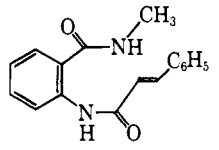
facile loss of carbon dioxide and rearrangement necessary in transforming cyclopenin (VI, R = H) to viridicatin (I, R = H) and not required of the previous proposals (II, III, and IV) which contained the viridicatin skeleton intact. Synthesis of the postulated structure was undertaken to resolve these doubts.

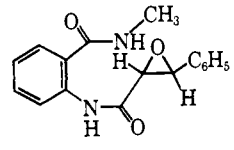
2-Amino-N-methylbenzamide with *trans*-cinnamoyl chloride gave 2-(N-methylcarboxamido)-*trans*-cinnamanilide (VII) (mp 187°)[8] which was epoxidized with *m*-chloroperbenzoic acid to the glycidamide VIII (mp 166–167°). Excess potassium *t*-butoxide in *t*-butyl alcohol (to form the diamidate anion) lead to ring closure to 3,4-dihydro-3-hydroxybenzyl-4-methyl-1H-1,4-benzodiazepin-2,5-dione (IXa) (mp 199°); only one of the two possible diastereomers was obtained. A small amount of dehydroxybenzylated product, X,[9] was produced, presumably from IXa by a retroaldol reaction.

Acetylation of IXa provided the O-acetyl derivative IXb (mp 233–235°) which thermally underwent elimination to 3-benzylidene-3,4-dihydro-4-methyl-1H-1,4-benzodiazepine-2,5-dione (XI) (mp 208–209°); over-all yield from VII to XI was 58%. Only one stereoisomer of the benzylidene compound XI was isolated; it was assigned the *trans* configuration shown on the following evidence.

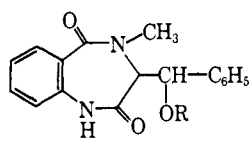
The *trans*-cinnamate retained its configuration during amide formation and epoxidation as indicated by the coupling constants for the vinyl protons of VII (J = 16 cps) and the α and β hydrogens of the β-phenylglycidamide VIII (J = 2.5 cps). A single diastereomer was



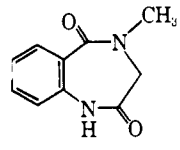
VII



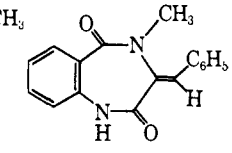
VIII



IXa, R = H
b, R = $COCH_3$



X



XI

obtained for IXa and its configuration is unchanged by acetylation. Pyrolytic *cis* elimination then yields the *trans*-benzylidene XI. Confirmation for this assignment was obtained by isolation of both isomers from condensation of X and benzaldehyde.[10] The major isomer (identical with XI) had N-methyl and vinyl hydrogen resonances at δ 3.2 and 6.95, respectively, while in the minor isomer they were at δ 3.5 and 6.72. The upfield shift for the N-methyl signal in the *trans* isomer is due to shielding from the benzene ring π cloud; the downfield shift of the vinyl hydrogen signal in the *trans* isomer is due to deshielding by the carbonyl.[11]

(8) Satisfactory elemental analyses were obtained for all compounds in the synthetic sequence, and in each case the spectroscopic data (uv, ir, nmr) supported the assigned structures.

(9) P. M. Carabateas and L. S. Harris, *J. Med. Chem.*, **9**, 6 (1966).

(10) J. L. Wong, unpublished work, this laboratory.

(11) Similar observations have been made with 2-acetyl-5-benzylidenecreatinine [A. R. Frasca and E. B. Dennler, *Chem. Ind.* (London), 509 (1967)].

The epoxidation of XI was complicated by adverse steric and electronic factors, and no precedent exists for epoxidation of a double bond so substituted. A large variety of methods gave no reaction, overoxidation, or traces of epoxide. Finally, conditions were found (*m*-chloroperbenzoic acid, room temperature, 14 days) which gave a 37% yield of epoxide. That this material was *dl*-cyclopenin (VI, R = H) (mp 194–195°) was established by comparison with natural *l*-cyclopenin [mp 179–180°, $[\alpha]^{23}_{5462}$ −301° (*c* 1.0, methanol)].[12] The ir ($CHCl_3$), uv (C_2H_5OH), and nmr ($CDCl_3$) spectra of the two compounds were identical, the R_f's on tlc were the same, and both gave viridicatin with acid. This synthesis establishes the structure of cyclopenin beyond doubt and confirms the previous proposal.[4] It also allows the assignment of relative stereochemistry as shown in VI.

