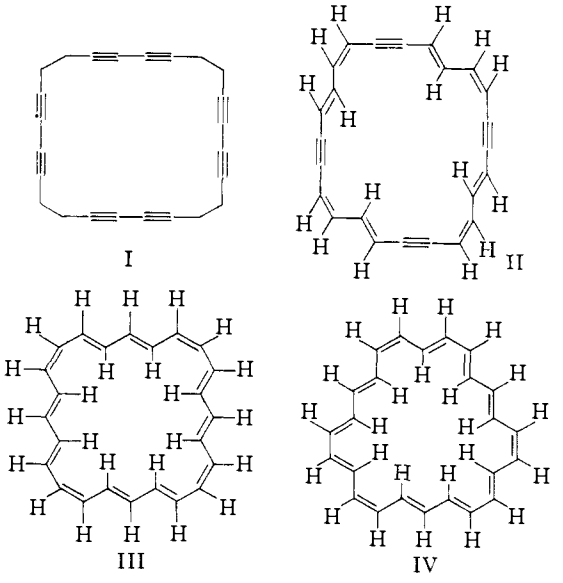
The empirical formula was $C_{24}H_{16}$ (Found: C, 94.65; H, 5.20): $\lambda_{max.}^{chloroform}$ 240, 330 and 346 mμ (ϵ = 28,000, 125,000 and 206,000); $\lambda_{max.}^{benzene}$ 333 and 350 mμ (ϵ = 120,000 and 208,000), with absorption up to *ca.* 600 mμ ($\epsilon_{400\ m\mu}$ = 2,270, $\epsilon_{450\ m\mu}$ = 2,020, $\epsilon_{500\ m\mu}$ = 1,070, $\epsilon_{550\ m\mu}$ = 275). The infrared spectrum (KBr) showed bands at 3.31(m), 4.63 (w), 6.28(m), 7.07(m), 7.72(m), 8.49(m), 9.11(m), 10.27(s), 10.75(s), 11.81(m), 13.11(m) and 13.24 (m). Hydrogenation in dioxane over platinum smoothly yielded cyclotetracosane, m.p. and mixed m.p. 46–47°.



I II III IV

This rearrangement product is clearly a completely conjugated octaene-tetrayne. It is most likely cyclotetracosa-1,7,13,19-tetra-(*cis*)-ene-3,9-15,21-tetra-(*trans*)-ene-5,11,17,23-tetrayne (II), a molecule which may be not completely planar in view of the presence of four *cis*-double bonds.

Partial hydrogenation of II in benzene over a "Lindlar" palladium catalyst[4] followed by chromatography on alumina gave first a yellow crystalline compound ($\lambda_{max.}^{pentane}$ 306 and 314 mμ), then unchanged II and finally *ca.* 15% of a substance crystallizing from ether as very dark-blue, almost black, needles (dark violet in solution). The last compound, which decomposed when heated, had empirical formula $C_{24}H_{24}$ (Found: C, 92.14; H, 7.62); $\lambda_{max.}^{isooctane}$ 264, 350, 363 and 512 mμ (ϵ = 12,100, 195,000, 201,000 and 1,740); $\lambda_{max.}^{benzene}$ 360, 375 and 530 mμ (ϵ = 183,000, 195,000 and 1,720), with absorption up to *ca.* 750 mμ ($\epsilon_{600\ m\mu}$ = 1,270, $\epsilon_{650\ m\mu}$ = 610, $\epsilon_{700\ m\mu}$ = 180). The infrared spectrum (KBr) showed bands at 3.32 (m), 7.06(w), 7.73(m), 10.13(s), 10.36(s), 10.55(s), 10.77(w), 10.90(w), 11.47(w), 12.03(w), 12.25(w), 12.85(w) and 13.28(m). Full hydrogenation gave cyclotetracosane, m.p. and mixed m.p. 44–46°.

The properties of the blue substance show it to be cyclotetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecaene (CTD). The ultraviolet spectrum and color indicate that all 12 double bonds are part of one chromophoric system and *trans*-addition of hydrogen therefore appears to have taken place, as in the synthesis of cycloöctadecanonaene (CON).[5] The present evidence does not permit a definite distinction to be made between the 1,7,13,19-tetra-(*cis*)-ene structure III and the 1,9,17-tri-(*cis*)-ene structure IV. We consider, however, that the spectral evidence favors IV (requiring the inversion of one *cis*-double bond of II during the hydrogenation), the more planar structure of the two. It should be noted that CTD cannot be converted to a more stable isomer, *e.g.*, with iodine in boiling benzene.

