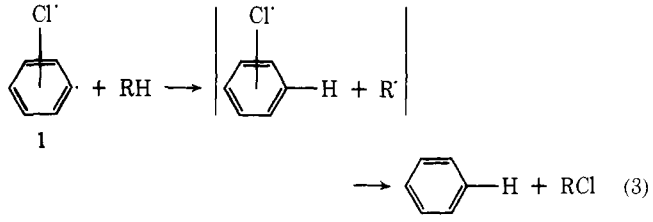
$$ArX^* \rightarrow Ar^\cdot + X^\cdot \qquad (1)$$

$$D + ArX^* \rightarrow D^{+\cdot} + ArX^{-\cdot} \rightarrow Ar^\cdot + X^- \qquad (2)$$

The fate of the aryl radical depends on the medium. In aromatic solvents, arylation occurs,[5] while in solvents liable to hydrogen abstraction, reductive dechlorination is the major reaction pathway.[2,3,6] Under certain circumstances, the aryl radical may combine with a nucleophile, leading ultimately to substitution by the $S_{RN}1$ mechanism.[7]

Recently, Fox et al. suggested a third possible reaction pathway.[8] Photolysis of chlorobenzene in cyclohexane solution gave a remarkably high yield of chlorocyclohexane. Cleavage according to eq 1 seemed to be ruled out, on the grounds that both phenyl and chlorine are reactive radicals and should both

abstract hydrogen readily from the solvent. They proposed the intermediate π-complex **1**, which they argued would abstract hydrogen predominantly through the phenyl moiety, as seen in eq 3.



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$$\rightarrow \bigcirc\!\!-H + RCl \quad (3)$$

However, a statement in their paper, to the effect that the photoreaction was sensitive to concentration, led us to consider an alternative mechanism involving excimers as intermediates (Scheme I).

Scheme I

$$ArCl^* + ArCl \rightarrow (ArCl)_2^* \leftrightarrow (ArCl^{+\cdot}\cdot ArCl^{-\cdot})^*$$

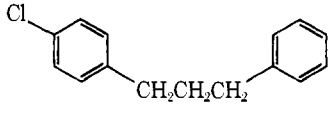
$$(ArCl^{+\cdot}\cdot ArCl^{-\cdot})^* \rightleftharpoons ArCl^{+\cdot} + ArCl^{-\cdot}$$

$$ArCl^{-\cdot} \rightarrow Cl^- + Ar\cdot \xrightarrow{RH} ArH + R\cdot$$

$$R\cdot + ArCl^{+\cdot} \rightarrow ArCl + R^+ \xrightarrow{Cl^-} RCl$$

This scheme suggests that photodecomposition of chlorobenzene will be more efficient (i) at high chlorobenzene concentrations (ii) in the presence of electron donors, to increase the ionic contribution $(D^{+\cdot}\cdot ArCl^{-\cdot})^*$ of the exciplex. Additionally, we reasoned (iii) that intramolecular exciplex interactions would be reflected especially clearly in the reactivity.

We therefore prepared compounds **2** and **3** by standard reactions.[9] The presence of three methylene groups separating donor and acceptor has been shown to cause pronounced excimer or exciplex character in their fluorescence spectra.[10]



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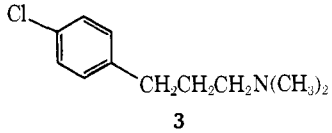

3

Isooctane solutions of both **2** and **3** had emission characteristic of chlorobenzene fluorescence (λ_{max} 295 nm) together with a broad long wavelength component, indicating intramolecular complexation. Concentrated (0.06 M) solutions of chlorobenzene and of *p*-chlorotoluene at −60 °C had emission spectra similar to that of **2**. Triethylamine quenched the fluorescence of chlorobenzene ($k_q\tau$ = 2.7 M^{-1} in isooctane), but in this case, no exciplex emission was observed. These results indicate that both intra- and intermolecular complexes can be formed, but do not show whether the complexes are involved in the photoreaction.

