COMMUNICATIONS TO THE EDITOR

TETRAFLUOROHYDRAZINE

Sir:

To date there have been reported and verified only four binary compounds composed of nitrogen and fluorine: nitrogen trifluoride,[1] *cis*- and *trans*-difluorodiazine[2] and fluorine azide.[2] We wish to report the preparation and properties of a fifth such compound, tetrafluorohydrazine.

Tetrafluorohydrazine is made by the thermal reaction of nitrogen trifluoride with various metals such as stainless steel, copper, arsenic, antimony and bismuth according to the equation $2NF_3 + M \rightarrow N_2F_4 + MF$. In a flow reactor packed with copper turnings at 375° with a residence time of 13 minutes tetrafluorohydrazine was produced from nitrogen trifluoride in 42–62% conversion and a yield of 62–71%.

Tetrafluorohydrazine was purified by distillation of the residual nitrogen trifluoride from a *n*-pentane slush bath (−131.5°) which retained the tetrafluorohydrazine. Further purification was carried out by gas phase adsorption chromatography using a column of Linde Molecular Sieve 13X.[3]

The identity of tetrafluorohydrazine has been established by elemental analysis and molecular weight determination: F, calcd. 73.06%, found 71.92%; mol. wt. calcd. 104, found 107. The molecular weight differentiates this compound from the NF_2 reported by Ruff,[4] as do the reported physical properties.

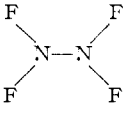
The vapor pressure of tetrafluorohydrazine was measured and can be expressed by a Clausius–Clapeyron equation

$$\log P_{(mm)} = -692/T + 6.33$$

The boiling point of tetrafluorohydrazine is calculated to be −73° and the heat of vaporization is estimated to be 3170 cal./mole. The critical temperature of tetrafluorohydrazine by the Cagniard de la Tour tube method is 36°. From an extrapolation of the vapor pressure data a critical pressure of 77 atmospheres is estimated.

The infrared absorption spectrum of tetrafluorohydrazine consists of a very strong complex band between 9.75 and 10.75 μ and a strong broad band at 13.60 μ.

The mass spectrum of tetrafluorohydrazine given in Table I obtained on a Consolidated Model 620 Mass Spectrometer is consistent with the proposed structure



(1) O. Ruff, J. Fischer and F. Luft, *Z. anorg. allgem. Chem.*, **172**, 417–428 (1928).

(2) J. F. Haller, Ph.D. Thesis, Cornell University, 1942.

(3) Trade Mark of Union Carbide and Carbon Corporation, New York, N. Y.

(4) O. Ruff and L. Staub, *Z. anorg. allgem. Chem.*, **198**, 32–38 (1931).

TABLE I

FRAGMENTATION PATTERN OF N_2F_4

m/e	Ion	Pattern
52	NF_2^+	90.6%
33	NF^+	100.0%
28	N_2^+	7.7%
19	F^+	4.7%
14	N^+	8.5%

Sensitivity div./μ 19.0

Instrument sensitivity 100 div./μ for *m/e* 43 of *n*-butane

The F^{19} nuclear magnetic resonance spectrum of tetrafluorohydrazine consisted of a single broad unresolved band at a field of approximately 75 p.p.m. lower than that of the F^{19} nuclei of trifluoroacetic acid. Resolution of the expected triplet was not observed, probably because of the low symmetry of tetrafluorohydrazine.

The mechanism of formation of this compound and its chemical and physical properties are under investigation; results will be prepared at a later date.

The authors wish to express their appreciation to Dr. Keith S. McCallum for the analyses and n.m.r. spectrum of tetrafluorohydrazine.

