neutrons[1] and $Si(CH_3)_4$ + neutrons;[2] the ^{31}Si reactions with the starting materials were reported.

We report here a reaction of thermally vaporized silicon atoms. In an apparatus essentially as described for carbon vaporizations[3] a p-type semiconductor grade of silicon[4] was heated resistively to 1400° *in vacuo* (2×10^{-5} torr) while trimethylsilane was deposited on the liquid nitrogen cooled walls as a trapping agent. Aside from the presence of unidentified products, totaling 5%, the sole reaction product (20–30% based on silicon vaporized) isolated by gas chromatography is 1,1,1,3,3,3-hexamethyltrisilane, ($(CH_3)_3SiSiH_2Si(CH_3)_3$, I). I was identified by analysis of its nmr, infrared, and mass spectra. The nmr spectrum showed two singlets, area ratio 8.85:1, at τ 9.80 and 7.01, respectively, in benzene. The infrared spectra showed absorptions at 3.4, 3.5, 4.8 (Si–H), 7.1, 8.0, 10.9, 11.7–12.0, 13.4, 14.5, and 15.0 μ.

The mass spectrum (70 ev) consisted of a parent peak, *m/e* 176, with P + 1 and P + 2 of expected intensities for three silicon atoms; the $(CH_3)_3Si^+$ peak is the most prominent peak of the spectrum.

The insertion of silicon atoms into the Si–H bond of trimethylsilane is analogous to the earlier reports of insertion into Si–H bonds by carbenes[5,6] and dimethylsilene;[7] it is probably a two-step insertion.

$$(CH_3)_3SiH + Si \longrightarrow (CH_3)_3SiSiH$$

$$(CH_3)_3SiSiH + (CH_3)_3SiH \longrightarrow (CH_3)_3SiSiH_2Si(CH_3)_3$$

The study of silicon atom chemistry with other substrates is in progress.

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(1) P. P. Gaspar, B. D. Pate, and W. Eckelman, *J. Am. Chem. Soc.*, **88**, 3878 (1966).

(2) D. Snediker, "The Chemical Effects of Neutron Capture in Tetramethyl Silane," Ph.D., Thesis, The Pennsylvania State University, 1965.

(3) P. S. Skell, L. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *J. Am. Chem. Soc.*, 87, 2829 (1965).

(4) We gratefully acknowledge the assistance of Texas Instruments Inc., Dallas, Texas, in providing samples of silicon.

(5) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **85**, 2667 (1963).

(6) K. Kramer and A. Wright, *Angew. Chem.*, **74**, 468 (1962); *Tetrahedron Letters*, 1095 (1962).

(7) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442, 1443 (1964).

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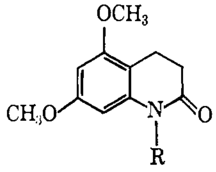
Synthesis of Acronycine

Sir:

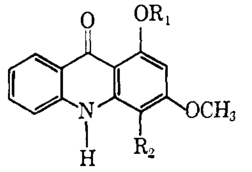
Acronycine,[1–5] an alkaloid isolated from *Acronychia Baueri* Schott, is reported to show significant antitumor activity in experimental animals.[6] We wish to report a synthesis of this natural product.

5,7-Dimethoxy-3,4-dihydrocarbostyril (**1a**, mp 194–195°) is formed in 30% yield by fusing the 3-bromopropionyl derivative of 3,5-dimethoxyaniline with zinc chloride–sodium chloride at 150° for 30 min. Reaction of **1a** with 2-iodobenzoic acid in nitrobenzene with cuprous iodide as the catalyst at 170° for 6 hr yields 1-(2-carboxyphenyl)-5,7-dimethoxy-3,4-dihydrocarbostyril (**1b**, mp 227–229°, 53% yield). Ring closure with polyphosphoric acid at 100° for 2 hr followed by treatment with refluxing 1 *N* methanolic hydrogen chloride for 2.5 hr yields methyl 1,3-dimethoxy-9-oxoacridan-4-propionate (**2a**, mp 244–245°, 83% yield).

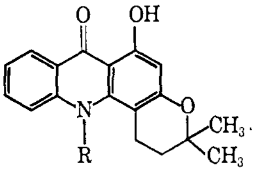
The methoxyl function at C-1 is selectively hydrolyzed with boron trichloride[7] in methylene chloride to form methyl 1-hydroxy-3-methoxy-9-oxoacridan-4-propionate (**2b**, mp 194–195°, 80% yield). Treatment of **2b** with excess methyllithium in tetrahydrofuran at −20° gives the corresponding tertiary carbinol **2c** (mp 213–214°, 82% yield). Fusion of **2c** with pyridine hydrochloride at 200° for 2 hr yields 6-hydroxy-3,3-dimethyl-2,3-dihydro-7(12H)-1H-pyrano[2,3-*c*]acridinone (**3a**, mp 278–280° dec). Owing to its tendency to crystallize on the column during silica gel chromatography, **3a** is not ordinarily isolated. Instead, the crude product is allowed to react with methyl iodide and potassium carbonate in refluxing acetone[2] to give nordihydroacronycine (**3b**, mp 213–215°, 20% over-all yield). This compound is identical by the usual physical comparisons with an authentic sample prepared from acronycine.[2]



