0 °C (~6 h), zone 1 was filled with dry ice, F_2 at 0.5 cm^3/m was started, and the helium flow was reduced to 20 cm^3/m. Every 24 h the F_2 was increased by 0.5 cm^3/m to a maximum of 2.0 cm^3/m; the helium was reduced to 10 cm^3/m and 5 cm^3/m and then stopped; and one additional zone each 24 h was not replenished with dry ice/alcohol.[9] Zone 5 initially at −130 °C was warmed to −120, −110, and −100 °C at 24-h intervals until the liquid nitrogen dewar (Linde, LS-160) connected to the temperature controller was exhausted; it was then filled with dry ice/alcohol and not replenished in sequence. The day that zone 6 began to warm from −78 °C the helium was restarted at 5.0 cm^3/m.[10] The product was collected in a liquid-nitrogen-cooled trap, transferred to the vacuum line, and fractionated through −96 and −196 °C traps. The −96 °C fraction was dissolved in CCl_4 and separated by GLC on a Fluorosilicone QF-1, 10% on Chromosorb P column $^3/_8$ in. × 7 m long. The yields are *F*-neopentane (I), 0.32 g (6.7%), 1-hydryl-*F*-neopentane (II), 1.9 (24%), and 1,3-dihydryl-*F*-neopentane (III), 1.17 g (28%). Complete characterizations for compounds II and III are given in Tables I and II, respectively.

F-Neopentyl iodide was prepared as follows: 1-Hydryl-*F*-neopentane (0.545 g, 2.02 mmol) was dissolved in 5 mL of anhydrous ethyl ether under a nitrogen atmosphere. That solution was added dropwise to $CH_3Li/LiBr$ (3.0 mL, 4.8 mmol, 1.6 M Alfa Ventron) diluted in 5 mL of ether cooled to −50 to −55 °C. The mixture was magnetically stirred until 45 mL of gas, CH_4, had been evolved (about 2 h). A slight excess of iodine (1.27 g, ca. 5 mmol) was dissolved in 40 mL of dry ether and added to the −50 °C mixture dropwise until the iodine color persisted. The product was isolated by vacuum-line fractionalization followed by gas–liquid chromatography on Fluorosilicone QF-1, 10% on Chromosorb P, yielding *F*-neopentyl iodide (0.285 g, 35.6% yield; 48% yield based on 1-hydryl-*F*-neopentane recovered). Complete characterization is given in Table III.

F-Neopentyl bromide was synthesized and purified in an analogous way except that the bromine–ether solution was added to the reaction mixture at −78 °C. Its characterization is given in Table IV. In contrast to *F*-neopentyl iodide which slowly decomposes at room temperature, the bromide is stable indefinitely.[11]

Acknowledgment. The authors would like to acknowledge the support of the Research Corporation, Cottrell Research Fund, and the Office of Naval Research for partial support of this work. ^{19}F NMR spectra were run with the assistance of Professor Richard J. Lagow and Mr. Bob Smithwick.

Registry No. I, 374-51-6; II, 2993-15-9; III, 71076-43-2; *F*-neopentyllithium, 71076-44-3; perfluoroneopentyl iodide, 71076-45-4; perfluoroneopentyl bromide, 71076-46-5; perfluoro-2,2,5,5-tetramethylhexane, 71076-47-6.

(8) The vapor pressure of neopentane at −65 °C is such that the helium flow carries the vapor to the reactor so that it deposits as a fine snow-like solid of high surface area. This step is very important for good yields.

(9) These steps bring about a gradually increasing concentration and quantity of fluorine, a gradually increasing temperature at a given point, and an overall temperature gradient. The temperature gradient volatilizes the more highly (75%) fluorinated species exposing less highly fluorinated species to fluorination.

(10) The dilution step at final warmup is very important in shifting the product mixture toward the mono- and dihydryl-*F*-neopentanes.

