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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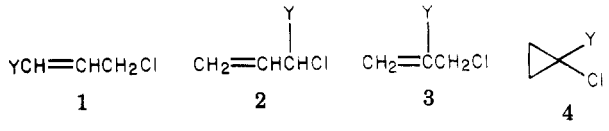
Received January 3, 1979

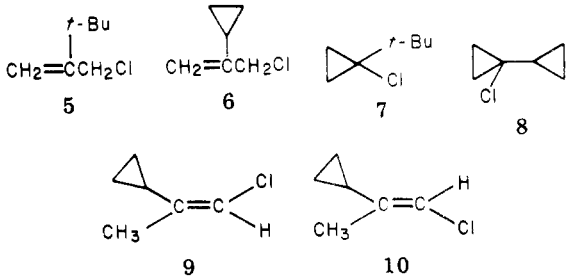
Some years ago,[2] workers from this laboratory reported that allylic chlorides were transformed to cyclopropyl chlorides under appropriate photosensitization conditions. That and subsequent work[3] indicated that acetone or acetophenone sensitization of the allylic chlorides in acetonitrile solvent 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

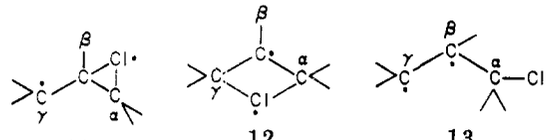
(1) Paper 22: S. J. Cristol, D. P. Stull, and R. D. Daussin, *J. Am. Chem. Soc.*, **100**, 6674 (1978).
(2) S. J. Cristol and G. A. Lee, *J. Am. Chem. Soc.*, **91**, 7554 (1969).
(3) S. J. Cristol, G. A. Lee, and A. L. Noreen, *J. Am. Chem. Soc.*, **95**, 7067 (1973).
(4) The yield in this rearrangement-cyclization 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).

0022-3263/79/1944-3434$01.00/0

N-chloro-*N*-cyclohexylbenzenesulfonamide and **6** by chlorination with the same reagent of 2-cyclopropylpropene. When **5** and **6** were irradiated in acetone or in acetone–acetonitrile, each was converted to its cyclopropyl analogue (**7** and **8**, respectively) in good yield and with fairly high quantum efficiency.[4]

Thus the photoreaction described earlier may be assumed to occur with all compounds of type **3** to give the otherwise difficultly accessible tertiary chlorocyclopropanes **4**, with the limitation that Y is a saturated alkyl or cycloalkyl group. As mentioned above, when Y is phenyl or chlorine as a β substituent, 1,2-rearrangement–cyclization is not observed, although allylic (1,3-) rearrangement and cis–trans isomerization both occur on photosensitization. On the other hand, all three reaction channels are observed when alkyl, phenyl, or chlorine substituents are present in α or γ positions on the allylic chloride.

Among the plausible triplet intermediates for the various interconversions is the biradical **11**[8] for the (stereoselective[8]) allyl to cyclopropyl rearrangement and the biradical **12**[5,9] for the 1,3- and cis–trans isomerizations, although the latter could arise from the biradical **13**, as well. Failure of 3-Ph or 3-Cl to suffer photocyclization–rearrangement, while the other paths remain open, can be rationalized by consideration of such intermediates. Comparison of **11** with **13** suggests that an electron-de-



11 **12** **13**

localizing substituent, such as chlorine or phenyl, should stabilize **12** or **13** relative to **11** and thus reduce the probability of the reaction channel involving **11**, compared with those involving **12** or **13**.[10]

Experimental Section

2-Chloromethyl-3,3-dimethyl-1-butene (5). *N*-Chloro-*N*-cyclohexylbenzenesulfonamide, prepared from 110 g (0.46 mol) of *N*-cyclohexylbenzenesulfonamide by the usual method,[12] was dissolved in 100 mL of benzene in a 1-L flask. 2,3,3-Trimethyl-1-butene[13] (67 mL, 0.48 mol) and 100 mg of benzoyl peroxide were added. The solution was heated at reflux for 15 h, during which time two more batches (100 mg each) of benzoyl peroxide were added. After usual workup[12] and distillation, about 26 g (43%) of crude **5** was obtained, boiling at 93 °C (300 torr). Pure **5** [^{1}H NMR (CCl_4) δ 5.23 (m, 1 H, H-1), 5.15 (m, 1 H, H-1), 4.08 (d, J = 1.2 Hz, 2 H, CH_2Cl), 1 17 (s, 9 H, *t*-Bu); in good agreement with literature data[14]] could be separated by gas chromatography on a 7.5% Carbowax on Chromosorb W column from the contaminating 4-chloro-2,3,3-trimethyl-1-butene [^{1}H NMR δ 4.85 (m, 2 H, H-2), 3.45 (s, 2 H, H-4), 1.75 (d, J = 2 Hz, 3 H, C-2-CH_3), 1.17 (s, 6 H, C-3-CH_3)], which had a longer retention time than **5**.

