The Diterpene Alkaloids. The Structure of Atidine[1]

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Degradative work has shown atidine to be a ketodihydroatisine. Huang-Minlon reduction of atidine furnishes dihydroatisine (II). Reduction of atidine with sodium borohydride furnishes a mixture, one of the components of which is identical with dihydroajaconine (V). The correlation of atidine (VI) with dihydroajaconine allows the keto function to be assigned to position 7 in atidine.

The well-known diterpene alkaloids[3] of *Aconitum heterophyllum* Wall include atisine, hetisine, heteratisine, and benzoylheteratisine. Recently we reported the isolation of a new diterpene alkaloid, atidine, from *A. heterophyllum*.[4] This paper details the elucidation of the structure of this alkaloid and its correlation with the delphinium alkaloid, ajaconine.[5]

Atidine crystallizes from ether or benzene as heavy, truncated prisms, m.p. 182.5–183.5°, $[\alpha]D$ −47°. The analysis indicates a molecular formula of $C_{22}H_{33}NO_3$. The equivalent weight determined by electrometric titration with hydrochloric acid was 356.3 (required, 359.5), and the pK_a', 7.53. The infrared spectrum in KBr suggested the presence of the following functional groups: ν_{max}, 3544 and 3454 (OH), 1695 (>C=O), 3086, 1658, and 900 (>C=CH_2), and 1376 cm.$^{-1}$ (C—CH_3).

Two of the oxygen atoms in atidine were shown to be of primary or secondary character by formation of an amorphous diacetate, ν_{max} (film from $CHCl_3$) 3050 and 1656 (>C=CH_2), 1706 (>C=O), 1742 and 1235 (OAc), and 1372 cm.$^{-1}$ (C—CH_3), which showed the absence of hydroxyl absorption in the infrared; and a crystalline diacetate hydrochloride, m.p. 182–190°, ν_{max} (Nujol), 3058, 1653, and 907 (>C=CH_2), 1701 (>C=O), and 1741, 1235, and 1250 cm.$^{-1}$ (OAc). Hydrolysis of the latter under acidic conditions gave 2 molar equiv. of acetic acid. That a rearrangement had not occurred during acetylation was shown by hydrolysis of the diacetate with potassium carbonate in aqueous methanol to atidine.

The presence of an exocyclic methylene and C-methyl groups which were suggested by infrared absorption bands in atidine and several of its derivatives were confirmed by p.m.r. data[6]; thus a two-proton double triplet with centers at τ 4.93 and 4.80 (J = 2 c.p.s.) corresponding to >C=CH_2, and a three-proton singlet at τ 9.23 (C—CH_3). Moroever, oxidation of atidine with permanganate–periodate gave formaldehyde.

The nature of the carbonyl group indicated by absorption at 1695 cm.$^{-1}$ in atidine was shown to be ketonic by preparation of an oxime. Since the ultraviolet absorption of atidine is uneventful, it is clear that the low infrared frequency at 1695 cm.$^{-1}$ is not due to conjugation. That it is probably attributable to hydrogen bonding is suggested by the fact that the ketonic carbonyl group in the diacetate (1706 cm.$^{-1}$) and the diacetate hydrochloride (1701 cm.$^{-1}$) absorbs in the usual range. It is therefore safe to assign the 1695 cm.$^{-1}$ absorption in atidine to a six-membered or larger ketone function.

Reduction of atidine with sodium borohydride in 80% methanol afforded an amorphous "dihydroatidine"[4] whose infrared spectrum showed the absence of carbonyl absorption. Reduction in acetic acid in the presence of prereduced Adams catalyst furnished an amorphous tetrahydro derivative which also showed the absence of carbonyl absorption in the infrared. Electrometric titration of the tetrahydro derivative showed a molecular weight of 369 (calcd. 363.5) and pK_a of 8.47. "Dihydroatidine" presumably arose by reduction of the carbonyl function and the tetrahydro derivative by reduction of both the carbonyl and exocyclic methylene functions. Oxidation of "tetrahydroatidine" with lead tetraacetate in acetic acid at 60° furnished a mixture from which glyoxal was isolated as the bis-*p*-nitrophenylhydrazone in 26% yield. Initially, this fact was accepted as evidence[7,8] for the presence of a β-hydroxyethylamine system in the tetrahydro derivative.[4] Subsequent work by Wiesner, however, has shown that this reaction has no diagnostic value for the presence of β-hydroxyethylamine group since several alkaloids bearing an N-ethyl group also furnish glyoxal when oxidized with lead tetraacetate.[9] However, examination of the p.m.r. spectrum[6] of atidine confirms the presence of the β-hydroxyethyl side chain. Thus, there is a characteristic triplet (τ 6.42, 6.32, and 6.22; J = 6 c.p.s.) with an area of two protons which also occurs in dihydroatisine (II) (τ 6.45, 6.35, and 6.25; J = 6 c.p.s.) and α- and β-tetrahydroatisine (τ 6.45, 6.35, and 6.25; J = 6 c.p.s.) and can be assigned to the two protons adjacent to the hydroxyl in a β-hydroxyethyl side chain.

