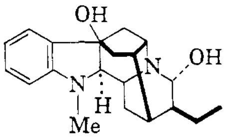
spectral properties. This method should prove to be a useful one in alkaloid chemistry. In this particular instance it leads to a novel proof of the structure and stereochemistry of ajmaline. Both ajmaline and its C-ethyl epimer, isoajmaline[1] were degraded to the β-carbolinium salts (VII). The one obtained from isoajmaline proved to be identical in all respects with *d-trans*-2,3-diethyl-1,2,3,4-tetrahydro-12-methylindolo[2,3-a]quinolizinium perchlorate (VIIb) which was derived in two steps from dihydrocorynantheane whose absolute stereochemistry is known.[2a] As expected the corresponding *cis*-indoloquinolizinium perchlorate prepared from corynantheidane was identical with (VIIa). Thus the stereochemistry of the hexacyclic system and the C-ethyl in ajmaline must be as depected in (I). The carbinolamine hydroxyl is placed *trans* to the ethyl since presumably it is able to take up the thermodynamically more stable position via the intermediacy of the open chain aldehyde form.[3] The assignment of configuration of the secondary hydroxyl is tentative and is derived from the chemistry of the sodium borohydride reduction product of ajmalidine.[4] The details of the reactions outlined above are as follows. Deoxyajmaline[1] was oxidized by means of lead tetraacetate in benzene to furnish deoxyajmalal-A (IIa),[5,6] m.p. 180–181°, $[\alpha]_D$ +39°, which epimerized as expected in base to deoxyajmalal-B (IVa), m.p. 210–212°, $[\alpha]_D$ −1 ±1°. The aldehydes upon reduction with sodium borohydride gave the respective alcohols, deoxyajmalol-A (IIIa), amorphous, $[\alpha]_D$ −53° (picrate, m.p. 218–220°) and deoxyajmalol-B (Va), m.p. 217–8° $[\alpha]_D$ −7°. O-Tosyldeoxyajmalol-B, m.p. 149–151°, after a two-hour reflux in collidine underwent a fission[7] and an aerial oxidation to furnish *l-cis*-3-ethyl-1,2,3,4-tetrahydro-12-methyl-2-vinylindolo[2,3-a]-quinolizinium perchlorate (VIa), m. p. 201–202°, $[\alpha]_D$ −27°, which upon hydrogenation using Adams catalyst gave the *l-cis*-diethyl derivative (VIIa), m.p. 212–213°, $[\alpha]_D$ −27°. In a similar fashion deoxyisoajmaline[1] afforded deoxyisoajmalal-A (IIb), m.p. 143–4°, $[\alpha]_D$ +126°, deoxyisoajmalal-B (IVb), m.p. 179–180° $[\alpha]_D$ +80°, deoxyisoajmalol-A (IIIb), m.p. 175–6°, $[\alpha]_D$ +55°, deoxyisoajmalol-B (Vb), m.p. 246–7°, $[\alpha]_D$ +86°, O-tosyldeoxyisoajmalol-B, m.p. 167–8°, *d-trans*-3-ethyl-1,2,3,4-tetrahydro-12-methyl-2-vinylindolo[2,3-a]quinolizinium perchlorate (VIb), m.p. 167–9°, $[\alpha]_D$ +64°, and the *d-trans*-diethyl derivative (VIIb), m.p. 201–202°, $[\alpha]_D$ +16°.



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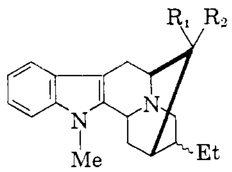

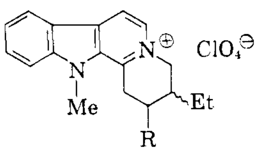

II, R_1 = CHO; R_2 = H
III, R_1 = CH_2OH; R_2 = H
IV, R_1 = H; R_2 = CHO
V, R_1 = H; R_2 = CH_2OH

VI, R = $CH{=}CH_2$
VII, R = Et

a = *cis* form b = *trans* form

Treatment of the potassium salt of dihydrocorynantheane[2a] with excess methyl iodide gave a product which upon pyrolysis at 300–340° *in vacuo* yielded the N_a-methyl derivative, m.p. 109–111.5°, $[\alpha]_D$ −22°. Ring C dehydrogenation of this using the palladium and maleic acid method[8] furnished (VIIb), m.p. 198–200°, $[\alpha]_D$ +15°. Similarly corynantheidane[9] gave (VIIa), m.p. 213–4°, $[\alpha]_D$ −27°, via its oily N_a-methyl compound. It is theoretically satisfying that ajmaline and its congeners, as well as corynantheidine, form no exception to the rule[2a,b] that there is a common stereochemical denominator (C_{15} of yohimbine) among the indole alkaloids.

