(ϵ 20,400), $\lambda_{\max}^{\mathrm{pH}\ 7-12}$ 269 mμ (ϵ 20,000). The infrared spectra of the synthetic compound and that of the isolated compound are superimposable in every detail.

The isolated product was converted to the free base by first treating it with a 3-mole excess of periodate in neutral aqueous solution, then heating the reaction mixture at 100° for 30 min in 0.1 *N* sodium hydroxide solution. The free base cochromatographed in solvent systems A–E (ref 3) with 6-N-(3-methyl-2-butenylamino)purine. This sample was synthesized by condensing the corresponding amine with 6-chloropurine, mp 212–214° (reported 213–215).[8] *Anal.* Calcd for $C_{10}H_{13}N_5$: C, 59.09; H, 6.45; N, 34.46. Found: C, 59.02; H, 6.34; N, 34.65. When compound I is hydrolyzed in 1 *N* hydrochloric acid for 15 min at 100°, the free base of I is not obtained but rather two new bases are formed. These products, termed A and B for the sake of discussion, have been partially characterized.

Compound A was crystallized from ethanol, mp 200–202° dec. *Anal.* Found: C, 58.95; H, 6.58; N, 34.60. Ultraviolet absorption spectra showed $\lambda_{\max}^{\mathrm{pH}\ 1.5}$ 264 mμ (ϵ 14,750), $\lambda_{\max}^{\mathrm{pH}\ 7.0}$ 270 mμ (ϵ 13,120), $\lambda_{\max}^{\mathrm{pH}\ 11.8}$ 276 mμ (ϵ 14,700). The elemental analysis fits the empirical formula of the free base of I, and since the spectra are similar to those of N^1,N^6-dimethyladenine,[9] compound A probably has a cyclized side chain attached to the N^1 and N^6 position of adenine. The formation of such a product would be analogous to the formation of pyrotriacanthine from triacanthine, 6-amino-3-(3-methyl-2-butenyl)purine, under acidic conditions.[10] Compound B was crystallized from acetonitrile–ethanol (1:1), mp 173–174°. *Anal.* Calcd for $C_{10}H_{15}N_5O$ (mol wt 221.26): C, 54.28; H, 6.83; N, 31.66; Found: C, 54.71; H, 6.77; N, 31.24. The ultraviolet absorption spectra [$\lambda_{\max}^{\mathrm{pH}\ 1.0}$ 272 mμ (ϵ 16,800), $\lambda_{\max}^{\mathrm{pH}\ 7.0}$ 268 mμ (ϵ 17,700), $\lambda_{\max}^{\mathrm{pH}\ 11.5}$ 274 mμ (ϵ 17,300)] are similar to those of an N^6-(alkyl-substituted) adenine. The mass spectrum shows a parent peak at *m/e* 221 and major peaks at *m/e* 203 (loss of H_2O) and 162 (loss of $(CH_3)_2COH$). These data suggest that compound B is a product formed by addition of water according to the Markovnikov rule to the double bond of the isopentenyl side chain. Further work on the chemistry of these compounds is in progress and will be communicated shortly.

The amount of compound I in yeast s-RNA was estimated more accurately by spectrophotometric analysis of the initial column isolate. It comprises 0.1 mole % of the nucleotides. We also isolated compound I from s-RNA prepared from calf liver.[11] It is present at a level of 0.05 mole %. Compound I can occur, statistically, in only certain s-RNA molecules and it is of interest that it occurs in serine transfer RNA.[12] Although the isolated natural product has structure I, it is conceivable that in the s-RNA molecule it could exist as the N^1 isomer since N^1-methyladenosine can rearrange to N^6-methyladenosine under alkaline conditions.[13] We cannot rule out the possibility that an analogous rearrangement occurs under the conditions of enzymic hydrolysis of s-RNA.

The occurrence of natural compounds containing an isopentenyl unit attached to adenine has been reported previously. 6-N-(4-Hydroxy-3-methyl-2-butenylamino)purine, called zeatin, occurs in *Zea mays.*[4] 6-Amino-3-(3-methyl-2-butenyl)purine, termed triacanthine, occurs in *Gleditsia triacanthos.*[10] Leonard and Fujii have synthesized the N isomers of triacanthine including the N^6 isomer,[8] the free base of compound I. This synthetic compound is a more potent cytokinin than kinetin [6-furfurylamino)purine].[14]

Compound I, which possesses cytokinin activity,[15] represents the first naturally occurring cytokinin to be found as an integral part of a nucleic acid. Whether there is any relationship between the capacity of compound I to promote cell division and differentiation in plants and its presence in RNA is an open question. Nevertheless, the chemical reactivity of the isoprene–adenine unit may be of considerable importance to the biochemical function of those s-RNA molecules in which it is located.

