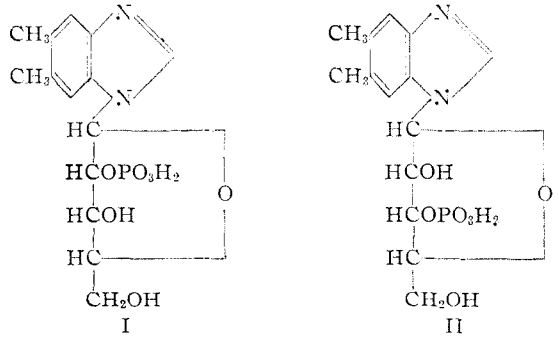
gen sulfide. The product crystallized from water–acetone. After one recrystallization, α-ribazole phosphate melted at 235–236° dec. (capillary) 240–241° (micro-block). The melting point of this material in admixture with the vitamin $B_{12}$ degradation product was not depressed. *Anal.* Found: C, 46.72; H, 5.25; N, 7.81; P, 8.33. The absorption spectra of aqueous solutions were: at *ca.* *p*H 2, maxima at 277 mμ and 285 mμ; at *ca.* *p*H 11, maxima at 249 mμ, 280 mμ, and 288 mμ.

The phosphorylation of 5′-trityl-α-ribazole was also effected by means of dibenzylchlorophosphonate.[3] The benzyl groups were subsequently removed by hydrogenolysis. The product was purified as the crystalline dibrucine salt, m.p. 169–173° (capillary). *Anal.* Found: C, 62.66; H, 6.34; N, 7.31; P, 2.46.

Brown and Todd[4] have separated adenylic acids a and b by paper chromatography using a solvent system (5% aqueous disodium hydrogen phosphate–isoamyl alcohol) developed by Carter.[5] Paper strip chromatography of the crystalline phosphate from vitamin $B_{12}$ and the synthetic α-ribazole phosphate with this system showed that the two samples were identical and consisted of only one isomer (2′ or 3′ phosphate), having an $R_F$ value of 0.74. The α-ribazole phosphate was detected as a fluorescent spot after the dried paper chromatogram had been sprayed with 2% acetic acid. Furthermore, when the two samples of α-ribazole phosphate were treated by the method of Brown and Todd[4] for the isomerization of the adenylic acids, *i.e.*, by heating under reflux in 80% acetic acid for ten minutes, each was converted into a mixture of approximately equal parts of the 2′- and 3′-isomers. The isomers had $R_F$ values of 0.78 and 0.74.

The identification of this crystalline phosphate as the 2′-phosphate (I) or the 3′-phosphate (II) is



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not possible on this evidence, and this differentiation is comparable to the situation on adenylic acids a and b.[4] Furthermore, the possibility of phosphoryl migration during the acid hydrolysis of vitamin $B_{12}$ indicates that the position of the linkage of the phosphate group to ribose in this crystalline α-ribazole phosphate is not necessarily the same as it is in vitamin $B_{12}$.

Dr. Gladys A. Emerson of the Merck Institute for Therapeutic Research tested α-ribazole phosphate for vitamin $B_{12}$ activity[6] in rats and found that it has substantially the same activity as α-ribazole, or about one four-hundredth the activity of vitamin $B_{12}$.

(3) F. R. Atherton, H. T. Openshaw and A. R. Todd, *J. Chem. Soc.*, 384 (1945).

(4) D. M. Brown and A. R. Todd, *ibid.*, 44 (1952).

(5) C. E. Carter, THIS JOURNAL, **72**, 1466 (1950).

(6) G. Emerson, F. W. Holly, C. H. Shunk, N. G. Brink and K. Folkers, *ibid.*, **73**, 1069 (1951).