These data indicate that atidine is a pentacyclic, tertiary base of the dihydroatisine type and contains a carbonyl group in a six-membered ring.[4] In view of the above, it became of interest to relate directly atidine

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(3) Recent review articles on the diterpene alkaloids are: (a) S. W. Pelletier, *Tetrahedron*, **14**, 76 (1961); (b) H.-G. Boit, "Ergebnisse der Alkaloid-Chemie bis 1960," Academie-Verlag, Berlin, 1961, pp. 851–905, 1009–1011; (c) E. S. Stern in "The Alkaloids," Vol. VII, R. H. F. Manske, Ed., Academic Press Inc., New York, N. Y., 1960, pp. 473–503; (d) K. Wiesner and Z. Valenta, "Progress in the Chemistry of Organic Natural Products," Vol. XVI, Springer-Verlag, Vienna, 1958, pp. 26–63.

(4) S. W. Pelletier, *Chem. Ind.* (London), 1016 (1956).

(5) J. A. Goodson, *J. Chem. Soc.*, 245 (1945).

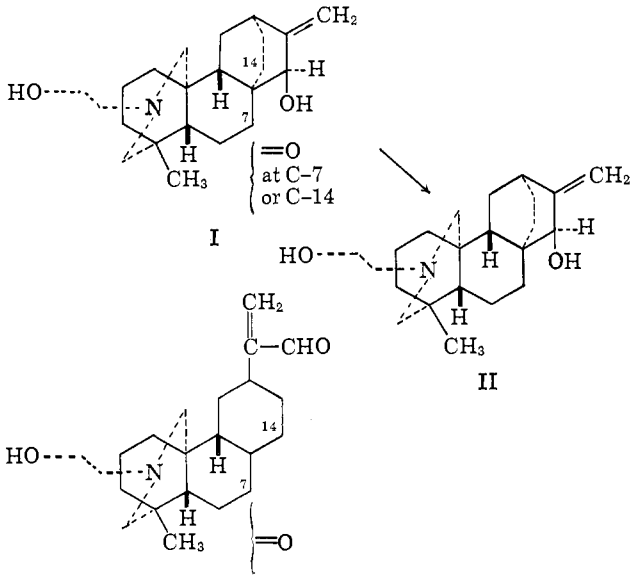
(6) The author is grateful to Dr. P. C. Parthasarathy for taking these p.m.r. spectra.

(7) N. J. Leonard and M. A. Rebenstoff, *J. Am. Chem. Soc.*, **67**, 49 (1945).

(8) O. E. Edwards and T. Singh, *Can. J. Chem.*, **32**, 465 (1954).

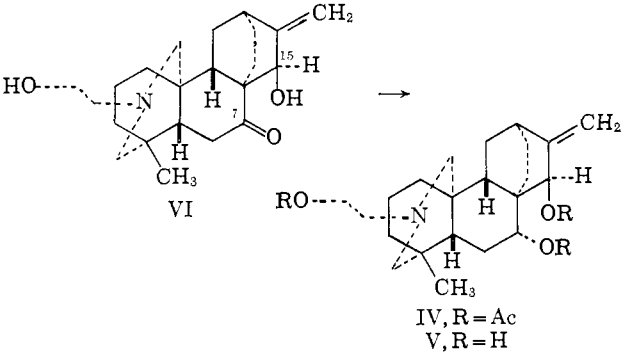
(9) K. Wiesner, S. Ito, and Z. Valenta, *Experientia*, **14**, 167 (1958).

to dihydroatisine (II).[10] This was accomplished by reduction of atidine by the Huang-Minlon procedure. The product, m.p. 156.5–159°, $[\alpha]D$ −43.8°, was identical in every respect, including infrared spectrum, with that of an authentic sample of dihydroatisine.[14] The diacetate of the product, m.p. 122.5–123.5°, $[\alpha]D$ −81°, was identical with an authentic specimen of dihydroatisine diacetate as shown by mixture melting point, rotation, and infrared spectrum. Clearly atidine may thus be represented by structure I.