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[8] N. J. Leonard and T. Fujii, *Proc. Natl. Acad. Sci. U. S.*, **51**, 73 (1964).

[9] A. D. Broom, L. B. Townsend, J. W. Jones, and R. K. Robins, *Biochemistry*, 3, 494 (1964).

[10] N. J. Leonard and J. A. Deyrup, *J. Am. Chem. Soc.*, **84**, 2148 (1962).

[11] R. H. Hall, *Biochemistry*, **3**, 876 (1964).

[12] H. G. Zachau, private communication. The material isolated by Dr. Zachau is identical with our isolated sample of compound I on the basis of ultraviolet spectroscopy, cochromatography, and its breakdown in acid to form compounds A and B. Dr. Zachau has independently obtained evidence that supports the structure of I.

(13) P. Brookes and P. D. Lawley, *J. Chem. Soc.*, 539 (1960).

(14) H. Q. Hamzi and F. Skoog, *Proc. Natl. Acad. Sci.* U.S., **51**, 76 (1964).

(15) Full details of the biological activity will be published elsewhere.

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The Structures of Some Presumed 9,10-Dihydro-9,10-*o*-xylyleneanthracene Derivatives. A Case of 1,5 Participation by Bromine in a Free Radical Bromination

Sir:

The synthesis of a number of derivatives of 9,10-dihydro-9,10-*o*-xylyleneanthracene (I) has been reported and a detailed conformational analysis of these compounds has been made on the basis of spectral properties.[1] In the course of a study of various synthetic approaches to 9,10-benzocyclobutenoanthracene,[2] we encountered reactions of some derivatives of I which could not be reconciled with their previously assigned structures. We now wish to report a revision of the structures of all but one of the above derivatives[3] and the transformation of some of these compounds into a novel new hexacyclic hydrocarbon for which we propose the name triskelene (II).[4] In the course of this work an unusual rearrangement reaction has been found in which a bromine-stabilized radical plays a key role.

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(1) K. Sisido, R. Noyori, and H. Nozaki, *J. Am. Chem. Soc.*, **84**, 3562 (1962).

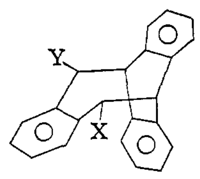
(2) M. P. Cava and R. Pohlke, *J. Org. Chem.*, **28**, 1012 (1963).

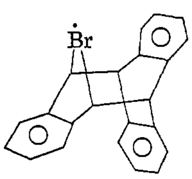
(3) For the sake of brevity, several compounds described in ref 1 (a diacetate, a diol, a hydroxy ketone, and an acetoxy ketone) are not specifically discussed in this communication, although they must now be regarded as semitriskelene structures since they were all obtained from either Xb or IXb.

(4) Derived from the word *triskelion:* a symbolic figure consisting of three curved branches or bent legs or arms radiating from a center. Its systematic name is: 5,10-(*o*-benzeno)-4b,5,9b,10-tetrahydro-7H-indeno-[2,1-*a*]indene.

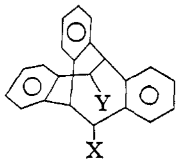
The reaction of I with 1 equiv of N-bromosuccinimide (NBS) in CCl_4 (tungsten lamp) gave the previously reported monobromide III, mp 183°.[5,6] Lithium aluminum hydride (LAH) reduction of III gave I, confirming the unrearranged skeletal structure of III. Acetolysis of III gave the monacetate IV, mp 172°,[1] assigned the rearranged structure IVb instead of the originally assigned structure IVa for the following reasons. Alkaline hydrolysis of IVb gave alcohol Vb (rather than Va), mp 191°,[1] converted by thionyl chloride (*via* the uncharacterized VIb) followed by LAH reduction to the new hydrocarbon 3,7-*o*-benzeno-1,2,5,6-dibenzocyclooctadiene ("semitriskelene," VII), mp 235°. Chromic acid oxidation of Vb gave monoketone VIIIb (rather than VIIIa), mp 193°;[1] further oxidation of VIIIb gave diketone IXb, mp 224–225°. The isomeric unrearranged diketone IXa, mp 213–214°, was obtained by direct chromic acid oxidation of hydrocarbon I.[7]

