TABLE I

MÖSSBAUER DATA FOR *cis-trans* ISOMERIC PAIRS [Cu(Co^{57})] SOURCE AT ROOM TEMPERATURE

Compound	Temp., °K.	Effect, %	Q.S., mm. sec.$^{-1}$	I.S., mm. sec.$^{-1}$	Shift from Na$_2$[Fe(CN)$_5$NO]·2H$_2$O, mm. sec.$^{-1}$
cis-{C$_5$H$_5$FeCOP(C$_6$H$_5$)}$_2$	78	12	1.60 ± 0.05	−0.04 ± 0.05	+0.52 ± 0.05
trans-{C$_5$H$_5$FeCOP(C$_6$H$_5$)$_2$}$_2$	78	9	1.66 ± 0.05	−0.04 ± 0.05	+0.52 ± 0.05
cis-{C$_5$H$_5$FeCOAs(CH$_3$)$_2$}$_2$	78	3	1.42 ± 0.05	+0.05 ± 0.05	+0.61 ± 0.05
trans-{C$_5$H$_5$FeCOAs(CH$_3$)$_2$}$_2$	78	3	1.57 ± 0.05	+0.05 ± 0.05	+0.61 ± 0.05

source and an SnO$_2$ absorber, both at room temperature.

The two absorber pairs used were *cis-* and *trans-*{C$_5$H$_5$FeCOP(C$_6$H$_5$)$_2$}$_2$ and *cis-* and *trans-*{C$_5$H$_5$FeCOAs(CH$_3$)$_2$}$_2$ synthesized by methods described elsewhere.[7] The infrared spectra of these compounds in CS$_2$ solution all show a single absorption band in the region 1900 to 1950 cm.$^{-1}$ which is ascribed to a terminal carbonyl group, and no absorption in the bridging carbonyl region. The dimeric and diamagnetic nature of these compounds leads to the conclusion that the two iron atoms are joined by two bridging phosphorus (or arsenic) atoms, and from the resultant nearly tetrahedral environment around the iron atom it is seen that *cis* and *trans* isomers can be formulated. The assignment of configuration is based largely on proton nuclear magnetic resonance data, which show, for example, a single methyl resonance for *trans*-{C$_5$H$_5$FeCOAs(CH$_3$)$_2$}$_2$ and two methyl resonances for the *cis* isomer.

As has been previously noted, organometallic iron compounds do not show an appreciable resonance effect at room temperature, presumably due to the fact that the Debye temperature of these compounds is well below 300°K. For this reason, the present samples were examined at liquid nitrogen temperature in the usual transmission geometry.

The Mössbauer data at 78°K are summarized in Table I. In each case two well-defined peaks of essentially equal intensity were observed, from which it is concluded that the Gol'danskii effect[8] in these compounds is of only minor importance. From these data it is also evident that the isomer shift is identical for the *cis* and *trans* compounds within the limits of accuracy of the experiment, in consonance with the requirements of the partial isomer shift correlation previously reported.[5] The indicated error of ±0.05 mm. sec.$^{-1}$ represents an uncertainty of about 0.6 channel in the position of each of the two resonance maxima required to define the isomer shift or the shift from the centroid of the spectrum of the standard. The small shift from zero velocity arises from the particular choice of a host matrix for the Co^{57} activity and is thus not related directly to the magnitude of the error in the position of the resonance maximum. Recent comparison studies[9] have shown that nominally identical sources of Co^{57} diffused into copper are not identical with respect to their isomer shifts from zero velocity for a given absorber. We have therefore included in the last column of Table I the apparent isomer shift from the center of the Na$_2$[Fe(CN)$_5$NO]·2H$_2$O spectrum as an additional reference point. These data should permit the direct comparison of the present data with those obtained using other recoil-free sources of Co^{57}.

Moreover, using the relationship between the nuclear magnetic resonance shift of the cyclopentadienyl pro-

tons in CS$_2$ [with respect to an internal standard of (CH$_3$)$_4$Si] and the partial isomer shift appropriate for the cyclopentadienyl group,[5] it is possible to calculate a value for the partial isomer shift for a bridging phosphorus atom. This value is −0.010 mm. sec.$^{-1}$ for the *cis* isomer and −0.020 mm. sec.$^{-1}$ for the *trans* isomer, in good agreement with that calculated earlier.[5] A similar calculation for the arsine bridged compounds yields a value of −0.04 mm. sec.$^{-1}$ for both the *cis* and the *trans* isomer. The apparent reversal in the isomer shifts—that is, the fact that the phosphorus bridged compounds with more negative isomer shifts than the arsenic bridged compounds give rise to less negative partial isomer shifts of the bridging groups—is due to the difference in the cyclopentadienyl proton n.m.r. shifts and hence to the relative value of the appropriate partial isomer shift of the cyclopentadienyl group.