Possible sites for location of the keto group were suggested by the observation that treatment of atidine with alkali under mild conditions led to extensive formation of polymeric material.[3a] With a keto group at either position 7 or 14, one would expect the β-hydroxyketone to undergo facile cleavage of the retroaldol type to give the unstable acrolein derivative (III), thus accounting for the rapid destruction of atidine. Subsequent events showed that the keto group did indeed occupy one of these sites.

We return now to a reconsideration of the amorphous "dihydroatidine"[4] described earlier in this paper. Subsequent work has shown that this material is a mixture which after acetylation is separable by chromatography over alumina.[14] One of the components is a triacetate,[14] m.p. 133.5–135.5°, $[\alpha]D$ −88° (EtOH), which is identical, by all the usual criteria, with the triacetate of the borohydride reduction product of ajaconine, *viz.*, dihydroajaconine (IV).[15–17] Moreover, saponification of the triacetate with potassium carbonate in methanol under very mild conditions furnishes a crystalline hydrate,[14] m.p. 94–95°, which is identical with dihydroajaconine hydrate (V).[15–17] At the time, this conversion demonstrated that the site of the exocyclic methylene and the site and stereochemistry of the 15-hydroxyl are identical in atidine and



ajaconine. It also showed that the carbonyl oxygen of atidine and the then unknown[15] hydroxyl of ajaconine are on the same carbon atom. Since Edwards has subsequently proven that this oxygen function is at C-7 in ajaconine,[16] the corresponding keto function in atidine is also located at C-7. Thus the complete structure of atidine is represented by VI.

Experimental

General Experimental Procedures. Melting points are corrected and were taken on a hot-stage equipped with a microscope and polarizer. Finely powdered samples were placed on the stage 15° below the melting point and the temperature was raised at a rate of about 4°/min. Rotations were taken in chloroform unless otherwise noted. Ultraviolet spectra were determined in 95% ethanol on a Beckman Model DU spectrophotometer and infrared spectra on Perkin-Elmer Model 21 and Infracord spectrophotometers. P.m.r. spectra[6] were taken on a Varian A-60 spectrometer in deuteroichloroform with tetramethylsilane as an internal standard. Petroleum ether refers to a light petroleum fraction of b.p. 30–70°. Ligroin refers to a light petroleum fraction of b.p. 60–70°. The removal of solvents *in vacuo* was accomplished with a Craig-type rotating flash evaporator at 15–20 mm. and with the water bath usually at 35–50°.

Atidine.[4,14] The alkaloid crystallized from benzene or ether as heavy prisms: m.p. 182.5–183.5°, $[\alpha]^{31}D$ −47°; ν_{max}^{KBr} 3544 and 3454 (OH), 1695 (>C=O), 3086, 1658, and 900 (>C=CH_2), 1376 cm.$^{-1}$ (—C—CH_3); p.m.r. 3-proton singlet τ 9.23 (C—CH_3); 2-proton triplet at τ 6.42, 6.32, 6.22 (J = 6 c.p.s.) (NCH_2—CH_2OH) and 2-proton double triplet, with centers at τ 4.93 and 4.80 (J = 2 c.p.s.) (>C=CH_2).

Anal. Calcd. for $C_{22}H_{33}NO_3$: C, 73.50; H, 9.25; N, 3.90; equiv. wt., 359.5. Found: C, 73.57, 73.74; H, 9.42, 9.39; N, 3.93; equiv. wt., 356.3.

Atidine Hydrochloride. A solution of 52 mg. of atidine in 3.0 ml. of acetone was treated with a slight excess of concentrated hydrochloric acid. Evaporation *in vacuo* gave a residue which crystallized from methanol–acetone as rosettes, m.p. 200–210°. Recrystallization afforded rosettes, m.p. 204–215° dec.

Anal. Calcd. for $C_{22}H_{33}NO_3 \cdot HCl$: C, 66.73; H, 8.66. Found: C, 66.74; H, 8.82.

