Anal. Calcd for $C_8H_{14}OCl_2$: C, 48.75; H, 7.16. Found: C, 48.91; H, 7.22.

Continued elution with benzene led to 159 mg whose distillation [bath temperature 80° (0.2 Torr)] gave alcohol **8**: mp 41–42°; infrared (Nujol) OH 2.91 (m) μ, fingerprint region vastly different from that of **7**; pmr δ 3.85 (m, 1, oxymethine).

Anal. Calcd for $C_8H_{14}OCl_2$: C, 48.75; H, 7.16. Found: C, 48.73; H, 7.12.

A mixture of 1.00 g of ketone **10** and 0.38 g of lithium aluminum hydride in 100 ml of ether was stirred at 0° for 1 hr. Work-up as above gave 970 mg of alcohol **6**, mp 61–62°.

A mixture of 270 mg of alcohol **6** and 50 mg of 10% palladium–charcoal in 5 ml of ethanol was hydrogenated at room temperature and atmospheric pressure. Usual work-up yielded 270 mg of alcohol **7**, mp 43–44°.

A solution of 5.00 g of ketone **2** in 10 ml of ether was added over a 1.5-hr period to a suspension of 500 mg of lithium aluminum hydride in 50 ml of ether under nitrogen in a Dry Ice–acetone bath. The mixture was stirred for 3 hr, 3 ml of methyl formate added, and the stirring continued for 30 min. After the mixture was warmed to 0°, 1 ml of water and 1 ml of 10% sodium hydroxide solution were added and the mixture was filtered. The filtrate was washed with 5% sodium bicarbonate solution and with water, dried, and evaporated. Crystallization of the residue from 5 ml of 3:1 hexane–benzene yielded 1.74 g of **10**. Chromatography of the mother liquor on Florisil and elution with petroleum ether gave 0.87 g more of **10**. Elution with 3:1 petroleum ether–benzene led to 1.64 g of a solid whose sublimation [45° (0.1 Torr)] yielded dienol **11a**: mp 57–57.5°; infrared (Nujol) OH 3.01 (s) μ; pmr δ 1.21 (s, 3, Me), 4.09 (m, 1, oxymethine), 5.95–6.15 (m, 4, olefinic H's), 6.23 (s, 1, $CHCl_2$); pmr (pyridine) δ 1.27 (s, 3, Me), 4.20 (m, 1, oxymethine), 5.85–6.10 (m, 4, olefinic H's), 6.64 (s, 1, $CHCl_2$).

Anal. Calcd for $C_8H_{10}OCl_2$: C, 49.76; H, 5.23. Found: C, 49.64; H, 5.24.

A mixture of 88 mg of **11a** and 600 mg of manganese dioxide in 75 ml of ether was stirred at room temperature for 3 hr and then filtered. Evaporation of the filtrate gave 86 mg of the dienone **2**.

A mixture of 70 mg of **11a** and 10 mg of 10% palladium–charcoal in 5 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure. After cessation of hydrogen uptake the mixture was filtered and the filtrate evaporated. A benzene solution of the residue was passed through a column of silica gel and evaporated. Pmr analysis of the residual mixture, 64 mg, showed it to consist of 90% alcohol **7** and 10% ketone **9**.

A solution of 13.6 g of ketone **2** in 40 ml of tetrahydrofuran was added over a 10-min period to a suspension of 1.95 g of lithium aluminum hydride in 140 ml of tetrahydrofuran under nitrogen. The mixture was stirred for 0.5 hr, sodium sulfate decahydrate then added, and the mixture filtered. The filtrate was dried and evaporated and the residue chromatographed on Florisil. Elution with petroleum ether yielded 500 mg of liquid diene **11b**: infrared ($CHCl_3$) C=C 6.01 (s), 6.12 (m) μ; pmr δ 1.20 (s, 3, Me), 2.38 (q, 2, J = 18.0, 2.5 cps, methylene), 5.4–6.0 (m, 4, olefinic H's), 5.66 (s, 1, $CHCl_2$). It was characterized as a maleic anhydride adduct (*vide infra*). Elution with 20:1 petroleum ether–ether gave 7.6 g of ketone **10**, while elution with a 4:1 mixture afforded 1.2 g of alcohol **6**.

