maintained by use of an appropriate cooling bath: 0 to −5 °C in an ice–salt bath, −30 to −35 °C in a CH_3CN–liquid N_2 slush bath,[8] and −78 °C in a dry ice–acetone bath. *n*-Butyllithium (1.0 equiv)[9] in hexane was placed in the addition funnel via syringe and added dropwise to the reaction mixture followed by addition of HMPA (1.1 equiv). The mixture was stirred for 30–40 min, and a THF solution of the unsaturated acid (0.5 equiv) or unsaturated ester (1.0 equiv) was added dropwise over 10 min. The resulting mixture was stirred for an additional 10 min followed by the addition of MeI (1.0 equiv). After being stirred for 30 min, the mixture was allowed to warm to −10 °C and was quenched by the addition of water. The resulting mixture was acidified with dilute HCl and extracted with Et_2O. The combined Et_2O extracts were washed with saturated NaCl, dried (Na_2SO_4), and evaporated to give the crude product.

3-Methylindene-2-acetic Acid (6). 2-Indeneacetic acid[10] (0.96 g, 5.5 mmol) was methylated as described above at 0 to −5 °C, affording 0.80 g (79%) of a mixutre of methylated products as described in the text. Two recrystallizations from hexane afforded an analytical material: mp 113–115 °C; NMR ($CDCl_3$) δ 2.02 (3, m, CH_3), 3.41 (4, m, $2CH_2$), 7.18 (4, m, aromatic), 9.70 (1, s, COOH).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.72; H, 6.51.

α-Methyl-2-indeneacetic Acid (8). 2-Indeneacetic acid (3.0 g, 17.2 mmol) was treated according to the general procedure at −78 °C, affording 3.1 g (96%) of a yellow oil which solidified on standing. Recrystallization from hexane after treatment with charcoal afforded an analytical sample: mp 104–106 °C (lit.[10] mp 106–106.5 °C); NMR ($CDCl_3$) δ 1.43 (3, d, J = 7 Hz, CH_3), 3.38 (2, s, CH_2), 3.54 (1, q, J = 7 Hz, CH), 6.69 (1, s, vinyl H), 7.25 (4, m, aromatic), 11.0 (1, s, COOH).

α,α-Dimethyl-2-indeneacetic Acid (12). Ester 9[10] (1.0 g, 5.3 mmol) was treated according to the general procedure twice in succession. The resulting yellow oil (1.02 g) was then heated at gentle reflux for 16 h in 20 mL of a 4:1 mixture of HOAc and concentrated HCl. The resulting mixture was cooled to ambient temperature, poured onto ice, and filtered when the ice had melted, affording 0.77 g (72%) of crude acid after vacuum drying. Three recrystallizations from hexane afforded an analytical sample: mp 143–146 °C; NMR ($CDCl_3$) δ 1.57 (6, s, $2CH_3$), 3.49 (2, s, CH_2), 6.78 (1, s, vinyl H), 7.05–7.55 (4, m, aromatic), 10.5 (1, br s, COOH).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.25; H, 7.00.

Registry No.—**4,** 57932-05-5; **6,** 69381-20-0; **7,** 69381-21-1; **8,** 24040-29-7; **9,** 24040-30-0; **10,** 24040-28-6; **11,** 69381-22-2; **12,** 69381-23-3.

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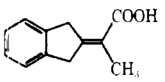

i

in HO-*t*-Bu–Me_2SO, as would be anticipated from results obtained with the phenylbutenoic acids.

(6) The presence of **7** in the reaction product mixture was assigned on the basis of the NMR spectrum. After substraction for spectral characteristics equivalent to those for **6** and **8,** an additional doublet was seen at δ 1.73 and the total integration of the methyl region (δ 2.5–1.0) was found to be equivalent to about three protons relative to the aromatic and downfield (acid) protons. The total integration of the vinyl resonance and the region from δ 3.0 to 4.2 was four protons with the vinyl region (broad singlet) accounting for about 0.75 proton.

(7) Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. NMR spectra were recorded with a Hitachi Perkin-Elmer Model R-24 spectrometer, using Me_4Si as an internal standard.

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Alkyl Nitrite–Metal Halide Deamination Reactions. 6. Direct Synthesis of Arenediazonium Tetrafluoroborate Salts from Aromatic Amines, *tert*-Butyl Nitrite, and Boron Trifluoride Etherate in Anhydrous Media

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Arenediazonium tetrafluoroborate salts have been prepared by a wide variety of methods.[3] The most commonly employed procedures involve diazotization of aromatic amines with sodium nitrite in 40–50% aqueous fluoroboric acid[4] or diazotization in aqueous hydrochloric or sulfuric acid followed by addition of sodium tetrafluoroborate or fluoroboric acid to precipitate the arenediazonium tetrafluoroborate salt.[5] Although these procedures generally give good yields of water-insoluble diazonium salts, a large excess of fluoroboric acid or sodium tetrafluoroborate is required to precipitate the tetrafluoroborate salts and the process for obtaining the anhydrous salt is laborious. In addition, aromatic amines that do not dissolve in aqueous mineral acid are not amenable to these procedures. In these instances, alternate processes that employ either sodium nitrite in concentrated acids[6] or nitrosonium tetrafluoroborate in anhydrous solvents[7] have been advanced. Modified procedures for the preparation of arenediazonium tetrafluoroborates that are appreciably soluble in water have also been described.[8]

