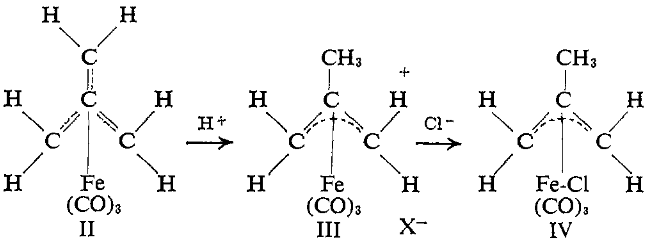
methylene proton peaks of π-allyl-π-cyclopentadienyliron monocarbonyl seen at τ 7.33 (*syn*) and 9.32 (*anti*);[12] and to the band at τ 6.09 of cyclobutadieneiron tricarbonyl.[1]

The $C^{13}$ spectrum[13] of II consists of a singlet at $-18.8 \pm 1.0$ ppm ($CS_2 = 0$), another singlet at $+87.8 \pm 1.0$ ppm, and a triplet at $+139.8 \pm 1.0$ ppm with a splitting of $158 \pm 10$ cps. From the $C^{13}$ satellites in the proton spectrum, each appearing as a doublet with a splitting of 5 cps, $J_{C,H} = 162 \pm 1$ cps; this coupling value is typical for olefin π complexes.[14,15] The low-field $C^{13}$ singlet is at a position typical for metal carbonyls,[14] while the triplet appears at a value intermediate to those of the carbons of butadieneiron tricarbonyl and slightly higher than that of cyclobutadieneiron tricarbonyl.[15] Although the central carbon falls at an unusually low position for a π complex, the difference in shift (52 ppm) between it and the methylene carbons is rather less than would be theoretically predicted[16] for the free molecule (64 ppm) and far less than would be predicted from an empirical comparison with allene.[17] This suggests that the central carbon signal may be furthest shifted upfield, reflecting a stronger interaction with the metal.[14,15]

In view of the extraordinarily facile valence tautomerism seen in some iron carbonyl complexes,[18] structures other than the symmetrical one in which the iron atom is situated directly below the central carbon may be considered. The compound would then be observed as the symmetrical average of three rapidly equilibrating asymmetric structures. In one conceivable set of structures the $Fe(CO)_3$ grouping might be bonded only to an allyl portion of the ligand, in another set to the double bond of methylenecyclopropane. In both cases, however, the inert gas configuration of iron would be violated; and in the first case the average of the nmr signals might be expected at lower field than is found, while the second possibility requires the twisting of methylene groups in and out of plane and the rapid formation and cleavage of carbon–carbon bonds. No broadening of the proton signal was observed at −60°.[19]



Protonation of the ligand occurs in strong acids, as with butadieneiron tricarbonyl and derivatives;[20] a solution of the complex II in 96% $H_2SO_4$ exhibits an nmr spectrum nearly identical with that of π-2-methylallyliron tricarbonyl perchlorate (III),[21,22] with three singlets at τ 8.0, 7.3, and 5.0, the relative intensities being 3:2:2. Treatment of the complex II with $H_2SO_4$, followed by concentrated HCl, gave rise to the known covalent chloride (IV)[21,22] in high yield; the nmr spectrum of IV consists of three singlets at τ 8.01, 6.73, and 5.68.

Further investigations of this and related systems are presently underway.

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[12] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, 3, 1 (1965).

[13] Measurements were taken at 25.143 Mc.

[14] P. C. Lauterbur and R. B. King, *J. Am. Chem Soc.*, **87**, 3266 (1965).

[15] H. G. Preston and J. C. Davis, *ibid.*, **88**, 1585 (1966).

[16] (a) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963); (b) J. A. Pople, *Mol. Phys.*, 7, 301 (1964).

[17] R. A. Friedel and H. L. Retcofsky, *J. Am. Chem. Soc.*, **85**, 1300 (1963).

[18] C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**. 1388 (1965).

[19] That the complex II has a higher melting point and narrower liquid range than either cyclobutadieneiron tricarbonyl or butadieneiron tricarbonyl might be taken to indicate higher symmetry.

[20] G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962).

[21] G. F. Emerson, Dissertation, University of Texas, 1964.

[22] G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind.* (London), 836 (1964).

