gel with hexane–ethyl acetate (85/15) gave a product which was further recrystallized from ligroin: yield 0.48 g (44%); mp 76–77 °C (lit.[9] mp 84 °C). Spectral data were in good agreement with literature data: IR (KBr) 2220, 2160 (C≡C), 1715 (CO$_2$R), 1605, 1515 (C=C) cm^{-1}; NMR (CCl$_4$) δ 2.09 (brs, 3 H, 9-CH$_3$), 2.43 (s, 3 H, SCH$_3$), 3.79 (s, 3 H, CO$_2$CH$_3$), 5.96 (brd, 1 H, 5-H), 6.14 (d, 1 H, 1-H), 7.00 (q, 1 H, 2-H, $J_{1\text{-H},2\text{-H}}$ = 15.6 Hz, $J_{2\text{-H},5\text{-H}}$ = 2.8 Hz).

Methyl (1*Z*,5*Z*)-6-(methylthio)-1,5-nonadiene-3,7-diyne carboxylate (3) was prepared in the same way as **2** from (*E*)-methyl 3-bromoacrylate by using the same amounts of starting materials. Purification was carried out by chromatography on silica gel with hexane–ethyl acetate (85/15); yield 0.49 g (45%). Spectral data were in good agreement with those reported in the literature: IR (film) 2220, 2160 (C≡C), 1715 (CO$_2$R), 1605, 1525 (C=C) cm^{-1}; NMR (CCl$_4$) δ 2.09 (d, 3 H, 9-CH$_3$), 2.39 (s, 3 H, SCH$_3$), 3.69 (s, 3 H, CO$_2$CH$_3$), 5.92 (brd, 1 H, 5-H), 5.95 (d, 1 H, 2-H), 6.26 (q, 1 H, 2-H, $J_{1\text{-H},2\text{-H}}$ = 11 Hz, $J_{2\text{-H},5\text{-H}}$ = 2.8 Hz, $J_{5\text{-H},9\text{-CH}_3}$ = 0.6 Hz).

Acknowledgment. Grants from the Swedish Natural Science Research Council to T.F. and S.G. are gratefully acknowledged.

Registry No. 2, 3102-40-7; **3**, 2739-61-9; **4**, 3140-92-9; **5**, 79916-95-3; **6**, 73882-40-3; **7**, 79916-96-4; **7** methyl ester, 79916-97-5; **8**, 79916-98-6; **8** methyl ester, 79916-99-7; **9**, 79917-00-3; **10**, 23229-66-5; **11**, 79917-01-4; **12**, 79917-02-5; **13**, 79917-03-6; **14**, 79917-04-7; **15**, 79917-05-8; methyl (*E*)-3-bromoacrylate, 6213-87-2; methyl (*Z*)-3-bromoacrylate, 6214-22-8.

A Convenient Synthesis of Hexafluoroacetone

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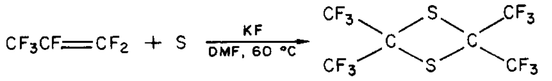
Hexafluoroacetone (HFA) is a powerful electrophile and, as such, has been used as an efficient trapping agent and useful synthetic reagent. Of the many methods which have been reported for the preparation of HFA,[1] several are based on hexafluoropropene (HFP) as the raw material due to its commercial availability, although the first industrial-scale preparation involved the fluorination of hexachloroacetone. Among the former methods is the nitric oxide oxidation of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (1) or hexafluorothioacetone dimer (HFTA dimer) at 600 °C.[2] We have discovered that HFTA dimer can readily be converted by NO and other oxidants to HFA at much lower temperatures, and have also developed a simple and convenient synthesis of HFTA dimer.[3]

HFTA Dimer

When HFP was bubbled into dry DMF containing KF and sulfur at 40 °C, an exothermic reaction occurred, and HFTA dimer was produced in 72–83% yields after workup (eq 1). HFP could be added at a rate such that a reaction temperature of 50–60 °C was maintained without external heating and HFP was consumed as rapidly as it was added.



(1)

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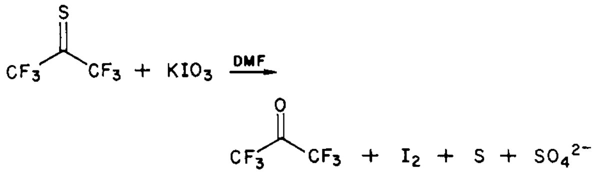
When KF, S, and DMF are mixed, a bluish hue is imparted to the solution. The color rapidly disappears upon the addition of HFP or HFTA dimer. The blue color did not appear if the DMF was wet (0.05% H$_2$O) although the reaction to produce HFTA dimer still occurred. The reaction takes place under similar conditions in dimethyl sulfoxide, dimethylacetamide, and *N*-methylpyrrolidinone, but little or no reaction took place in sulfolane, acetone, or HFTA dimer. When CsF was substituted for the less soluble KF, the reaction took place in CH$_3$CN but with considerable byproduct formation.

