

gave only the *threo* hydrocarbon **2**. Since this transformation is well documented⁷ as an over-all *syn* addition, it follows that the tetrasubstituted olefin (mp 278–279°) must possess the *E* or *trans* configuration (**5**).

While 1,2-diferrocenyl-1,2-diphenyl-1,2-ethanediol has been suggested as a possible intermediate in the Clemmensen reduction of benzoylferrocene (**6**),⁸ its isolation from that reaction has recently been accomplished in this laboratory.⁵ As expected the pinacol was produced in two diastereomeric forms (mp 202–204 and 207–209°).

In another example of asymmetric selection brought about by the presence of an optically active solvent, it was found that only the higher melting pinacol is optically active, and therefore must be the *threo* isomer **8**.

Treatment of a solution of benzoylferrocene (**6**) in (+)-(*S*)-1-methoxy-2-methylbutane (**4**) with zinc dust and aqueous hydrochloric acid gave the two diastereomeric pinacols in good yield. Separation was achieved by fractional crystallization: the less soluble isomer (mp 207–209°) was optically active (*threo*-**8**, $[\alpha]^{21}_{546}$ 9.2 ± 1.0° (c 1.0, benzene)), while no optical activity could be detected in the more soluble isomer (mp 202–204°, *erythro*-**7**).

Thus, the relative stereochemical features of all the relevant compounds involved in the Clemmensen reduction of benzoylferrocene have been rigorously elucidated by novel means.⁹

(7) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 128 ff.

(8) M. D. Rausch and D. L. Admas, *J. Org. Chem.*, **32**, 4144 (1967).

(9) R. W. Murry, R. D. Youssefyeh, and P. R. Story (*J. Amer. Chem. Soc.*, **88**, 3655 (1966)) have assigned the relative configurations to *cis*- and *trans*-2,5-dimethylhexene-3 ozonides by means of kinetic resolution, a process similar in principle to that used in the present work.

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On the Pyramidal Stability of Allylmethylphenylphosphine¹

Sir:

It has been suggested² that the facile racemization² of allylmethylphenylphosphine (**1**) relative to methylphenyl-*n*-propylphosphine (**2**) might be attributed to an intramolecular allylic rearrangement.³ We wish to report that the thermal racemization of **1** is actually somewhat *slower* than that of **2**, and that allylic rearrangements play no significant role in the racemization of **1**.

Optically active (+)-(*R*)-**1**, prepared by hexachlorodisilane reduction⁴ of (+)-(*R*)-allylmethylphenylphosphine oxide,⁵ undergoes racemization in benzene with first-order kinetics:⁶ $k_{\text{rac}} \times 10^5$ (sec⁻¹) = 1.69 (130°), 7.48 (145°), and 28.0 (160°), whence E_a =

(1) We are grateful to the Air Force Office of Scientific Research for support of this research under Grant No. AF-AFOSR-1188-B.

(2) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Lett.*, 161 (1961).

(3) For a related rearrangement, see T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Amer. Chem. Soc.*, **88**, 3832 (1966).

(4) K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 2788 (1969).

(5) A. W. Herriott and K. Mislow, *Tetrahedron Lett.*, 3013 (1968).

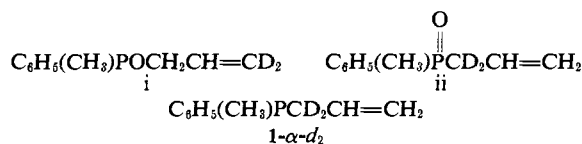
(6) The phosphine **1** is extraordinarily susceptible to decomposition in air, and all measurements must be performed under rigorous exclusion of oxygen.

32.2 kcal/mol and $\log A = 12.8$. In decalin (*cis*:*trans* = 2:1) at 130°, **1** racemizes with $k_{\text{rac}} = 1.44 \times 10^{-5}$ sec⁻¹, compared to $k_{\text{rac}} = 3.34 \times 10^{-5}$ sec⁻¹ for the racemization of **2** under identical conditions.⁷

That an allylic rearrangement is not implicated in the racemization of **1** was demonstrated by the observation that the pmr spectrum of the labeled compound,⁸ **1- α - d_2** , suffered no perceptible change when solutions in C₆D₆ were heated⁶ for prolonged periods of time at temperatures up to 150°. At 175°, a slow exchange of protons at the α - and γ -allylic positions (τ 7.6–7.8 and 4.95–5.36, respectively) was noted, accompanied by slight decomposition. The half-life for exchange at 175°, *ca.* 50 hr, is about 300 times the half-life for racemization at the same temperature, *ca.* 10 min. The allylic rearrangement, whatever its mechanism, is therefore too slow⁹ to account for the racemization, which must occur by pyramidal inversion.

(7) This value is in good agreement with the rate constant, $k_{\text{rac}} = 3.78 \times 10^{-5}$ sec⁻¹, previously reported for the racemization of **2** in decalin at 130° (L. Horner and H. Winkler, *Tetrahedron Lett.*, 461 (1964)).

(8) Reaction of methylphenylbromophosphine with allyl- γ - d_2 alcohol, followed by rearrangement⁵ of the allyl- γ - d_2 methylphenylphosphinite (i) at 100°, gave a phosphine oxide (ii), reduction of which with hexachlorodisilane⁴ afforded the specifically deuterated phosphine (**1- α - d_2**).



(9) In a related observation, M. P. Savage and S. Trippett, *J. Chem. Soc., C*, 1998 (1967), found that in the absence of catalysts diphenyl-(1-phenylallyl)phosphine does not rearrange to cinnamylidiphenylphosphine on heating at 220° for 15 hr.

(10) National Science Foundation Trainee, 1968–1969.

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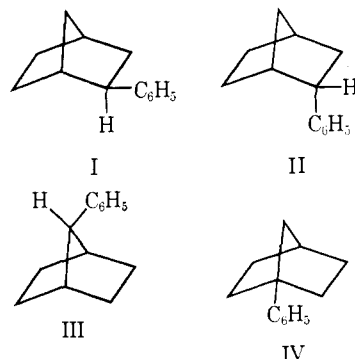
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Stabilization via Carbon–Carbon Hyperconjugation

Sir:

Investigation of the aluminum chloride catalyzed benzylation of the phenylnorbornanes I–IV has re-



vealed some significant findings. These results will be discussed in terms of (a) the general importance of differential solvent effects in stabilization of a charge developed either at or adjacent to an aromatic ring, (b) the importance of C–C hyperconjugation where the C–C bond(s) involved contain an "abnormal" high degree of p character.