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## Isoindole Formation by a Novel Rearrangement

*Sir:*

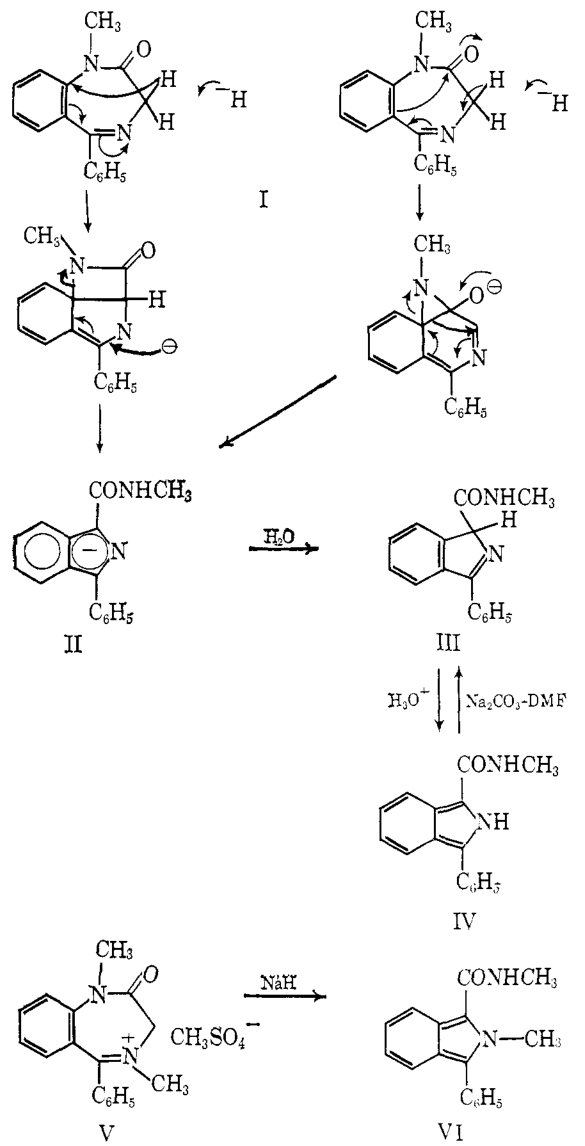
We have found that 1-alkyl-substituted 2,3-dihydro-5-phenyl-(1H)-1,4-benzodiazepin-2-ones of type I readily undergo rearrangement to give N-alkyl-3-phenyl-1-isoindolecarboxamides of type IV, mp 218–220°, $\nu_{NH}^{CHCl_3}$ 3420 and 3480 $cm^{-1}$; $\nu_{C=O}^{CHCl_3}$ 1630 and 1540 $cm^{-1}$; nmr spectrum (DMF-$d_7$) $NHCH_3$, three-proton doublet centered at δ 3.01 ($J = 5$ cps); $\lambda_{max}$ (2-propanol) 221 (ε 14,600), 230 (ε 15,200), 258 (ε 33,000), 295 (ε 5900), and 369 mμ (ε 22,500). *Anal.* Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64. Found: C, 76.88; H, 5.99. This rearrangement was carried out at about 60° in N,N-dimethylformamide solution with 1 equiv of sodium hydride. The yield of isolated product was >80%. Unlike most isoindoles, these compounds are extremely stable and easy to purify. This is probably due to the resonance stabilization imparted to the molecule by the carboxamido function.

There has been much discussion as to whether or not isoindole is more stable than the tautomeric isoindolenine.[1] Lwowski was able to show by nmr studies that, in solution, 1-phenylisoindoles are in equilibrium with the tautomeric isoindolenines,[1] while Bender and Bonnett have recently reported that 1,3,4,7-tetramethylisoindole exists mainly as the isoindolenine tautomer.[2] For the first time, we have been able to isolate both possible tautomers of an isoindole. By treating a solution of IV in N,N-dimethylformamide with sodium carbonate we obtained the isoindolenine III,[3] mp

[1] See D. F. Veber and W. Lwowski, *J. Am. Chem. Soc.*, **86**, 4152 (1964), and references cited therein.

[2] C. O. Bender and R. Bonnett, *Chem. Commun.*, 198 (1966).

[3] Structure III is preferred to the other possible isoindolenine structure on the basis of the shift in the frequency of the carbonyl absorption in the infrared spectrum and the chemical shift of the methyl group in the nmr spectrum when compared to the corresponding spectra for com-


I II III IV V VI

223–228°, mmp with IV 190–202°; $\nu_{NH}^{CHCl_3}$ 3410 cm$^{-1}$; $\nu_{C=O}^{CHCl_3}$ 1680 and 1530 cm$^{-1}$; nmr spectrum ($CDCl_3$) $NHCH_3$, three-proton doublet centered at $\delta$ 2.65 ($J$ = 5 cps), NH $\delta$ 6.55, 10 protons in aromatic region (band) centered at $\delta$ 7.5; $\lambda_{max}$ (2-propanol) 253 m$\mu$ ($\epsilon$ 13,700). *Anal.* Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64. Found: C, 76.79; H, 5.34.