HFTA dimer is appreciably soluble in DMF at room temperature. Under the conditions of our experiments, the mixture was homogeneous (except for undissolved KF) at the end of the reaction. Cooling the solution to about –20 °C precipitates nearly all of the dimer (mp 23 °C), which can then be filtered, washed with water, and distilled (bp 110 °C). The recovered DMF can be reused.

Hexafluoroacetone

In the presence of fluoride ion, HFTA dimer is in equilibrium with its monomer in DMF solution. Since HFTA is much more reactive than HFTA dimer, we felt that oxidation of the monomer, generated in situ from the dimer, would provide a convenient method for the preparation of HFA, since the ketone (bp –28 °C) would distill out of the reaction mixture. Of the several metallic and nonmetallic reagents used for the oxidation, nearly all reacted. However, most gave a mixture of HFA and CF$_3$COF (Ag$_2$O, PbO, SnO, PbO$_2$, Fe$_2$O$_3$) or of HFA and (CF$_3$)$_3$CH[4] (P$_2$O$_5$, Cu$_2$O, CuO). These same products were also formed in low yield when no oxidant was present. The oxidants alter the product ratios from about 6:2:1 (HFA/CF$_3$COF/(CF$_3$)$_3$CH) with DMF, HFTA dimer, and KF alone to nearly all CF$_3$COF in the presence of PbO$_2$ and to nearly all HFA in the presence of KIO$_3$, NaIO$_4$, NO$_2$, or HgO. These oxidants substantially increased the amount of volatile products.

A convenient reagent for the conversion of HFTA to HFA was KIO$_3$. Thus, when 1 was added to a mixture of KF and KIO$_3$ in DMF and the solution heated to reflux, HFA distilled out of the flask (eq 2). Yields were 74–89%.



(2)

Interestingly, SO$_2$ was not a reaction product. However, sulfur was recovered from the product mixture, in addition to I$_2$ and K$_2$SO$_4$. Elemental sulfur was a substantial byproduct in the oxidation of HFTA with NO$_2$ also, permitting its recycle in the synthesis of 1.

The two reactions (HFTA dimer synthesis and conversion to HFA) could be combined in a one-pot procedure in which 1 was not isolated. After preparation of the dimer from HFP, KIO$_3$ was added and the mixture heated to reflux as before during a period of 0.5–1 h during which HFA distilled out of the reaction mixture. We found that the purity of HFA was reduced in this procedure, being contaminated with (CF$_3$)$_3$CH (bp 11–12[5]). For most purposes, this is not likely to adversely effect reactions intended with HFA.

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(1) For a review, see Krespan, C. G.; Middleton, W. J. *Fluorine Chem. Rev.* **1967**, *1*, 145.

(2) Middleton, W. J.; Sharkey, W. H. *J. Org. Chem.* **1965**, *30*, 1384.

(3) During the course of our work, England reported the synthesis of HFTA dimer under similar conditions. England, D. C. *J. Org. Chem.* **1981**, *46*, 147.

(4) Identified by IR, ^{1}H NMR, and ^{19}F NMR.

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Experimental Section

Caution: HFTA dimer and HFA are toxic!

HFTA Dimer (1). A 500-mL, three-necked flask was fitted with a mechanical stirrer, thermometer, a water-cooled condenser, and a gas inlet tube. The outlet of the condenser was attached to a -78 °C cold trap. Under an atmosphere of nitrogen, the flask was charged with 200 mL of dry DMF, 23 g (0.72 mol) of sulfur, and 5.0 g of KF. The mixture was warmed to 40 °C, the heat source removed, and HFP bubbled in at a rate of about 1 g/min. The temperature rose and leveled off in the range of 52-57 °C. After 96 g of HFP had been added, an additional 23 g of sulfur was added (total sulfur charged 1.44 mol). Hexafluoropropene was added until a total of 199.5 g (1.33 mol) was used (2.3 h). The whole mixture was cooled to -20 °C and filtered. The solid was washed with cold DMF. After allowing the solid to melt, it was filtered, and the lower layer was washed twice with 50 mL of H_2O. This gave 199.7 g of pale yellow product (82.5% yield) of 98% purity by GC.

Hexafluoroacetone. From KIO_3. In an apparatus like that described above except for the gas inlet tube was charged 1 g of anhydrous KF, 30 g (0.14 mol) of KIO_3, 20.0 g of HFTA dimer (distilled, bp 110 °C, 0.055 mol), and 100 mL of dry DMF (water content 0.004%). The mixture was then heated to 140 °C over 20 min. The temperature rose gradually to 149 °C during an additional 100 min. The mixture turned dark brown as iodine was formed. In the cold trap 16.3 g (0.098 mol) of HFA (95% by GC) was collected (89% yield).