The absorbers used in this work were made up to have essentially the same quantity of Fe^{57} per unit area, and thus the magnitudes of the resonance effect should be directly comparable. From the data in Table I it is seen that the resonance effect in the arsenic compounds is lower by a factor of 3–4 than that in the analogous phosphorus compounds. This effect is due to the strong K-edge absorption of the 14.4 kev. γ-ray of Fe^{57} by arsenic, and thus high-precision data on arsenic-containing compounds are difficult to obtain since long periods of data accumulation (with the concomitant problems of electronic drift) are required to achieve good counting statistics. For this reason the present data are being extended to related antimony compounds in a further test of the additivity of partial isomer shifts in Mössbauer spectra of iron–organic compounds.

(10) Shell Development Corporation, Emeryville, California.

RUTGERS, THE STATE UNIVERSITY   R. H. HERBER
NEW BRUNSWICK, NEW JERSEY
MELLON INSTITUTE   R. G. HAYTER[10]
PITTSBURGH 13, PENNSYLVANIA

Chimonanthine. A One-Step Synthesis and Biosynthetic Model

Sir:

The suggested[1,2] biosynthesis of the calycanthaceous alkaloids is represented by an oxidative dimerization of N-methyltryptamine (II), itself a natural product (dipterin[3]). The various members of the group are derivable from the tetraaminodialdehyde (IV). However, the dimer (III) would be expected to yield chimonanthine (I) directly in conditions unfavorable to hydrolytic cleavage of the indolenine or di-(N-acetal) groupings. Thus by achieving the much sought β,β'-radical coupling of the indole nucleus, we are now able

(7) R. G. Hayter, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963; *J. Am. Chem. Soc.*, **85**, 3120 (1963.)

(8) This effect, which is experimentally observed as an unequal intensity of the two peaks of a quadrupole split resonance line, even in the absence of preferred crystal orientation, was first accounted for by Gol'danskii, *et al.*, *J. Exptl. Theoret. Phys.* (USSR), **43**, 448 (1962); *Phys. Letters*, **3**, 344 (1963).

(9) The authors are indebted to Dr. G. K. Wertheim and Professor R. L. Collins for data regarding their Cu(Co^{57}) sources prior to publication.

(1) R. Robinson and H. J. Teuber, *Chem. Ind.* (London), 783 (1954).

(2) R. B. Woodward, N. C. Yang, T. J. Katz, V. M. Clark, J. Harley-Mason, R. J. F. Ingleby, and N. Sheppard, *Proc. Chem. Soc.*, 76 (1960).
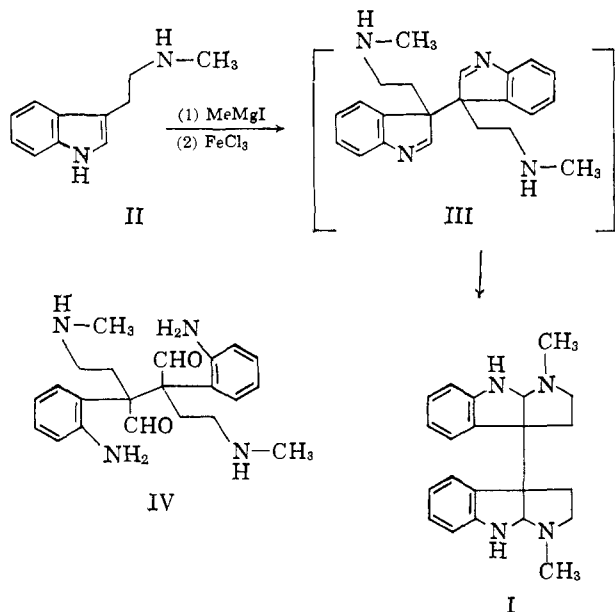
(3) N. K. Yurashevskii, *J. Gen. Chem. USSR*, **10**, 781 (1940).

to report a dramatically simple synthesis of *dl*-chimonanthine.

In view of the difference in acidity between the secondary amino and indolic hydrogens, it was assumed that addition of one equivalent of methylmagnesium iodide to the dibasic dipterin would form the ionic[4] "magnesylindole" derivative. N-methyltryptamine, prepared[5] in high yield from tryptamine,[6] was added in ether solution to an equivalent amount of methylmagnesium iodide under anhydrous conditions. Treatment of the mixture with ethereal ferric chloride, then aqueous ammonium chloride, and isolation by ether extraction gave as major product (20% yield) *dl*-chimonanthine, m.p. 183–185° from ether or benzene. Comparison of the mass spectrum,[7] showing the very characteristic symmetrical scission, with the published data,[8] gave complete correspondence of cracking pattern and abundance. The ultraviolet (λ_{max} 248, 305 mμ) and infrared (CHCl$_3$) spectra were also superimposable on those of natural *l*-chimonanthine.[9] Investigation of a crude sample[10] of the latter afforded a small amount of optically inactive material, m.p. 201–203°, which displayed small but significant differences in its n.m.r. spectrum, while retaining the other properties[11] of *l*-chimonanthine. We consider this new alkaloid to be *meso*-chimonanthine, and comparison of this with one of our synthetic fractions, m.p. 201–202°, reveals that these are identical.