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[1] F. A. L. Anet, D. Chakravarti, R. Robinson and E. Schlittler, *J. Chem. Soc.*, 1242 (1954).

[2] (a) E. Wenkert and N. V. Bringi, THIS JOURNAL, **81**, 1474 (1959); (b) E. Wenkert, E. W. Robb and N. V. Bringi, *ibid.*, **79**, 6570 (1957).

[3] In isoajmaline also, the hydroxyl group would be expected to be *trans* to the C-ethyl.

[4] M. Gorman, N. Neuss, C. Djerassi, J. P. Kutney and P. J. Scheuer, *Tetrahedron*, **1**, 328 (1957).

[5] This reaction was first described by R. B. Woodward, K. Schenker, *Angew. Chem.*, **68**, 13 (1955), but no melting point was given and experimental details are presently only available for the case of the oxidation of dihydrosandwicine in acetic acid, ref. 4.

[6] Good analyses were obtained for all compounds reported. The optical rotations were measurd at 25 ± 2° in methanol unless otherwise stated.

[7] For related examples in simple cases, see C. A. Grob, *Experientia*, **13**, 126 (1957).

[8] E. Wenkert and D. K. Roychaudhuri, THIS JOURNAL, **80**, 1613 (1958).

[9] M.-M. Janot, R. Goutarel, J. Chabasse-Massonneau, *Bull. Soc. Chim.*, **20**, 1033 (1953).

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RECEIVED JUNE 1, 1960

A NITROGEN ANALOG OF SESQUIFULVALENE[1]

Sir:

We wish to record the synthesis of 2-cyclopentadienylidene-1-methyl-1,2-dihydropyridine (II), a simple nitrogen analog of the unknown hydrocarbon sesquifulvalene (I).[2]

2-Bromopyridine methiodide (one mole) suspended in 1,2-dimethoxyethane reacts with sodium cyclopentadienide (2 moles) to give 31% of II, orange needles from ether or hexane. II is obtained in two dimorphic modifications: A, m.p. 56–57°, *Anal.* Calcd. for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91; neut. equiv., 157. Found: C, 84.05; H, 7.16; N, 8.94; neut. equiv., 156. B,

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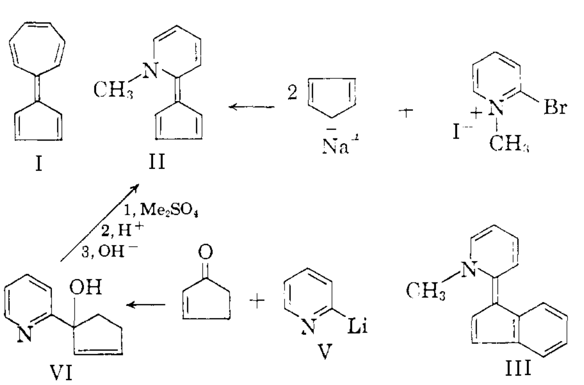
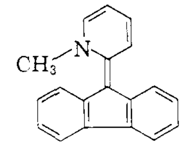
[1] This work was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 49(638)-828. Reproduction in whole or in part is permitted for any purpose of the United States Government. Also sponsored in part by the Office of Ordnance Research under contract No. DA-04-495-ORD-532. We are indebted to these agencies for support.

[2] *Cf.* (a) W. von E. Doering in "Theoretical Organic Chemistry: papers presented to the Kekulé Symposium," Butterworths Scientific Publications, London, 1959, p. 35; (b) B. Pullman, A. Pullman, E. D. Bergmann, H. Berthod, E. Fischer, Y. Hirschberg, D. Lavie and M. Mayot, *Bull. Soc. chim. France*, **19**, 73 (1952).