From NO_2. A 250-mL, three-necked flask was equipped with a thermometer, stirrer, gas inlet tube, and a cold-finger condenser containing acetone held to -10 to -20 °C. A dry ice and acetone trap (-78 °C) was connected to the -20 °C condenser. The flask was charged with 125 g of HFTA dimer (85% purity, 0.29 mol), 3.5 g of KF, and 100 mL of dry DMF. The mixture was heated to 100-120 °C and 70 g (1.52 mol) of NO_2 was passed subsurface into the liquid over a period of 5.5 h. At the end of this period, the -20 °C condenser was allowed to warm to room temperature and the apparatus flushed with nitrogen. The -78 °C trap contained 113.5 g, which after distillation, afforded 77.3 g (0.466 mol, 80% yield from 1) of HFA (bp -28 °C) and 36 g of NO_2 (bp 21 °C).

Acknowledgment. We acknowledge R. E. Eibeck and M. A. Robinson for helpful discussions.

Registry No. 1, 791-50-4; hexafluoropropene, 116-15-4; hexafluoroacetone, 684-16-2.

Anomalous Course of Leuckart Reduction of Anthraquinones by Formamide

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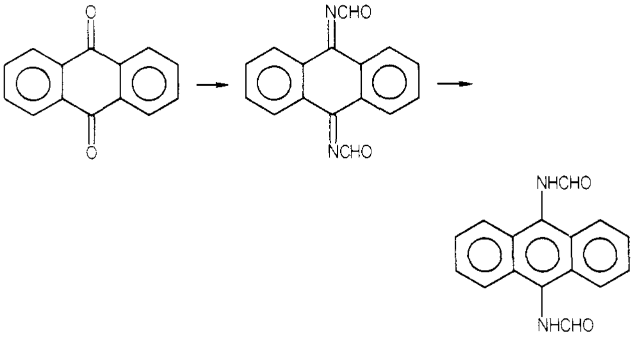
Reactions of such alkyl- and dialkylamides as methylformamide, dimethylformamide, and hexamethylphosphoric triamide with a variety of chloroanthraquinones have been described;[1,2] these give (methylamino)- and (dimethylamino)anthraquinones, depending on the reagent and conditions. Formamide, presumably because of its demonstrated capacity for reacting with the carbonyl groups in the parent anthraquinone,[3] has apparently not been used in comparable experiments. It has, however, been known for some time that aminoanthraquinones can be produced from chloroanthraquinones by reaction with *p*-toluenesulfonamide[4] or phthalimide,[5] followed in each case by hydrolysis.

Schiedt[3] had originally reported 1 as the product obtained from reaction of anthraquinone with formamide. This was unfortunately misquoted on review as the 9,10-dihydro derivative, i.e., the compound anticipated from a double Leuckart reaction of anthraquinone.[6] We have now confirmed (microanalysis, IR, and mass spectroscopy) Schiedt's original formulation. Evidently, two molecules of formamide have condensed, one at each carbonyl group, with anthraquinone and a third molecule of formamide (or formic acid) has effected 9,10 reduction (or, equivalently, a single Leuckart reaction followed by proton shift) to produce an aromatic central ring.



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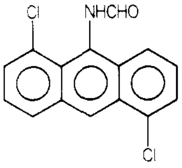

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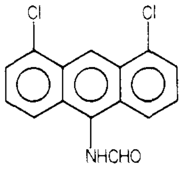

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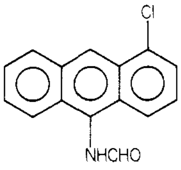

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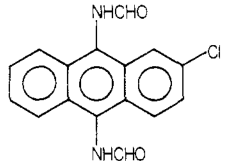

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We now report our results on the reaction of formamide with chloroanthraquinones. The symmetrical 1,5-dichloroanthraquinone gave, after 3-h reflux with formamide, a mixture containing 2 and 1,5-dichloroanthracene, together with some unreacted quinone. The course of reaction was thus following that noted by Schiedt (reaction at carbonyl)[3] rather than that observed with methylformamide and dimethylformamide (displacement of chlorine),[1,2] but further stages of reduction were apparent. The yield of 1,5-dichloroanthracene increased with lengthening reaction time. With the assumption that 2 is derived from the product of an initial Schiedt-type sequence, these observations may be rationalized as a conversion of the Schiedt-type intermediate by formamide (or formic acid) to the 9,10-dihydro derivative, a reduction equivalent to tautomerization and Leuckart reduction. The dihydro derivative then eliminates a molecule of formamide.

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