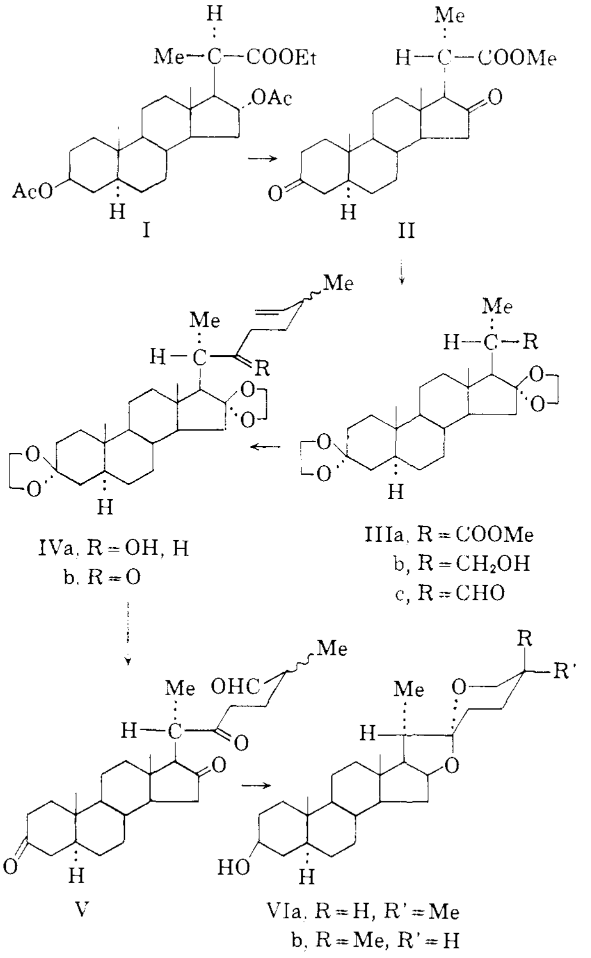
We have described[2,3] recently the conversion by a three-step sequence of $3\beta,16\alpha$-diacetoxyandrostan-17-one to the 20-iso ethyl ester I,[4] which was transformed by three further steps to the 20-normal diketoester II.[3,5] The latter now has been converted to the corresponding di-cycloethylene ketal IIIa (60%) (m.p. 196–198°, $[\alpha]_D$ − 24°[6]).[7]


I
II
IIIa, R = COOMe
b, R = CH_2OH
c, R = CHO
IVa, R = OH, H
b, R = O
V
VIa, R = H, R' = Me
b, R = Me, R' = H

Lithium aluminum hydride (LAH) reduction yielded the primary alcohol IIIb (70%) (m.p. 235–237°, $[\alpha]_D$ − 18°),[8] which was oxidized with chromium trioxide–pyridine to the aldehyde IIIc (70%) (m.p. 183–184°, $[\alpha]_D$ − 21°).[9]

3-Methyl-4-pentenoic acid [b.p. 78–80° (25 mm.), n^{20}_D 1.4366][10] was reduced with LAH to 3-methyl-4-penten-1-ol [b.p. 63–64° (25 mm.), n^{20}_D 1.4369], which on treatment with phosphorus tribromide in pyridine yielded 1-bromo-3-methyl-4-pentene [b.p. 138–140° (764 mm.), n^{20}_D 1.4680]. The corresponding magnesium derivative on condensation with the aldehyde IIIc produced the alcohol IVa (70%) as a mixture of C-25 isomers (m.p. 143–157°, $[\alpha]_D$ − 18°),[11] which on oxidation with chromium trioxide–pyridine furnished the ketones IVb (85%) (m.p. 145–148°, $[\alpha]_D$ − 16°). Ozonolysis at − 18° in ethyl acetate–pyridine, and then decomposition with Raney nickel and treatment with dilute acetic acid, led to the triketo-aldehydes V which were reduced directly with sodium borohydride in isopropyl alcohol–tetrahydrofuran. Short heating of the product with dilute hydrochloric acid produced a 1:1 mixture of tigogenin (VIa) and neotigogenin (VIb) (25% from IVb.) Crystallization of the acetates[12] and saponification furnished neotigogenin (VIb) (m.p. 201–203°, $[\alpha]_D$ − 76°) identical with an authentic sample. Refluxing the synthetic mixture with ethanolic hydrochloric acid[13] for 120 hr. yielded tigogenin (VIa) (m.p. 202–204°, $[\alpha]_D$ − 68°), identical with an authentic specimen.

This work constitutes a total synthesis of the two steroidal sapogenins, since androstan-3β-ol-17-one is available by a number of total synthetic routes.[14] Further, in view of known interconversions, our work leads to the steroidal alkaloids of the tomatidine–solasodine type[15] as well as of the solanidine type.[16]

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[2] N. Danieli, Y. Mazur and F. Sondheimer, *Chemistry & Industry*, 1724 (1958).

