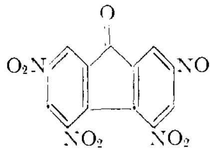
(−) and (+)-(isopropylideneaminoöxy)-propionic acid, II, respectively, in the presence of *p*-toluenesulfonic acid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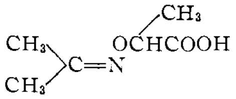
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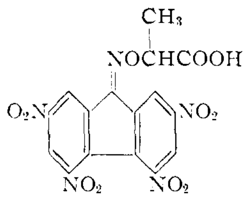
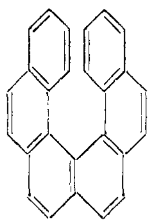

III

When a solution of two equivalents of 1-naphthyl-*sec*-butyl ether and one equivalent of (−)-III, $[\alpha]^{29}\mathrm{D}$ −91.4° (*c*. 1.6, dioxane), in acetic acid was cooled a purple complex separated. The ethers recovered from the complex and the mother liquor were optically active, $[\alpha]^{31}\mathrm{D}$ −7.8° (*c*, 6.4 ethyl acetate) and $[\alpha]^{32}\mathrm{D}$ +6.4° (*c*, 11, ethyl acetate), respectively. Similarly, methyl 2-(1-anthryl)-propionate was partly resolved into the corresponding (+)- and (−)-forms, $[\alpha]^{24}\mathrm{D}$ +101° and $[\alpha]^{27}\mathrm{D}$ −66.0° by means of (+)-III, $[\alpha]^{23}\mathrm{D}$ +84° (*c*, 1.5, dioxane). The above rotations are undoubtedly not maximal but represent the result of a single separation of complex.


IV

When a solution of phenanthro[3,4-*c*]phenanthrene,[2] IV, m.p. 231–231.5° (uncor.), in benzene was treated with one-half equivalent of the complexing agent the solution became dark red. Upon the addition of ethanol, the hydrocarbon separated as hexagonal plates. Three further applications of this treatment followed by nine conventional recrystallizations afforded IV, m.p. 263–267°, $[\alpha]^{24}\mathrm{D}$ −3640° (*c*, 0.0988, chloroform). The optical stability of this compound is indicated by the fact that it remelts at 234–250°, showing that even at its m.p. racemization is not complete. This is the first example of the resolution of a hydrocarbon which owes its asymmetry to intramolecular overcrowding.

N-*sec*-Butylpicramide, a compound which might have been used for resolution by means of complex formation has been prepared.[3] Racemic N-*sec*-butylpicramide was partially resolved by complex formation with (+)-β-naphthylcamphylamine but the partially resolved reagent was never used to resolve any other compound.

Because of the considerable complexing ability of III, this reagent should prove valuable for the resolution of a variety of racemic aromatic compounds. The extensions and limitations in the use of III and analogous compounds is under study as well as the exchange reaction represented by equation (1).

The reagent II was made by treating the sodium salt of acetoxime with methyl 2-bromopropionate.[4] 2-(Isopropylideneaminoöxy)-propionic acid, II, m.p. 58–61°, (Found: C, 49.5; N, 9.7), was resolved by treating two equivalents of racemic II with 1.5 equivalents of (−)-ephedrine in 1:1 benzene–Skellysolve B. The resulting salt, m.p. 116–119°, was decomposed with hydrochloric acid. The acid thus produced was recrystallized from 5:1 Skellysolve B–acetone to give (+)-II, m.p. 83.5–85.5°, $[\alpha]^{26}\mathrm{D}$ +30.8° (*c*, 7.6, water, 2 dm.).

(−)-2-(2,4,5,7-Tetranitro-9-fluorenylideneaminoöxy)-propionic acid, m.p. 198–200° cor.,[5] (Found: C, 43.0, H, 2.0, N, 15.8), $[\alpha]^{28}\mathrm{D}$ −97.1° (*c*, 1.5, dioxane), was made by gently refluxing a mixture of one equivalent of 2,4,5,7-tetranitrofluorenone, 1.5 equivalents of (+)-2-(isopropylideneaminoöxy)-propionic acid and 1.7 equivalents of *p*-toluenesulfonic acid monohydrate, in glacial acetic acid. The product was then precipitated with water and the yellow solid recrystallized from a mixture of acetic acid and butyl chloride. The (+)-III was made similarly by starting with I and (−)-II.