(12) Prepared from a crude isolate obtained by H. R. while a guest in the laboratory of Dr. H. Raistrick in March 1956.

Herman Smith, Paul Wegfahrt, Henry Rapoport

Department of Chemistry
University of California, Berkeley, California

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Hydrogen–Deuterium Exchange in a Cobalt–Nitrogen Complex

Sir:

The recently reported nitrogen complexes of cobalt[1–5] are useful models for the nitrogen-binding site of the nitrogenase enzyme.[6] The activation energies for coordination of N_2 are very low, and the relative affinities for N_2, H_2, and NH_3[4] seem to be similar to those of the enzyme. Therefore, it was of interest to study the exchange of D_2 with the hydridonitrogen complex, $HCo(N_2)(PPh_3)_3$.[5]

Surprisingly, when benzene solutions of $HCo(N_2)(PPh_3)_3$ were allowed to equilibrate with deuterium gas at 25°, the amount of hydrogen introduced into the gas far exceeded the amount available by exchange with the lone Co–H. Indeed, the extent of exchange corresponded to roughly 19 hydrogens per mole of cobalt complex. For example, the gases from incubation of 5.1×10^{-5} mol of $HCo(N_2)(PPh_3)_3$ with 6.5×10^{-5} mol of D_2 (25°, 24 hr) contained 88% H_2, 11% HD, and 0.5% D_2. The calculated values for random statistical exchange of 19 H's are 87% H_2, 12% HD, and 1% D_2. This result suggests that not only the Co–H but also six aryl H's per phosphine ligand exchange with the D_2 atmosphere.

The extent and position of aromatic deuteration were confirmed by the following experiment. A solution of 1.0 mmol of $HCo(N_2)(PPh_3)_3$ in 50 ml of benzene was stirred with 21 mmol of D_2 at 25° for 6 days.

(1) A. Misono, Y. Uchida, and T. Saito, *Bull. Chem. Soc. Japan*, **40**, 700 (1967).

(2) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967).

(3) A. Sacco and M. Rossi, *ibid.*, 316 (1967).

(4) A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Am. Chem. Soc.*, **89**, 3071 (1967).

(5) J. A. Ibers, *Chem. Commun.*, 96 (1968).

(6) R. W. F. Hardy and R. C. Burns, *Ann. Rev. Biochem.*, in press.

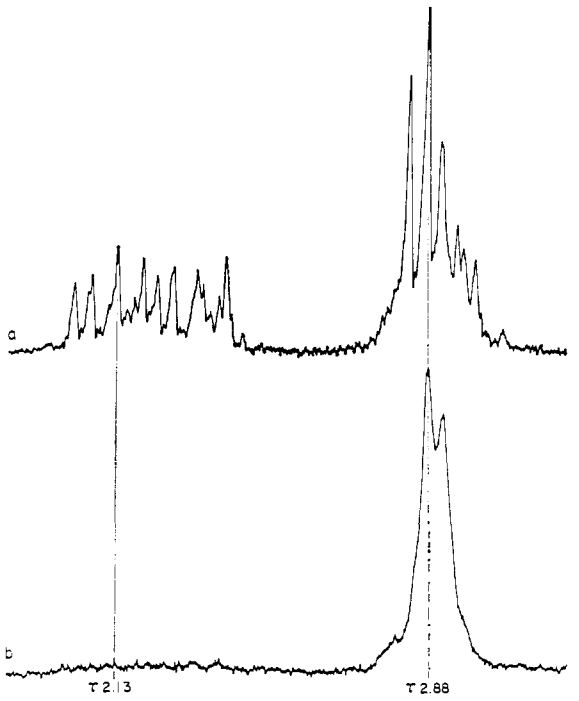
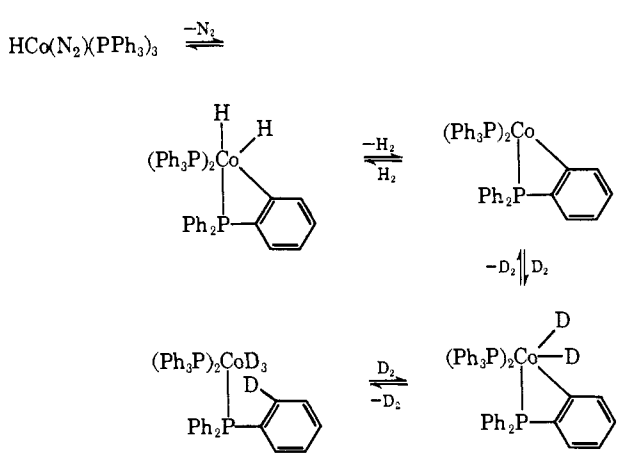


Figure 1. Proton nmr spectra of normal (a) and deuterated (b) triphenylphosphine oxide at 60 MHz in C_6D_6 solution with $(CH_3)_4Si$ internal standard.

