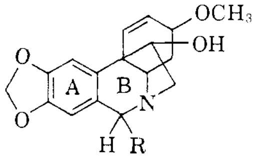
TABLE I

Fraction	Phenylalanine fed % Incorp.	Phenylalanine fed Dilution[a]	Tyrosine fed % Incorp.	Tyrosine fed Dilution
Chloroform-insoluble alkaloids	0.45		1.02	
Chloroform-soluble alkaloids	0.95		1.42	
Lycorine	0.095	5.46×10^3	0.11	1.55×10^4
Belladine	0.42	1.33×10^3	0.82	3.33×10^3

[a] Specific activity of compound fed (μc./mM.) divided by specific activity of compound isolated.

incorporation of these amino acids in *Nerine bowdenii*, where at least two alkaloid ring systems could be examined simultaneously.



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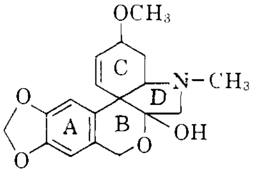

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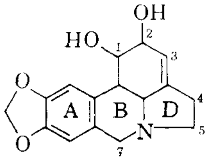
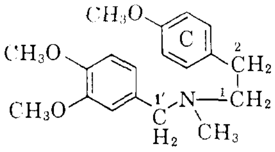


III



IV

Solutions of the hydrochlorides of 3-C^{14}-DL-phenylalanine (0.3 mc.) and 3-C^{14}-DL-tyrosine (0.1 mc.) were injected into the bulbs of blooming *N. bowdenii*. After one month the bulbs were harvested and processed in the usual way.[6] Total incorporation of radioactivity of phenylalanine and tyrosine into the various alkaloid fractions is given in Table I. The lycorine (III) and belladine (IV), after appropriate dilution with inactive alkaloids, were degraded by the methods described in a previous paper.[6] The relative specific activities of pertinent degradation products are listed in Table II. These data show conclusively that phenylalanine can serve as a precursor of ring A and the benzylic carbon atom in both the lycorine and belladine ring systems but is unable to provide the C_6–C_2 fragment (ring C and the two-carbon side chain) in these alkaloids. In agreement with our earlier results in *S. formosissima*,[2] tyrosine can serve as the precursor of the C_6–C_2 unit, but not the C_6–C_1 unit of belladine.

Superficially, these findings are in conflict with the fact that in most Amaryllidaceae alkaloids ring A possesses a greater degree of hydroxylation than ring C. However, similar findings have been reported in the biosynthesis of the phenolic cinnamic acids related to lignin.[7] A more detailed study of the processes by which oxygen is introduced into the C_6–C_1 unit of these alkaloids is in progress.

TABLE II[a]

Fragment	Isolated and counted as	Relative activity Phenylalanine	Relative activity Tyrosine
IV	Belladine (IV)	1.00	1.00
IV	Belladine methiodide	0.96	0.95
IV, Ring A + C_1'	N,N,N-Trimethylveratrylammonium iodide	.92	.00
IV, Ring C + C_1, C_2	1-(*p*-Methoxyphenyl)-1,2-dibromoethane	.01	.99
IV, Ring C + C_1, C_2	1-(*p*-Methoxyphenyl)-1,2-ethanediol	.01	1.00
IV, C_1	Formaldehyde (methone)	.00	0.00
IV, Ring C + C_2	Anisaldehyde (octahydroxanthene)	.01	0.98
III	Lycorine	1.00	..
III	4-(1,2-Dihydroxyethyl)-5,6-dihydro-5-methyl-8,9-methylenedioxyphenanthridine	0.99	..
III, C_5	Formaldehyde (methone)	0.00	..
III, less C_5	4-Carboxy-5-methyl-8,9-methylenedioxyphenanthridinone	1.02	..
III, C_4	Barium carbonate	0.00	..
III, less C_4, C_5	5-Methyl-8,9-methylenedioxyphenanthridinone	1.04	..
III, less C_4, C_5	5-Methyl-8,9-methylenedioxy-6-phenylphenanthridinium perchlorate	0.95	..
III, C_7	Benzoic acid	0.97	..

