rinsed with a 1.0- and a 0.5-ml portion of benzene to give a total liquid residue of 4.8 ml in the pot. Analysis by glpc showed that approximately 0.011 g of toluene and 0.006 g of benzonitrile were present in the liquid residue.

A control identical with the above photolysis run, except that the solution was refluxed without irradiation, gave no change in the hydrochloric acid titer. Other control experiments showed that (1) no additional ammonia was evolved after 24 hr; (2) under the conditions of the photolysis, both triphenyltriazine (II) and triphenylimidazole (III) were stable and benzonitrile did not cyclize to triphenyltriazine (II); and (3) toluene and benzonitrile in benzene could be photolyzed and recovered as above in 85 and 97% yields, respectively.

**Effect of Added Triphenyltriazine (II) upon the Decomposition of I.**—A mixture of 0.9304 g (0.0030 mole) of the dihydrotriazine I and 1.8609 g (0.00602 mole) of the triphenyltriazine (II) contained in the flask of apparatus A was decomposed for 1.75 hr to yield 20.6 cc (STP) of gas (91.5% relative to that obtained from pure I). The pentane extract of the residue upon evaporation gave 0.1480 g of benzonitrile (106% relative to that obtained from pure I).

**Thermal Decomposition of 1,2-Diphenylethylamine.**—Purified 1,2-diphenylethylamine (8.6739 g, 0.044 mole) contained in the flask (25 ml.) of apparatus B was refluxed for 21 hr. After flushing the system, the titration of 10-ml aliquots of the acid solution indicated that 0.0232 mole of ammonia had been evolved. That the gas was ammonia was shown in a second experiment in which the gas was collected and identified by its infrared spectrum. A portion (4.1758 g) of the residue remaining in the flask was dissolved in ether and extracted with 10% hydrochloric acid to yield ultimately 1.6028 g of recovered 1,2-diphenylethylamine. The neutral fraction gave 2.3021 g of material which was separated by column chromatography into several compounds of which the major ones were 1,2-diphenylethane, stilbene, and deoxybenzoin. Their identification was based upon their infrared spectra and mixture melting point with authentic samples.

**Acknowledgment.**—The author wishes to thank Dr. Carl J. Olsen for his helpful suggestions and Mr. Larry D. Miller for his assistance.

# Fluorinated 1,2,3-Triazolines

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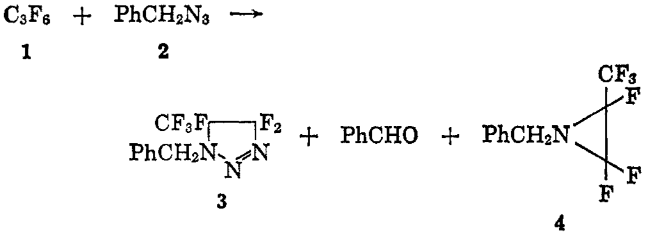
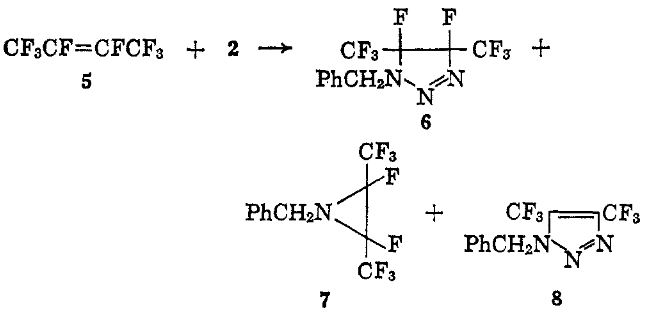
Benzyl azide reacted slowly with perfluoropropene and perfluorobutene-2 at 150° to produce the triazolines **3** and **6**, respectively. The triazolines have been defluorinated to the triazoles, **10** and **8**, and have been pyrolyzed on glass beads to the corresponding aziridines, **4** and **7**. The pyrolysis of **3** on nickel balls gives an unusual type of cleavage wherein both nitrogen and difluorocarbene are eliminated, leaving N-benzyltrifluoroacetimidoyl fluoride as the major product. Difluorocarbene was isolated as tetrafluoroethylene. When tetramethylethylene was present, the difluorocarbene was trapped as 1,1-difluorotetramethylcyclopropane.