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RECEIVED SEPTEMBER 30, 1952

## ON THE INTERNAL ROTATION OF A POLYPEPTIDE CHAIN

*Sir:*

A recent publication[1] states that an 11-atom ring structure of a polypeptide chain is possible, consistent with the published X-ray data, if the azimuthal angle of internal rotation about –NH–CO– axis is different by about 30° from that of the planar peptide structure. However, Pauling and Corey consider that such a structure is unacceptable.[2] During the past years we have carried out some experimental work to determine the internal rotation about various single bonds contained in a polypeptide chain. For example, in the case of $CH_3$–CO–NH–$CH_3$ it was proved by the ultraviolet measurement that this molecule has a planar configuration and the deviation of 30° from the planar position seems improbable.[3] According to our infrared, Raman and dipole measurements on this substance, the two $CH_2$– groups are in the *trans* position with respect to each other in the liquid state and in aqueous and carbon tetrachloride solutions of various concentrations.[3] We can derive the same conclusion for the structure of the peptide bonds of a polypeptide chain from the infrared measurement. Therefore, we cannot agree with those Pauling and Corey models which have the *cis* configurations of peptide bonds.[4]

Pauling and Corey also discussed the internal rotation about single bonds of a polypeptide chain other than that about peptide bonds.[5] As to the internal rotation we have been publishing many papers[6] and our polypeptide model is based on the conclusion of these papers.[7] The presence of six potential minima in one rotation about a single bond suggested by Pauling and Corey[5] is not compatible with our experimental result. Generally we have three potential minima in one complete internal rotation.[6] We are planning to publish further our experimental results concerning the

(1) M. L. Huggins, THIS JOURNAL, **74**, 3963 (1952).

(2) L. Pauling and R. B. Corey, *ibid.*, **74**, 3964 (1952).

(3) S. Mizushima, T. Shimanouchi, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba and O. Fujioka, *ibid.*, **72**, 3940 (1950).

(4) L. Pauling and R. B. Corey, *Proc. Nat. Acad. Sci.*, **38**, 86 (1952).

(5) L. Pauling and R. B. Corey, *ibid.*, **37**, 729 (1951).

(6) As to the summary of these works see S. Mizushima, Reilly Lectures, University of Notre Dame, 1951. See also S. Mizushima, Y. Morino, I. Watanabe, T. Shimanouchi and S. Yamaguchi, *J. Chem. Phys.*, **17**, 591 (1949).

(7) T. Shimanouchi and S. Mizushima, *Kagaku*, **17**, 24, 52 (1947); *J. Chem. Soc., Japan*, **21**, 1 (1948). See also S. Mizushima, T. Shimanouchi, M. Tsuboi, T. Sugita and E. Kato, *Nature*, **164**, 819 (1949); *J. Chem. Soc. Japan*, **23**, 176 (1950).

internal rotation of simple molecules closely related to the polypeptide chain.[8]

(8) See also S. Mizushima, T. Shimanouchi, *et al.*, THIS JOURNAL, **73**, 1330 (1950); **74**, 270 (1952); *Nature*, **169**, 1058 (1952).

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## HYDROGEN TRANSFER REACTIONS ACCOMPANYING THE COBALT CATALYZED SYNTHESIS FROM ACETYLENE, CARBON MONOXIDE AND METHANOL

*Sir:*

Acetylene reacts with carbon monoxide and methanol in presence of a cobalt catalyst and it is known that in this reaction a mixture of esters can be obtained.[1] Using a dissolved cobalt catalyst, *e.g.*, $(Co(CO)_4)_2$ the reaction proceeds much more rapidly and no metallic cobalt is found in the reaction products.

Acting at very low temperature (90–110°) and at high CO pressure (200–300 atm.) in presence of 2% dissolved $[Co(CO)_4]_2$ as catalyst the following products are identified, the yield being dependent primarily on the concentration of the acetylene:

| | Product | Yield, g./100 g. $C_2H_2$ | Notes |
|---|---|---|---|
| 1 | Methyl acrylate | 14–24 | Identification by reaction with $CH_2N_2$[2] |
| 2 | Cyclopentanone | Traces | 2,4-Dinitrophenylhydrazone m.p. 146°[3] mix. m.p. with an authentic sample, 146° |
| 3 | $\Delta^2$-Cyclopentenone-1 | 2–10 | B.p. (760 mm.) 154–155°; $n^{20}D$ 1.4787; U.V. spectrum[4] $\lambda$ = 309 m$\mu$, log $\epsilon$ = 1.50; 2,4-dinitrophenylhydrazone m.p. 165–166°,[5] *anal.* N: found 21.8; calcd. for $C_{11}H_{10}O_4N_4$: 21.37 |
| 4 | Dimethyl fumurate | 1–14 | M.p. 101.2–101.4°; mixture m.p. with an authentic sample, 101.2° |
| 5 | Dimethyl succinate | 70–250 | M.p. 19°, $n^{20}D$ 1.4484 |
| 6 | Trimethyl ethanetricarboxylate | 35–50 | M.p. 34.5°; *anal.* found C, 47.19; H, 5.89; calcd. for $C_8H_{12}O_6$, C, 47.058; H, 5.882 |
| 7 | Dimethyl $\gamma$-ketopimelate | 40–60 | M.p. 56°; *anal.* found: C, 53.3; H, 6.85; calcd. for $C_9H_{14}O_5$: C, 53.46; H, 6.93 |