A previous route[12,13] to this series of alkaloids involving coupling at the oxindole level would seem to be a less relevant biosynthetic model than the extremely direct *indole* dimerization. The present demonstration of the reaction affirms the possibility of such a mecha-

(4) M. G. Reinecke, H. W. Johnson, and J. F. Sebastian, *Tetrahedron Letters*, 1183 (1963).

(5) This preparation was devised by Dr. A. C. Day, University of Oxford, England.

(6) We are grateful to Dr. A. Brossi, of Hoffmann–LaRoche, Nutley, New Jersey, for a lavish gift of this material.

(7) Thanks are due to Dr. H. Budzikiewicz, Stanford University, for his kind determination of this spectrum.

(8) E. Clayton, R. I. Reed, and J. M. Wilson, *Tetrahedron*, **18**, 1495 (1962).

(9) We thank Dr. G. F. Smith, Manchester University, England, for a very generous gift of *l*-chimonanthine.

(10) Dr. G. F. Smith also has this sample under study.

(11) H. F. Hodson, B. Robinson, and G. F. Smith, *Proc. Chem. Soc.*, 465 (1961).

(12) J. B. Hendrickson, R. Rees, R. Goschke, *ibid.*, 383 (1962).

(13) J. B. Hendrickson, R. Goschke, and R. Rees, to be published. We thank Dr. Hendrickson for a copy of his manuscript before publication, and a sample of synthetic chimonanthine for comparison.

nism *in vivo* providing an exact analogy for incorporation experiments.

The resolution of our synthetic materials, and further aspects of this convenient route to the "parent" member of the series (and, by interconversion, the other structural isomers) are under investigation.

UNIVERSITY OF BRITISH COLUMBIA   A. I. SCOTT
VANCOUVER 8, BRITISH COLUMBIA   FRANK McCAPRA
CANADA   E. S. HALL

RECEIVED NOVEMBER 22, 1963

Reaction Pathways in the Photochemical Conversion of Diphenylamines to Carbazoles

Sir:

Quantum yield and flash-photolytic studies have been made of the effects of oxygen and temperature on the photoconversion of diphenylamines to carbazoles, using diphenylamine itself (DPA) and the N-methyl and N-phenyl (TPA) derivatives. These experiments confirm our suggestion[1] that a transient species absorbing at 610 mμ (probably a closed-ring, polar structure) is an intermediate in the reaction and establish the existence of two concurrent pathways for the conversion. One pathway requires oxygen as reagent, while the other appears to involve a unimolecular step with very low or zero activation energy. This work also resolves an apparent contradiction between our aerobic oxidation studies,[1] done mainly on N-meDPA, and the recent work of Bowen and Eland[2] on DPA, in which it is stated that oxygen inhibits the reaction.

In hexane at room temperature, in the presence of oxygen, the quantum yield of carbazole production (φ), as $f(O_2)$ concentration, passes through a maximum whose location depends on the particular amine. For DPA, $\varphi_{max} \approx 0.08$ at $[O_2]_{max} \approx 2 \times 10^{-5}$ M, while for N-meDPA, $\varphi_{max} = 0.30$ at $[O_2]_{max} = 6 \times 10^{-4}$ M. In air-saturated hexane ($[O_2] = 3 \times 10^{-3}$ M), φ (DPA) is less than 0.02, but φ (N-meDPA) is much less oxygen-sensitive. In order to reduce φ (N-meDPA) to 0.02, oxygen pressures in excess of 3 atm. are required. The residual φ-values, in exhaustively degassed solution, are about 0.05 for DPA and less than 0.01 for N-meDPA. The maximum is thus much more pronounced for the methyl derivative, while oxygen inhibition is more apparent for DPA.[2]

Flash experiments, under favorable conditions of yield and lifetime (TPA in degassed glycerol, at −60°) show that 610 is formed from the amine triplet. Moreover, in TPA solutions containing oxygen, the disappearance of 610 and formation of carbazole take place at the same rate. The maximum in the φ *vs.* $[O_2]$ curve can thus be understood as a combined effect of oxygen quenching of the triplet (yield-limiting at high $[O_2]$) and oxygen-dependent conversion of 610 to carbazole (yield-limiting at low $[O_2]$).

In degassed solution, down to −70°, 610 decays back to the parent amine by a first-order process, with $E_A = 10$ kcal. Below −70°, 610 decay becomes independent of temperature and irreversible. Steady ultraviolet irradiation of N-meDPA in degassed hexane at −76° produces N-me carbazole with $\varphi \approx 0.2$. The temperature-independent 610 decay appears to correspond to this carbazole-forming reaction.

All these observations are consistent with the reaction scheme shown at the top of the next page. Using this mechanism, with values of k_4, k_6/k_5, k_7, k_8, and k_9 measured directly in flash experiments, and taking k_2 and k_5 to be diffusion-controlled, the φ *vs.*

(1) K. H. Grellmann, G. M. Sherman, and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 1881 (1963).

(2) E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc.*, 202 (1963).