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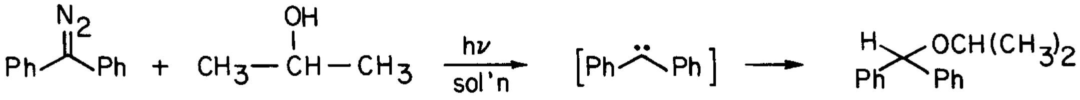
The Chemistry of Diphenylcarbene in Polycrystalline (S)-2-Butanol. The Formation of an Enantiomerically Pure Product of Radical-Radical Coupling

Jose′ Zayas and Matthew S. Platz[1*]

The Department of Chemistry, Ohio State University, Columbus, Ohio 43210

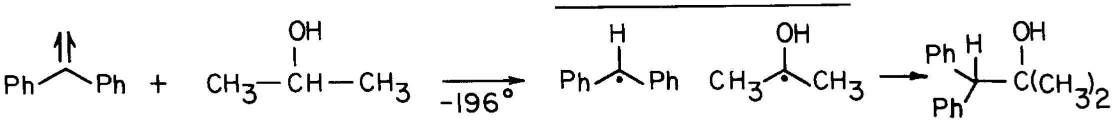
Summary: Photolysis of diphenyldiazomethane 1 in RS-2-butanol in solution between room temperature and -115°C gives ether 5 as the only volatile product. Photolysis of 1 in polycrystalline (S)-2-butanol at -196° gives 5 as well as the 5 products derived from formal CH insertion of the carbene into the matrix. Tertiary alcohol 6 was formed in 15% yield and was shown to be enantiomerically pure.

The unusual low temperature solid state chemistry of aromatic carbenes was first discovered by Moss and coworkers.[2] A few years later the Tomioka group studied the chemistry of aryl carbenes in alcoholic solutions and low temperature polycrystals.[3] For example photolysis of diphenyldiazomethane 1 in a solution of 2-propanol releases diphenylcarbene (DPC) which reacts to form ether 2 in near quantitative yield. This is generally regarded as a diffusion controlled reaction of the low lying singlet state of DPC.



1 DPC 2

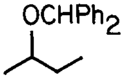
Rapid cooling of the solution of 1 in 2-propanol to -196° produces a polycrystal. Irradiation of the solid again releases DPC, but, under these conditions the major product is alcohol 4. This compound is thought to be formed via reaction of triplet DPC with the matrix to give radical pair 3, followed by radical-radical coupling.[4]



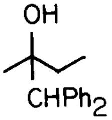
3 4

It appeared to us that if a chiral alcohol was employed as the matrix, a radical pair would again be formed. However, the limited motion available to the radical pair might lead to an adduct with high enantiomeric purity. These expectations were based upon the pioneering work in solid state chemistry of Schmidt.[5] Bartlett and McBride[6] and Lahav and Leiserowitz[7] have found enantiomerically enriched products of radical chemistry formed in chiral single crystals.

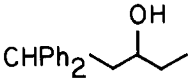
Accordingly, the chemistry of DPC in 2-butanol was examined. Photolysis of 1 in (RS)-2-butanol at room temperature gives ether 5 in quantitative yield. Triplet sensitization (xanthone) of 1 also leads to ether 5 in quantitative yield, pointing to rapid singlet-triplet carbene equilibration under these conditions.[8] Ether 5 is the only product observed upon photolysis of 1 at -74, -100 and -115° in (RS)-2-butanol solution (pure 2-butanol, mp -114°). However, upon crystallization of the matrix, product alcohols such as 6 are observed. At -120° the ratio of 5/ 6 is 3. At -196°, photolysis of a 0.1M solution of (S)-2-butanol gives the product distribution shown below (absolute yields by VPC, the remainder of the material balance is unreacted 1 consumed by the addition of acrylonitrile).[9]



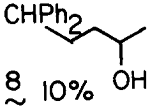
5 9%



6 14%



7 10 %

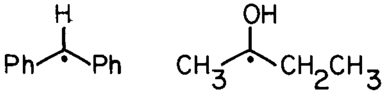


8 10%

All compounds were identified based on comparison with authentically prepared materials. The two diastereomeric alcohols derived from formal CH insertion into the methylene position of (S)-2-butanol were formed in only 1% yield.