Atidine Oxime. A solution of 50 mg. of atidine in 3 ml. of ethanol was boiled under reflux for 3 hr. with

(10) For the stereochemistry of dihydroatisine see ref. 3a, 11, 12, and 13.
(11) A. J. Solo and S. W. Pelletier, *Chem. Ind.* (London), 1108 (1960).
(12) D. Dvornik and O. E. Edwards, *Tetrahedron*, **14**, 54 (1961).
(13) H. Vorbrueggen and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 2990 (1962).
(14) S. W. Pelletier, *Chem. Ind.* (London), 1670 (1957).
(15) D. Dvornik and O. E. Edwards, *ibid.*, 952 (1957).
(16) D. Dvornik and O. E. Edwards, *Tetrahedron*, **14**, 54 (1961).
(17) The author wishes to thank Dr. O. E. Edwards for kindly placing samples of dihydroajaconine and its triacetate at our disposal for comparison purposes.

an excess of hydroxylamine hydrochloride and sodium acetate. The mixture was filtered, taken to dryness *in vacuo*, and treated with water. Extraction with benzene gave an amorphous oxime.

Anal. Calcd. for $C_{22}H_{34}N_2O_3$: C, 70.55; H, 9.15; N, 7.50. Found: C, 70.42; H, 9.29; N, 7.63.

Atidine Diacetate Hydrochloride. A solution of 52 mg. of atidine in 2 ml. of dry pyridine and 2 ml. of acetic anhydride was allowed to stand for 18 hr. After evaporation *in vacuo* and working up in the usual way, there was obtained 62 mg. of resin which did not crystallize from the usual solvents. After treatment in acetone with hydrochloric acid, there was obtained 53 mg. of thin plates, m.p. 182–194°. Recrystallization from methanol–acetone afforded the hydrochloride: 45 mg.; m.p. 182–190°; infrared spectrum (Nujol) ν_{max} 907, 1653, and 3058 (>C=CH_2), 1701 (>C=O), and 1250, 1235, and 1741 cm.$^{-1}$ (OAc); ν_{max}^{KBr} 907 and 1654 (>C=CH_2), 1248, 1232, and 1742 (OAc), and 1376 cm.$^{-1}$ (C—CH_3).

Anal. Calcd. for $C_{26}H_{37}NO_5 \cdot HCl$: C, 65.06; H, 7.98; 2 Ac, 17.93. Found: C, 65.24; H, 8.29; Ac, 17.50.

Atidine Diacetate. A small sample of the hydrochloride was converted in water to the base with sodium bicarbonate. Extraction gave a resin: infrared (film from $CHCl_3$), ν_{max} 1656 and 3050 (>C=CH_2), 1706 (>C=O), 1235 and 1742 (OAc), and 1372 cm.$^{-1}$ (C—CH_3).

Saponification of Atidine Diacetate. A solution of 47 mg. of atidine diacetate in 2.0 ml. of methanol was treated with 50 mg. of potassium carbonate in 0.5 ml. of water and allowed to stand for 5 hr. at room temperature and 2 days in the refrigerator. The mixture was evaporated *in vacuo*, taken up in water, and extracted with chloroform. Evaporation of the chloroform gave 39 mg. which crystallized from ether to give atidine, m.p. 178–182.5° cor.

Test for Exocyclic Methylene Group in Alkaloids. To a series of 25-ml. volumetric flasks containing (1) 5.0 mg. of isoatisine, (2) atidine, (3) blank, was added 1.0 ml. of pyridine. At zero time, 10 ml. of a solution of 0.02 *M* sodium metaperiodate and 10 ml. of a solution of 0.005 *M* potassium permanganate were added to each flask. The flasks were made up to volume with distilled water and 5-ml. aliquots were transferred to 10-ml. volumetric flasks. After 10 min. and 45 min., the reaction was stopped by the addition of 2.0 ml. of 1 *M* sodium arsenite solution and 2.0 ml. of 2 *N* sulfuric acid. The contents were allowed to stand for 15 min. Each flask was made up to 10 ml. Then 2.0 ml. aliquots were transferred to test tubes and 10 ml. of freshly prepared chromatropic acid[18] solution was added to each tube. After heating in a water bath at 100° for 30 min., the color of each tube was observed. A purple color indicated an exocyclic methylene group (see Table I).

Conversion of Atidine to Dihydroatisine. In a 10-ml. test tube fitted with a reflux condenser was placed 130 mg. of atidine, 2.0 ml. of 99.8% hydrazine hydrate, and 3.4 ml. of diethylene glycol. The contents were maintained at 130° (inside temperature) for 1 hr.

(18) F. Feigl, "Spot Tests in Organic Analysis," 5th Engl. Ed., Elsevier Publishing Co., New York, N. Y., 1956, p. 331.