[a] Samples were counted in a Packard Tri-carb Scintillation Counter in toluene or dioxane–naphthalene scintillator solutions.

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(6) W. C. Wildman, H. M. Fales, R. J. Highet, S. W. Breuer and A. R. Battersby, *Proc. Chem. Soc.*, 180 (1962).

(7) D. R. McCalla and A. C. Neish, *Can. J. Biochem. and Physiol.*, **37**, 537 (1959).

DOUBLE ADDITION OF A CARBENE TO AN ACETYLENE

Sir:

Hydrocarbon bicyclobutanes have recently been prepared by double carbene sequences.[1,2] We wish to report the formation of a perfluorobicyclobutane by adding difluorocarbene twice to hexafluoro-2-butyne.

Difluorocarbene was generated by pyrolysis of $(CF_3)_3PF_2$ at 100°[3] and added to hexafluoro-2-butyne in the gas phase to give 1,2-bis-(trifluoro-

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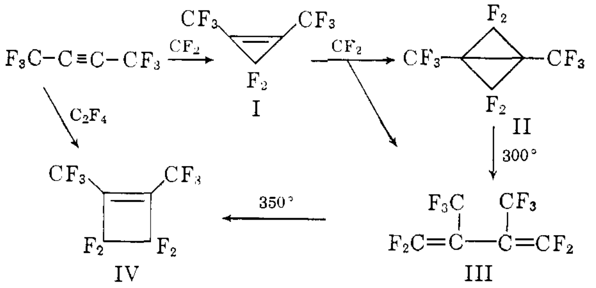
(1) R. Breslow, Organic Symposium, Bloomington, Indiana, June, 1961.

(2) W. R. Moore, H. R. Ward and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

(3) W. Mahler, Abstracts, 2nd International Symposium on Fluorine Chemistry, Estes Park, Colo., 1962, p. 90.



methyl)-3,3-difluorocyclopropene (I), b.p. 11°, m.p. −86°, double bond absorption at 1820 cm.$^{-1}$, mol. wt. (vapor density), observed 212, calcd. for C_5F_8, 212. The cyclopropene I was chlorinated in ultraviolet light to give 1,2-bis(trifluoromethyl)-1,2-dichloro-3,3-difluorocyclopropane as a 1:5 *cis-trans* mixture.

Anal. Calcd. for $C_5Cl_2F_8$: C, 21.20; Cl, 25.08; F, 53.72; mol. wt., 283. Found: C, 21.76; Cl, 24.93; F, 54.09; mol. wt., 287.

The *cis*-dichloro compound, isolated by gas chromatography, has m.p. −72°, 23 mm. vapor pressure at 0° and shows non-equivalent CF_2 fluorines with coupling of 172 c.p.s., characteristic of cyclopropanes.[4,5] The *trans* isomer has m.p. −56°, 27 mm. vapor pressure at 0°, and equivalent *gem* fluorines by n.m.r.

Difluorocarbene adds to the cyclopropene I at 100° in the gas phase to give a 25% yield of 1,3-bis-(trifluoromethyl)-2,2,4,4-tetrafluorobicyclobutane (II), b.p. 39°, m.p. −90°, together with an 8% yield of 2,3-bis-(trifluoromethyl)-1,1,4,4-tetrafluorobutadiene (III), b.p. 52°, m.p. −91°.

Anal. Calcd. for C_6F_{10}: C, 27.48; F, 72.52; mol. wt., 262. Found for II: C, 28.11; F, 72.50; mol. wt., 262. Found for III: C, 27.82; F, 72.30; mol. wt., 263.

No band characteristic of unsaturation appears in the infrared or Raman spectra of the bicyclobutane II. The F^{19} magnetic resonance spectrum of the CF_2 groups of the bicyclobutane in the first approximation is of the type AB[6] with a splitting of 150 c.p.s. In detail, it is A_2B_2[7] further complicated by sevenfold multiplicity due to the equivalent CF_3 groups. The pattern for the CF_3 groups is a triplet of triplets.

