Fig. 1.

laboratory over a temperature range 55–85°, the thermal decomposition of acetyl peroxide being used to generate the radicals. Recently this work was repeated with the certain changes: photolysis of azomethane was used to generate methyl radicals and the temperature range was extended from 6 to 95°. The method applied in the present studies was similar to that developed in previous investigations and the evidence for its justification as well as the details of the experimental technique are given in a paper by Steel and Szwarc.[5]

TABLE I

ACTIVATION ENERGIES AND FREQUENCY FACTORS CALCULATED BY THE LEAST SQUARE METHOD

Compound	k_2/k_1 at $50°$ [a]	$E_2 - E_1$, kcal./mole	A_2/A_1
Ethylene	39.2	−1.03	2×4.3
Propylene	25.7	−1.00	5.55
Isobutene	42.9	−1.29	5.8
Styrene	1070	−3.22	7.6
α-Methylstyrene	1090	−3.36	5.7
Butadiene-1,3	2440	−3.15	2×9.2
Isoprene	2450	−3.38	2×6.3

[a] The k_2/k_1 values are intrapolated from the respective Arrhenius lines.

In this communication we present only the final results of our studies, shown in Fig. 1 and 2 and Table I, and discuss their significance. The rate constant of methyl radicals addition to the respective substrate is denoted by k_2, whereas k_1 is the rate constant of hydrogen abstraction from isooctane, the latter being used as a solvent in all these experiments. Inspection of Fig. 1 and Table I shows clearly that (1) the same species are responsible for the observed reactions whether acetyl peroxide or azomethane is used to generate the radicals. This means that all these reactions are due indeed to methyl radicals. The suggestion of some workers that acetate radicals are responsible for methylation in the acetal peroxide systems is disproved. (2) The accuracy of activation energies

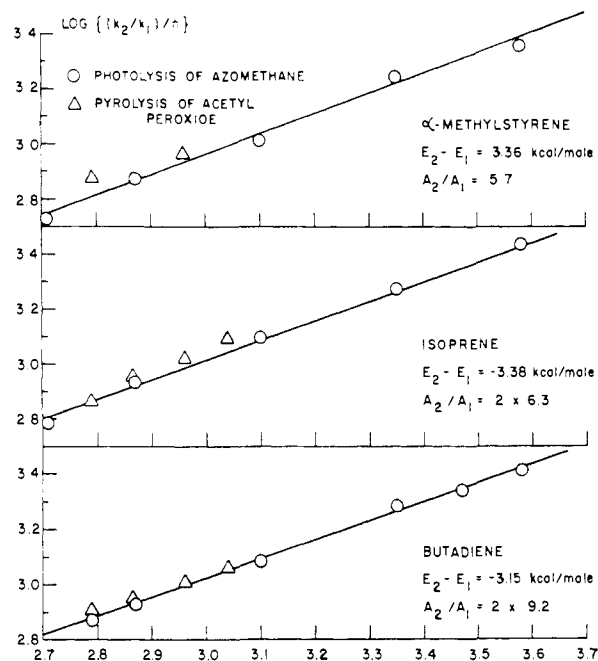(5) C. Steel and N. Szwarc, J. Chem. Phys., in press.

Fig. 2.

determination is greatly improved in this work as compared with the previous studies. This is obvious from inspection of Fig. 1. Indeed, the present values of $E_2 - E_1$ are reliable within ±0.1–0.2 kcal./mole, whereas the errors in the previous one are ±1–2 kcal./mole. (3) Consequently, the present values of A_2/A_1 are reliable within a factor smaller than 1.3, and inspection of Table I definitely shows that in a series of additions, each involving the same center, A_2/A_1 is nearly constant in spite of a 100-fold change in the reactivities of the investigated substrates. The constancy of A_2/A_1 was assumed in our previous discussions[6,7] but now this assumption is verified experimentally. This shows that the entropy of activation is constant for methyl radical addition reactions to a series of substrates possessing the same type of reaction center.

(6) M. Szwarc and J. H. Binks, in "Theoretical Organic Chemistry—Kekule Symposium, 1958," Butterworth Publ., 1959, p. 262.
(7) J. H. Binks and M. Szwarc, J. Chem. Phys., 30, 1494 (1959).

DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY COLLEGE OF FORESTRY
    AT SYRACUSE UNIVERSITY   M. FELD
SYRACUSE 10, NEW YORK   M. SZWARC
   RECEIVED JUNE 13, 1960

RAUWOLFIA ALKALOIDS. XXXII. THE ABSOLUTE STEREOCHEMISTRY OF AJMALINE AND A NEW PROOF OF ITS STRUCTURE

Sir:

In connection with our current interest in Hunteria alkaloids, we have developed a facile experimental method for the recognition of heterocyclic alcohols related to (III). Ajmaline (I) was used as a source of stereoisomers of this type. We have found that O-tosyl derivatives of the alcohols (III) and (V) may be converted in two steps into N_a-methyl-β-carbolinium salts (VI) which can be recognized through their characteristic ultraviolet

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°, [α]D +39°, which epi-

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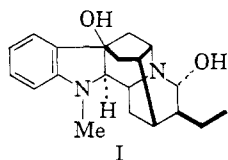
merized as expected in base to deoxyajmalal-B (IVa), m.p. 210–212°, [α]D −1 ±1°. The aldehydes upon reduction with sodium borohydride gave the respective alcohols, deoxyajmalol-A (IIIa), amorphous, [α]D −53° (picrate, m.p. 218–220°) and deoxyajmalol-B (Va), m.p. 217–8° [α]D −7°. O-Tosyldeoxyajmalol-B, 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°, [α]D −27°, which upon hydrogenation using Adams catalyst gave the l-cis-diethyl derivative (VIIa), m.p. 212–213°, [α]D −27°. In a similar fashion deoxyisoajmaline[1] afforded deoxyisoajmalal-A (IIb), m.p. 143–4°, [α]D +126°, deoxyisoajmalal-B (IVb), m.p. 179–180° [α]D +80°, deoxyisoajmalol-A (IIIb), m.p. 175–6°, [α]D +55°,

(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).
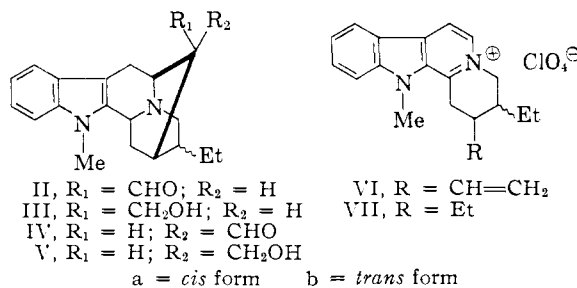
(3) In isoajmaline also, the hydroxyl group would be expected to be trans to the C-ethyl.

(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).

II, R₁ = CHO; R₂ = H
III, R₁ = CH₂OH; R₂ = H
IV, R₁ = H; R₂ = CHO
V, R₁ = H; R₂ = CH₂OH

VI, R = CH=CH₂
VII, R = Et

a = cis form   b = trans form

deoxyisoajmalol-B (Vb), m.p. 246–7°, [α]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°, [α]D +64°, and the d-trans-diethyl derivative (VIIb), m.p. 201–202°, [α]D +16°.

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 Na-methyl derivative, m.p. 109–111.5°, [α]D −22°. Ring C dehydrogenation of this using the palladium and maleic acid method[8] furnished (VIIb), m.p. 198–200°, [α]D +15°. Similarly corynantheidane[9] gave (VIIa), m.p. 213–4°, [α]D −27°, via its oily Na-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 (C₁₅ of yohimbine) among the indole alkaloids.

(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).

RESEARCH DEPARTMENT   M. F. BARTLETT
CIBA PHARMACEUTICAL PRODUCTS, INC.   E. SCHLITTLER
SUMMIT, NEW JERSEY   R. SKLAR
DEPT. OF CHEMISTRY   W. I. TAYLOR
IOWA STATE UNIVERSITY   ROBERT L. S. AMAI
AMES, IOWA   ERNEST WENKERT

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 C₁₁H₁₁N: 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,

(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).