The condensation of organic azides with olefins to produce 1,2,3-triazolines has been studied extensively.[1] However, the use of perfluorinated olefins has not yet been described. The present investigation involves the condensation of benzyl azide with perfluoropropene and perfluorobutene-2.

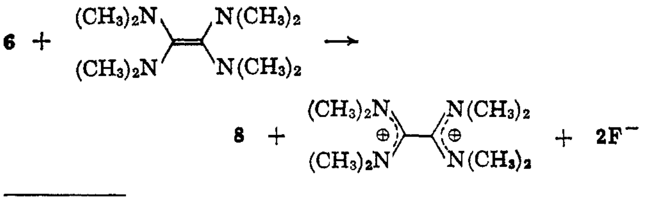
Perfluoropropene (**1**) reacts with benzyl azide (**2**) to produce 1-benzyl-4,4,5-trifluoro-5-trifluoromethyl-1,2,3-triazoline (**3**) in 85% yield based on the benzyl azide present. Benzaldehyde and N-benzyl-2,2,3-trifluoro-2-trifluoromethylaziridine (**4**) were also detected by gas chromatography as minor products.


$C_3F_6 + PhCH_2N_3 \longrightarrow$ + PhCHO +
1 2 3 4


$CF_3CF{=}CFCF_3 + 2 \longrightarrow$
5 6 7 8

Perfluorobutene-2 (**5**) reacts with **2** under the same conditions to give 1-benzyl-4,5-difluoro-4,5-bistrifluoromethyl-1,2,3-triazoline (**6**) in 65% yield. N-Benzyl-2,3-difluoro-2,3-bistrifluoromethylaziridine (**7**) and 1-benzyl-4,5-bistrifluoromethyl-1,2,3-triazole (**8**) were formed in 7 and 5% yield, respectively. Benzaldehyde, 6%, and benzyl azide, 2%, were also detected as constituents of the product mixture. The mechanism by which **8** was formed was not determined. Its structure was confirmed by an alternate synthesis from benzyl azide and hexafluorobutyne-2. The triazole was also formed by extracting two fluorine atoms from **6** with tetrakis(dimethylamino)ethylene (**9**), a compound capable of halogen abstractions.[2]

$$CF_3{\equiv}CCF_3 + 2 \longrightarrow 8$$


6 + → 8 + + 2F⁻

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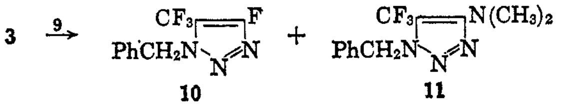
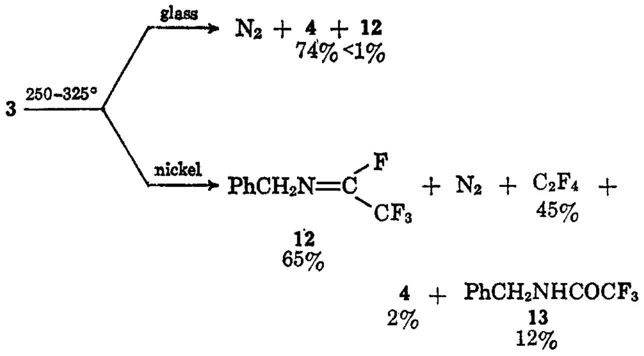
(1) (a) K. Alder and G. Stein, *Ann.*, **485**, 211 (1931); (b) R. Fusco, G. Bianchetti, and D. Pocar, *Gazz. Chim. Ital.*, **91**, 849, 933 (1961); **92**, 1040 (1962); *Chem. Ber.*, **96**, 802 (1963); (c) J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964); (d) L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat, and R. L. Hale, *Chem. Ind.* (London), 1556 (1964); (e) P. Scheimer, *J. Org. Chem.*, **30**, 7 (1965); (f) R. Huisgen, L. Möbius, and G. Szeimies, *Chem. Ber.*, **98**, 1138, 1153 (1965).