(11) The decomposition of pure *F*-neopentyl iodide is to iodine and presumably *F*-2,2,5,5-tetramethylhexane. This was deduced from the mass spectra: Chemical Ionization gave: 519, 2, $C_{10}F_{21}$, and 319, 100, C_6F_{13}. Electron Impact gave: 319, 22, C_6F_{13}; 269, 10, C_5F_{11}; 231, 47, F_5F_9; 181, 100, C_4F_7; 119, 60, C_2F_5; 69, 31, CF_3. Major peaks in the infrared spectrum (cm^{-1}) were: 1285 vs, 1270 vs, 1247 sh, 1218 m, 1182 w, 1163 mw, 1033 w, 988 s, 784 mw, 748 m, 734 m, and 707 ms. Homolytic cleavage of the C–I bond is a common reaction of *F*-alkyl iodides on photolysis or thermolysis.

2,2,6,6-Tetramethylpiperidine-*N*-oxyl-4-carboxylic Anhydride

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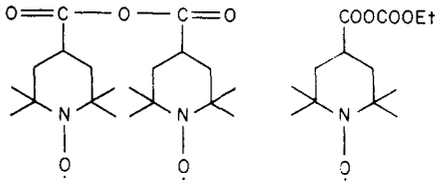
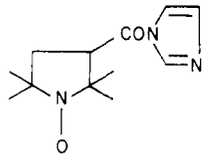
Reagents for "spin labeling" are of some interest.[1] We wish to report preparation and characterization of the title compound **1**. It is: (1) easily prepared; (2) crystalline; (3) stable and easily stored under ambient conditions; (4) easily weighed and simply manipulated; (5) modestly water soluble (see below); and (6) achiral.



1 **2**

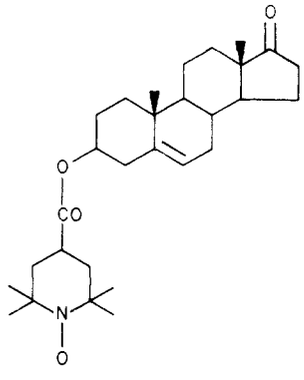
Anhydride **1** is in fact the product of a reaction described by Rauckman and Rosen,[2] who reported the preparation and in situ use of the mixed anhydride **2** as a spin acylating agent. We stumbled across **1**, the actual acylating agent, as a result of investigating the influence of reagent ratios on yields in the preparation of "**2**".

The virtues of **1** are listed above. Its lack of chirality is in our eyes of some importance if one is contemplating spin acylation of a chiral system (e.g., proteins). This virtue is not shared by the spin acylating reagent **3** recently reported by Adackaparayil and Smith.[3]



3

Anhydride **1** reacts smoothly with primary and secondary alcohols in the presence of 4-(dimethylamino)-pyridine as catalyst.[4] Esters are formed in high yield in this fashion as is exemplified by the acylation of 3-hydroxy-17-ketoandrost-5-ene (**4**); the ester **5** is isolated in 93% yield.



5

(1) J. F. W. Keana, *Chem. Rev.*, **78**, 37 (1978).
(2) E. J. Rauckman and G. M. Rosen, *Synth. Commun.*, **6**, 325 (1976).
(3) M. Adackaparayil and J. H. Smith, *J. Org. Chem.*, **42**, 1655 (1977).
(4) W. Steglich and G. Höfle, *Angew, Chem., Int. Ed., Engl.*, **8**, 981 (1969).

The water solubility of 1 is also of some potential utility. Thus, aqueous *n*-butylamine reacts with 1 with little competing hydrolysis to afford the butyl amide in 80% yield. This finding is particularly useful in that the reagent may find application in the spin acylation of proteins.

