Table I. Product Composition (Absolute Yields) of Peroxylactone **1a**

Mode of decomp	α-Methylstyrene oxide (**4a**)	Acetophenone (**5a**)	Propiophenone (**6a**)	Phenylacetone (**7a**)	Methyl to phenyl ratio[a]
Photolysis[b]	49.5 ± 1.9	11.5 ± 0.9	7.1 ± 0.2	7.6 ± 0.2	0.94
Piperylene-quenched photolysis	47.0 ± 1.3	5.6 ± 0.2	7.1 ± 0.4	15.9 ± 0.9	0.45
Thermolysis[c]	<0.5	7.6 ± 0.2	77.4 ± 1.0	13.8 ± 0.1	5.6

[a] Ratio of methyl (**6a**) to phenyl (**7a**) migration. [b] Irradiation of 1.0 *M* solution in benzene at 350 nm (Rayonet RPR-100) in Pyrex vessel for 24–30 hr. [c] Heating of a 1.0 *M* solution in benzene at 125° (ref 5).

was hydrolyzed with 0.1 *N* $HClO_4$ back to diol **9** (mp 93–93.5°, $[\alpha]^{26}D$ +138.9° in benzene). Since control experiments showed that diol **9** is optically stable under these hydrolytic conditions and since it is known that hydrolysis of epoxides by 0.1 *N* $HClO_4$ results in inverted diol with negligible racemization,[8] epoxide **4b** is 93% optically pure (2*S*)-(+)-1,1-diphenylepoxypropane. Additional control experiments indicated that (2*S*)-(+)-**4b** did not photoracemize under the photolysis conditions of **1b**, although prolonged photolysis converts **4b** into benzhydryl methyl ketone (**8**). Finally, no reacemization of **4b** could be provoked on irradiation in the presence of the individual photoproducts, a synthetic or authentic photoproduct mixture. In short, epoxide **4b** was produced in racemic form in the photolysis of optically active **1b** rather than photoracemized after its production.

The stereochemical results exclude formation of epoxide **4** directly from excited **1** *via* concerted photodecarboxylation. This mechanistic interpretation requires that optically active **1b** must lead to optically active **4b** with retained or inverted configuration.[9] Similarly, **4** cannot be derived from diradical **3**, since decarboxylation with concurrent cyclization must give optically active **4b** from active **1b**. Thus, the stereochemical results demand that the 1-oxatrimethylene diradical **2** serves as a precursor to epoxide **4** and that diradical **2** is sufficiently long-lived to racemize completely before cyclization into **4** takes place. Furthermore, fragmentation into ketone **5** and rearrangement into ketones **6** and **7** compete with cyclization (Table I) and, as expected, racemic **7b** is formed in the photolysis of (*S*)-(−)-**1b** since racemized diradical **2b** is the precursor to the photoproducts. On the contrary, in the thermolysis[5] of (*S*)-(−)-**1b** ketone **7b** was produced with quantitative inversion of configuration since diradical **3b**, the precursor to the thermoproducts, exclusively decarboxylates with concurrent migration of the β substituent. No epoxide is formed in the thermolysis.

It is of interest to compare the methyl–phenyl migratory aptitudes, *i.e.*, the ratio of rearrangement ketones **6a** (methyl migration) and **7a** (phenyl migration). In the last column of the table these data are summarized for the photolysis, piperylene-quenched photolysis, and thermolysis of peroxylactone **1a**. Clearly, in the photolysis of **1a** no differentiation between methyl and phenyl migration is made, yet in the thermolysis, methyl migration outweighs by a factor of 5.6 phenyl migration; however, in the piperylene-quenched photolysis phenyl predominates over methyl migration by a factor of 2.2. As already discussed,[5] the diradical 2-keto-1,5-dioxapentamethylene intermediate **3a** serves as precursor to the thermoproducts of **1a**, for which methyl migrates in preference to phenyl since β scission is the principal driving force for transposing the β substituent as **3a** decarboxylates. Probably in the unquenched photolysis a triplet 1-oxatrimethylene intermediate is the precursor which fails to discriminate between phenyl and methyl migration, while in the piperylene-quenched photolysis a singlet 1-oxatrimethylene intermediate intervenes. However, elaborate photomechanistic experiments are essential to settle the finer details of this novel reaction.

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(10) M.S. Thesis, University of Puerto Rico, June 1970. Part of this work was presented by G. S. A. at the Fifth Junior Technical Meeting, administered by the Puerto Rico Section of the American Chemical Society (Aug 1970), and was awarded the first prize.