Table I

	15 min.	45 min.
1. Isoatisine	Purple	Purple
2. Atidine	Faint purple	Purple
3. Blank	Faint brown	Faint brown

and then hydrazine was distilled as the temperature was raised to 150°. At this point 700 mg. of powdered potassium hydroxide was added and the temperature raised to 200° over a period of 30 min. The temperature was maintained at 200 ± 3° for 1 hr. The dark brown mixture was cooled, poured into 50 ml. of water, and extracted with chloroform. Evaporation gave 119 mg. of a yellow resin which was dissolved in ether and chromatographed over 3.0 g. of Woelm neutral alumina. The first six fractions of 25 ml. each contained 72 mg. of material which crystallized from ether. This was combined with 42 mg. of similar material from another run and rechromatographed in benzene over 2.0 g. of neutral alumina. The first five fractions (94 mg.) were combined and crystallized three times from ether to give 41 mg. of dihydroatisine, m.p. 156–158.5°. Recrystallization gave 27 mg. of pure dihydroatisine, m.p. 156.5–159°, $[\alpha]^{27}D$ −43.8° (*c* 1.25), undepressed by an authentic sample of m.p. 156–158.5°, $[\alpha]^{27}D$ −43.9° (*c* 1.41). The infrared spectrum in KBr was identical with that of an authentic sample of dihydroatisine.

Diacetate. Dihydroatisine (26 mg.) prepared from atidine was boiled with acetic anhydride for 15 min. After working up the reaction mixture in the usual fashion there was obtained 31 mg. of resin. Crystallization from ether gave heavy prisms of the diacetate, m.p. 122.5–123.5°, $[\alpha]D$ −81° (*c* 1.4, $CHCl_3$). An authentic sample showed m.p. 123.5–124°, $[\alpha]^{27}D$ −82° (*c* 1.2, $CHCl_3$). The infrared spectrum in KBr was identical with that of an authentic sample of dihydroatisine diacetate.

Reduction of Atidine to Dihydroatidine Epimers. A solution of 125 mg. of atidine in 10 ml. of 80% methanol was treated with 250 mg. of sodium borohydride and allowed to stand for 3 hr. The methanol was removed *in vacuo* and the residue was taken up in water and extracted with chloroform. Since evaporation gave 140 mg. of foam containing inorganic contaminents, the product was dissolved in aqueous methanol, diluted with water, and extracted with benzene. The benzene extract was washed twice with water, dried over sodium sulfate, and evaporated *in vacuo* to give 120 mg. of the mixed epimers.

Anal. Calcd. for $C_{22}H_{35}NO_3$: C, 73.09; H, 9.76. Found: C, 73.35; H, 9.74.

Catalytic Reduction of Atidine to Tetrahydro Isomers. A solution of 102 mg. of atidine in 6 ml. of acetic acid was hydrogenated in the presence of 102 mg. of prereduced Adams catalyst. After the absorption of 2 moles of hydrogen, the solution was filtered, taken to dryness *in vacuo*, and processed in the usual manner. The product did not crystallize from the usual solvents. The infrared spectrum in chloroform showed the absence of carbonyl and exocyclic double bond absorption, ν_{max} 1372 (C—CH_3) and 3333 cm.$^{-1}$ (OH); pK_a' 8.47.

Anal. Calcd. for $C_{22}H_{37}NO_3$: C, 72.68; H, 10.26. Found: C, 72.68; H, 10.26.

Formation of Glyoxal from Tetrahydroatidine. A solution of 83 mg. of the above "tetrahydroatidine" in 10 ml. of glacial acetic acid was treated with 217 mg. of lead tetraacetate and maintained at 62° for 22 hr. After dilution with 10 ml. of water, 200 mg. of *p*-nitrophenylhydrazine was added and then the mixture was heated at 100° for 21 hr. After cooling the bis-*p*-nitrophenylhydrazone of glyoxal was collected, m.p. 315–318°, 19.6 mg. (26%). Recrystallization from 125 ml. of boiling acetic acid gave 12.4 mg. of reddish purple crystals, m.p. 317–318°, with an infrared spectrum in Nujol identical with that of the authentic bis-*p*-nitrophenylhydrazone prepared from glyoxal.