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RECEIVED APRIL 21, 1955

BISCYCLOPENTADIENYLRHENIUM HYDRIDE—A NEW TYPE OF HYDRIDE

Sir:

When rhenium pentachloride (0.03 mole) is allowed to react with sodium cyclopentadienide (0.2 mole) in tetrahydrofuran solution and the evaporated purple reaction mixture is heated at 120–170° in vacuum, a yellow crystalline sublimate, m.p., 161–162°, is obtained in yields ~20% based on the halide. The molecular weight of the compound by the isothermal distillation method in benzene and ether is 312 ± 5. The compound cannot, however, be biscyclopentadienylrhenium, $(C_5H_5)_2Re$, since it is diagmagnetic in the crystal and the melt from 77 to 510°K., and in organic solvents. The only reasonable explanation of this fact is that the compound is a hydride. Chemical analysis does not, however, provide an unequivocal answer [*Anal.* Found: C, 37.7; H, 3.6; Re, 58.75. Required for $(C_5H_5)_2ReH$; C, 37.85; H, 3.49; Re, 58.66; mol. wt., 317.5].

Proof of the hydridic nature of the compound comes from studies with a Varian Associates high resolution nuclear magnetic resonance spectrometer. In carbon disulfide solutions, a resonance peak attributable to the protons of the cyclopentadienyl rings is observed with a shift relative to the reference, water, of −1.17 p.p.m. $(H–H_r/H_r)$; a second resonance peak of approximately one-tenth the intensity is observed with a displacement of

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[2] The synthesis of this hydrocarbon will be described later.

[3] R. Weiss and A. Abeles, *Monatsh.*, **59**, 238 (1932).

[4] Compare E. Borek and H. T. Clark, THIS JOURNAL, **58**, 2020 (1936).

[5] The substance also melts and resolidifies or sinters between 125° and 135°.

+17.2 p.p.m., and must be attributed to a hydrogen atom of an unusual character.

Biscyclopentadienylrhenium hydride is unaffected by water and reacts moderately quickly with air; it is readily soluble in, and may be crystallized from solvents such as petroleum ether, benzene and ether. It is only sparingly soluble in liquid ammonia and the solutions do not conduct electricity. It does not react with ferrous chloride in tetrahydrofuran solution to form ferrocene.

While a rhenium carbonyl hydride has been reported,[1] neither this compound nor the carbonyl hydrides of other second and third group transitional metals have been rigorously characterized and their properties studied. However, unlike the carbonyl hydrides of iron and cobalt, biscyclopentadienylrhenium hydride appears to have no basic properties and is unaffected by 6 *N* sodium hydroxide. On the contrary, it behaves as a proton acceptor (*cf.* NH_3) and will dissolve in dilute hydrochloric or sulfuric acids without evolution of hydrogen to form a unipositive cation $[(C_5H_5)_2ReH_2]^+$; on addition of sodium hydroxide to those solutions biscyclopentadienylrhenium hydride is liberated and can be recovered by solvent extraction. The ion gives precipitates with large anions such as silicotungstate, and a rose-pink reineckate has been characterized. That the hydridic hydrogen atoms are attached to the rhenium atom in the ion is indicated by a single proton resonance peak in the aqueous solution at a displacement of +18.9 p.p.m. relative to water.

The most reasonable structure for biscyclopentadienylrhenium hydride would seem to be one similar to that of ferrocene, with metal to ring bonds of the "sandwich bond" type. The nuclear magnetic resonance studies show that the hydridic hydrogen is unusually well diamagnetically shielded and the hydrogen atom is presumably buried in the electron density surrounding the metal atom in the exposed region between the cyclopentadienyl rings.

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[1] W. Hieber and A. Fuchs, *Z. anorg. Chem.*, **248**, 256 (1941).