I II VI V III

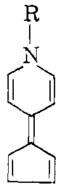


IV

m.p. 74.5–75°, *Anal.* Found: C, 84.12; H, 7.11; N, 8.97. Form A is converted to form B by seeding. The infrared and ultraviolet spectra of the two forms are identical.

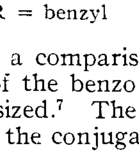
The structure of II is established (i) by its method of synthesis; (ii) by its alternative formation (in only spectroscopically detectable amount) by the sequence V → VI → II (compound VI had m.p. 34–35°, *Anal.* Calcd. for $C_{10}H_{11}ON$: C, 74.52; H, 6.88. Found: C, 74.47; H, 6.93); and (iii) by its conversion *via* catalytic hydrogenation (5.1 moles) to 1-methyl-2-cyclopentylpiperidine, isolated as the hydroiodide (VII) and identified by comparison (mixed m.p., infrared spectrum) with an authentic sample (m.p. 141–142°, *Anal.* Calcd. for $C_{11}H_{22}NI$: C, 44.75; H, 7.17. Found: C, 44.88; H, 7.51) prepared by hydrogenation (4.0 moles) of 2-cyclopentenylpyridine methiodide (m.p. 109–110°, *Anal.* Calcd. for $C_{11}H_{14}NI$: C, 46.01; H, 4.91. Found: C, 46.14; H, 4.88). The latter is prepared from the known[3] substance 2-cyclopentenylpyridine.

Compound II appears to be the first simple sesquifulvalene analog of proven structure. Two previously reported substances of this type, assigned structures VIII[4] and IX,[5b] were prepared by addition of cyclopentadiene to the corresponding pyridinium salts followed by oxidation of the intermediate dihydropyridine and, in principle, could be 2- instead of 4-cyclopentadienylidene derivatives. Compound IX, originally thought[5a] to be *either* the 2- or 4-isomer, was later assigned[5b] the 4-structure for unstated reasons. Compound VIII apparently was assigned[4] the 4-structure partly by analogy to the condensations of α-methyleneketones with acylpyridinium salts, which are known from the work of Doering and McEwen to produce 4-substituted dihydropyridines.[6] In our opinion, this analogy is unsafe, for Doering and McEwen accounted for the absence of the 2-isomer from their reaction mixtures by proposing that *it was formed but rapidly rearranged to an enol ester and pyridine.* Such a rearrangement is not a factor in the reactions leading to the substances assigned structures VIII and IX and, therefore, there appear to be no compelling grounds for excluding the 2-structures.



VIII, R = 2,6-dichlorobenzyl
IX, R = benzyl

Table I records a comparison of the properties of II with those of the benzo analogs III and IV previously synthesized.[7] The effect of annelation on the acidities of the conjugate acids (all referred to the water scale by the methods given in Table I) is the same as in the series cyclopentadiene > indene > fluorene,[8] but the positions of the long wave-length maxima of the visible spectra of the anhydrobases follow a sequence which is the reverse of that observed[9] (at least for simple alkyl derivatives) and theoretically justified by molecular orbital calculations[10] for the series fulvene > benzofulvene > dibenzofulvene. The spectral sequence is, however, in accord with that theoretically expected[11] for the series of hydrocarbon anions cyclopentadienide[12] < indenide < fluorenide and actually observed in the isoelectronically corresponding series pyrrole < indole < carbazole. The order of spectral transition energies is thus in qualitative agreement with the idea that the electronic distribution in the II, III, IV (*cf.* X) series is similar to that predicted[2b] for the parent hydrocarbon I. The extent to which steric factors, especially in III and IV, contribute to the order of acidities and spectral transition energies is not known. We hope to eliminate these factors in a study of the isomeric 4-cyclopentadienylidene-1,4-dihydropyridine series now in progress.



X

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[3] B. Emmert and E. Pirot, *Ber.*, **74**, 714 (1941); H. L. Lochte, P. E. Kruse and E. N. Wheeler, THIS JOURNAL, **75**, 4477 (1953).