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Partial Resolution of Racemic Tertiary Phosphines with an Asymmetric Palladium Complex

Sir:

Optically active tertiary phosphines can serve as key ligands in the transition metal catalyzed asymmetric hydrogenation of olefins.[1,2] They have been prepared through asymmetric syntheses[3–5] or by resolution of racemates,[6,7] most of which require tedious steps. Here we propose a simple method of resolving racemic tertiary phosphines through stereospecific reactions of an asymmetric palladium(II) complex.

Cope and Friedrich[8] reported the preparation of a chelated complex, di-μ-chloro-bis(*N*,*N*-dimethylbenzylamine-2-*C*,*N*)-dipalladium (**1**), from *N*,*N*-dimethylbenzylamine and lithium tetrachloropalladate(II). A similar reaction of *N*,*N*-dimethyl-α-phenethylamine [$[\alpha]^{26}D$

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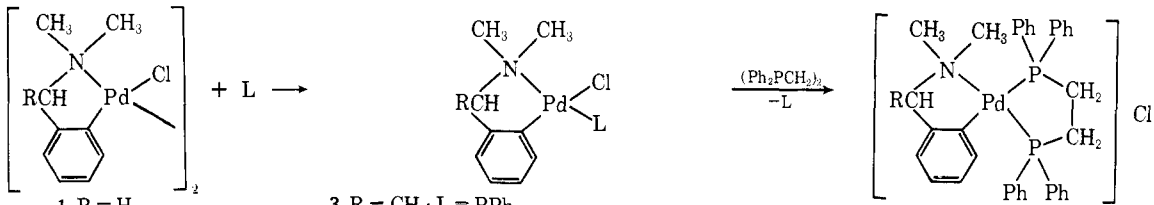

1, R = H
2, R = CH_3

3, R = CH_3; L = PPh_3
4, R = CH_3; L = PPh(α-naphthyl)(o-tolyl)[10]
5, R = CH_3; L = PPh(α-naphthyl)(p-$EtOC_6H_4$-)[11]

6, R = CH_3

-54.4 (neat); lit.[9] $[\alpha]^{25}D$ -71.2 (neat)] with sodium chloropalladate(II) afforded an analogous yellow complex (**2**), mp 194–204° dec, $[\alpha]^{26}D$ +53.4° (*c* 1.22, benzene), in good yield (>90%). The structure of **2** is assigned on the basis of molecular weight determination (vapor pressure osmometry), elemental analyses, and ^1H nmr ($CDCl_3$) which contains signals at δ 1.56 (6 H, d, J = 6.0 Hz, $CHCH_3$), 2.65 (6 H, s, NCH_3), 2.92 (6 H, s, NCH_3), 3.87 (2 H, q, J = 6.0 Hz, CH), and 6.70–7.25 ppm (8 H, m, aromatic). The resonances resemble those of **1**; in particular, the intensity of aromatic protons supports the ortho metalation.

Tertiary phosphines react with **2** in benzene at room temperature, producing mononuclear complexes **3**, **4**, and **5**.

The nmr spectrum ($CDCl_3$) of **3** shows resonances at δ 1.76 (3 H, d, J = 6.3 Hz, $CHCH_3$), 2.76 (3 H, d, J_{PH} = 3.0 Hz, NCH_3), 2.82 (3 H, d, J_{PH} = 1.5 Hz, NCH_3), 3.78 (1 H, m, CH), and 6.3–7.85 ppm (19 H, m, aromatic). The long-range coupling between the *N*-methyl protons and the phosphorus atom strongly favors the trans alignment of the two ligand atoms. A similar geometry was observed in a structurally related palladium complex containing σ metalated allylamine and PPh_3.[12] The two *N*-methyl groups are diastereotopic, owing to the presence of an asymmetric carbon, and are nonequivalent.