The photolyses[11] indicated clearly that the exciplexes are *not* intermediates along the usual photoreaction pathway. Thus fulfillment of each of the conditions (i) to (iii) led to a decrease in the quantum yield of reaction rather than the increase predicted by Scheme I. The results are shown in Table I. Increase of chlorobenzene concentration in either cyclohexane (entries 1–4) or isooctane (entries 5 and 6) leads to a reduction in the quantum efficiency for chlorobenzene decomposition. Compound **2**, which can form an intramolecular excimer, is substantially more stable to photolysis than chlorobenzene. Likewise, addition of the electron donor triethylamine to the solution decreases the quantum yield for disappearance of chlorobenzene (entries 3, 9, and 10), and the effect is exaggerated for the amino compound **3**.

Table I. Photolysis of Chlorobenzene and Derivatives in Cyclohexane

Entry	Compound (M)	Additives	Φ_r
1	PhCl (8×10^{-3})	–	0.52
2	PhCl (1×10^{-2})	–	0.49
3	PhCl (2×10^{-2})	–	0.42
4	PhCl (5×10^{-2})	–	0.33
5	PhCl (1×10^{-2})[a]	–	0.28
6	PhCl (5×10^{-2})[a]	–	0.14
7	**2** (1×10^{-2})	–	0.01
8	**3** (2×10^{-2})	–	0.22
9	PhCl (2×10^{-2})	Et_3N (0.01)	0.32
10	PhCl (2×10^{-2})	Et_3N (0.05)	0.25

[a] Solvent was isooctane.

We thus conclude that excimer/exciplex formation in the case of chlorobenzene leads to protection against photodecomposition. This is in contrast to the situation for 1-chloronaphthalene,[3] where excited state complexation appears to enhance photodecomposition. The explanation may well be found in the absolute values of the quantum yields for direct photolysis of these aryl chlorides: ~0.4 for chlorobenzene, $\sim 10^{-3}$ for 1-chloronaphthalene. If the excited state complexes were to decompose with an intermediate efficiency, say $\sim 10^{-2}$, then complexation could conceivably promote the photodegradation of 1-chloronaphthalene and retard that of chlorobenzene.

Very recently, Arnold and Wong[12] have proposed a more conventional explanation for the formation of chlorocyclohexane in these photolyses. They suggest that, instead of a π-chlorobenzene intermediate, there is the normal hydrogen abstraction by both phenyl radicals and chlorine atoms. Abbreviated, their scheme is:

$$PhCl^* \rightarrow Ph\cdot + Cl\cdot \xrightarrow{C_6H_{12}} PhH + HCl + 2C_6H_{11}\cdot \quad (4)$$

$$2C_6H_{11}\cdot \rightarrow \text{cyclohexene} + \text{cyclohexane } \textit{or} \text{ bicyclohexyl} \quad (5)$$

$$\text{cyclohexene} + HCl \xrightarrow[PhH]{h\nu} \text{chlorocyclohexane} \quad (6)$$

Our observations are in complete accord with their scheme. We find (i) substantial yields of bicyclohexyl, (ii) faster decomposition of chlorobenzene than formation of chlorocyclohexane, and (iii) suppression of chlorocyclohexane in the presence of triethylamine or of solid sodium carbonate.

In summary, our results show that excited state complexation can intervene in the photochemistry of chlorobenzene, but that loss of the substituent from the complexes appears to be less efficient than from the uncomplexed substrate. Full experimental details will appear in a later paper.