[4] F. Kröhnke, K. Ellegast and E. Bertram, *Ann.*, **600**, 176 (1956).

[5] (a) D. N. Kursanov, N. K. Baranetskaya and V. N. Setkina, *Proc. Acad. Sci. U.S.S.R.*, **113**, 191 (1957); (b) D. N. Kursanov and N. K. Baranetskaya, *Bull. Acad. Sci. U.S.S.R.*, 341 (1958).

[6] W. von E. Doering and W. E. McEwen, THIS JOURNAL, **73**, 2104 (1951).

[7] J. A. Berson and E. M. Evleth, *Chemistry and Industry*, 901 (1959).

[8] (a) W. K. McEwen, THIS JOURNAL, **58**, 1124 (1936); (b) A. Streitwieser, *Tetrahedron Letters*, No. 6, 23 (1960).

[9] For a summary, see E. D. Bergmann in "Progress in Organic Chemistry," Volume 3, edited by J. W. Cook, Academic Press, Inc., New York, N. Y., 1955, p. 103.

[10] B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, p. 496, and references therein cited.

[11] Reference 10, p. 644.

[12] *Cf.* R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, spectra nos. 1, 2, 192, 193, 338, 339, 340.

TABLE I

Compound	pK_a	λ_{max} (mμ) (log ϵ)[e]
II	9.1 ± 0.2[a]	410–425 (3.88)[d]
III	11.1 ± 0.2[b]; 10.8 ± 0.2[c]	510 (3.89)
IV	11.5 ± 0.2[a]; 11.6 + 0.1[b]; 11.3 ± 0.1[c]	533 (3.90)

[a] By titration in acetonitrile with dioxane–perchloric acid, according to the method of H. K. Hall, *J. Phys. Chem.*, **60**, 63 (1956). [b] Spectrophotometric, in dioxane, using piperidine–piperidine perchlorate as internal buffer, according to the method of L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932). [c] Spectrophotometric, as in footnote *b*, in acetonitrile. [d] Shoulder. [e] In isoöctane.

Compound II gives a colorless solution (λ_{max} 342, no shoulder at 410–425 mμ) in ethanolic perchloric acid, signifying conversion to the conjugate acid; the change is quantitatively reversed by alkali, even after storage of the acidic solution. The unstable crystalline perchlorate of II is obtained as needles (from ethyl acetate–ethanol) which decompose above about 80°. *Anal.* Calcd. for $C_{11}H_{12}O_4NCl$: C, 51.26; H, 4.69. Found: C, 51.50; H, 5.20. This substance shows no $\equiv^+N$-H absorption in the infrared (KBr disc). Presumably, protonation occurs in the five-membered ring.

Further properties and reactions of II and related substances are being investigated.

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RECEIVED JUNE 10, 1960

A NEW SYNTHESIS OF ARYLPHOSPHONOUS DICHLORIDES[1]

Sir:

A few years ago,[2] Doak and Freedman announced an aromatic phosphonic acid synthesis destined to become the most widely useful of the several methods known.[3] Readily prepared aryldiazonium fluoroborates are the starting materials; these are treated with phosphorus trichloride or tribromide in a dry solvent in the presence of a cuprous halide as catalyst. The mixture is then hydrolyzed and the phosphonic acid obtained generally in 30–50% yield. The intermediate of this reaction has not been subjected to study but has been suggested by Crofts[4] to be $ArPX_3^+BF_4^-$.

We reasoned that the intermediate, if hydrolyzable to a phosphonic acid, may well bear chemical similarity to an aryl tetrahalophosphorane, and hence might be reducible to an arylphosphonous dichloride, $ArPCl_2$.[5] We have indeed found that magnesium shavings added to the diazonium fluoroborate–phosphorus trichloride reaction product in ethyl acetate solvent effect this reduction. The reaction is exothermic but easily controlled. These known phosphonous dichlorides thus have been prepared: *p*-chlorophenyl-, b.p. 132–133° at 20 mm. (reported,[6] 133° at 20 mm.), 37% crude yield; *p*-tolyl-, b.p. 109–110° at 11 mm. (reported,[7] 107–110° at 10 mm.), 11% yield. Both compounds were analyzed and gave the correct values. Additional proof of their identity was obtained by hydrolysis to the corresponding phosphonous acids, each of which had melting points in agreement with literature values.