Bromination of I (tungsten lamp) with 2 equiv of NBS (or better, bromine) in CCl_4 gave the rearranged dibromide Xb, mp 235° (reported[1] as Xa, mp 216–217°). Further light-catalyzed bromination of Xb afforded tribromide XI, mp 217°, and finally tetrabromide XII, mp 224–225° dec; solvolysis of XII in moist methanol gave diketone IXb. Bromides Xb, XI, and XII were all reduced by LAH (or zinc) to give the same hydrocarbon, triskelene (II),[4] mp 207°. Zinc reduction of tetrabromide XII could be effected in two stages, allowing the isolation of 6,12-dibromotriskelene (XIII), mp 233°. The structure of XIII has been confirmed by a complete X-ray crystallographic analysis.[8]



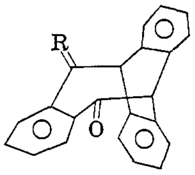


XIV

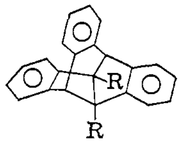


Series a
I, X = Y = H
III, X = Br, Y = H
IV, X = $OCOCH_3$, Y = H
V, X = OH, Y = H
X, X = Y = Br

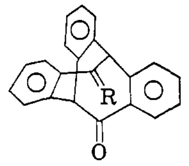
Series b
IV, X = $OCOCH_3$, Y = H
V, X = OH, Y = H
VI, X = Cl, Y = H
VII, X = Y = H
X, X = Y = Br



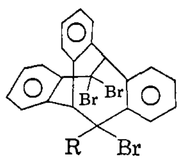
VIIIa, R = H_2
IXa, R = O



II, R = H
XIII, R = Br



VIIIb, R = H_2
IXb, R = O



XI, R = H
XII, R = Br

The bromination of I under free radical conditions takes place rapidly (within a few minutes) and cleanly to give only either the *unrearranged* monobromide III or the *rearranged* dibromide Xb. Clearly the bromine atom in III must play a critical part in the rearrangement to the semitriskelene skeleton which accompanies bromination of III to Xb. We suggest that the radical formed by abstraction of a hydrogen atom from III is stabilized considerably by neighboring group participation of the bromo substituent. The resulting strainless but rigid bridged radical (XIV) has a geometry particularly conducive to a transoid rearrangement to the energetically more favorable semitriskelene system.[9] Evidence has been reported previously in support of three-membered-ring bromine radical intermediates produced during photobromination.[10] The conversion of III to Xb is, to our knowledge, the first example of a reaction involving a five-membered-ring bridged bromine radical.

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[5] Satisfactory elemental analyses were obtained for all compounds reported in this paper except for tribromide XI which was not obtained entirely free of Xb.

[6] This melting point is at variance with that (141–142°) previously reported.

[7] The diketone (mp 213–214°) previously assigned structure IXa (ref 1) must be regarded as a slightly impure sample of our diketone IXb (mp 224–225°). The ultraviolet spectrum reported for this material is identical with that of our rearranged diketone IXb. In contrast, the ultraviolet spectrum of our unrearranged diketone IXa shows the following values in isooctane solution: λ_{max} 203 mμ (log ε 4.69), 221 (4.34), 230 (4.25), and 273 (4.14). Apparently, the carbonyl groups of diketone IXa show very little conjugation with the adjacent aromatic ring, indicating a bent structure for the *o*-phthaloyl system.

[8] This work was carried out by R. Henriques, F. Paton, and R. Gosling at the Department of Physics, University of the West Indies. A complete analysis of the structure of XIII will be published elsewhere.

[9] Molecular models indicate that no appreciable nonbonded interactions exist in semitriskelene (VII). On the other hand, such interactions are present in hydrocarbon I (see ref 1).

[10] P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2849 (1963); P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964).

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Ethylene Episulfoxide[1]

Sir:

Reported attempts to oxidize ethylene episulfide to either the episulfoxide or the episulfone have consistently failed.[2] Several examples of ethylene episulfones are now known, but these were prepared by reaction of a diazomethane with sulfur dioxide.[3] The only characterized examples of an episulfoxide or an episulfone obtained by oxidation of the corresponding episulfide are those resulting from the hydrogen peroxide oxidation of dibenzoylstilbene episulfide.[4]

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[1] Thiirane 1-oxide.

[2] (a) G. Hesse, E. Reichold, and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957); (b) C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

[3] (a) G. Hesse, E. Reichold, and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957); (b) H. Staudinger and F. Pfenninger, *ibid.*, **49**, 1941 (1916); (c) N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966); (d) N. P. Neureiter, *J. Am. Chem. Soc.*, **88**, 558 (1966).