(2) W. Carpenter, *J. Org. Chem.*, **30**, 3082 (1965).

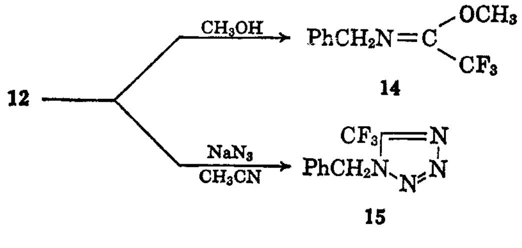
The triazole **10** was generated from the triazoline **3** by treatment with tetrakis(dimethylamino)ethylene. A second product, **11**, was also isolated from this reaction in good yield. Apparently the fluorine atom in the 4-position of **10** has considerable reactivity, being easily replaced by amines. The exact means by which the dimethylamino group enters the triazoline was not determined.



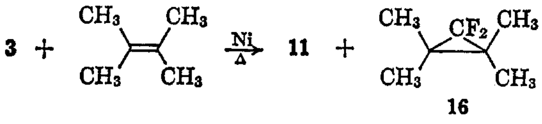
Both of the triazolines, **3** and **6**, can be pyrolyzed easily on glass beads to give the corresponding aziridines, **4** and **7**, respectively, whose structures were confirmed by elemental analyses, nmr, and infrared spectroscopy. The course of the ring cleavage of **3** depends on the type packing in the pyrolysis tube.



If the pyrolysis tube is filled with glass balls, the main product is the expected aziridine, **4**. If nickel balls are used, the ring cleaves mainly to give N-benzyltrifluoroacetimidoyl fluoride (**12**). Under the reaction conditions some N-benzyltrifluoroacetamide (**13**) was always produced. The formation of **12** proved the structure of **3** by showing the position of the trifluoromethyl group in **12** and in **13**. The structure of **13** was easily demonstrated by alternate synthesis from benzylamine and trifluoroacetic anhydride. Furthermore, **12** was converted to the methyl imidoate and the tetrazole[3] by treatment with methanol and sodium azide, respectively.



The formation of tetrafluoroethylene invites the proposal that difluorocarbene is an intermediate in the pyrolysis of **3** on nickel balls. In order to substantiate this idea a pyrolysis was carried out with added tetramethylethylene. The major product besides **12** was 1,1-difluorotetramethylcyclopropane (**16**), obtained in 18% yield. It is conceivable that difluorocarbene arises from difluorodiazomethane, which, at the temperature of pyrolysis, would decompose into difluorocarbene and nitrogen. Cleavage of a triazoline to an imine and a substituted diazomethane was previously noted by Fusco.[1b]



The type of catalytic effect of nickel balls on the pyrolysis of **3** was not observed with the other triazoline,

$$6 \xrightarrow[300\text{–}325°]{\text{glass or nickel}} 7 \quad 67\text{–}80\%$$

**6**. Even at 325° only a very small yield of **13** was produced. None of **12** was detected by gas chromatography. The major product was again the aziridine, **7**.

The fluorinated triazolines form rather sluggishly from the olefins and the azides. Under the reaction conditions of 150° for 3 days not all of the azide was consumed even in the presence of a large excess of olefin. Nonfluorinated triazolines generally form under much milder conditions. The stability of the fluorinated triazolines is greater than that of their nonfluorinated analogs, which generally decompose somewhere between 100 and 200°. The fluorinated triazolines must be heated over 200° before serious decomposition begins. Ultraviolet light does cause the triazolines to go to aziridines,[1e] but the reaction is so slow that it is impractical.