The infrared spectrum of the butadiene III shows absorption at 1750 and 1725 cm.$^{-1}$, indicative of two double bonds. The CF_2 fluorines are non-equivalent by n.m.r. with no detectable spin-spin interaction with each other.

At 300° the bicyclobutane II slowly rearranges to the butadiene III (20% conversion, 95% yield in 16 hours). At 350° the butadiene III cyclizes to 1,2-bis-(trifluoromethyl)-3,3,4,4-tetrafluorocyclobutene (IV) (15% conversion, 100% yield in 48 hours). This cyclobutene was prepared independently by the cycloaddition of hexafluoro-2-butyne to tetrafluoroethylene at 230° (3% yield in 4 hours); b.p. 36°, m.p. −66°, absorption at 1715 cm.$^{-1}$, mol. wt., observed, 259. The *gem* fluorines of IV are equivalent by n.m.r. In ultraviolet light, chlorine adds to give the dichloro adduct as a solid *cis–trans* mixture.

Anal. Calcd. for $C_6Cl_2F_{10}$: Cl, 21.32; F, 57.06. Found: Cl, 21.36; F, 56.72.

In further demonstration of the structure, the bicyclobutane II reacts in the dark at 200° to add chlorine across the diagonal bond.

Anal. Calcd. for $C_6Cl_2F_{10}$: C, 21.62; Cl, 21.32; F, 57.06. Found: C, 21.37; Cl, 21.65; F, 57.04.

F^{19} magnetic resonance shows this to be a *cis–trans* mixture, different from the 1,2 isomers derived from the cyclobutene. The *cis* 1,3 isomer has non-equivalent CF_2 fluorines with coupling constants of 211 c.p.s. characteristic of cyclobutanes.[4] The *trans* 1,3 isomer shows equivalent *gem* fluorines as expected.

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[4] W. D. Phillips, *J. Chem. Phys.*, **25**, 949 (1956).

[5] E. G. Brame, Jr., unpublished observations.

[6] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 122.

[7] *Ibid.*, p. 146.

THE XENON RADIOSENSITIZED EXCHANGE OF DEUTERIUM ATOMS WITH METHANE

Sir:

In a recent paper[1] describing studies of the deuterium–methane exchange initiated by tritium β-rays, the absence of the abstraction reaction (1) was reported. This surprising conclusion is contradictory to what recently has been

$$D + CH_4 \longrightarrow HD + CH_3 \qquad (1)$$

thought to be a well-established reaction[2–4] and is based mainly on the observations that no ethane was detected and that the only initial exchange product was CH_3D. With evidence against (1), these authors[1] propose that the exchange proceeds *via* a non-abstraction mechanism (other than a high activation energy inversion[5]), *viz.*

$$D + CH_4 \longrightarrow CH_3D + H \qquad (2)$$

$$H + D_2 \longrightarrow HD + D \qquad (3)$$

Moreover, temperature dependence studies of this exchange system[1] were found to be inconsistent with the results of Berlie and Leroy,[2] who found E_1 = 4.5 kcal./mole and a steric factor of the order of 10^{-5}.

In studies of the xenon radio-sensitized deuterium–methane exchange at room temperature we have obtained evidence consistent with LeRoy's contention[3] that (1) occurs at room temperature and above. Furthermore, our results are in accord with the low values of E_1 and P_1 found by Berlie and LeRoy,[2] with Whittle and Steacie's estimate[6] of E_1 = 7.8 kcal./mole and $P_1 \sim 10^{-3}$ to

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[1] R. F. Firestone, C. F. Lemr and G. J. Trudel, *J. Am. Chem. Soc.*, **84**, 2279 (1962).

[2] M. J. Berlie and D. J. LeRoy, *Can. J. Chem.*, **32**, 650 (1954).

[3] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Edition, Reinhold Publishing Corp., New York, N. Y., 1954, pp. 454–455.

[4] D. W. Coillet and G. M. Harris, *J. Am. Chem. Soc.*, **75**, 1486 (1953).

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