β-Cyclopropylallyl Chloride (6). A solution containing 0.088 mol of *N*-chloro-*N*-cyclohexylbenzenesulfonamide,[12] 7.2 g (0.088 mol) of 2-cyclopropylpropene,[15] and a small amount of benzoyl peroxide in 10 mL of benzene was heated at reflux for 3 h. Workup as usual,[12] followed by distillation, gave 4.0 g of a monochloride mixture that appeared (^{1}H NMR spectrum) to contain approximately 50% of **6** and 25% each of the *E* and *Z* isomers of 1-chloro-2-cyclopropylpropene. Preparative gas chromatography on a 10% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb W column led to separation of (*Z*)-1-chloro-2-cyclopropylpropene (**9**)[16] from a mixture of **6** and (*E*)-1-chlorocyclopropylpropene (**10**).[16] ^{1}H NMR spectra (CCl_4) were assigned as follows: **9**, δ 5.80 (m, 1 H, H-1), 1.66, (d, J = 1.2 Hz, 3 H, CH_3), 1.4 (m, 1 H), 0.52 (m, 4 H); **10**, δ 5.80 (m, 1 H, H-1), 1.43 (d, J = 1.3 Hz, 3 H, CH_3), 1.9 (or 1.4) (m, 1 H), 0.6 (m, 4 H); **6**, δ 5.01 (m, 1 H, H-3), 4.79 (m, 1 H, H-3), 4.01 (d, J = 1.0 Hz, 2 H, H-1), 1.4 (or 1.9) (m, 1H), 0.6 (m, 4 H).

Irradiations. Preparative irradiations were conducted with **5** and **6** to give satisfactory yields of **4** analogues, substantially as described elsewhere[5,18] for 3-Me. We report here details on small-scale irradiations, isolations, and properties of products. Irradiations were carried out in NMR tubes in a small Griffin–Srinivasan Rayonet reactor (Model RPR-100) with 300-nm lamps.

A solution of 0.15 mL of **5** in 0.50 mL of acetone-d_6 was deaerated by nitrogen bubbling. After the solution had undergone 12 h of irradiation, 25% of **7** was formed; after 45 h, about 65% of **7** was formed; longer irradiations led to complete disappearance of **5**, with little evidence of substantial byproduct formation. Pure 1-chloro-1-*tert*-butylcyclopropane (**7**) was isolated by use of a $^3/_8$ in. 7.5% Carbowax on Chromosorb W column at 65 °C: mp 75–77 °C; ^{1}H NMR (CCl_4) δ 1.02 (s, 9 H), 0.89 (m, 4 H). Anal.[19] Calcd for $C_7H_{13}Cl$: C, 63.39; H, 9.88. Found: C, 63.50; H, 10.00. A rough comparison of the rate of **7** production with that of 4-Me[3,5] suggests that the quantum yield of formation of **7** from **5** is about 0.15.

As described above, our sample of **6** was mixed with substantial amounts of **10**. Nonetheless, irradiation of the mixture, as described above for **5**, in acetone-d_6 led to a mixture of **8**, **9**, and **10**. Analysis indicated that **8** undoubtedly formed from **6** and **9** from **10**, and this was confirmed by irradiation of **9** which led to partial isomerization to **10** but not to formation of **8**. **8** could be separated from **9** and **10** on a 10% TCEP on Chromosorb W column at 120 °C and had ^{1}H NMR and mass spectra in agreement with those reported by Landgrebe and Becker.[20]

Acknowledgment. This investigation was supported in part by Grant CA-13199, awarded by the National Cancer Institute, DHEW, and by Grant CHE77-20854, awarded by the National Science Foundation.

Registry No. 3 (Y = Me), 563-47-3; **4** (Y = Me), 50915-28-1; **5**, 26356-27-4; **6**, 42161-98-8; **7**, 71130-02-4; **8**, 16492-07-2; **9**, 71130-03-5; **10**, 71130-04-6; *N*-chloro-*N*-cyclohexylbenzenesulfonamide, 15963-66-3; *N*-cyclohexylbenzenesulfonamide, 3237-31-8; 2,3,3-trimethyl-1-butene, 594-56-9; 4-chloro-2,3,3-trimethyl-1-butene, 71130-05-7; 2-cyclopropylpropene, 4663-22-3.

(7) The reactions which they undoubtedly undergo[6] are degenerate (cis–trans and allylic rearrangements).

(8) S. J. Cristol and C. S. Ilenda, *Tetrahedron Lett.*, 3681 (1976).

(9) S. J. Cristol and R. P. Micheli, *J. Am. Chem. Soc.*, **100**, 850 (1978).

(10) A referee has suggested that the electron-delocalizing power of a chlorine substituent may not be large compared with an alkyl group, citing the comparable effects[11] on hydrogen abstraction by phenyl radicals on substituted methanes He suggested the results may be a reflection of polar character.

(11) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

(12) W. Theilacker and W. Wessel, *Justus Liebigs Ann. Chem.*, **703**, 34 (1967).

(13) G. Edgar, G. Calingaert, and R. E. Marker, *J. Am. Chem. Soc.*, **51**, 1483 (1929).

(14) H. Bilke, G. Collin, Ch. Duschek, W. Hobold, R. Hohn, W. Pritzkow, H. Schmidt, and D. Schnupfeil, *J. Prakt. Chem.*, **311**, 1037 (1969).

(15) R. Van Volkenburgh, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 172 (1949).

(16) This structure is assigned on the assumption[17] that the methyl group cis to the chlorine atom would absorb upfield of the absorption peak of an otherwise equivalent *trans*-methyl group.

(17) S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **31**, 581 (1966).

(18) S. J. Cristol and R. J. Daughenbaugh in "Organic Photochemical Synthesis", Vol. 2, R. Srinivasan, Ed., Wiley, New York, 1976, p 23.

(19) Analysis by Galbraith Laboratories, Knoxville, Tenn.

(20) J. A. Landgrebe and L. W. Becker, *J. Am. Chem. Soc.*, **90**, 395 (1968).