The differences in behavior between the derivatives of perfluoropropene and those of perfluorobutene-2 are remarkable. The presence of the extra $CF_3$ group in **6** renders it more susceptible to loss of two atoms of fluorine or of nitrogen than is **3** since the yield of **4** compared with **1** was very low and no triazole corresponding to **8** was formed in the reaction between **1** and **2**. However, the extra $CF_3$ group renders **6** much less susceptible to 4,5 carbon-carbon bond cleavage during pyrolysis on nickel balls.

## Experimental Section

**Gas Chromatographic Separations.**—The gas chromatographic separations and analyses were performed on a Wilkins A-700 gas chromatograph equipped with the following columns: A, 5.5 ft × 0.25 in. aluminum tube packed with 20% Dowfax 9N9[4] on Chromosorb W[5]; B, 8 ft × 0.5 in. nickel tube packed with 20% Apiezon N on Chromosorb W; C, 10 ft × 0.25 in. aluminum tube packed with 5% DC-200 Silicone Fluid (8000 cstokes) on Teflon-6[6]; D, 15 ft × $^3/_8$ in. aluminum tube filled with 20% DC-200 Silicone Fluid (8000 cstokes) and 1% Dowfax 9N9 on Chromosorb P; and E, 6 ft × 0.25 in. aluminum tube filled with the same packing as column D. Columns A, C, and E were operated at a helium flow rate of 60 cc/min, column B at 240 cc/min, and column D at 180 cc/min.

The gas chromatographic analyses were calculated with the area normalization method, wherein the integrated peak areas were corrected according to the relative thermal response of the various compounds in the mixture. The percentage of each component was assumed to be the percentage of its corrected peak area in the total corrected area of the chromatogram. The relative response of each component was determined by integrating a chromatographic trace of a mixture of known composition of the various components. The component peak area divided by its proportion of the mixture was used to correct the peak area of that component in the analytical trace. Where there were unknown peaks, their response was assumed to be

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(3) J. von Braun and W. Rudolf, *Ber.*, **74**, 264 (1941).

(4) Dow Chemical Co., Midland, Mich.

(5) Johns-Manville Products Corp., Celite Division.

(6) E. I. du Pont de Nemours and Co., Washington, W. Va.

unity. The error in making this assumption is small if the total percentage of unknowns is small.

Nmr spectra were obtained with neat samples containing tetramethylsilane as a proton reference and trichlorofluoromethane as a fluorine reference. Proton resonance spectra were run on a Varian A-60 spectrometer, F$^{19}$ spectra on a Varian DP-60 spectrometer operating at 56.4 Mcps. Chemical shift values for F$^{19}$ spectra are given in $\phi$ units (parts per million relative to $CFCl_3$).

**Benzyl Azide.**[7]—A mixture of 127 g (1.00 mole) of benzyl chloride, 130 g (2.00 moles) of sodium azide, and 500 ml of diethylene glycol was stirred 2 hr on the steam bath. The mixture was then steam distilled. The benzyl azide was separated from the water, dried over $MgSO_4$, and filtered. The yield was 114 g. By gas chromatography on column A at 165° (retention time, 10.5 min), it was shown to be quite pure and was used in the subsequent reactions without further purification.

**Hexafluorobutyne-2.**—Hexafluorobutyne-2, originally prepared by dechlorination of 1,1,1,4,4,4-hexafluoro-2,3-dichlorobutene-2 with zinc in dioxane,[8] was much more rapidly and conveniently prepared by use of zinc and dimethylformamide as described for the preparation of trifluoropropyne.[9]

**1-Benzyl-4,4,5-trifluoro-5-trifluoromethyl-1,2,3-triazoline (3).**—Hexafluoropropene (75.0 g, 0.50 mole) was condensed in a large test tube cooled to −70°. The tube was quickly removed, wiped dry, and placed in a prechilled reaction bomb containing 50 g (0.38 mole) of benzyl azide. The sealed bomb was heated at 150° for 70 hr. Distillation of the dark brown liquid yielded 103 g of material boiling at 75–95° (9 mm). Gas chromatographic analysis on column A at 165° showed that the product was 95% **3**, retention time 6.8 min. The yield based on benzyl azide was 85% of theory. The major impurities were benzyl azide, benzaldehyde, and **4**. An analytical sample was prepared by gas chromatography on column A.