The isoindolenine III could be reconverted quantitatively to the thermodynamically more stable isoindole IV simply by treatment with dilute acid or strong aqueous base.

The mechanism of the rearrangement can be explained by an initial attack of hydride ion at the 3 position of the benzodiazepinone nucleus (removal of one of the acidic protons) followed by a ring contraction to give either of the tricyclic intermediates as shown. Either intermediate would then undergo further rearrangement to give the salt of the isoindole carboanion II.

The 1,4-dimethyl-2-oxo-1,4-benzodiazepinium salt V could also, by treatment with sodium hydride, be rearranged to the corresponding 2,N-dimethyl-3-phenyl-1-isoindolecarboxamide (VI), mp 185–188°; $\nu_{NH}^{CHCl_3}$ 3460 cm$^{-1}$; $\nu_{C=O}^{CHCl_3}$ 1640 and 1530 cm$^{-1}$; nmr spectrum ($CDCl_3$) N-$CH_3$, $\delta$ 4.08; $NHCH_3$, three-proton doublet centered at $\delta$ 3.05 ($J$ = 5 cps); $\lambda_{max}$ (2-propanol) 222 ($\epsilon$ 23,200), 260 ($\epsilon$ 25,750), 298 ($\epsilon$ 5000), 306 ($\epsilon$ 5050), and 356 m$\mu$ ($\epsilon$ 19,000). *Anal.* Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10. Found: C, 77.59; H, 5.85. The isoindole structure of VI was proved by comparison with an authentic specimen, prepared from the known 2-methyl-1-phenylisoindole and methyl isocyanate.[4]

A detailed account of this investigation will be the subject of a forthcoming publication.

**Acknowledgment.** We wish to thank Professor G. Büchi for many helpful suggestions and his valuable advice.

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pound IV. These shifts indicate that the $CONHCH_3$ group is attached to a saturated center on the isoindolenine nucleus.

(4) W. Theilacker and O. R. Leichtle, *Ann.*, **572**, 124 (1951).

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## The Pinacol Rearrangement of 2-*p*-Anisylnorbornane-2,3-*cis,exo*-diol[1]

*Sir:*

Collins, *et al.*[2] have aptly demonstrated that the rearrangement of 2-phenylnorbornane-2,3-*cis,exo*-diol (I) in concentrated sulfuric acid at 0° takes place with rearrangement of the norbornane carbon skeleton *via* a hydride shift from the 6 to the 1 position,[3] accompanied by an intramolecular migration of hydrogen from C-3 to C-2 to give 3-*endo*-phenyl-2-norbornanone (II). Roberts[4] has suggested that the 2,4-dimethoxy analog of I could give *endo*-3-hydrogen migration during the pinacol rearrangement, as it is conceivable that the two methoxy groups could stabilize the tertiary classical open carbonium ion III at the expense of the bridged ion IV.

In connection with another study in the norbornane system we had prepared 2-*p*-anisylnorbornane-2,3-*cis,exo*-diol (V) and have carried out its rearrangement in concentrated sulfuric acid at 0°. While some sulfonation did take place, the only nonacidic compound isolable was 3-*endo*-*p*-anisyl-2-norbornanone (VI) in *ca.* 50% yield. The preparations of the compounds involved in this study and their structural assignments are as follows.

Peracetic acid oxidation of 2-*p*-anisylnorbornene followed by lithium aluminum hydride reduction gave the diol V. The performic acid oxidation procedure which previously afforded I[5] proved unsatisfactory as a pathway to V, apparently due to the more rapid alkene dimerization reaction.[6]

The structure of V was confirmed by comparison with I in the 3-$\mu$ region of the infrared, where both showed strong intramolecular OH···O hydrogen bonds,[7] and

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[1] This work was supported by a research grant from the National Science Foundation.

[2] C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Am. Chem. Soc.*, **86**, 4913 (1964); B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966).

[3] If one renumbers the carbon atoms after the initial Wagner–Meerwein rearrangement, it is apparent that a 6,1-hydride shift becomes a classical 6,2-hydride shift.

[4] See ref 2, p 4915.

[5] D. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961).

[6] D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

[7] L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954); **80**, 5950 (1958).