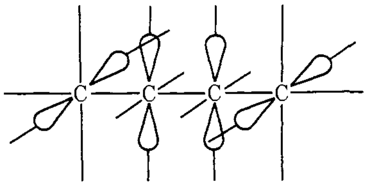
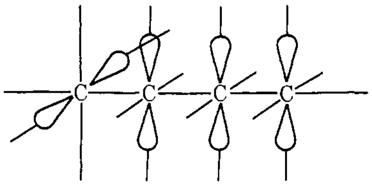


1a



1b

lower in energy than those of type **1a**.[8] Triplets **1b** can account for the results only if the nonplanar distortion is rapidly transferred from one end of the molecule to the other.[2,9]

Acknowledgment. This research was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by National Science Foundation Grant GP-7941.

(8) R. Hoffmann, *Tetrahedron*, **22**, 521 (1966). The calculations were for 1,3-butadiene and no distinction between triplets and singlets was made.

(9) NOTE ADDED IN PROOF. We have discussed our results with Professor G. S. Hammond and Dr. B. M. Monroe. Since, it appears, the main difference in operation is our use of freshly distilled 2,4-hexadienes and since we have some indication that undistilled diene isomerizes somewhat faster than distilled diene, we agree that it is probable that distillation eliminated some photoactive impurity.

(10) (a) Petroleum Research Fund Fellow. (b) Petroleum Research Fund Scholar.

Jack Saltiel, Lewis Metts,[10a] Mark Wrighton[10b]
Department of Chemistry, The Florida State University
Tallahassee, Florida 32306

Received July 23, 1969

Differentiation of Relative Configurations in the *erythro* and *threo* Forms of 1,2-Diferrocenyl-1,2-diphenylethane and 1,2-Diferrocenyl-1,2-diphenyl-1,2-ethanediol

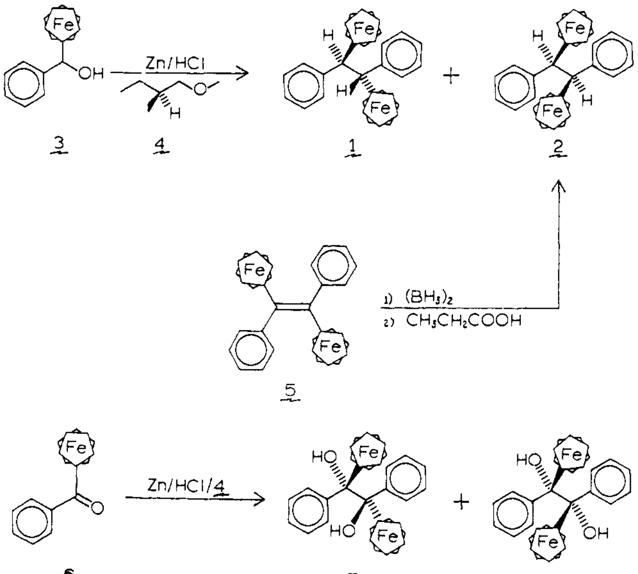
Sir:

A little explored area of stereoselectivity lies in the use of optically active solvents in reaction processes. In principle, one might expect to observe enantiomeric enrichment (asymmetric selection[1]) in the chiral products of such processes if the diastereomeric transition states, resulting from interaction of a chiral solvent with the transition states leading to enantiomeric products, give rise to a $\Delta\Delta G^{\ddagger}$ large enough to provide a significant rate difference in the formation of each enantiomer.[2]

We report now two examples of this type of asymmetric selection which are noteworthy not only because they serve as illustrations of the principle stated above but also because they provide rigorous bases for assignments of relative stereochemistry to previously unassigned stereomers.

The diastereomeric forms (*erythro* and *threo*) of 1,2-diferrocenyl-1,2-diphenylethane[3] occur among the products of Clemmensen reduction of benzoylferrocene.[4] While these stereomers have been separated[5] (mp[3] 218–220° and 276–278°), no configurational assignments have been made. In the present work it has been shown that the lower and higher melting isomers are the *erythro* (**1**) and *threo* (**2**) forms, respectively.

Treatment of (±)-ferrocenylphenylcarbinol (**3**) in (+)-(*S*)-1-methoxy-2-methylbutane (**4**) ($[\alpha]^{21}\text{D}$ 0.032°; lit.[6] $[\alpha]^{18}\text{D}$ 0.34°) with zinc and hydrochloric acid gave the lower melting diastereomer (mp 218–222°) in 45% yield and the higher melting form (mp 276–278°) in 31% yield. Of the two purified products, only the higher melting isomer was optically active ($[\alpha]^{22}_{546}$ 26.1 ± 1.7° (*c* 0.176, benzene)), showing it, therefore, to be the *threo* form **2**.