A solution of 5.00 g of ketone **2** in 10 ml of ether was added over a 30-min period to a suspension of 500 mg of lithium aluminum hydride in 50 ml of ether at *ca.* −5°. The mixture was stirred for 30 min, 1 ml of 10% sodium hydroxide solution added, and the mixture filtered. The filtrate was washed with sodium bicarbonate solution and with water, dried, and evaporated. Distillation [45° (0.5 Torr)] of the residue yielded 1.86 g of a mixture, shown by gas phase chromatography (SE-30 column) to consist of 90% **11b** and 10% **10**. Chromatography of the distillation residue on silica gel and elution with petroleum ether gave 56 mg of diene **11b**. Elution with 1:1 benzene–petroleum ether led successively to 338 mg of **10** and 1.08 g of a complex alcohol mixture whose distillation [75° (0.4 Torr)] afforded 577 mg of a mixture shown by manganese dioxide oxidation (*vide supra*) to contain *ca.* 40% dienol **11a**.

Anhydride 12.—A solution of 340 mg of diene **11b** and 350 mg of maleic anhydride in 1 ml of benzene was refluxed for 48 hr and then evaporated. Chromatography of the residue on Florisil and elution with 4:1 benzene–petroleum ether gave 215 mg of a mixture of Diels–Alder adducts from which 120 mg of **12** could be obtained on crystallization from benzene–petroleum ether. Recrystallization from benzene yielded **12**: mp 146–146.5°; infrared (Nujol) C=O 5.38 (w), 5.46 (w), 5.64 (s) μ; pmr δ 1.37 (s, 3, Me), 1.4–1.7 (m, 2, methylene), 3.0–3.7 (m, 4, methines), 5.42 (s, 1, $CHCl_2$), 6.2–6.5 (m, 2, olefinic H's).

Anal. Calcd for $C_{12}H_{12}O_3Cl_2$: C, 52.38; H, 4.39. Found: C, 52.53; H, 4.31.

Analysis of the pmr spectrum of the first mother liquor showed it to contain predominantly **12** but also some of its isomer epimeric at the methyl-substituted site: pmr δ 1.18 (s, 3, Me), 5.63 (s, 1, $CHCl_2$).

A mixture of 100 mg of **12** and 10 mg of 10% palladium–charcoal in 5 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure. The mixture was filtered and the filtrate evaporated. A benzene solution of the residue, 100 mg, was passed through a Florisil column and evaporated. Sublimation [80° (0.1 Torr)] of the residue yielded **dihydro-12**: mp 161–162°; infrared (Nujol) C=O 5.37 (m), 5.63 (s) μ; pmr δ 1.31 (s, 3, Me), 5.82 (s, 1, $CHCl_2$).

Anal. Calcd for $C_{12}H_{14}O_3Cl_2$: C, 52.00; H, 5.09. Found: C, 51.98; H, 5.22.

Registry No.—**3a**, 24463-33-0; semicarbazone of **3a**, 24463-34-1; *p*-toluenesulfonylhydrazone of **3a**, 24463-35-2; **3b**, 24147-13-5; **3c**, 24463-37-4; **3d**, 24463-38-5; **4a**, 24463-39-6; **4b**, 24463-40-9; **5b**, 24463-41-0; **6**, 24463-42-1; **7**, 24463-43-2; **8**, 24463-44-3; **11a**, 24463-45-4; **11b**, 24463-46-5; **12**, 24463-47-6; dihydro-12, 24463-48-7.

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Iodonium Salts from Organolithium Reagents with *trans*-Chlorovinyliodoso Dichloride[1,2]

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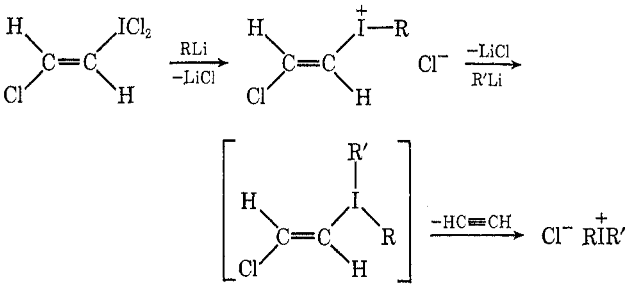
The aim of the present work was to adapt a recently reported synthesis of diaryliodonium salts[3] to the synthesis of iodonium salts having one or two heterocyclic, alkyl, or bicycloalkyl groups, according to the following scheme.