Treatment of **2** with 4 mol of racemic α-naphthylphenyl-*o*-tolylphosphine in benzene followed by isolation with *n*-hexane afforded a pale yellow crystalline complex **4**, mp 138–141°, $[\alpha]^{26}D$ +24.6° (*c* 6.33, benzene), in 70% yield. The mother liquor was concentrated and chromatographed on a "Florisil" column using an *n*-hexane–benzene (1:3) mixture as the solvent. The eluate was then concentrated and treated with a small amount of *n*-pentane to give the free phosphine as colorless crystals, mp 107–109°, $[\alpha]^{26}D$ +2.39° (*c* 1.78, CH_2Cl_2), in 65% yield. The analytical and molecular weight data of **4** conformed to the calculated values. The nmr spectrum indicated a trans geometry as found for **3** and also the presence of two isomers in a ratio of 5.7:4.3. The somewhat broad spectrum (C_6D_6) gives rise to a well-defined one at 55° showing resonances at δ 1.45 (1.3 H, d, J = 6.0 Hz, $CHCH_3$), 1.62 (1.7 H, d, J = 6.0 Hz, $CHCH_3$), 2.44 (*a* H, s, CH_3 ring), 2.47 (*b* H, d, J_{PH} = 1.5 Hz, NCH_3), 2.52 (*c* H, d, J_{PH} = 3.0 Hz, NCH_3), 2.62 (*d* H, d, J_{PH} = 1.5 Hz, NCH_3), 2.67 (*e* H, d, J_{PH} = 3.0 Hz, NCH_3), 2.74 (*f* H, s, CH_3 ring) (the total intensity of δ 2.44–2.74 = $a + b + c + d + e + f$ = 9 H), ~3.2 (1 H, broad CH), and 6.50–7.65 ppm (20 H, m, aromatic). The presence of two asymmetric centers in **4** (also in **5**) should create two diastereoisomers. However, such diastereoisomerism does not necessarily lead to the observation of a chemical shift difference in the ligand protons of two isomers.

In addition to the diastereoisomerism, other possible isomerisms indicated by the nmr spectrum of **4** may be geometrical and conformational. The long-range P–H coupling observed at every *N*-methyl proton resonance excludes other geometries for the ligand alignment. The optically active (+)-α-naphthylphenyl-*o*-tolylphosphine recovered from reaction 1, which gives **4a** of an isomer ratio of 5.7:4.3, was used for reaction 2, to give the complex **4b**, whose isomer ratio should be inversed (4.3:5.7), if the origin of isomerism observed in the nmr spectrum is of diastereoisomers. The identical isomer

$$(+)\text{-}\mathbf{2} + 2\text{L} \rightarrow \mathbf{4a} + (+)\text{-L}^* \quad (1)$$

$$(+)\text{-}\mathbf{2} + (+)\text{-L}^* \rightarrow \mathbf{4b} \quad (2)$$

ratio found in the nmr spectra of **4a** and **4b** excludes the possibility of diastereoisomerism. Thus, a conformational isomerism remains which is consistent with the temperature dependence of the nmr spectrum. The steric requirement of the bulky phosphine must be responsible for this isomerism.[13]

The yellow complex **5**, mp 228–230°, $[\alpha]^{26}D$ +46.8° (*c* 5.2, benzene), for which good analytical data were obtained, showed an nmr spectrum (C_6D_6) consistent with a structure analogous to **3** and **4**: δ 0.95 (3 H, t, J = 7.0 Hz, CH_2CH_3), 1.51 (3 H, d, J = 7.0 Hz, $CHCH_3$), 2.57 (6 H, unresolved signal, NCH_3), 3.35 (3 H, m, CH and CH_2), and 6.5–8.3 ppm (20 H, m, aromatic). The α-naphthylphenyl-*p*-ethoxyphenylphosphine, isolated from the reaction of **2** with 4 mol of the racemate, was also optically active, $[\alpha]^{26}D$ −2.57° (*c* 6.80, CH_2Cl_2). Each type of proton in **5** indicates the absence of the isomerism found in **4**. Thus, the *o*-tolyl group appears to exert a particularly efficient steric effect; the large steric requirement compared to the para-substituted aryl group has been embodied by the tris(aryl)phosphines.[14]

Treatment with bis(diphenylphosphino)ethane of **4** and **5** provided optically active α-naphthylphenyl-*o*-tolylphosphine, $[\alpha]^{26}D$ −1.04° (*c* 7.72, CH_2Cl_2) and α-naphthylphenyl-*p*-ethoxyphenylphosphine, $[\alpha]^{26}D$ +0.91° (*c* 6.06, CH_2Cl_2) together with a chelated complex **6**, mp 185° dec, $[\alpha]^{26}D$ +39.9° (*c* 2.68, CH_2Cl_2), Λ_M (molar conductance) 36.9 ohm^{-1} cm^2 mol^{-1} (CH_2Cl_2, 25°). The nmr spectrum ($CDCl_3$) of **6**, being consistent with the structure, contains signals at δ 1.73 (3 H, d, J = 7.0 Hz, CCH_3), 2.55 (6 H, broad s, N-

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$(CH_3)_2$, ~2.6 (4 H, broad, $-CH_2CH_2-$), 3.85 (1 H, m, CH), and 6.55–8.10 ppm (24 H, m, aromatic).