In another experiment where a higher molar ratio of the optically active solvent **4** to **3** was used (51 as compared to 32 in the initial experiment), the *threo* isomer **2** was produced in lower material yield but in higher optical yield ($[\alpha]^{22}_{546}$ 57.3 ± 5.5° (*c* 0.183, benzene)), indicating perhaps the presence of an interesting dependence of optical yield on the concentration of the chiral solvent.

These results have also allowed assignment of stereochemistry to 1,2-diferrocenyl-1,2-diphenylethene, another product of the Clemmensen reduction of benzoylferrocene[4] which is produced in that reaction in only one of its two diastereomeric forms. Hydroboration of the olefin, followed by treatment with propionic acid,

---

(1) S. I. Goldberg and M. S. Sahli, *J. Org. Chem.*, **32**, 2059 (1967).

(2) Optically active solvents, or solvent additives, that have been used successfully are: (+)-bornyldimethylamine (M. Betti and E. Lucchi, *Boll. Sci. Fac. Chim. Ind. Bologna*, 2 (1940)); (+)-2,3-dimethoxybutane (H. L. Cohen and G. F. Wright, *J. Org. Chem.*, **18**, 432 (1953); A. G. Brook, H. L. Cohen, and G. F. Wright, *ibid.*, **18**, 447 (1953); K. R. Bharucha, H. L. Cohen, and G. F. Wright, *ibid.*, **19**, 1097 (1954); N. Allentoff and G. F. Wright, *Can. J. Chem.*, **35**, 900 (1957); N. Allentoff and G. F. Wright, *J. Org. Chem.*, **22**, 1 (1957)); (+)-mannitol hexamethyl ether and (−)-arabitol pentamethyl ether (N. Allentoff and G. F. Wright, *ibid.*, **22**, 1 (1957)). For an account of others see J. Mathieu and J. Weill-Raynal, *Bull. Soc. Chim. Fr.*, 1211 (1968). For an account of some early unsuccessful experiments in this area see P. D. Ritchie, "Asymmetric Synthesis and Asymmetric Induction," Oxford University Press, 1933, p 78 ff.

(3) A. Berger, W. E. McEwen, and J. Kleinberg, *J. Amer. Chem. Soc.*, **83**, 2274 (1961).

(4) S. I. Goldberg and M. L. McGregor, *J. Org. Chem.*, **33**, 2568 (1968).

(5) S. I. Goldberg and W. D. Bailey, unpublished.

(6) H. G. Rule, E. B. Smith, and J. Harrower, *J. Chem. Soc.*, 376 (1933).

gave only the *threo* hydrocarbon **2**. Since this transformation is well documented[7] 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.

Stanley I. Goldberg, William D. Bailey
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

Received June 30, 1969

On the Pyramidal Stability of Allylmethylphenylphosphine[1]

Sir:

It has been suggested[2] that the facile racemization[2] 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 reduction[4] of (+)-(*R*)-allymethylphenylphosphine 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 = 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 C_6D_6 were heated[6] 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 slow[9] to account for the racemization, which must occur by pyramidal inversion.

---

[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).

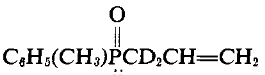
[5] A. W. Herriott and K. Mislow, *Tetrahedron Lett.*, 3013 (1968).

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

[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 rearrangement[5] of the allyl-γ-d_2 methylphenylphosphinite (i) at 100°, gave a phosphine oxide (ii), reduction of which with hexachlorodisilane[4] afforded the specifically deuterated phosphine (**1**-α-d_2).

$C_6H_5(CH_3)POCH_2CH{=}CD_2$
i



$C_6H_5(CH_3)\overset{\overset{\displaystyle O}{\|}}{P}CD_2CH{=}CH_2$

ii

$C_6H_5(CH_3)PCD_2CH{=}CH_2$
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 cinnamyldiphenylphosphine on heating at 220° for 15 hr.

[10] National Science Foundation Trainee, 1968–1969.

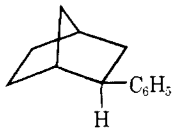
Raymond D. Baechler, William B. Farnham,[10] Kurt Mislow
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received July 22, 1969

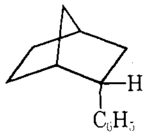
Stabilization *via* Carbon–Carbon Hyperconjugation

Sir:

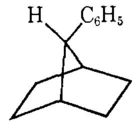
Investigation of the aluminum chloride catalyzed benzoylation of the phenylnorbornanes I–IV has revealed some significant findings. These results will be discussed in terms of (a) the general importance of differential solvent effects in stabilization of a charge developed either at or adjacent to an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



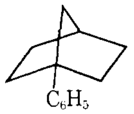
I



II



III



IV