Di-2-thienyliodonium and phenyl-2-thienyliodonium salts, previously obtained by direct electrophilic substitution of thiophene,[4] were prepared in 72 and 38%

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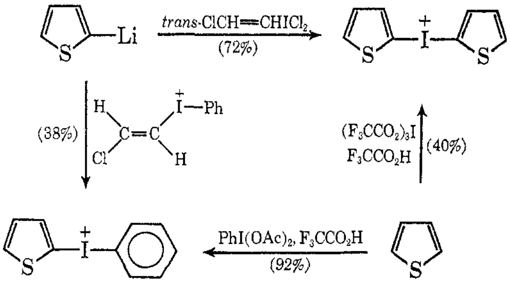
[1] Supported in part by National Science Foundation Grant No. GP-4425 to F. M. B. and by American Chemical Society Petroleum Research Fund Grant No. 231 to R. A. N.

[2] Taken from the dissertation of R. A. Nathan submitted in partial fulfillment of the requirements for the Ph.D. degree, 1969.

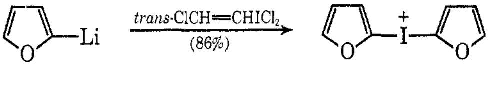
[3] F. M. Beringer and R. A. Nathan, *J. Org. Chem.*, **34**, 685 (1969).

[4] F. M. Beringer, H. E. Bachofner, R. A. Falk, and M. Leff, *J. Amer. Chem. Soc.*, **80**, 4279 (1958).

yields, respectively, by the reaction of 2-thienyllithium with *trans*-chlorovinyliodoso dichloride and phenyl(*trans*-chlorovinyl)iodonium chloride.



By this method it has been possible to prepare for the first time an iodonium salt from furan. The mixed



iodonium chloride–bromide, isolated as soon as the reaction mixture warmed to room temperature, could not be successfully recrystallized, but metathesis to the iodide gave a pure salt. Attempts to prepare phenyl(2-furanyl)iodonium salts from phenyl(2-chlorovinyl)iodonium chloride with 2-furanyllithium were unsuccessful.

Pyridyliodonium salts could not be prepared by the use of 2-pyridyllithium with the iodoso and iodonium reagents. It is not known whether the difficulty lay in an inherent shortcoming of the synthesis or in the instability of 2-pyridyliodonium salts.

In attempts to form iodonium salts with one or two bonds to sp^3 carbon, the same iodoso and iodonium reagents containing the *trans*-chlorovinyl masking group were treated with neopentyllithium and with 1-bicyclo[2.2.1]heptyllithium but gave no iodonium salt. Also, unsuccessful were reactions using vinyllithium, 1-cyclohexenyllithium, 1-perfluoroheptyllithium, and 3,3,3-trifluoropropynyllithium; the causes of these failures are not known.

Experimental Section

Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Gas chromatography was done on 6-ft columns, packed with 20% SE-30 on Chromosorb W (DMCS-treated), with an Aerograph 1520-A gas chromatograph. Melting points[5] were taken in capillary tubes on a Thomas–Hoover apparatus and corrected.

Neopentyllithium.—Since the low-temperature (10°) synthesis of neopentyllithium[6,7] could not be repeated, a new procedure at higher temperature[8] was developed. A 250-ml round-bottom three-necked flask equipped with a septum cap, reflux condenser, and pressure-equalizing addition funnel was flushed well with argon, flamed, charged with 8.0 g of lithium dispersion[9] and 80 ml of benzene, and kept under a positive pressure of argon. Neopentyl chloride (21.32 g, 200 mmol) in 40 ml of benzene was placed in the addition funnel. After approximately 20% of the alkyl chloride solution had been added, the temperature was raised slowly to the point of exotherm (usually between 75 and 80°), at which time the heat was removed, and gentle reflux was maintained (about 82°) by regulating the rate of addition of the alkyl halide. After this addition, the mixture was heated overnight under reflux. The cooled reaction mixture was filtered through sintered glass under argon. Titration of aliquots from different runs showed a variation from 60 to 90% in the yield of neopentyllithium. Neopentyl bromide gave much lower yields, about 10%.