To demonstrate the versatility of the new method, two new and otherwise difficultly obtainable phosphonous dichlorides were prepared: *m*-chlorophenyl-, b.p. 124–125° at 18 mm., 33% yield (*Anal.* Calcd. for $C_6H_4Cl_3P$: C, 33.76; H, 1.89; P, 14.51. Found: C, 34.04; H, 2.06; P, 14.65). *p*-Cyanophenyl-, b.p. 127–128° at 4.5 mm., 25% yield (*Anal.* Calcd. for $C_7H_4Cl_2NP$: C, 41.21; H, 1.98; P, 15.19. Found: C, 41.42; H, 2.03; P, 15.17). Each was hydrolyzed to the phosphonous acid: *m*-chlorophenyl-, recrystallized from carbon tetrachloride, m.p. 90.5–91.5° (*Anal.* Calcd. for $C_6H_6ClO_2P$: C, 40.80; H, 3.43; P, 17.54. Found: C, 41.17; H, 3.65; P, 17.11). *p*-Cyanophenyl-, recrystallized from ethanol–carbon tetrachloride, m.p. 166–167° (*Anal.* Calcd. for $C_7H_6NO_2P$: C, 50.31; H, 3.62; P, 18.54. Found: C, 50.61; H, 3.87; P, 18.20).

The following experimental procedure is typical. All operations were conducted in a nitrogen atmosphere. To 200 ml. of dry ethyl acetate, 0.20 mole of *p*-cyanobenzenediazonium fluoroborate and 1.7 g. of cuprous bromide, was added 0.23 mole of phosphorus trichloride. After stirring for 30 min., the mixture was warmed to 40°, a vigorous reaction commencing. When complete, 0.20 mole of magnesium was added slowly with cooling to hold the temperature at 40–50°. The reaction mixture was freed of solvent and the residual semi-solid mass extracted with three 100-ml. portions of benzene–heptane mixture, 1:1 v./v., The extract was flash-distilled to remove solvent and the residual liquid then vacuum-distilled. There was obtained first a 2-g. fraction, b.p. 44–61° at 6 mm., solidifying at room temperature. This product is independent of the structure of the starting diazonium fluoroborate and variable in quantity; it is a fuming, phosphorus-free substance, and is believed to be the boron trifluoride–ethyl acetate complex (b.p. 123° at 772 mm., m.p. 37.5°[8]). The phosphonous dichloride (10 g.) was collected at 130–137° at 6 mm. It was redistilled through a 6 in. packed column, and after a small forerun the main cut was collected at 127–128° at 4.5 mm.; it provided the analytical data listed above. An alternative isolation procedure is to distill the solvent-free reaction product directly, eliminating the extraction. The large solid residue, however, makes this distillation somewhat difficult.

It appears that we have here a new method of synthesis of arylphosphonous dichlorides, and

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(1) Supported by a grant from the Duke University Research Council.

(2) G. O. Doak and L. D. Freedman, THIS JOURNAL, **73**, 5658 (1951).

(3) L. D. Freedman and G. O. Doak, *Chem. Rev.*, **57**, 479 (1957).

(4) P. C. Crofts, *Quart. Reviews*, **12**, 341 (1958).

(5) L. D. Quin and C. H. Rolston, *J. Org. Chem.*, **23**, 1693 (1958), and references cited therein. E. P. Komkov, K. U. Karavanov and S. Z. Even, *Zhur. obshchei Khim.*, **28**, 2963 (1958), have reported a somewhat similar preparation of alkylphosphonous dichlorides by reducing with metals the complex salts $RPCl_3^+ AlCl_4^-$ (J. P. Clay, *J. Org. Chem.*, **16**, 892 (1951)).

(6) D. R. Nijk, *Rec. trav. chim.*, **41**, 461 (1922).

(7) B. Buchner and L. B. Lockhart, Jr., THIS JOURNAL, **73**, 755 (1951).

(8) G. T. Morgan and R. Taylor, *J. Soc. Chem. Ind.*, **50**, 869 (1931).