

pound crystallized on standing, and a sample recrystallized from pentane/dichloromethane melted at 51 °C. Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.02; H, 9.46; N, 8.74. Spectral data: IR 1655 cm^{-1} ; NMR δ 4.5 (broad s, 1 H), 3.72 (s, 2 H), 3.50 (t, 2 H), 2.4 (t, 2 H), 2.0 (m, 2 H), 1.28 (s, 6 H).

Synthesis of 4 from Ethyl 4-Bromobutanoate. Ethyl 4-bromobutanoate (5.0 g, 0.025 mol) and 1 (5.94 g, 0.067 mol) were dissolved in 50 mL of 95% ethanol and the mixture refluxed for 20 h, or until starting ester had completely reacted (as determined by GC). The mixture was cooled, acidified with dilute HCl, and extracted with ether to remove neutral compounds. The aqueous layer was made basic with NaOH and extracted with ether. The extract was dried (K_2CO_3) and distilled, yielding pure 5 as a liquid, bp 95 °C (22 mm). The product crystallized on standing.

A sample was purified for analysis by recrystallization from pentane and dichloromethane, mp 25–26 °C. Anal. Calcd for $C_{10}H_{21}NO_3$: C, 59.08; H, 10.41. Found: C, 58.95; H, 10.78. Spectral data: IR 1730 cm^{-1} ; NMR δ 4.15 (q, 2 H), 3.28 (s, 2 H), 2.7–1.7 (overlapping multiplets, 8 H), 1.27 (t, 3 H), 1.05 (s, 6 H).

The remaining sample of 5 was heated in a 150 °C oil bath under a reflux condenser for 20 h and then distilled. After an ethanol forerun, the entire sample was collected at 110 °C (0.25 mm). This product crystallized on cooling, and was identical with 4 prepared from butyrolactone as described above.

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Registry No.—1, 124-68-5; 3a, 51849-54-8; 3b, 61484-26-2; 4, 61484-27-3; 5, 61484-28-4; *cis*-4,5-dimethyltetrahydrofuran-2-one, 10150-95-5; γ -butyrolactone, 96-48-0; ethyl 4-bromobutanoate, 2969-81-5.

References and Notes

- S. P. McManus, P. J. Kelly, W. J. Patterson, and C. U. Pittman, Jr., *J. Org. Chem.*, **41**, 1642 (1976).
- See, for example, A. I. Meyers and E. D. Mihelich, *J. Org. Chem.*, **40**, 1186 (1975).
- The amine 1 has a boiling point of 165 °C.
- The oxazoline 3a is also converted cleanly to 4 simply by extended heating in the presence of 1 and water.
- Interestingly, the triplet corresponding to the ring methylene of 4 adjacent to the carbonyl group shifts nearly as much as the hydroxymethylene signal does.
- Mass spectra were kindly supplied by Dr. M. L. Druehlinger of the Chemistry Department, Indiana State University.
- This lactone was prepared in 33% yield from diethyl malonate and *trans*-2,3-dimethyloxirane. For a similar preparation of the compound, see P. L. Pacini and R. G. Ghirardelli, *J. Org. Chem.*, **31**, 4133 (1966).
- Published analytical results for this compound in ref 1 are inconsistent,¹⁰ at least partially because of the hygroscopic nature of the material, but there is no doubt that the compound we isolated is the same reported there.
- These data match those given in ref 1 quite well, and are included here only to emphasize the similarity between the spectra of 3a and 4.
- Personal communication from S. P. McManus.

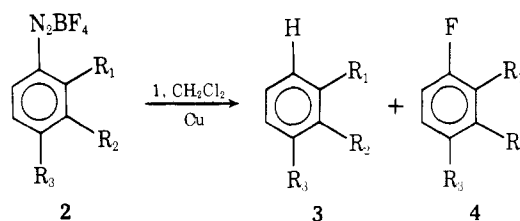
Crown Ether-Copper-Catalyzed Decomposition of Arenediazonium Fluoroborates