[3] N. Danieli, Ph.D. Thesis, Hebrew University, Jerusalem, June, 1958.

[4] The corresponding methyl ester now has been synthesized by a different route by V. Schwarz, V. Cerny and F. Sorm (*Chem. Listy*, **52**, 1633 (1958)).

[5] N. Danieli, Y. Mazur and F. Sondheimer, *Chemistry & Industry*, 1725 (1958).

[6] All rotations were measured in chloroform.

[7] J. W. Corcoran and H. Hirschmann, This Journal, **78**, 2325 (1956).

[8] All new compounds gave satisfactory analytical results and the infrared spectra were compatible with the assigned structures. Yields are given to the nearest 5%.

[9] That no inversion at C-20 had occurred during the conversion of II to IIIc was shown through LAH reduction of IIIc to IIIb, which with dilute acetic acid and then with LAH yielded the same bisnorallocholane-$3\beta,16\beta$,22-triol (m.p. 247–250°, $[\alpha]_D$ +15°) as had been obtained[3] by the LAH reduction of II.

[10] *Cf.* W. J. Croxall and J. O. Van Hook, This Journal, **72**, 803 (1950).

[11] The 22-hydroxyl group was apparently introduced stereospecifically, since the corresponding condensation of IIIc with isoamyl magnesium bromide yielded one single alcohol (m.p. 195–196°, $[\alpha]_D$ −20°).

[12] *Cf.* L. H. Goodson and C. R. Noller, *ibid.*, **61**, 2420 (1939); R. K. Callow and V. H. T. James, *J. Chem. Soc.*, 1671 (1955).

[13] *Cf.* R. B. Woodward, F. Sondheimer and Y. Mazur, This Journal, **80**, 6693 (1958), and references cited there.

[14] *Cf.* J. W. Cornforth, "Progress in Organic Chemistry," Ed. J. W. Cook, Butterworths Scientific Publications, London, 1955, Vol. 3, Chapter 1.

[15] (a) F. C. Uhle, This Journal, **76**, 4245 (1954); (b) F. C. Uhle and J. A. Moore, *ibid.*, **76**, 6412 (1954).

[16] Y. Sato and H. G. Latham, *ibid.*, **78**, 3146 (1956); see also F. C. Uhle and W. A. Jacobs, *J. Biol. Chem.*, **160**, 243 (1945).

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1,2-DIFERROCENYLETHANE FROM AN UNUSUAL REACTION

Sir:

Ferrocene condenses with formaldehyde in either concentrated sulfuric acid[1] or liquid hydrofluoric acid[2] to give a compound (I) containing two ferrocene nuclei and two methylene groups (from two moles of formaldehyde). This condensation product (I) was originally assigned the structure 1,1'-bis-ferrocenylenemethane (Ia).[1,2,3] Subsequently, Nesmeyanov and co-workers[4] revised their assign-

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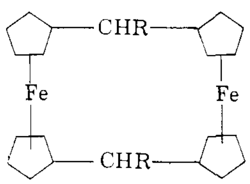
[1] A. N. Nesmeyanov and I. I. Kritskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 253 (1956).

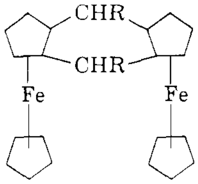
[2] V. Weinmayr, This Journal, **77**, 3009 (1955).

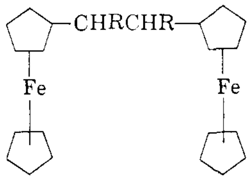
[3] Y. T. Struchkov, *Zhur. Obshchei Khim.*, **27**, 2039 (1957).

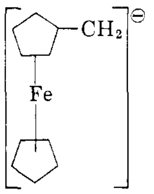
[4] A. N. Nesmeyanov, L. A. Kazitsyna, B. V. Lokshin and I. I. Kritskaya, *Doklady Akad. Nauk S.S.S.R.*, **117**, 433 (1957).

ment to structure Ib (1,2-bis-ferrocenylenemethane), on the basis of the presence of bands at 1110 and 1004 cm.$^{-1}$ (9 and 10μ bands)[5] in the infrared spectrum of I, indicative of at least one unsubstituted cyclopentadienyl ring. Both of these formulations (Ia and Ib) are incorrect; the structure of the condensation product (I) is 1,2-diferrocenylethane (Ic).