Di-2-thienyliodonium Iodide and Di-2-furanyliodonium Iodide.—These reactions were carried out at Dry Ice–acetone temperatures as described[3] for diphenyliodonium iodide, except that they were terminated immediately upon warming to room temperature. Work-up was rapid, and all salts were stored below 0°. **Di-2-thienyliodonium iodide** was obtained in 72% yield, mp 131–136° dec, lit.[4] 135–136°.

Di-2-furanyliodonium iodide was similarly obtained in 86% yield, mp 114–116° dec.[10]

Anal. Calcd for $C_8H_6O_2I_2$: C, 24.77; H, 1.56; I, 65.43. Found: C, 24.92; H, 1.45; I, 65.36.

Phenyl(2-thienyl)iodonium chloride was prepared as described previously for phenyl-1-naphthyliodonium chloride **3**, except that it was worked up immediately upon reaching room temperature, giving 1.6 g (38%), mp 149–150.5° dec, lit.[4] 140–141°.

Attempts to Prepare Alkyliodonium Salts.—The unsuccessful reactions of various alkyl- and perfluoroalkyllithium reagents with *trans*-chlorovinyliodoso dichloride and phenyl(*trans*-chlorovinyl)iodonium chloride were run like the successful preparations of diaryliodonium salts.[3] With these salts neopentyllithium gave no iodonium salt and no neopentyl halides. However, with phenyliodoso dichloride,[11] neopentyllithium gave neopentyl chloride and iodide (trace) along with iodobenzene.

When 1-bicyclo[2.2.1]heptyllithium was alllowed to react with *trans*-chlorovinyliodoso dichloride, while no solid was formed, vpc confirmed the presence of both bridgehead iodide and chloride (ratio of *ca.* 5:1). Presumably, the bridgehead iodide results from nucleophilic addition of the bicycloheptyl group to iodine in the iodoso or iodonium reagent.

Reactions of phenyliodoso dichloride and of phenyl(*trans*-chlorovinyl)iodonium chloride with 1-cyclohexenyllithium were equally unsuccessful. In the latter reaction quenching at low temperature with magnesium bromide etherate, with triphenylboron, and with methanol, in an attempt to help break the chlorovinyliodine bond, was also unsuccessful. In all three cases phenyl(*trans*-chlorovinyl)iodonium chloride was recovered.

Registry No.—*trans*-Chlorovinyliodoso dichloride, 24472-17-1; di-2-furanyliodonium iodide, 24472-18-2.

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[5] The technique involved in taking melting points of iodonium salts has been discussed previously: F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Sommer, *J. Amer. Chem. Soc.*, **81**, 342 (1959).

[6] D. E. Applequist and D. F. O'Brien, *ibid.*, **85**, 743 (1963).

[7] H. Gilman, H. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *ibid.*, **71**, 1499 (1949).

[8] H. Gilman, F. W. Moore, and O. Baine, *ibid.*, **63**, 2479 (1941).

[9] A dispersion of lithium containing 0.5% sodium in mineral oil. Due to the nonhomogeneity of the dispersion the exact amount of metal in the reaction mixture was unknown. The amount used, however, was in excess of stoichiometry.

[10] Previously unknown compound.

[11] J. Dehn, Jr., Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1964.

Reactions of 1,1-Bis(trifluoromethyl)alkenols in Sulfuric Acid

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We have recently had an interest in the preparation of fluorinated monomers, including 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene. At least two attempts to prepare this or similar compounds have appeared in the literature.[1,2] Plakhova and Gambaryan[2] reported the preparation of 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene by the phosphorus pentoxide or sulfuric acid dehydration of 1,1-bis(trifluoromethyl)-1-buten-3-ol, but this work may be in doubt (*vide infra*).

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[1] M. H. Kaufman and J. D. Brown, *J. Org. Chem.*, **31**, 3090 (1966).

[2] V. F. Plakhova and N. P. Gambaryan, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **4**, 681 (1962).