Tertiary alcohol 6 was isolated by MPLC. NMR analysis of the benzyhydryl proton of 6 (derived from reaction in racemic 2-butanol) is shown in Figure 1A. Tris[d,d-dicampholyl-methanato]europium (III)[10] (Eu(DCM)$_3$) shift reagent, shifts the benzyhydryl resonance, and splits it into two equally intense well separated resonances. Repetition of this experiment with 6 derived from the reaction of DPC with (S)(+)-2-butanol[11] is shown in Figure 1b. Within our limits of detection, only one enantiomer is present.

There are two possible explanations of this result. Compound 6 may be derived exclusively from singlet DPC. This would require that singlet DPC gives only ether 5 in solution, but both ether and alcohol 6 in the matrix. Kirmse has shown that singlet methylene inserts into CH bonds with retention.[12] However photolysis of 1 in (S)-2-butanol at -196° gives rise to the intense ESR signal of triplet DPC. The ESR signal of DPC is relatively long lived at -196° but has a half life of only 821 sec at -175°. Thus the reaction products are formed under matrix conditions and not upon thawing the sample. If the singlet-triplet splitting is as large as 3 kcal/mol, as has been reported, the equilibrium ratio of singlet to triplet DPC in the matrix is less than 10^{-7}.[13] Therefore, we feel it is unlikely that all of the tertiary alcohol 6 is singlet derived. A substantial amount of 6 must be formed from triplet DPC, via radical pair 9.

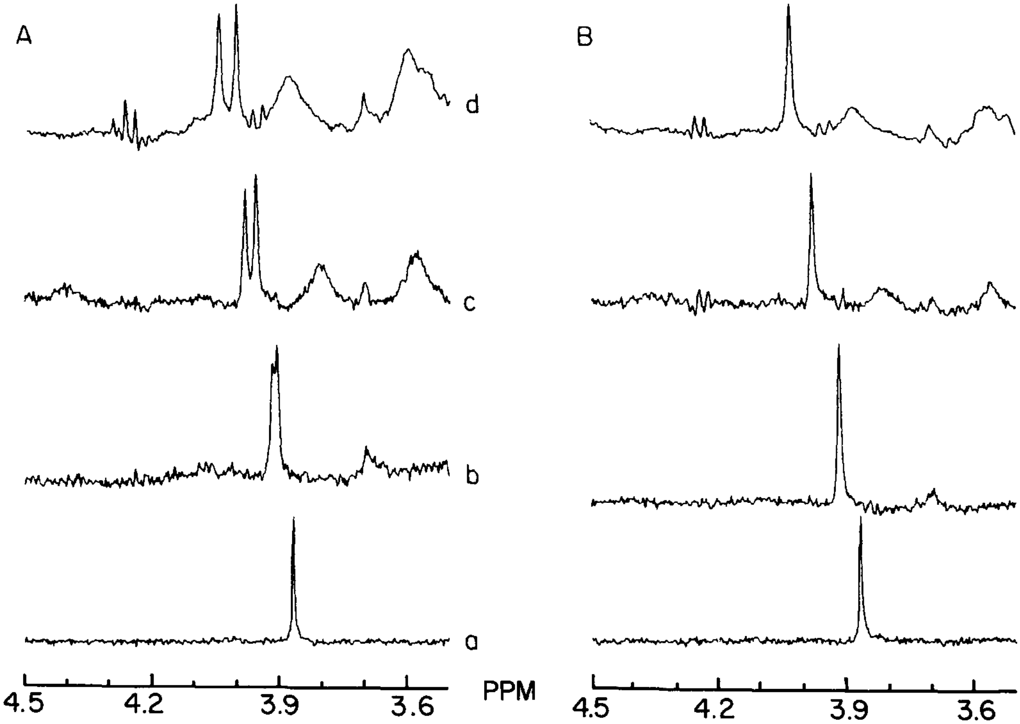


9

Although each component of 9 is itself achiral the radical pair is chiral. The solid state environment prevents motion of the radicals and allows radical-radical coupling in only one sense. Experiments are now in progress to establish the configuration of 6.

Acknowledgement Support of this work by the National Science Foundation is gratefully acknowledged. The authors wish to thank Professor David Hart for encouragement and help with MPLC. FT-NMR spectra (7 tesla) were obtained at The Ohio State University Chemical Instrument Center, using a Bruker WM-300 spectrometer funded in part by National Science Foundation Grant CHE7910019. The spectra were produced by Dr. C. E. Cottrell.

The benzyhydryl proton of 6 in the presence of (a) 0 (b) 5 (c) 10 and (d) 15 mg of europium shift reagent, obtained from (A) RS-2-butanol and (B) S-2-butanol at -196°.