Experimental Section

Preparation of 2,2,6,6-Tetramethylpiperidine-*N*-oxyl-4-carboxylic Anhydride. To a solution of 2.2 g (11 mmol) of 2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-carboxylic acid[5] and 1.88 mL (13.75 mmol) of triethylamine in 10 mL of dry benzene which was being stirred at room temperature was added dropwise 1.07 mL (13.75 mmol) of ethyl chloroformate. An immediate exothermic reaction ensued with the vigorous evolution of a gas and the deposition of a pink solid. The reaction was allowed to continue for 15 min after which it was diluted with dichloromethane and extracted with 5% hydrochloric acid, 4% sodium bicarbonate, and water. The organic layer was dried over anhydrous magnesium sulfate and evaporated to yield a solid which was immediately recrystallized from benzene/hexane to afford pink floculent needles (1.2 g, 57%, mp 146–148 °C; IR ν ($CHCl_3$) 1820, 1760; MS m/e 382.2476 (calcd for $C_{20}H_{34}N_2O_5$: 382.2466).

Anal. Calcd for $C_{20}H_{34}N_2O_5$: C, 62.80; H, 8.96. Found: C, 62.71; H, 9.03.

Reaction of the Nitroxyl Anhydride 1 with 3-Hydroxy-17-ketoandrost-5-ene. A solution of 58 mg (0.20 mmol) of 3β-hydroxy-17-ketoandrost-5-ene,[6] 4, 80 mg (0.21 mmol) of nitroxyl anhydride 1, and 5 mg (20 mol %) of 4-(dimethylamino)pyridine in 0.5 mL of dichloromethane was allowed to stir at room temperature for 15 min after which it was diluted with ether and extracted with 4% sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate and evaporated to afford 87 mg of product 5 (93%) melting at 186–188 °C. Recrystallization from methanol afforded material melting at 188–190 °C: IR ν ($CHCl_3$) 1720 (broad); ^1H NMR (270 MHz spectrum of hydroxylamine obtained by ascorbic acid reduction) ($CDCl_3$) δ 1.20 (s, 6 H), 1.14 (s, 3 H), 1.06 (s, 3 H), 0.89 (s, 3 H); MS m/e 470.3254 (calcd for $C_{29}H_{44}NO_4$: 470.3268).

Anal. Calcd for $C_{29}H_{44}NO_4$: C, 74.00; H, 9.42. Found: C, 74.03; H, 9.52.

Reaction of Nitroxyl Anhydride 1 with Aqueous *n*-Butylamine. To a solution of 84 μL (0.825 mmol) of *n*-butylamine in 3 mL of water was added 150 mg (0.39 mmol) of nitroxyl anhydride 1. The reaction was stirred for 1.5 h at room temperature during which time the anhydride dissolved, resulting in a yellow solution. The aqueous solution was extracted with chloroform which was in turn washed with 4% sodium bicarbonate, 5% hydrochloric acid, and water. The chloroform layer was dried over anhydrous magnesium sulfate and evaporated to yield 80 mg (80%) of a residue which crystallized upon sitting: mp (sublimed 60 °C (0.1 mm)) 83–85 °C; TLC (7.3 CCl_4/acetone) R_f 0.43; IR ν ($CHCl_3$) 3440, 1670, 1515, 1380, 1365; ^1H NMR (270 MHz of hydroxylamine-$CHCl_3$) δ 5.63 (hump, 1 H), 3.25 (t, 2 H), 2.46 (m, 1 H), 1.67 (bd, 4 H), 1.49 (m, 2 H), 1.36 (m, 2 H), 1.19 (s, 6 H), 1.13 (s, 6 H), 0.93 (t, 3 H); MS m/e 255.2072 (calcd for $C_{14}H_{27}N_2O_2$: 255.2071).

Anal. Calcd for $C_{14}H_{27}N_2O_2$: C, 65.84; H, 10.66. Found: C, 65.49; H, 10.33.

Registry No. 1, 70659-75-5; 4, 53-43-0; 5, 70659-76-6; 2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-carboxylic acid, 37149-18-1; butylamine, 109-73-9; *N*-butyl-2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-carboxamide, 70659-77-7.

