Evidence for Appreciable Phenyl Migration in the Rearrangements of *threo*- and *erythro*-1,2-Diferrocenyl-1,2-diphenylethane-1,2-diols

By S. I. GOLDBERG* and W. D. BAILEY

(*Department of Chemistry, University of South Carolina, Columbia, South Carolina* 29208)

Summary In addition to the predominant pinacolone resulting from ferrocenyl migration in diferrocenyldiphenyl pinacol, the isomeric pinacolone arising from phenyl migration is also established as an important product of the rearrangement.

A STRIKING property of the ferrocenyl group lies in its superiority as a migrating moiety. Thus, in all cases hitherto studied of rearrangements of pinacols corresponding to (I), the ferrocenyl group has been reported to migrate to the exclusion of R (IIa, but no IIb).[1] In view of the generally recognized ability of the phenyl group to migrate in the pinacol–pinacolone rearrangement,[2] it is remarkable that previous results would indicate that when the two groups are present in the same system (I; R = Ph) only ferrocenyl undergoes migration. In contradistinction to this impression we report that, along with the products [IV, V (*threo* and *erythro*),† VI (*trans*),† and VII], we have found ferrocenoylferrocenyldiphenylmethane (VIII) to be produced in the Clemmensen reduction of benzoylferrocene

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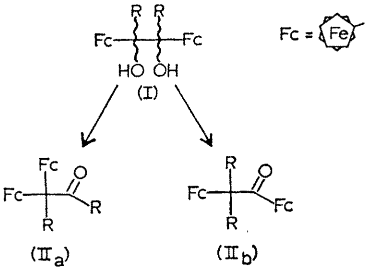
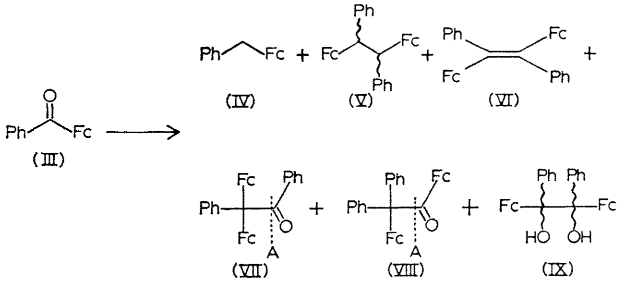
† Unequivocal stereochemical assignments have been made in this laboratory and will be reported elsewhere.

(III). This observation, along with a carefully determined material balance of the reaction, still attests to the superiority of ferrocenyl over phenyl in migration ability but only by a factor between seven and eight.



Compound (VIII) was shown to be isomeric with (VII) by combustion analyses and mass spectra [*m/e* 564 (M^+)]. The two are distinguished by m.p. [(VII) 204—206°; (VIII) 245—246° (dec.)] and other spectral data, the most important features of which are: (i) in the n.m.r. spectrum ($CDCl_3$) of (VII) at δ 4·02, 10H, singlet, unsubstituted rings of two equivalent ferrocene nuclei, while in that of (VIII) at δ 4·08 and 3·97, two 5H singlets, unsubstituted rings of two different ferrocene nuclei; (ii) carbonyl stretching frequency in the i.r. spectrum of (VII) at 1680 cm.$^{-1}$; at 1670 cm.$^{-1}$ for (VIII); (iii) the well known α-fragmentation displayed in the m.s. of ketones[3] (cleavage at bond A) is evidenced by major peaks at *m/e* 459 in the m.s. of (VII) and *m/e* 351 for (VIII).

Finally, each diastereomeric pinacol [*threo*-(IX) and *erythro*-(IX)]† was individually submitted to conditions (ethereal hydrogen chloride) under which rearrangement took place. No stereospecificity was apparent since each diastereomeric pinacol gave the same reaction products, (VI, VII, and VIII) in essentially identical yields. The ratio of (VII) : (VIII) was, however, slightly lower (4—5 : 1) than that found (7—8 : 1) in the Clemmensen reduction products.



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[1] N. Welikey and N. S. Gould, *J. Amer. Chem. Soc.*, 1957, **79**, 2742; M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, 1957, **22** 903; P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1962, 3880; A. N. Nesmeyanov and I. I. Kritskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1962, 352; L. R. Moffett, jun., *J. Org. Chem.*, 1964, **29**, 3626; M. D. Rausch and D. L. Adams, *ibid.*, 1967, **32**, 4144.

[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N.Y., 1953, p. 477.

[3] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, 1964, p. 191 ff.