*Anal.* Calcd for $C_{10}H_7F_6N_3$: C, 42.41; H, 2.49; F, 40.26; N, 14.84. Found: C, 42.66; H, 2.60; F, 40.12; N, 14.95.

The nmr spectra showed bands at $\tau$ 2.76 (phenyl) and 5.26 ($CH_2$) and $\phi$ 75.0 ($CF_3$), 93.0 (double doublet), 111.6 (double quartet, $CF_2$), and 158.3 (CF).

**1-Benzyl-4,5-difluoro-4,5-bistrifluoromethyl-1,2,3-triazoline (6).**—A mixture of 104 g (0.52 mole) of octafluorobutene-2 and 32.5 g (0.24 mole) of benzyl azide was treated according to directions in above procedure. The fraction boiling between 60 and 99° at 2 mm was shown by quantitative gas chromatographic analysis on column A at 172° to consist of 53.2 g (65%) of 1-benzyl-4,5-difluoro-4,5-bistrifluoromethyl-1,2,3-triazoline, retention time 4.0 min. By obtaining the infrared spectra of the various components separated by gas chromatography, the following compounds were also determined in the mixture: **7**, 7.0%; benzaldehyde, 5.7%; **8**, 5.3%; and benzyl azide, 2.0%. Many other peaks were evident but were quite small and therefore were not considered. The F$^{19}$ nmr spectrum of **6** showed it to be a mixture of *cis* and *trans* isomers. An analytical sample of **6** was prepared on column A. The nmr spectra showed bands at $\tau$ 2.76 (phenyl) and 5.26 ($CH_2$) and $\phi$ 72, 75 ($CF_3$), and 153 (complex multiplet, CF–CF).

*Anal.* Calcd for $C_{11}H_7F_8N_3$: C, 39.65; H, 2.12; F, 45.62; N, 12.61. Found: C, 39.50; H, 1.95; F, 45.37; N, 12.60.

**1-Benzyl-4,5-bistrifluoromethyl-1,2,3-triazole (8).**—An excess of hexafluorobutyne-2 was condensed with 1.0 g of benzyl azide in a test tube chilled to −70°. The tube was sealed and allowed to stand 2 days at room temperature. The tube was then rechilled, opened, and allowed to warm up to room temperature to drive off excess hexafluorobutyne. The residue was almost pure **8**. No azide remained as shown by its infrared spectrum. The spectrum was identical with those of the same compound produced in the reaction of octafluorobutene-2 with benzyl azide and by defluorination of **6** with tetrakis(dimethylamino)ethylene. An analytical sample was prepared on column B at 182°, retention time 5.0 min. The nmr spectra showed bands at $\tau$ 2.76 (phenyl) and 4.46 ($CH_2$) and $\phi$ 55.9 and 59 ($CF_3$).

*Anal.* Calcd for $C_{11}H_7F_6N_3$: C, 44.76; H, 2.39; F, 38.62; N, 14.23. Found: C, 44.58; H, 2.25; F, 38.82; N, 14.15.

**Attempted Reaction of Zinc with 6.**—Five grams of zinc dust and 5.0 g of **6** were heated together in 20 ml of dimethylformamide for 12 hr between 115–145°. The mixture was diluted with water and extracted with methylene chloride. A gas chromatographic analysis of the extract showed that some reaction had occurred to give **8**, but the conversion was very low.