(5) E. J. Rauckman, G. M. Rosen, and M. B. Abou-Donia, *J. Org. Chem.*, 41, 564 (1976).
(6) We thank Professor A. Wilds for a generous sample of this material.

Photochemical Transformations. 23. β-Substituent Effects in the Photorearrangement-Cyclizations of Allylic Chlorides to Cyclopropyl Chlorides[1]

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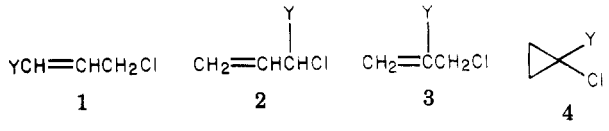
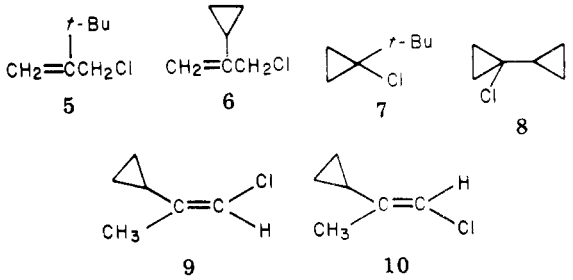
Some years ago,[2] workers from this laboratory reported that allylic chlorides were transformed to cyclopropyl chlorides under appropriate photosensitization conditions. That and subsequent work[3] indicated that acetone or acetophenone sensitization of the allylic chlorides in acetonitrile solvent gave high yields of chlorocyclopropanes for a variety of substituted acyclic allylic chlorides. These included, for example, besides allyl chloride (1-H) itself,



1 2 3 4

the γ-substituted compounds, crotyl chloride (1-CH_3), cinnamyl chloride (1-Ph), and 1,3-dichloropropene (1-Cl), and the α-substituted compounds, α-methylallyl chloride (2-CH_3), α-phenylallyl chloride (2-Ph), and allylidene chloride (2-Cl). On the other hand, while β-methylallyl chloride (3-CH_3) gives 1-chloro-1-methylcyclopropane (4-CH_3) in good yield,[4] neither β-chloroallyl chloride (3-Cl) nor β-phenylallyl chloride (3-Ph) undergo the corresponding rearrangements to the 4 species, even though it is clear[6] that these substances accept triplet excitation from sensitizer and are undoubtedly photoactive. As the photorearrangement cyclization offers a potentially very useful method for the preparation of cyclopropyl chlorides, in particular for the relatively inaccessible 1-substituted cyclopropyl chlorides, we now wish to report our experiments with two other β-substituted allyl chlorides and to comment briefly upon our results.

The compounds we chose to study were 2-chloromethyl-3,3-dimethyl-1-butene (β-*tert*-butylallyl chloride, 5) and β-cyclopropylallyl chloride (6). 5 was prepared by



5 6 7 8 9 10

free-radical chlorination of 2,3,3-trimethyl-1-butene with

(1) Paper 22: S. J. Cristol, D. P. Stull, and R. D. Daussin, *J. Am. Chem. Soc.*, **100**, 6674 (1978).
(2) S. J. Cristol and G. A. Lee, *J. Am. Chem. Soc.*, **91**, 7554 (1969).
(3) S. J. Cristol, G. A. Lee, and A. L. Noreen, *J. Am. Chem. Soc.*, **95**, 7067 (1973).
(4) The yield in this rearrangement-cyclization was found to be concentration dependent, falling off with increasing allylic chloride concentration, and has been discussed elsewhere.[5]
(5) S. J. Cristol, R. J. Daughenbaugh, and R. J. Opitz, *J. Am. Chem. Soc.*, **99**, 6347 (1977).
(6) S. J. Cristol and R. P. Micheli, *J. Org. Chem.*, **40**, 667 (1975).

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