CTD is a 24π-electron system and, unlike CON,[5] does not comply with Hückel's rule for aromaticity [presence of $(4n + 2)$ π-electrons]. In fact, CTD is much less stable than CON. Thus, CTD in daylight and air at room temperature after 24 hr. is over 99% destroyed, while CON is unchanged; CTD in dilute benzene solution in daylight after 12 days is 80% destroyed, while CON is largely unchanged.

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RECEIVED JULY 6, 1959

METABOLISM OF DL-PIPECOLIC ACID-2-C^{14} [1]

Sir:

Pipecolic acid (piperidine-1-carboxylic acid) was found to be a product of lysine catabolism in the rat,[2] in plants[3] and in *Neurospora*.[4] The suggestion that this compound was an intermediate between lysine and α-aminoadipic acid[2] was based only on the scanty evidence of a small conversion of lysine to α-aminoadipic acid observed in guinea pig liver homogenate,[5] and the fact that both lysine and α-aminoadipic acid form glutaric acid.[2,5] The present communication presents data which show that pipecolic acid does indeed lie on the lysine pathway to α-aminoadipic acid and confirms the role of the latter compound in lysine breakdown in the rat.

DL-Pipecolic acid-2-C^{14} (specific activity 0.3 mc./mmole) was prepared by enzymic deamination of DL-lysine-2-C^{14} and hydrogenation of the product.[6] The material was shown to be pure by paper chromatography and autoradiography.

Labeled pipecolic acid (1μc.) was incubated at 37° for 1.5 hours in each of three flasks containing: 2 ml. of rat liver mitochondria prepared in 0.25 *M* sucrose; 50 μmoles of phosphate buffer, *p*H 7.4; 3 μmoles of ATP; 3 μmoles of Versene; 12 μmoles of Mg^{++}; 25 μmoles of L-α-aminoadipate; the total volume was 3 ml./flask.

After deproteinization, the combined media were fractionally eluted from Dowex 50-(H^+) with 1 *N* HCl. The L-α-aminoadipic acid was located with ninhydrin.

(1) Aided by research grant (T-89A) from the American Cancer Society and the cancer research funds of the University.

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(4) R. S. Schweet, J. T. Holden and P. H. Lowy, *J. Biol. Chem.*, **211**, 517 (1954).

(5) H. Borsook, C. L. Deasy, A. J. Haagen-Smit, G. Keighley and P. H. Lowy, *ibid.*, **176**, 1383 (1948).

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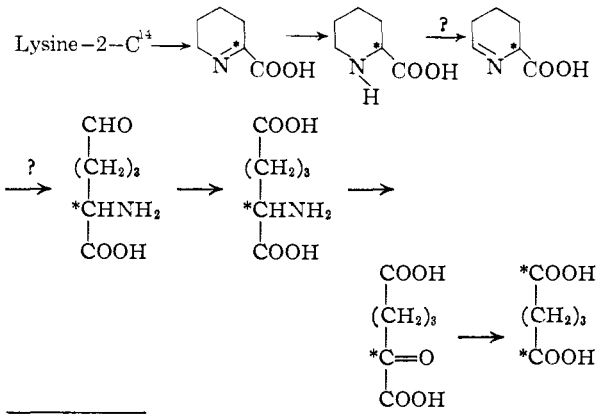
A major problem in the isolation of α-aminoadipic acid is the removal of traces of contaminating glutamic acid. The authors feel that this was not ruled out in the original isolation of this compound[5] since, in the present work, the criterion of constant specific activity by recrystallization was found not to be a guarantee of radiopurity. Therefore, isolation was undertaken. The combined fractions containing α-aminoadipic acid were run on six papers (Whatman no. 1) for 1.5 hours at *p*H 6.4 on a high voltage electrophoresis apparatus[7] under toluene (2000 v.). The α-aminoadipate (2500 c./m.) was located, eluted from the paper and converted to ornithine by the Schmidt reaction. Part of the product was treated on paper as above. The ornithine was eluted and then run on paper in butanol–pyridine–water (1:1:1) for two days (descending), located and eluted. A small amount of α,γ-diaminobutyric acid resulting from the Schmidt reaction with contaminating glutamic acid was found on the paper 2 inches below the ornithine. From approximately 250 c./m. put on the final paper, 145 c./m. was obtained after elution of the ornithine. There thus can be little doubt that α-aminoadipic acid is a product of pipecolic acid breakdown in rat liver mitochondria.