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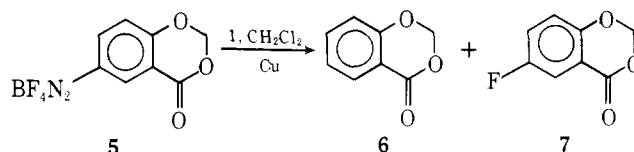
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We wish to report what appears to be the first example of arenediazonium tetrafluoroborate salt decomposition catalyzed by a macrocyclic polyether.¹ The arenediazonium salts shown in Table I were readily decomposed in methylene chloride under a nitrogen atmosphere in the presence of catalytic amounts (10 mol %) of dicyclohexyl-18-crown-6 (1) and powdered copper to afford varying proportions of reduction and Schiemann products as shown in Table I. We were also able to detect (VPC/mass spectrum) in each case the presence of minor amounts of chloroaromatic derivative (9)¹⁶ and 1,1,2,2-tetrachloroethane (10), apparently from dimerization of the dichloromethyl radical. It is also



- 2a, $R_1 = R_3 = F$; $R_2 = H$
 b, $R_1 = R_2 = H$; $R_3 = NO_2$
 c, $R_1 = H$; $R_2 = NO_2$; $R_3 = Cl$
 d, $R_1 = R_2 = R_3 = H$
 e, $R_1 = R_2 = H$; $R_3 = CH_3$



In addition, no reaction was observed when 15-crown-5 was substituted for 1. Decomposition was facilitated by the presence of electron-withdrawing groups in the aromatic nucleus. Evolution of nitrogen was complete for 2a, 2b, and 2c within a few minutes with gentle warming, while the remaining salts required longer periods of reflux (see Table I).

The initial report of an interaction between a polyether and a diazonium salt appears to be that of Martin and Bloch² who utilized 1 to aid in the decomposition of potassium diazocyclopentadiene-2-carboxylate. More recently, Gokel and Cram³ showed that arenediazonium salts were solubilized in nonpolar media by 18-crown-6 and binaphtho-20-crown-6 while binaphtho-17-crown-5 was ineffective. We have found that while use of 1 in the presence of copper leads to spontaneous decomposition of fluoroborate salt 2b, treatment with 15-crown-5 (8) results in no detectable reaction. As suggested by earlier workers,³ complexation of the diazonium species appears to involve insertion into the cavity of the crown ether as is known for complexation of metal ions.⁴ Complexation very likely affords a critical amount of solubilized diazonium salt which is necessary for further reaction.^{5,6} In the present case, the cavity of 1 is able to accommodate the diazonium species, while that of 8 is apparently too small.

Reaction in the case of salts 2a, 2b, and 2c led cleanly to the reduction product. The present method thus constitutes for these salts an extremely mild, nonaqueous way of replacing the diazonium group by hydrogen, a transformation which has attracted much attention.^{7–15} The remaining salts afforded mixtures of reduction and Schiemann products as shown in Table I. We were also able to detect (VPC/mass spectrum) in each case the presence of minor amounts of chloroaromatic derivative (9)¹⁶ and 1,1,2,2-tetrachloroethane (10), apparently from dimerization of the dichloromethyl radical. It is also

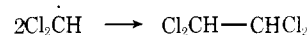
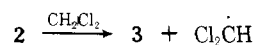
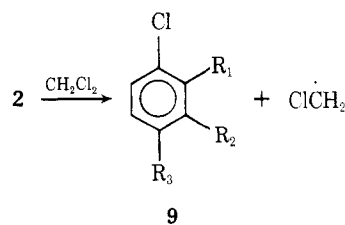


Table I. Products from the Crown Ether-Copper-Catalyzed Decomposition of Arenediazonium Fluoroborates

Reactant ^{a,b}	Registry no.	Reaction conditions	Products ^d (yields) ^e	Registry no.
2a	326-87-4	10 mol % 1, ^g CH ₂ Cl ₂ , 30 min, 40 °C	3a (95%); 4a (0)	372-18-9 (3a)
2b ^c	456-27-9	10 mol % 1, ^g CH ₂ Cl ₂ , 30 min, 40 °C	3b (91%); 4b (0)	58777-17-6 (3b)
2c	41136-80-5	10 mol % 1, ^g CH ₂ Cl ₂ , 30 min, 40 °C	3c (93%); 4c (0)	88-73-3 (3c)
2d	58801-43-7	10 mol % 1, ^g CH ₂ Cl ₂ , 3 h, 40 °C	3d (17%); 4d (60%)	71-43-2 (3d)
2e	459-44-9	10 mol % 1, ^g CH ₂ Cl ₂ , 3 h, 40 °C	3e (56%); 4e (29%)	462-06-6 (4d) 108-88-3 (3e)
5	61702-20-3	10 mol % 1, ^g CH ₂ Cl ₂ , 3 h, 40 °C	6 (83%); 7 (6%) ^f	352-32-9 (4e) 6009-10-5 (6) 61702-21-4 (7)