**Reaction of Tetrakis(dimethylamino)ethylene[10] with 6.**—A solution of 0.6 g (0.003 mole) of tetrakis(dimethylamino)ethylene and 0.5 g (0.0015 mole) of **6** and 3 ml of heptane was sealed in a small vial and heated to 100° for 2.5 hr. The reaction mixture turned from brown to nearly black. The contents of the vial were partitioned between water and ether. The water phase was very dark before being decolorized with Darco. It gave a strong fluoride test with zirconium–alizarin solution and gave a tan precipitate when 5 *M* sodium perchlorate was added. An infrared spectrum of the dried precipitate showed it to be octamethyloxamidinium diperchlorate. The ether solution from above was washed with dilute sulfuric acid and then water. It was decolorized with Darco and dried with magnesium sulfate before being filtered. The pale yellow filtrate was concentrated in a dry air stream to 0.34 g of viscous oil, which was found by gas chromatographic analysis to be 92% pure **8** (69% yield). Its retention time on column C (10.7 min at 153°) and its infrared spectrum are identical with those of **8** prepared by alternate syntheses.

**Reaction of Tetrakis(dimethylamino)ethylene with 3.**—A solution of 1.05 g (0.0053 mole) of **9**, 1.42 g (0.0050 mole) of **3**, and 2 ml of heptane was sealed in a glass vial and heated to 100° for 2 hr. The nearly black mixture was dissolved in water and ether. The ether phase was washed with water, then dried over magnesium sulfate, decolorized with activated charcoal, and then filtered. The filtrate was concentrated to 1.1 g of pale yellow oil. Gas chromatographic analysis showed two major peaks comprising 43 and 53% of the total peak area. The components were separated on column D at 191°, retention times 18.9 and 68.0 min, respectively. The first compound had nmr bands at $\phi$ 60 (doublet, $CF_3$) and 142 (quartet, CF), which are consistent with 1-benzyl-4-fluoro-5-trifluoromethyl-1,2,3-triazole (**10**).

*Anal.* Calcd for $C_{10}H_7F_4N_3$: C, 48.99; H, 2.88; F, 31.00; N, 17.14. Found: C, 48.97; H, 2.89; F, 31.00; N, 17.24.

The nmr spectrum of the second compound was consistent with 1-benzyl-4-dimethylamino-5-trifluoromethyl-1,2,3-triazole (**11**), with bands at $\tau$ 2.76, 4.64, and 7.36, which correspond in position and area to the phenyl, methylene, and methyl protons, respectively. The methyl proton peak under high resolution appears as a quartet due to the weak interaction of the trifluoromethyl group.

*Anal.* Calcd for $C_{12}H_{13}F_3N_4$: C, 53.33; H, 4.85; F, 21.09; N, 20.73; mol wt, 270. Found: C, 53.18; H, 4.73; F, 21.22; N, 20.88; mol wt, 280 (vapor osmometry in toluene).

**Conversion of 6 to 7 with Ultraviolet Light.**—One gram of **6** was stirred in a round-bottomed quartz flask while being irradiated with an unfiltered Hanovia mercury-vapor lamp. After 48 hr of this treatment, the conversion of **6** to **7** was only 20% as analyzed by gas chromatography on column A at 165°.

**Triazoline Pyrolyses.**—The heated portion of a 1-in. i.d. stainless steel tube used for the pyrolyses was 18 in. long. It was packed with either glass balls or nickel balls. The tube was positioned vertically and on the upper end had a ₮ 24/40 female joint to accommodate a dropping funnel. The lower end had a male ₮ 24/40 joint to which was attached a trap cooled in liquid nitrogen. A partial vacuum of about 100 mm was maintained throughout the run. Ten grams of the triazoline was used each time and required about 15–20 min for addition. The trapped material was then distilled from the trap under vacuum into a Dry Ice–acetone trap, which was followed by a liquid nitrogen trap. The distillate collected in a Dry Ice–acetone trap was analyzed by gas chromatography on column A. The material collected in the liquid nitrogen trap was weighed and then analyzed by mass spectroscopy. The yields are summarized in Table I.

Both the aziridines, **4** and **7**, were purified by preparative gas chromatography by using column A at 113°, retention times 6.0 and 5.1 min, respectively.