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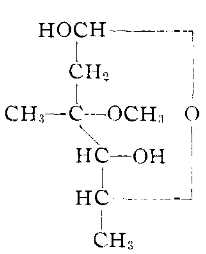
RECEIVED MAY 12, 1955

ERYTHROMYCIN. III. THE STRUCTURE OF CLADINOSE

Sir:

The isolation of cladinose from erythromycin was reported previously.[1,2] This is a $C_8H_{16}O_4$ compound containing two C–CH_3 groups, two hydroxyl groups and one methoxyl group. Evidence was presented for the presence of a hemiacetal grouping and the moiety $CH_3\overset{|}{C}HO$– with participation of this oxygen in the hemiacetal ring. These facts and further evidence given in this communication prove that cladinose has structure I.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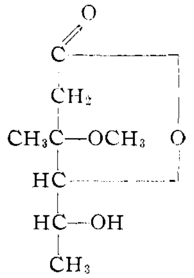
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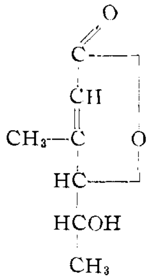
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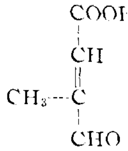
IV

Oxidation of cladinose with bromine formed a lactone (II). This compound lost the methoxyl group so readily that it was not possible to purify it, but it was characterized as its 3,5-dinitrobenzoate, m.p. 123–125° [Calcd. for $C_{15}H_{16}N_2O_9$: C, 48.91; H, 4.35; N, 7.62; CH_3O (1), 8.4. Found: C, 48.85; H, 4.33; N, 7.64; CH_3O, 8.7]. The infrared spectrum of the lactone was consistent with structure II, having absorption at 2.90 μ and 5.65 μ with a shoulder at 5.80 μ. The carbonyl absorption is indicative of a γ-lactone with a δ-lactone present as a minor component. Base treatment of II followed by neutralization resulted in the appearance of ultraviolet absorption at 211 mμ, ϵ 8400 which can be attributed to formation of a lactone having α,β unsaturation, probably III. Oxidation of base-treated II with periodate[3] formed two compounds. One of these was identified as acetaldehyde, 2,4-dinitrophenylhydrazone melting point and mixed melting point identical with an authentic sample. The other product, a liquid, formed a 2,4-dinitrophenylhydrazone, m.p. 250–251° dec. [Calcd. for $C_{11}H_{10}N_4O_6$: C, 44.90; H, 3.43; N, 19.03; mol. wt., 294. Found: C, 45.15; H, 3.68; N, 18.86; mol. wt., 289.6] and a semicarbazone, m.p. 214–215° [Calcd. for $C_6H_9N_3O_3$: C, 42.11; H, 5.26; N, 24.56. Found: C, 42.42; H, 5.36; N, 24.30]. An unambiguous synthesis proved that this compound is β-formylcrotonic acid (IV).

Ethyl β-hydroxymethylcrotonate[4] was oxidized to the aldehyde with manganese dioxide.[5] This was characterized by infrared and ultraviolet spectra and conversion to its 2,4-dinitrophenylhydrazone. The infrared spectrum showed aldehyde hydrogen absorption at 3.52 μ, ester carbonyl absorption at 5.85 μ, aldehyde carbonyl absorption at 5.90 μ and carbon–carbon double bond absorption at 6.08 μ. The ultraviolet absorption at 220 mμ, ϵ 10,170 (*cis*) and

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[1] E. H. Flynn, M. V. Sigal, Jr., P. F. Wiley and K. Gerzon, THIS JOURNAL, **76**, 3121 (1954).

[2] R. B. Hasbrouck and F. C. Garven, *Antibiotics and Chemotherapy*, **3**, 1040 (1953).

[3] It has been reported that cladinose does not react with periodate, but this is not absolute proof that there are not adjacent hydroxyl groups: see H. Klosterman and F. Smith, THIS JOURNAL, **74**, 5336 (1952).

[4] H. H. Sobotka and M. I. Rubin, U. S. Patent 2,390,335 (1945).

[5] J. Attenburrow, A. F. B. Cameron, J. H. Chapmau, R. M. Evans, B. A. Herns, A. B. A. Jansen and F. Walker, *J. Chem. Soc.*, 1094 (1952).