As additional evidence supporting the position assigned to pipecolic acid, we have ascertained that DL-pipecolic acid-2-C^{14} is converted to carboxy-labeled glutaric acid both by rat liver mitochondria and the intact rat.

Taken together these data lend strong support to the degradative pathway for lysine outlined here



(7) H. Michl, *Monatsh. Chem.*, **82**, 489 (1951).

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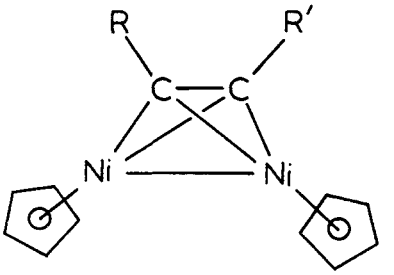
CYCLOPENTADIENYLNICKEL–ACETYLENE COMPLEXES

Sir:

In a recent communication[1] it was suggested that the bridging groups in dicobalt octacarbonyl are not coplanar with the two metal atoms, but occupy two of the octahedral sites about each metal atom, whilst three others are occupied by terminal carbonyl groups and the sixth is unoccupied. The same arrangement would be expected for the isoelectronic di-iron octacarbonyl anion. Both these substances are noted for their catalytic activity[2] and for the ease with which they react with acetylenes.[3] These properties may be explained by the suggested geometry as the unoccupied octahedral position should be readily attacked by the substrate.

An infrared spectral study of the neutral isoelectronic dicyclopentadienyldinickel dicarbonyl (I), first prepared by Fischer and Palm,[4] suggests that it also belongs to the same group. Thus (I) exhibits two carbonyl stretching frequencies in the bridging carbonyl region (at 1879(m) and 1838(s) $cm.^{-1}$), in contrast to the related dicyclopentadienyldi-iron tetracarbonyl in which the two bridging carbonyl groups have been shown to lie in a plane which contains the metal atoms which are essentially fully octahedrally coördinated.[5] These considerations led us to study the reactions of (I) with various acetylenes. The components react smoothly on heating in toluene and in every case both carbonyl groups are replaced by one molecule of acetylene. Tolan yields the complex (II, R = R′ = C_6H_5) as black crystals, m.p. 149–150° (Found: C, 68.0; H, 5.2; M, 409. $C_{24}H_{20}Ni_2$ requires: C, 67.7; H, 4.7; M, 426). Phenylacetylene similarly affords (II, R = C_6H_5, R′ = H) as black needles m.p. 132–133° (Found: C, 62.1; H, 4.3; $C_{18}H_{16}Ni_2$ requires: C, 61.8; H, 4.6) whilst hexyne-3 gives a dark green oil (II, R = R′ = C_2H_5) (Found: C, 58.3; H, 6.3. $C_{16}H_{20}Ni_2$ requires: C, 58.3; H, 6.1). Complexes of the type (II) form black crystals or dark green oils, and the solids are stable in air. The oils, or solutions of solid complexes in hydrocarbon solvents, are, however, slowly decomposed in air and solutions in ethanol or acetic acid are rapidly oxidized. Reduction of (II, R = R′ = C_6H_5) with sodium and alcohol in liquid ammonia yields dibenzyl showing that the diphenylacetylene residue is bonded only to the nickel atoms.

This reduction together with the formal analogy of the reactions of (I) and of cobalt octacarbonyl with acetylenes leads us to propose structure (II) for our products, analogous to that of the cobalt complexes.[6]



(1) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 156 (1959).

(2) H. W. Sternberg, R. Markby and I. Wender, THIS JOURNAL, **78**, 5704 (1956); H. Adkins and H. Krsek, *ibid.*, **70**, 383 (1948).

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