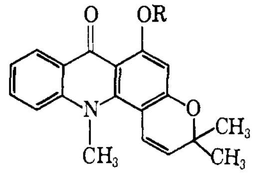
1a, R = H
b, R = 2-HOOCC$_6$H$_4$



2a, R$_1$ = CH$_3$
R$_2$ = CH$_2$CH$_2$COOCH$_3$
b, R$_1$ = H
R$_2$ = CH$_2$CH$_2$COOCH$_3$
c, R$_1$ = H
R$_2$ = CH$_2$CH$_2$C(CH$_3$)$_2$OH



3a, R = H
b, R = CH$_3$



4a, R = H
b, R = CH$_3$

Alternately, **3a** is prepared by treating 1,3-dihydroxy-9-acridanone,[8] prepared by hydrolysis of 1,3-dimethoxy-9-acridanone,[3] with 3,3-dimethylallyl chloride and zinc chloride in refluxing trifluoroacetic acid for 3 hr (18% yield).

Conversion of **3b** to noracronycine (**4a**) is accomplished with 2,3-dichloro-5,6-dicyanobenzoquinone in refluxing toluene (40% yield). The product obtained is identical with an authentic sample prepared from the natural product.[2] Methylation of **4a** to

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(1) F. N. Lahey and W. C. Thomas, *Australian J. Sci. Res.*, **A2**, 423 (1949).

(2) R. D. Brown, L. J. Drummond, F. N. Lahey, and W. C. Thomas, *ibid.*, **A2**, 622 (1949).

(3) L. J. Drummond and F. N. Lahey, *ibid.*, **A2**, 630 (1949).

(4) P. L. Macdonald and A. V. Robertson, *Australian J. Chem.*, **19**, 275 (1966).

(5) T. R. Govindachari, B. R. Pai, and P. S. Subramaniam, *Tetrahedron*, **22**, 3245 (1966).

(6) G. H. Svoboda, G. A. Poore, P. J. Simpson, and G. B. Boder, *J. Pharm. Sci.*, **55**, 758 (1966).

(7) F. M. Dean, J. Goodchild, L. E. Houghton, J. A. Martin, R. B. Morton, B. Parton, A.W. Price, and N. Somvichien, *Tetrahedron Letters*, 4153 (1966).

(8) W. Baczynski and S. von Niementowski, *Ber.*, **38**, 3009 (1905).

form acronycine (**4b**) is brought about by a procedure described in the literature.[2] The product obtained is identical with acronycine.

Microanalytical data and nmr, ultraviolet, and infrared spectra are all in agreement with the structural assignments.

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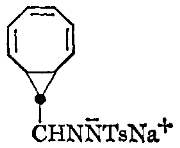
Three Bicyclic Nonatrienes from Bicyclo[5.1.0]octa-2,4-dien-8-yl Carbene[1,2]

Sir:

A preliminary report on the synthetic utility of rearrangements of highly unsaturated bicyclic carbenes has been made.[3] Bicyclo[4.2.2]deca-2,4,7,9-tetraene and the 9,10-dihydronaphthalenes were shown to be the products of thermal decomposition of I. We describe here a further example of such a rearrangement, the synthesis of three bicyclic nonatrienes, and comment upon the mechanism of these remarkable changes.