The nmr spectrum of **4** had bands at $\tau$ 2.76 (phenyl) and 5.84 (doublet $CH_2$) and $\phi$ 75.9 ($CF_3$), 116.6 (double doublet), 130.3 (double quartet, $CF_2$), and 184.9 (CF). The nmr spectrum of **7** showed the presence of *cis* and *trans* isomers in a ratio of about 1:2. The *cis* isomer had bands at $\tau$ 2.76 (phenyl) and 5.79

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[7] The improved procedure given here is a modification of that of T. Curtius and G. Ehrhart, *Ber.*, **55**, 1559 (1922).

[8] A. L. Henne and W. G. Finnegan, *J. Am. Chem. Soc.*, **71**, 298 (1949).

[9] W. G. Finnegan and W. P. Norris, *J. Org. Chem.*, **28**, 1139 (1963).

[10] E. I. du Pont de Nemours and Co., Wilmington, Del.

Table I

Triazoline Pyrolyses

| Compd | Tube packing | Temp, °C | Yields, % | | |
|---|---|---|---|---|---|
| | | | **4** or **7** | **12** + **13** | $C_2F_4$ |
| **3** | Glass | 325 | 74 | Very little[a] | Not investigated |
| **3** | Ni | 250 | 2 | 77 | 45 |
| **6** | Glass | 300 | 80 | None | None |
| **6** | Ni | 325 | 67 | Very little[b] | None |

[a] 22% of triazoline was unreacted. [b] 14% of triazoline was unreacted.

(triplet, $CH_2$) and $\phi$ 73.0 ($CF_3$) and 163.6 (CF). The *trans* isomer showed bands at $\tau$ 2.76 (phenyl) and 5.95 ($CH_2$) and $\phi$ 75.1 ($CF_3$) and 177.4 (CF).

*Anal.* Calcd for $C_{10}H_7F_6N$: C, 47.07; H, 2.77; F, 44.67; N, 5.50. Found: C, 46.89; H, 2.96; F, 44.43; N, 5.75.

*Anal.* Calcd for $C_{11}H_7F_8N$: C, 43.29; H,2.31; F, 49.80; N, 4.59. Found: C, 43.29; H, 2.47; F, 49.72; N, 4.49.

The pyrolysis of **3** on nickel balls furnished the highest yield of **12**, **13**, and tetrafluoroethylene and, therefore, was used to obtain these materials. Compound **12** shows nmr spectral bands at $\tau$ 2.81 (phenyl) and 5.49 ($CH_2$) and $\phi$ 73.4 ($CF_3$) and 51.1 (CF). The C=N bond absorbs at 5.9 $\mu$. Unfortunately, **12** was too reactive with atmospheric moisture to obtain a good analysis. However, it was converted into the imidoyl ester and tetrazole. See below. Tetrafluoroethylene was easily identified in the liquid nitrogen trapped material by mass spectroscopy. N-Benzyltrifluoroacetamide[11] (**13**) was identified by a comparison of its physical and spectral properties with those of an authentic sample prepared by slowly adding an excess of trifluoroacetic anhydride to benzylamine in ether. The volatiles were removed and the residue was sublimed to give white crystals, mp 70–71°. Its nmr spectra show bands at $\tau$ 2.35 (NH), 2.87 (phenyl), and 5.78 ($CH_2$) and $\phi$ 76.2 ($CF_3$).

**1-Benzyl-5-trifluoromethyltetrazole (15).**—A mixture of 2.0 g (0.0098 mole) of N-benzyltrifluoroacetimidoyl fluoride (**12**), 0.7 g (0.011 mole) of sodium azide, and 25 ml of acetonitrile was stirred in a stoppered flask overnight at room temperature. The mixture was filtered and the filtrate was evaporated to 2.1 g of yellow oil. This was purified by preparative gas chromatography on column D at 190°, retention time 18.5 min. Its nmr spectrum shows one band at $\phi$ 61.3 ($CF_3$).

*Anal.* Calcd for $C_9H_7F_3N_4$: C, 47.37; H, 3.09; F, 24.8; N, 24.56. Found: C, 47.44; H, 3.02; F, 24.70; N, 24.76.