Acetylation of Dihydroatidine to Give Dihydroajaconine Triacetate. A solution of 139 mg. of the mixture of epimeric dihydroatidines in 2.0 ml. of dry pyridine and 1.0 ml. acetic anhydride was allowed to stand overnight. Evaporation *in vacuo* gave a resin which was dissolved in chloroform and washed with dilute ammonium hydroxide. The chloroform phase yielded 180 mg. which on standing in methanol several days deposited heavy prisms, 52.8 mg., m.p. 122–127°. Recrystallization from methanol gave 44.5 mg., m.p. 131.5–133°. It was later observed that the crystalline isomer could be obtained easily by chromatography in benzene over Woelm neutral alumina. Recrystallization gave prisms of m.p. 133.5–135.5°, $[\alpha]_D$ −88.7° (*c* 1.9, EtOH), undepressed with an authentic sample of dihydroajaconine diacetate.[17] The infrared spectrum in KBr was identical with that of dihydroajaconine diacetate, ν_{max} 3448 (OH), 1745 and 1242 (OAc), 1718 (>C=O), and 1372 cm.$^{-1}$ (C—CH_3). Later experiments showed that acetylation of 257 mg. of dihydroatidine and work-up by chromatography gave 116 mg. of the dihydroajaconine triacetate, m.p. 131.5–134° cor.

Saponification of Dihydroajaconine Triacetate (from Dihydroatidine). A solution of 24.4 mg. of the triacetate in 1 ml. of methanol was treated with 69 mg. of potassium carbonate in 2 ml. of methanol and 1 ml. of water and allowed to stand for 17 hr. The reaction mixture was evaporated *in vacuo*, taken up in water, and extracted with chloroform. The product (19.3 mg.) was dissolved in a few drops of acetone, diluted until turbid, and seeded. Dihydroajaconine crystallized as fine needles, m.p. 90–91°. Recrystallization from aqueous acetone gave needles, m.p. 94.0–95.0°, undepressed by an authentic sample of m.p. 94.5–97.5°.[17]

A New Stable Radical, Bis(trifluoromethyl) Nitroxide[1]

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The stable free radical bis(trifluoromethyl) nitroxide has been synthesized, isolated, and characterized for the first time. This material is a stable purple gas at room temperature. It is unreactive with glass, stainless steel, copper, water, air, mercury, Freon 11, and 10% aqueous sodium hydroxide. Only reactions with other free radicals such as nitric oxide and nitrogen dioxide have been confirmed to date, the former yielding the known compound $(CF_3)_2NONO$.

Bis(trifluoromethyl) nitroxide ($(CF_3)_2NO$, I), a perfluorinated stable nitroxide radical, has been synthesized and isolated as a purple gas at room temperature. On cooling, the gas condenses to a brown liquid (b.p. −25°) and solidifies to a yellow solid (m.p. −70°). It is not affected chemically by water, 10% aqueous sodium hydroxide, air, stainless steel, copper, glass, fluorotrichloromethane, or benzene. However, it readily undergoes reactions with other free radical species. It combines readily with nitric oxide to form O-nitrosobis(trifluoromethyl)hydroxylamine ($(CF_3)_2NONO$, II) and with nitrogen dioxide to form a compound believed to be the oxygen-substituted adduct O-nitrobis(trifluoromethyl)hydroxylamine ($(CF_3)_2NONO_2$, III).

To the knowledge of the authors this is the first reported isolation of a stable nitroxide radical containing fluorinated substituents. The stable nature of this material cannot be ascribed to steric hindrance, but is believed to result from the strong electronegative character of the CF_3 groups and some delocalization of the unpaired electron by the six fluorine atoms as evidenced by its nine-line symmetrical electron spin resonance pattern.[2]

Nitroxide free radicals, R_2NO, have been known for many years. Prior to the present synthesis of I, a few such nitroxide radicals had been prepared and isolated, whereas several others had been observed as transient species in e.s.r. studies. Diphenyl nitroxide ($(C_6H_5)_2NO$) was first prepared by Wieland and Offenbacher.[3] It has a half-life of about 50 hr. in cumene at 100° according to Thomas and Tolmann.[4] Baird and Thomas[5] have recently made an e.s.r. study of seven disubstituted nitric oxide free radicals of unreported stability. The stable free radical di-*t*-butyl nitroxide has been synthesized by Hoffmann and

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(2) We are indebted to a referee for pointing out that delocalization of the unpaired electron by the fluorine atoms is reasonable but is not proved by the observation of fluorine e.s.r. hyperfine splitting since β-substituent hyperfine splitting can occur *via* a spin-polarization mechanism without electron delocalization [A.D. McLachlan, *Mol. Phys.*, **1**, 233 (1958)].

(3) H. Wieland and M. Offenbacher, *Ber.*, **47**, 2111 (1914).

(4) J. R. Thomas and C. A. Tolmann, *J. Am. Chem. Soc.*, 84, 2930 (1962).

(5) J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, **35**, 1507 (1961).