Following the procedure of Korte,[4] ethyl or methyl diazoacetate was catalytically decomposed in tropilidene to give IIa. This compound could be converted *via* IIb–e in conventional steps to the salt IIf. Decomposition of IIf under vacuum at 90–120° led to a complex mixture of isomers from which the four major products could be isolated by preparative gas–liquid partition chromatography. These are, in order of elution from a 3.5-m, 10% Carbowax 20M on 45–60 Chromosorb P column operated at 100° with a helium flow of 100 cc/min, tropilidene (19%; relative retention time 1.00), bicyclo[5.2.0]nona-2,4,8-triene (III, 27%; relative retention time 3.38; infrared: 3010, 2920, 2900, 2850, 1640, 1445, 1375, 1284, 1222, 998, 922, 715, and 675 cm^{-1}), bicyclo[4.2.1]nona-2,4,7-triene (IV, 37%; relative retention time 4.66), and bicyclo[3.2.2]nona-2,6,8-triene (V, 12%; relative retention time 5.25; infrared 3030, 3005, 2945, 2910, 2860, 2800, 1630, 1610, 1422, 1378, 1366, 1325, 1276, 1249, 1195, 1040, 980, 959, 886, 870, 715, and 688 cm^{-1}). The over-all yield of hydrocarbons was *ca.* 35%. Compound IV was identified by comparison of infrared and nuclear magnetic resonance spectra with those of authentic material[5,6] and by hydrogenation to bicyclo[4.2.1]nonane identical with that prepared from bicyclo[4.2.1]nonan-9-one[7] by Wolff–Kishner reduction. Compound V absorbed 3 moles of hydrogen to give a hydrocarbon identical with that prepared from bicyclo[3.2.2]non-6-en-2-one[8] by hydrogenation and Wolff–Kishner reduction. The structure of III was determined in a similar fashion. *cis*-Bicyclo[5.2.0]non-8-ene (VI) was synthesized from cycloheptene by the method of Kirmse.[9] This material had an infrared spectrum identical with that of the compound prepared by Fonken by photolysis of the cyclononadienes[10] or by thermal cyclization of *cis*,-*trans*-1,3-cyclononadiene.[11] Hydrogenation of VI gave *cis*-bicyclo[5.2.0]nonane (VII), again identical with material made by Fonken.[11] Allinger[12] originally synthesized both *cis*- and *trans*-bicyclo[5.2.0]nonanes from the known and characterized[13] *cis*- and *trans*-1,2-dicarboxycyclobutanes. Fonken identified his materials by comparison of spectra with those of Allinger. Accordingly, the assignment of stereochemistry in VI and VII is secure. Hydrogenation of III led to the uptake of 3 moles of hydrogen and the formation of VII as the sole product. The skeleton and stereochemistry of III can therefore be assigned with confidence. In all cases infrared and nmr spectra were consistent, if not uniquely so, with the assigned structures.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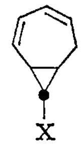
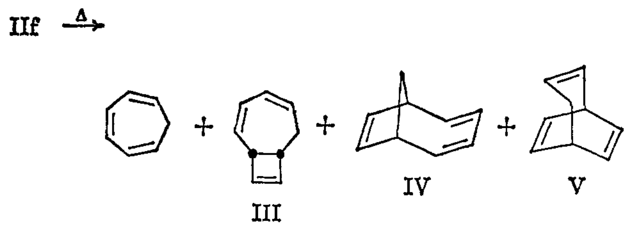
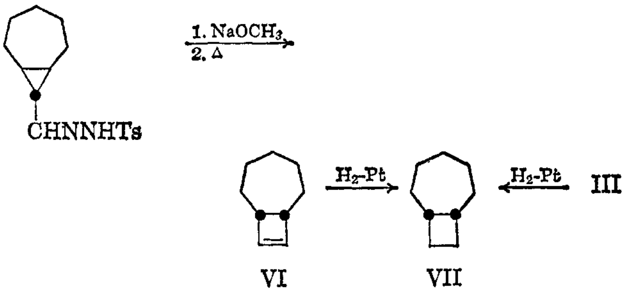

IIa, X = $COOCH_3$
b, X = COOH
c, X = COCl
d, X = CHO
e, X = CHNNHTs
f, X = $CHN\bar{N}TsNa^+$





Isolation of III allows some comments to be made on the mechanism of the changes observed in this and previous[3] work. The possible paths for the formation of IV and V include the sigmatropic rearrangement of the cyclobutene III. A thermally allowed shift of the order [1,5] would lead to IV, while V is the product of a hypothetical shift of the order [1,3], an event expected

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[1] We are pleased to thank the Lilly Research Laboratories for most generous support of this work.

[2] Taken in part from the A.B. Thesis of S. D. Reich, Princeton University, 1967.

[3] M. Jones, Jr., and L. T. Scott, *J. Am. Chem. Soc.*, **89**, 150 (1967).

[4] F. Korte, K.-H. Büchel, and F. F. Wiese, *Ann.*, **664**, 114 (1963).

[5] W. Grimme, *Chem. Ber.*, 100, 113 (1967). We are particularly grateful to Dr. Grimme for informing us of his work prior to publication and for supplying us with many excellent spectra.

[6] L. G. Cannell, *Tetrahedron Letters*, 5967 (1966).

[7] C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960).

[8] J. A. Berson and M. Jones, Jr., *ibid.*, **86**, 5017, 5019 (1964). We thank Professor Berson for a sample of this compound.

[9] W. Kirmse and K.-H. Pook, *Chem. Ber.*, **98**, 4022 (1965).

[10] K. M. Shumate and G. J. Fonken, *J. Am. Chem. Soc.*, **88**, 1073 (1966).

[11] K. M. Shumate, P. N. Neuman, and G. J. Fonken, *ibid.*, **87**, 3996 (1965). We thank Professor Fonken for copies of these spectra.

[12] N. L. Allinger, M. Nakazaki, and V. Zalkow, *ibid.*, **81**, 4074 (1959).

[13] W. H. Perkin, Jr., *J. Chem. Soc.*, 572 (1894).