The final gas composition was 12% H_2, 43% HD, and 45% D_2 *vs.* a calculated random composition of 10% H_2, 43% HD, and 47% D_2. The complex was decomposed with 30% H_2O_2, and the spectrum of the recovered triphenylphosphine oxide was recorded in C_6D_6 solution in which the *ortho*-proton signal is well separated from those of the *meta* and *para* protons (Figure 1a). The *ortho*-proton signal is almost eliminated in this spectrum (Figure 1b) and the *meta* + *para* signal is collapsed because coupling with the *ortho* protons does not occur. Hence, it appears that most, if not all, of the deuterium introduced into the triphenylphosphine ligands is in the positions *ortho* to the phosphorus atoms.

The most likely explanation for this result is that a rapid equilibrium occurs in which the *ortho* C–H bonds add to a "coordinately unsaturated" cobalt complex (Scheme I). The final complex shown in this series of equilibria is an *o*-deuterioaryl analog of $(Ph_3P)_3CoD_3$ reported by Sacco and Rossi.[3] The irreversible addition of an *ortho* proton of an aryl ligand in a square-planar d^8 complex, $(Ph_3P)_3IrCl$, has been reported by Bennett and Milner.[7] An equilibrium involving addition of a methyl CH of a methylphosphine ligand has been shown by Chatt and Davidson.[8]

Scheme I



(7) M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967).
(8) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

G. W. Parshall

Contribution No. 1425, Central Research Department Experimental Station, E. I. du Pont de Nemours and Company Wilmington, Delaware 19898

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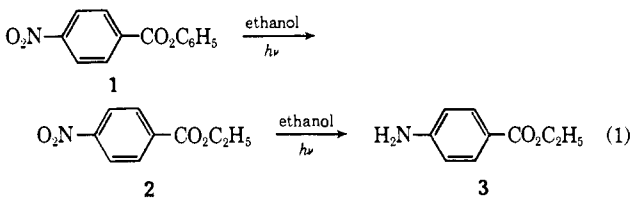
Photochemistry of Nitrobenzoate Esters and Related Nitroaromatic Compounds. Some Novel Reduction and Esterification Reactions[1]

Sir:

During studies to assess qualitatively the influence of solvent and substituents on the course of the photo-Fries reaction,[1b,2-4] we irradiated[5] an ethanol solution of phenyl 4-nitrobenzoate (**1**) and found that, rather than a Fries rearrangement, a relatively rapid transesterification, followed by reduction of the nitro group to an amino group, comprised the major reaction pathway (eq 1). That the observed solvolysis step was indeed



light mediated was indicated by noting that a solution of **1** in ethanol after being heated at 50–55° for 21.5 hr provided **2** in only 2.3% conversion, while during irradiation approximately one-third of **1** was converted to a mixture of **2** and **3** in only 2 hr. After 11.5-hr irradiation, the starting material was completely consumed and the major product consisted of a mixture of phenol, **2**, and **3** in the molar ratio 2.26:1:1.39. The yield of phenol was approximately 60%; a number of minor products have not yet been characterized. The reduction step in eq 1 was realized separately by the irradiation of ethanol solutions of **2**. In less than 1 hr about 25% of **2** had been converted to **3**, and after 12 hr the yield of **3** was greater than 60% as determined gas chromatographically. Work-up of the reaction mixture, which involved acid treatment of the crude product, regeneration of basic material, silica gel

(1) (a) Photochemical Studies. VI. (b) For part V, see, R. A. Finnegan and D. Knutson, *J. Am. Chem. Soc.*, **89**, 1970 (1967). (c) This work was supported by Grant GP-5785 from the National Science Foundation.
(2) H. Kobsa, *J. Org. Chem.*, 27, 2393 (1962).
(3) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963).
(4) R. A. Finnegan and J. J. Mattice, *Tetrahedron*, **21**, 1015 (1965).
(5) In all cases, solutions approximately 1% (w/v) were irradiated with a 450-W, medium-pressure mercury lamp (Hanovia 79A36) housed in a double-walled quartz immersion well. Progress of reaction was followed by infrared and gas chromatographic analysis of aliquots.