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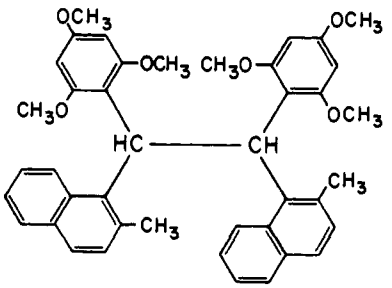
Partial Resolution of a Racemic Compound by Crystallization from (+)-α-Pinene: a Novel Use of Inclusion Compounds

Sir:

It is well known that racemic compounds may be resolved by way of diastereomeric inclusion compounds, in which the compound to be resolved functions as the guest and an enantiomerically pure compound or crystal lattice as the host.[1] We now report what to our knowledge is the first example of the converse, and potentially useful, procedure: resolution of a racemic host compound by crystallization of the inclusion compound from an enantiomerically enriched solvent which furnishes the guest molecules. Such a resolution ultimately depends on the differential effect of "active solvents" on the solubility of enantiomers, an effect which has been recognized as a principle since the dawn of stereochemistry.[2] This effect is also manifested in the enantiomeric enrichment of configurationally labile compounds by asymmetric transformations,[3] in the unequal partitioning of configurationally stable enantiomers between an achiral and a chiral liquid phase,[4] and in the preferential crystallization of one enantiomer of a configurationally stable compound through strong and specific (e.g., π-complexing or H-bonding) solute-solvent interactions.[5] In the present case, solvent and solute are both configurationally stable and form a stoichiometric complex in which there is no formal bonding association between solute and solvent.

In connection with our work on the dynamic stereochemistry of 1,1,2,2-tetraarylethanes,[6] we had occasion to prepare 1,2-bis(2-methyl-1-naphthyl)-1,2-bis(2,4,6-trimethoxyphenyl)ethane (**1**) by reductive dimerization ($CrCl_2$, HCl)[7] of racemic (2-methyl-1-naphthyl)(2,4,6-trimethoxyphenyl)methanol.[9] Ethane **1**, isolated in ca. 70% yield, proved to be a versatile inclusion host for a wide variety of guest molecules, e.g., benzene, cyclohexylamine, 2-butanone, cyclododecene, and ethyl acetate.[11] These inclusion compounds formed spontaneously, usually in a 1:1 ratio,[10] by crystallization from the appropriate solvent. The solvent-free ethane, mp 205–206 °C, could be prepared by heating the benzene solvate above its decomposition point (163–168 °C) under vacuum, followed by trituration with cold methanol. The ^{1}H NMR spectrum of **1** did not permit a decision between meso and racemic forms, the appearance of four C-CH_3 signals (solvent 1,2,4-trichlorobenzene, 92 °C), two of the same intensity and two others differing in intensity from the first two and from each other, being consistent with either *dl*- or *meso*-**1** but not with a mixture of the two (barring accidental isochrony).[12,13] We therefore resorted to crystallization of **1** from (+)-α-pinene ($[\alpha]^{22}_D$ +46.39°, neat), with which it forms a 1:1 inclusion compound,[10] mp 126–128 °C dec.[16]



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Successive recrystallizations from (+)-α-pinene gave crops of 1:1 inclusion compound which were examined polarimetrically[17] after chromatography on silica gel and elution with hexane–chloroform, to remove any residual pinene.[18] The initial crop had $[\alpha]^{27}_{350}$ −4.7° (*c* 0.6, $CHCl_3$),[20] a value which was not substantially increased on further recrystallization.[21] The ^{1}H NMR spectrum ($CDCl_3$) of the solvent-free, partially resolved **1** was the same as that of the unresolved sample. These results provide conclusive evidence that the product obtained by reductive dimerization is *dl*-**1**.[22,23]

The enantiomeric purity of the active samples, though unknown, is believed to be small. Nevertheless, the usefulness of the procedure is fully vindicated by the result, and the present technique should therefore be considered, where applicable, in situations where partial resolution would serve to distinguish between stereochemical alternatives.

Acknowledgment. We thank the National Science Foundation and the NATO Research Grants Programme for support of this work.

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(10) Elemental analysis and ^{1}H NMR spectrum were consistent with the assigned structure.
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