**Methyl N-Benzyltrifluoroacetimidoate (14).**—A mixture of 1.0 g of N-benzyltrifluoroacetimidoyl fluoride, 25 ml of methanol, and 2.0 g of sodium bicarbonate was stirred in a stoppered flask overnight at room temperature. The solvent was evaporated before filtration. The resulting pale yellow oil weighed 1.0 g and was nearly pure. It was further purified by gas chromatography on column D at 183°, retention time 8.7 min. It shows a C=N bond at 5.9 $\mu$.

*Anal.* Calcd for $C_{10}H_{10}F_3NO$: C, 55.30; H, 4.64; F, 26.24; N, 6.45. Found: C, 55.30; H, 4.85; F, 26.01; N, 6.72.

**1,1-Difluorotetramethylcyclopropane (16).**—A solution of 10 g (0.035 mole) of the triazoline **3** and 10 g (0.119 mole) of tetramethylethylene was pyrolyzed on nickel balls at 240–260° according to the procedure given above in the section on pyrolyses. The addition required 30 min. The material in the liquid nitrogen trap was redistilled at room temperature at 3 mm into another such trap cooled in liquid nitrogen. The distillate weighed 10.9 g, from which a yield of 18% was calculated by using integrated peak areas in the gas chromatographic analysis on column E at 70°, retention time 12 min. The pure material, which has a camphorlike odor, was isolated with column D at 70°, retention time 16.1 min. Its nmr spectrum showed a single triplet at $\tau$ 8.90 with a coupling constant of 2 cps owing to the interaction of two fluorine atoms. The nmr spectrum of 1,1-difluoro-2,2-dimethylcyclopropane shows a triplet for the methyl group absorption at $\tau$ 8.81 with $J = 2$ cps.[12] The mass spectrographic analysis showed a parent peak at 134 mass units. The infrared spectrum was identical with that of a sample prepared by a standard technique.[13] A mixture of 18.5 g of sodium chlorodifluoroacetate, 15 ml of tetramethylethylene, and 100 ml of diethylene glycol dimethyl ether was refluxed for 32 hr. The oil (10.4 g) which separated on the addition of ice-water (500 ml) was dried over $MgSO_4$ and then analyzed and purified by gas chromatography on column D at 143°, retention time 3.0 min, 11% yield based on the salt used.

*Anal.* Calcd for $C_7H_{12}F_2$: C, 62.66; H, 9.02; F, 28.32. Found: C, 62.72; H, 8.99; F, 28.30.

**Acknowledgment.**—The authors express their gratitude to Dr. R. A. Henry for his suggestions and encouragement and to Mr. Joe Johnson for obtaining the mass spectral data.

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# The Mass Spectra of Tetracyclines

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The mass spectra of nine tetracyclines were obtained. Eight of them exhibited strong molecular ion peaks. It is shown that the mass spectra of tetracyclines can be used to determine the nature and location of various functional groups in the molecule by examination of the changes that they cause in the fragmentation pattern and by application of the shift technique. The major fragmentations of the ring system are systematic and can be followed by the observation of metastable ions in 16-ev spectra.

The tetracyclines are one of the most important classes of broad spectrum antibiotics. The first tetracyclines were isolated from *Streptomyces* cultures, but it was soon discovered that the 5, 6, and 7 substituents could be greatly modified without decreasing the antibiotic activity of the compound. This finding has led to the syntheses, both chemical and biological, of a large number of modified tetracyclines in the search for new and more effective antibiotics. Because of the large number of functional groups present in the molecule, conventional methods of structure determination are laborious. However, in mass spectrometry one can take advantage of these functional groups because of the directing influences of the heteroatoms on the molecule's fragmentation processes. From the study of a combination of accurate mass measurements and fragmentation patterns it should be possible to determine both the nature and the location of the various functional groups in tetracyclines.

The mass spectra of nine different tetracyclines were obtained: tetracycline hydrochloride, chlortetracycline hydrochloride (aureomycin hydrochloride), oxytetra-

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