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MICROBIOLOGICAL TRANSFORMATIONS. II. THE MICROBIOLOGICAL AROMATIZATION OF STEROIDS[1]

Sir:

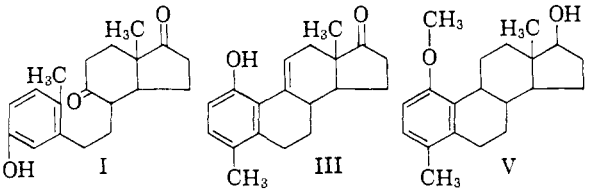
Although the transformation of steroids with microörganisms has been studied[1,2] extensively, no microbiological conversion of alicyclic steroids possessing an angular group at C_{10} to aromatic materials has as yet been reported. During our studies of the fermentation of 4-androstene-3,17-dione with a species of *Pseudomonas* isolated from cotton we obtained a phenolic compound (I), m.p. 123.5–125°; $\lambda_{max}^{methanol}$ 280 mμ (ε 2,320); $[\alpha]D$ +100.5° ($CHCl_3$); λ_{max}^{KBr} 2.92 μ (OH), 5.78 μ (17C=O), 5.92 μ (C=O), 6.23 μ, 6.66 μ (aromatic ring), 11.48 μ, 12.225 μ; (found: C, 76.14; H, 8.19). The phenolic compound (I) was prepared by the fermentation and extraction techniques previously described.[3] It was isolated by extraction with aqueous sodium hydroxide from a benzene–ether solution of the crude fermentation products, and was precipitated from the basic solution with either carbon dioxide or acetic acid. Acetylation of I

(1) Previous paper: R. M. Dodson, A. H. Goldkamp and R. D. Muir, THIS JOURNAL, **79**, 3921 (1957). For excellent reviews on the microbiological transformation of steroids, see reference 1 of this paper.

(2) P. Talalay, *Physiol. Revs.*, **37**, 362 (1957).

(3) D. H. Peterson, H. C. Murray, S. H. Eppstein, L. M. Reineke, A. Weintraub, P. D. Meister and H. M. Leigh, THIS JOURNAL, **74**, 5933 (1952).

with acetic anhydride and pyridine yielded a monoacetate (II), m.p. 147–147.5°; $\lambda_{max}^{methanol}$ 266 mμ (ε 650), 273 mμ (ε 650); $[\alpha]D$ +82.5° ($CHCl_3$); λ_{max}^{KBr} 5.70 μ, 8.225 μ (ester), 5.77 μ (17C=O), 5.90 μ (C=O), 6.225 μ, 6.325 μ, 6.71 μ (aromatic ring), 11.10 μ, 11.97 μ; (found: C, 73.34; H, 7.61).



The structure of I as 9,10-seco-3-hydroxy-1,3,5(10)-androstatriene-9,17-dione was established by this series of reactions: a solution of II in methanol:concd. hydrochloric acid (2:1) on standing deposited crystals of 1-hydroxy-4-methyl-1,3,5(10),9(11)-estratetraen-17-one[4] (III), m.p. 194–197°; $\lambda_{max}^{methanol}$ 255.5 mμ (ε 13,200), 300 mμ (ε 3,830), shoulders 265 mμ, 310 mμ; $[\alpha]D$ +264° ($CHCl_3$); λ_{max}^{KBr} 3.07 μ (OH), 5.79 μ (17C=O), 6.18 μ, 6.29 μ, 6.84 μ; (found: C, 80.55; H, 7.73). Compound III was converted, using methyl iodide and potassium carbonate in acetone, to 1-methoxy-4-methyl-1,3,5(10),9(11)-estratetraen-17-one, m.p. 123–124°; (found: C, 80.91; H, 8.22); which, in turn, was reduced with sodium borohydride to 1-methoxy-4-methyl-1,3,5(10),9(11)-estratetraen-17-ol, (IV) m.p. 144–145°; (found: C, 80.38; H, 8.95). Removal of the double bond from IV by reduction with potassium in liquid ammonia[5] gave the desired 1-methoxy-4-methyl-1,3,5(10)-estratrien-17-ol (V), m.p. 116.5–117.5°; $[\alpha]D$ +185.3° ($CHCl_3$); (found: C, 80.14; H, 9.67); 17-acetate, m.p. 148.5–150°. Compound V (and its acetate) was identical in all respects (m.p., mixed m.p., and infrared spectra) with a sample of 1-methoxy-4-methyl-1,3,5(10)-estratrien-17-ol (and its acetate, respectively) prepared from 1-hydroxy-4-methyl-1,3,5(10)-estratrien-17-one[6] via methylation and reduction (and acetylation).[7]