^a All diazonium salts were prepared by standard techniques see ref 7. ^b Identity confirmed by comparison of physical properties with literature values and by IR, ¹H NMR, and elemental analyses. ^c The authors thank Dr. D. Mulvey for a sample of this compound. ^d Identity determined by isolation and VPC/mass spectrum. ^e Yields determined by VPC vs. standard. ^f Decomposition occurred upon attempted distillation. ^g Registry no., 16069-36-6.

interesting to note the lack of biaryl coupling products, despite the assumed presence of aryl radicals.

We are currently exploring the synthetic utility of these crown ether catalyzed decompositions in the generation of coupling and Sandmeyer type products. We anticipate that crown ethers may also facilitate other gas evolving decompositions, such as those involving diazomethane, α -diazo ketones, and *p*-toluenesulfonylhydrazones.

Experimental Section

General. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Analysis of the products of decomposition of the diazonium salts was carried out on a Hewlett-Packard 6830 gas chromatograph with use of an SP-2401 column.

Preparation of Diazonium Salts. All salts were prepared by standard techniques (ref 7). The only compound which was prepared for the first time was 5, which had a decomposition point of 145–150 °C.

Arenediazonium Fluoroborate Decomposition. All salts were decomposed in identical fashion with the only variable being the heating period as shown in Table I. A representative procedure is given below for the decomposition of 2a.

Decomposition of 2,4-Difluorobenzediazonium Tetrafluoroborate (2a). A 100-mL round-bottom flask was charged with 1.33 g (5.9 mmol) of 2a, 11 mL of methylene chloride, and 0.19 g (0.5 mmol) of dicyclohexyl-18-crown-6 (1) under a nitrogen atmosphere. With continuous nitrogen flow, 0.1 g of copper powder was added in one portion and the reaction mixture was heated at 40 °C for 15 min with magnetic stirring. The cooled reaction mixture was then filtered and analyzed by VPC to indicate that 1,3-difluorobenzene (3a) was the sole product in 95% yield vs. internal standard. A portion of the reaction mixture was distilled to give a pure sample of 3a, which had boiling point, IR, and NMR identical with published values. Another portion of the reaction mixture was subjected to VPC/mass spectrum analysis, indicating a single peak at *m/e* 113, correct for 3a.

Registry No.—Copper, 7440-50-8.

References and Notes

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Reduction of Aryldiazonium Compounds in Nonpolar Media

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While studying diazonium ion reactivity in nonpolar media, we required a convenient method for protodediazotiation (reduction) of these substances. In particular, the method had to afford high yields of reduction product at low temperatures in a short period of time and be applicable in such nonpolar media as chloroform and methylene chloride. Numerous methods are available for reduction of aryldiazonium salts (particularly chlorides) in aqueous media,¹ but these are commonly ineffective for reduction of BF₄⁻ and PF₆⁻ salts which are more stable than chlorides but much less soluble in water. Reducing systems which have been reported for the reduction of BF₄⁻ or PF₆⁻ salts include zinc in ethanol,² tributyltin hydride in tetrahydrofuran or diethyl ether and triethylsilane in acetonitrile,³ rhodium complexes in dimethylformamide,⁴ tetramethylurea,⁵ sodium borohydride in methanol or dimethylformamide,⁶ 1,4-dioxane in the presence of Cu₂O,⁷ and 1,4-dioxane, tetrahydrofuran, 1,3-dioxolane, and 1,2-dimethoxyethane in aqueous sodium acetate.⁸ Moreover, the potential of hypophosphorous acid for our requirements could be inferred from Lamm's observation⁹ that 2-bromo-4,6-dichloro-, 2,4,5-trichloro-, and 2,4-dichloro-6-nitrobenzediazonium tetrafluoroborates were reduced by 10 equiv of hypophosphorous acid in 5 M HCl in 83, 77, and 64% yields, respectively.

We wish to report that hypophosphorous acid¹⁰ in chloroform solution in the presence of trace cuprous oxide fulfills the conditions set forth above. Thus, excellent yields of reduction products were obtained in eight of the nine cases examined (see Table I). The single exception is *p*-methoxybenzediazonium tetrafluoroborate, which undergoes reduction in only 67% yield. Apparently, electron-attracting substituents favor the reduction and mildly electron-releasing