The formulas of the products 1 and 5 are in agreement with the addition of one or two molecules of carbon monoxide and methanol to one molecule of acetylene.

On the contrary the composition of the other products does not correspond to the sum of molecules of acetylene, carbon monoxide and hydrogen but shows a higher or lower hydrogen content. Therefore any solid catalyst being absent the products 2, 4, 6, 7, must arise from some homogeneous hydrogen transfer reaction like the one observed[6] in the synthesis of esters or amides from olefins, carbon monoxide and alcohols or amines.

(1) G. Natta and P. Pino, Swiss Patent Ges. N. 46197 (June 24, 1949); *La Chimica e l'Industria*, **31**, 249 (1949).
(2) *Ber.*, **33**, 3595 (1901).
(3) THIS JOURNAL, **57**, 758 (1935).
(4) *Ibid.*, **74**, 514 (1952).
(5) *Ann.*, **539**, 207 (1939).
(6) G. Natta, P. Pino and R. Ercoli, THIS JOURNAL, **74**, 4496 (1952).

The hydrogen necessary for the synthesis of the cycloketones and $\gamma$-ketopimelic acid dimethyl ester, does not seem to be supplied by the dehydrogenation of methanol because no appreciable amounts of formaldehyde, or its derivatives, has been detected.

Also the formation of hydrogen by reaction between carbon monoxide and water cannot proceed to a large extent because anhydrous reagents were used, and no dehydration products of the reactants (for example, dimethyl ether) has been found in the liquid or gaseous reaction products.

Presently it seems more probable that the succinic acid dimethyl ester acts as hydrogen donor the first dehydrogenation product being the fumaric acid dimethyl ester.

Moreover, only a small amount of the last compound is detected in the reaction products, the most part being transformed in ethanetricarboxylic acid trimethyl ester, by reaction with carbon monoxide and methanol.

The very low temperature at which the synthesis of esters and ketoesters seems to take place,[7] from the intermediate olefinic compounds carbon monoxide and methyl alcohol, is not surprising if we consider the hydrogen transfer reactions as typical chain reactions.

We can conclude that hydrogen transfer reactions take place very easily with cobalt catalysts in presence of high carbon monoxide pressure. The cobalt catalysts probably act as hydrogen carriers according with the equilibrium

$$[Co(CO)_4]_2 + H_2 \rightleftarrows 2[Co(CO)_4]H$$

which can occur at high carbon monoxide pressure in presence of movable hydrogen atoms.

**Acknowledgment.**—The authors are indebted to the Lonza A.G., Basel, Switzerland, which generously supported this research.

(7) G. Natta, P. Pino and E. Mantica, *Gazz. Chim. Ital.*, **80**, 650 (1950); *La Chimica e l'Industria*, **32**, 201 (1950).

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RECEIVED SEPTEMBER 2, 1952

## THE MECHANISM OF VIRUS ATTACHMENT TO HOST CELLS. III[1]

*Sir:*

The chemical basis of virus attachment to its host cell has not previously been elucidated. Earlier studies from this laboratory have shown that the first phase of invasion of a host cell by a bacterial virus consists in establishment of strong electrostatic bonds between sites on the two surfaces.[2,3] Some of the evidence on which these conclusions were based is as follows: The initial attachment is exceedingly rapid, being diffusion-limited; its rate is constant between 0 and 37°; it can be readily reversed by appropriate changes of the ionic constituents of the medium; and its

(1) This work was supported by Research Contract No. AT-(29-1)-787 with the Division of Biology and Medicine, U. S. Atomic Energy Commission.
(2) T. T. Puck, A. Garen and J. Cline, *J. Exp. Med.*, **93**, 65 (1951).
(3) A. Garen and T. T. Puck, *ibid.*, **94**, 177 (1951).