Ia, IIa


Ib, IIb


Ic, IIc


IV

Ia, Ib, Ic, R = H; IIa, IIb, IIc, R = C_6H_5

Compound I, prepared by the sulfuric acid method,[1] melts 190–192° (lit.[1,2] m.p. 191°). Microanalyses agree better with its formulation as Ic than as Ia or Ib [*Anal.* Calcd. for $C_{22}H_{22}Fe_2$ (Ic): C, 66.37; H, 5.57; Fe 28.06. Calcd. for $C_{22}H_{20}Fe_2$ (Ia or Ib): C, 66.70; H, 5.09; Fe, 28.20. Found: C, 66.67; H, 5.77; Fe, 27.92; C-CH_3, 0.00].[6] Its infrared spectrum resembles closely that of ethylferrocene.[5,7] A mixture melting point of I with an authentic sample of 1,2-diferrocenylethane (Ic) [*Anal.* Found: C, 66.38; H, 5.59; Fe, 28.24], m.p. 193–195°, showed no depression and the infrared spectra (CS_2) of the compound (I $\equiv$ Ic) from the two routes were superimposable. The latter compound was prepared by hydrogenation of ferrocenylacetylferrocene (desoxyferrocoin) [*Anal.* Found: C, 63.95; H, 4.92; Fe, 27.20], m.p. 159–161°, the product of Friedel–Crafts' acylation of ferrocene with the acid chloride of ferrocenylacetic acid.[8]

The structure of the similar condensation product (II) from ferrocene and benzaldehyde (first assigned structure IIa,[1,2,3] later IIb[4]) is, presumably, analogous, *i.e.*, 1,2-diferrocenyl-1,2-diphenylethane (IIc) [*Anal.* Calcd. for $C_{34}H_{30}Fe_2$: C, 74.21; H, 5.50; Fe, 20.30. Calcd. for $C_{34}H_{28}Fe_2$: C, 74.48; H, 5.15; Fe, 20.38. Found: C, 74.37. H, 5.77; Fe, 20.10] since the infrared spectrum of this compound (II) is similar to that of I. Experiments now in progress are designed to establish unequivocally the structure of II.

Reflection on possible mechanisms for the formation of I and II suggests the reaction path shown, in which the key intermediate is the novel cation IV. In accord with this pathway,[9] α-hydroxymethylferrocene (III)[10] has been converted to I under conditions identical to those employed for the conversion of ferrocene and formaldehyde to I, and the blue-green, water-soluble di-cation (V) of I has been isolated as its dipicrate.

$$C_{10}H_{10}Fe + CH_2O \xrightarrow{H_2SO_4} \underset{III}{C_{10}H_9Fe{-}CH_2OH} \longrightarrow IV$$

$$2\ IV \xrightarrow[\text{zation}]{\text{dimeri-}} \underset{V}{(C_{10}H_9Fe{-}CH_2)_2} \xrightarrow{SnCl_2} I$$

Acknowledgment.—The authors wish to express their appreciation to the Me Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, for financial assistance.

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[5] M. Rosenblum, Ph.D. Thesis, Harvard University, August, 1953; M. Rosenblum and R. B. Woodward, THIS JOURNAL, **80**, 5443 (1958).

[6] Microanalyses for hydrogen reported by the earlier authors[1,2] are also higher than those expected for Ia or Ib.

[7] The present sample of ethylferrocene was prepared by D. J. Casey.

[8] K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, THIS JOURNAL, **79**, 3420 (1957).

[9] J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957).

[10] The electronic nature of the coupling intermediate (IV) is unspecified as to singlet or triplet state. Another attractive mechanistic possibility involves coupling of the neutral radical derived from IV in a chain sequence of intermolecular oxidation-reduction reactions.

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NOVEL HETEROCYCLO PENTADIENES

Sir:

Five-membered heterocyclic rings containing two conjugated double bonds in an alternating sequence with the hetero atom, as in thiophene, have been known for some time. However, preparation of such rings involving hetero atoms other than O, N, S, Se or Te in such ring systems have not been reported. We wish to report the synthesis of such five-membered heterocycles containing other hetero elements such as P, Ge, Sn, As or Sb. The method of preparation appears to be generally applicable with many elements having a positive valence of two or greater.

The procedure we have followed in preparing organometal (or organometalloid) heterocycles involves the condensation of an active metal (or metalloid) dihalide with a 1,4-dilithiobutadiene derivative. The dilithium derivative, 1,4-dilithio-1,2,3,4-tetraphenylbutadiene, is prepared as reported by Smith and Hoehn[1] by the dimerization of diphenylacetylene with lithium in ether. An ether solution of dihalide of the hetero atom having a molar concentration approximately equal to that of dilithium reagent solution is prepared. Using normal precautions to avoid exposure to air, carbon dioxide or moisture, the dilithium solution may be added dropwise to the dihalide solution under an atmosphere of dry nitrogen. The reaction is extremely rapid as indicated by the immediate disappearance of the dark red color characteristic of the organolithium reactant.

The reaction of dilithiumtetraphenylbutadiene (LTPBD) with SCl_2 formed tetraphenylthiophene. This previously has been prepared by other

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[1] L. I. Smith and H. H. Hoehn, THIS JOURNAL, **63**, 1184 (1941).