The conversion of 4-androstene-3,17-dione to I appears to proceed through 1,4-androstadiene-3,17-dione via 9-hydroxylation and a reverse-aldol type reaction. Paper chromatographic studies indicated the formation and utilization of 1,4-androstadiene-3,17-dione during the course of the fermentation. 1,4-Androstadiene-3,17-dione was isolated from incomplete fermentations. Preliminary experiments indicate that 1,4-androstadiene-3,17-dione is not formed via 1α-hydroxy-4-androstene-3,17-dione.[1]

It should be noted that the formation of I parallels closely the course postulated for the formation of estrone[8] from 4-androstene-3,17-dione except that hydroxylation occurs at C_9 rather than C_{19}. In fact, fermentation of 19-hydroxy-4-androstene-3,17-dione with this *Pseudomonas* species produced estrone, m.p. 260–262°, identical in all respects (m.p., mixed m.p., and infrared spectrum) with an authentic sample. It is possible that the physiological degradation of steroids via compounds similar to I is a very general process.

(4) The position of the double bond is not definitely established, but was assigned to $\Delta^{9(11)}$ on the basis of the fine structure in the ultraviolet spectrum: J. Heer and K. Miescher, *Helv. Chim. Acta*, **31**, 219 (1948).

(5) W. S. Johnson, A. D. Kemp, R. Pappo, J. Ackerman and W. F. Johns, THIS JOURNAL, **78**, 6312 (1956).

(6) A. S. Dreiding and A. Voltman, *ibid.*, **76**, 537 (1954).

(7) We are indebted to Dr. Willard Hoehn of this laboratory for a sample of 1-methoxy-4-methyl-1,3,5(10)-estratrien-17-ol acetate, prepared from 1-hydroxy-4-methyl-1,3,5(10)-estratrien-17-one.

(8) A. S. Meyer, *Experientia*, **11**, 99 (1955), see also ref. 2.

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THE REACTIVITY OF METHYLENE

Sir:

Differences have been noted between the reactivities of methylene produced from diazomethane and ketene toward various types of C–H bonds.[1,2,3] These have been ascribed to differences in excess energy of the methylene produced by the two methods.[2] Owing to the different conditions employed in the two methods there may be some objection to this comparison. Accordingly, the reactions of methylene from diazomethane under identical conditions to those used with ketene as a precursor have been investigated.

Mixtures of diazomethane with a large excess of the hydrocarbon being studied were photolysed using a medium pressure mercury arc and a Pyrex reaction vessel. Analyses were carried out gas chromatographically, and duplicate analyses indicated a high degree of reproducibility.

With propane the proportions of the main reaction products normal and isobutane did not vary with pressure in the range 200–1200 mm. and had a value of 2.62 ± 0.02:1. Similarly with *n*-butane the ratio of products, normal and isopentane, had a value of 1.25:1. With isobutane, iso- and neopentane were formed in the ratio 6.06:1. Hence methylene from diazomethane reacted 15 to 20% faster with secondary C–H bonds than with primary C–H bonds and approximately 50% faster with tertiary C–H bonds. These results compare favorably with those obtained in the liquid phase,[1] and indicate that the difference between the reactivities of methylene from the two precursors is real.

There are some discrepancies in the literature in relation to the reaction of methylene with the 2-butenes.[4,5] No evidence could be found for the formation of an associative complex between diazomethane and *cis*-2-butene. Both in liquid and gas phase (at pressures above 400 mm.) methylene reacted with both the *trans* and *cis* compounds similarly and gave *trans*-1,2-dimethylcyclopropane, *trans*-2-pentene and 2-methyl-2-butene in the former case and the corresponding *cis* compounds in the latter case, in agreement with the work of

(1) W. E. Doering, R. G. Butlery, R. G. Laughlin and N. Chaudhuri, THIS JOURNAL, **78**, 3224 (1956).

(2) H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957).

(3) J. H. Knox and A. F. Trotman-Dickenson, *Chemistry and Industry*, 1039 (1957).

(4) P. S. Skell and R. C. Woodworth, THIS JOURNAL, **78**, 4496 (1956).

(5) W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).