The opposite sign of rotation found in the phosphine recovered from reaction 1 compared to that from complex **4** or **5** demonstrates that the resolution was effected by a stereospecific reaction of the asymmetric complex **2** with the tertiary phosphines. Resolutions of some cyclic olefins[15–19] and asymmetric sulfoxides[20] have been achieved through separation of diastereoisomers of Pt(II) complexes. A stereospecific reaction of $PtCl_2$-(amine*) (C_2H_4) with some olefins has provided optically active olefins.[21] However, a successful extension of this type of reaction to resolution of phosphines is so far unknown. Resolutions of other monodentate racemic ligands with this system are currently under investigation.

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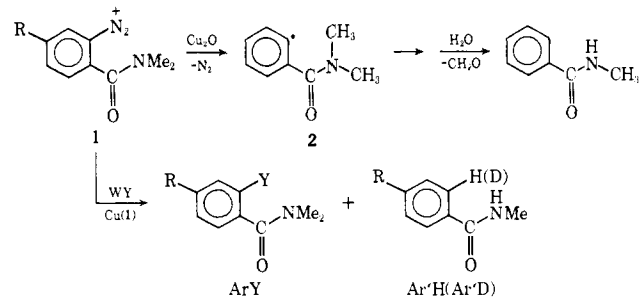
Isotope Effects after the Rate-Determining Step. The Role of Rotational Isomerism in a Hydrogen Transfer[1]

Sir:

Primary deuterium isotope effects are at present utilized in mechanistic studies very predominantly to gain information about rate-determining steps or pre-equilibria.[2] A potentially very informative use involves the study of competitive isotope effects in steps following the rate-determining step in order to discern whether or not a bond to hydrogen is being broken during the product-determining competition. In cases in which reactive intermediates are involved in hydrogen transfers, detailed mechanistic information can often be derived from such studies.

One application of this concept to the 1,5-hydrogen atom transfer which occurs in the radical **2**, produced by cuprous oxide promoted decomposition of the diazonium ion **1** (R = H), provided evidence that the rate of internal transfer is greater than that of rotation about the carbonyl CN bond but less than the rate of rotation about the methyl CN bond.[3]

We now report results which can be interpreted in terms of the behavior of the CC bond during this transfer. In the presence of a reagent WY capable of transferring an atom or radical group Y· to the



aryl radical, two products ArY and Ar'H (the product of internal hydrogen atom transfer) may result. If the same experiment is then performed utilizing the completely methyl-deuterated diazonium ion, the relative yields of ArY and Ar'H (or Ar'D) may or may not change, due to an isotope effect.

Case A. If the external and internal transfers occur either in the same intermediate or in different intermediates whose rate of interconversion is greater than the rate of internal transfer, then the apparent isotope effect will equal the true isotope effect (rate of H transfer/rate of D transfer). The product-determining competition would be between external and internal transfer.

$$\text{apparent isotope effect} = \frac{\text{yield of Ar'H/yield of ArY (unlabeled)}}{\text{yield of Ar'D/yield of ArY } (d_6 \text{ experiment})}$$

Case B. If the two types of transfer occur in different intermediates and if the rate of internal transfer is much greater than the rate of conversion of the intermediate undergoing this transfer to the other intermediate, then there will be no change of yields upon deuteration (apparent isotope effect = 1); in this case the product-determining steps would not include the internal transfer.

The apparent isotope effect at 30° defined as above is in parentheses following the substrate on which it was determined, the medium, and the external atom Y: (1) **1** (R = H), water 1.15 *M* in $CuCl_2$ and 0.64 *M* in NaCl. Y = Cl from $CuCl_2$[4] (14.4); (2) **1** (R = OMe), water 2.19 *M* in $CuCl_2$ and 0.61 *M* in NaCl, Y = Cl from $CuCl_2$[4] (4.7); (3) **1** (R = H), methanol, Y = H from methanol[5] (4.8). The catalyst was cuprous chloride and the solutions were homogeneous for 1 and 2, while solid cuprous oxide was used in 3. However, the state of the catalyst has no apparent effect on the ratio of the reduction product to that of internal transfer since the ratio was the same when CuCl–HCl was used under homogeneous conditions, but in the latter case some contamination with aryl chloride occurred.

The value in 1 is quite reasonable for a combination of a primary and a secondary isotope effect based on the isotope effect determined on the diazonium ion in which each methyl group was dideuterated.[3,6] This

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(5) Labeling studies indicate that the transferred hydrogen comes from the methyl group of the solvent.
(6) The apparent isotope effect in this example would be expected to be greater than 8.1 (this value has been corrected for the CH_2D and CD_3 content of the diazonium ion) found earlier[3] in water for decomposition of the diazonium ion in which both methyl groups are dideuterated, by a factor of about S^3 where S is the secondary isotope effect per deuterium atom. The value 8.1 is lower than the primary isotope effect by a factor S and the present value of 14.4 is greater than the primary effect