References

1. Fellow of the Alfred P. Sloan Foundation.

2. a. Moss, R. A.; Joyce, M. A. J. Am. Chem. Soc. (1978), 100, 4475-4480.
   b. Moss, R. A.; Huselton, J. K. ibid (1978), 100, 1314-1315.
   c. Moss, R. A.; Joyce, M. A. ibid (1977), 99, 1262-1264.
   d. Moss, R. A.; Dolling, U. H. ibid (1971), 93, 954-960.

3. a. Tomioka, H.; Griffin, G. W.; Nishiyama, K. J. Am. Chem. Soc. (1979), 101, 6009-6012.
   b. Tomioka, H.; Inagaki, T.; Nakamura, S.; Izawa, Y. J. Chem. Soc., Perkin Trans I (1979), 130-135.

c. Tomioka, H.; Izawa, Y. J. Am. Chem. Soc. (1977), 99, 6128-6129.
d. Tomioka, H. ibid (1979), 101, 256-257.
e. Tomioka, H.; Suzuki, H.; Izawa, Y. Chem. Lett. (1980) 293.

4. Platz, M. S.; Senthilnathan, V. P.; Wright, B. B.; McCurdy, C. W., Jr. J. Am. Chem. Soc. (1982), 104, 6494.
5. Schmidt, G. M. J., "Solid State Photochemistry," Monographs in Modern Chemistry 8 Ed., D. Ginsburg, Verlag Chemie, 1976.
6. a. Bartlett, P. D.; McBride, J. M. Pure. Appl. Chem. (1967) 15, 89.
   b. Tremelling, M. J.; McBride, J. M. J. Org. Chem. (1972) 37, 1073.
   See also Scheffer, J. R. Acc. Chem. Res. (1980) 13, 283.
7. a. Chang, H. C.; Popovitz-Biro, R.; Lahav, M.; Leiserowitz, L. J. Am. Chem. Soc. (1982) 104, 614.
   b. Popovitz-Biro, R.; Chang, H. C.; Tang, C. P.; Shochet, N. R.; Lahav, M.; Leiserowitz, L. Pure Applied Chem. (1980) 52 2693.
8. a. Bethell, D.; Stevens, G. and Tickle, P. Chem. Commun. (1970), 792.
   b. Closs, G. L. Top. Stereochem. (1968) 3, 193.
   c. Gaspar, P. D.; Whitsel, B. L.; Jones, M., Jr.; Lambert, J. B. J. Am. Chem. Soc. (1980), 102, 6108.
9. A 1.0 mL aliquot of an ~ 0.1 M diphenyldiazomethane solution in 2-butanol (S or RS) was syringed in equal quantities into three 3 mm pyrex tubes. Each pyrex tube contained sealed capillary tubes, this exposed more solution and shortened the photolysis time The tubes were degassed by cooling and thawing 2-3 times under vacuum then sealed and photolyzed under uv light ($\lambda_{max} \equiv 3500$ Å) at 77K for ~ 5-6 h. The tubes were thawed every 1-1.5 h. The photolyzed tubes were allowed to stand at 77K overnight, then opened. The unreacted DPDM **1** was quenched with acrylonitrile. The excess alcohol and acrylonitrile were removed under reduced pressure (0.01 mm Hg/80^{o}C). The residue was separated by MPLC on silica gel. The observed rotation of 1.8 mg **4** was $[\alpha]_D^{25} = -(9.72 \pm 2.78^{o})$ (C = 0.18 in CCl_4). The large uncertainty is due to the extreme dilution of the sample.
10. Sullivan, G. R., "Chiral Lanthanide Shift Reagents," Chapter in Topics in Stereochemistry Vol. 10, Ed. by E. L. Eliel and N. L. Allinger, Interscience - John Wiley and Sons, New York, 1978 pp 288-329.
11. The S-2-butanol prepared in this work had $[\alpha]_D = 12.45 \pm 0.01^{o}$.
    a. Pickard, R. H.; Kenyon, J. J. Chem. Soc. (T), (1911) 99, 45.
    b. Sprung, M. M.; Wallis, E. S. J. Am. Chem. Soc. (1934) 56, 1717.
    c. Leroux, P. J.; lucas, H. J. J. Am. Chem. Soc. (1951) 73, 41.
12. Kirmse, W.; Buschhoff, M. Chem. Ber. (1969) 102, 1098.
13. a. Closs, G. L.; Rabinow, B. E. J. Am. Chem. Soc. (1976) 98, 8190.
    b. Turro, N. J. Tetrahedron (1982) 38, 809.

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