We have recently reported that nitrosyl chloride and nitrosyl bromide are formed by an efficient halide–alkoxide exchange between titanium tetrahalides and alkyl nitrites.[1] Although titanium tetrafluoride is unreactive with alkyl nitrites, boron trifluoride is not similarly limited and when combined with alkyl nitrites provides convenient access to nitrosyl fluoride. When in situ generated nitrosyl fluoride is produced in the presence of an aromatic amine and excess boron trifluoride, arenediazonium tetrafluoroborate salts are formed in high yield (eq 1).

$$\mathrm{ArNH_2} \xrightarrow[\mathrm{BF_3}]{\mathrm{RONO}} \mathrm{ArN_2{}^+BF_4{}^-} \tag{1}$$

The diazotization reactions are performed under mild conditions in an anhydrous solvent, usually methylene chloride. Excess boron trifluoride, employed as the conveniently handled etherate complex, traps the alcohol and water produced in this diazotization procedure, and the arenediazonium tetrafluoroborates precipitate from the reaction solution as they are formed. The anhydrous tetrafluoroborate salts are obtained following simple filtration (Table I). The physical (decomposition temperature) and spectral (^1H NMR and IR) characteristics of the isolated salts are consistent with those previously reported in the literature.[3,9,10]

As seen from the yield data for isolated diazonium salts in Table I, the use of methylene chloride has significant yield advantages over other solvents. Ethers are susceptible to hydride abstraction by nitrosonium tetrafluoroborate,[11] and although their use as solvents for the preparation of arenediazonium tetrafluoroborate salts under aqueous conditions has been shown to improve the yields and purity of these salts,[8a] the present results do not indicate any unique advantage of ether solvents over methylene chloride in reactions performed under anhydrous conditions. However, amines such as the aminobenzoic acids that are insoluble in methylene chloride are preferably diazotized in the more polar ether solvents, and the isolated yields of the resulting arenediazonium tetrafluoroborate salts are superior to those reported

0022-3263/79/1944-1572$01.00/0

Table I. Isolated Yields of Arenediazonium Tetrafluoroborate Salts[a]

$ArN_2^+BF_4^-$, Ar =	registry no.	% yield[b] from CH_2Cl_2 solvent	% yield[b] from ether solvent	ether
p-$CH_3OC_6H_4$	459-64-3	98		
p-$CH_3C_6H_4$	459-44-9	93	77	Et_2O
2,4,6-$(CH_3)_3C_6H_2$	23755-18-2	94	86	Et_2O
C_6H_5	369-57-3	100	82	Et_2O
p-BrC_6H_4	673-40-5	92	78	DME
p-ClC_6H_4	673-41-6	94	76	DME
2,5-$Cl_2C_6H_3$	398-69-6	98	91	Et_2O
3,4-$Cl_2C_6H_3$	405-02-7	93	86	Et_2O
p-$HOOCC_6H_4$	456-25-7		89	THF
o-$HOOCC_6H_4$	14783-89-2		80	THF
p-$NO_2C_6H_4$	456-27-9		87	DME
m-$NO_2C_6H_4$	586-36-7	100	82	DME
o-$NO_2C_6H_4$	365-33-3	99	84	DME
4-NO_2-1-naphthyl	341-95-7		83	DME

[a] Reactions performed at −15 °C by addition of *tert*-butyl nitrite to the combination of $BF_3 \cdot Et_2O$ and arylamine in the indicated solvent. [b] Weight yield of isolated salt.

Table II. Proton NMR Spectral Characteristics of Benzenediazonium Tetrafluoroborate Salts[a]

$ArN_2^+BF_4^-$,	chemical shift, ppm[b]			
Ar =	$\delta_{2,6}$	$\delta_{3,5}$	δ_4	solvent
p-$CH_3OC_6H_4$[c]	8.45	7.35		CH_3CN
p-$CH_3C_6H_4$[d]	8.52	7.77		CH_3CN
2,4,6-$(CH_3)_3C_6H_2$[e]		7.58		CH_3CN
C_6H_5	8.43	7.65	7.87	CH_3COCH_3
p-BrC_6H_4	8.45	8.13		CH_3CN
p-ClC_6H_4	8.58	7.97		CH_3CN
2,5-$Cl_2C_6H_3$	8.65	8.00	8.28	CH_3CN
3,4-$Cl_2C_6H_3$	8.78,[f] 8.57[g]	8.13		CH_3CN
p-$HOOCC_6H_4$	8.93	8.53		CH_3COCH_3
o-$HOOCC_6H_4$	8.83	8.4–8.0		CH_3SOCH_3
p-$NO_2C_6H_4$	8.85	8.55		CH_3CN
m-$NO_2C_6H_4$	9.53,[f] 9.05[g]	8.23	8.90	CH_3CN
o-$NO_2C_6H_4$	8.87	8.7–8.2		CH_3CN

[a] Spectra were obtained on a Varian A-60A NMR spectrometer at 37 °C. [b] Relative to internal Me_4Si; δ values are referenced to the position of the diazo group. $J_{ortho} = 9 \pm 1$ Hz, $J_{meta} = 2.0 \pm 0.5$ Hz. [c] CH_3O at δ 4.07. [d] CH_3 at δ 2.66. [e] CHinfn3 absorptions at δ 2.80 (6 H) and 2.62 (3 H). [f] 2-H. [g] 6-H.

for reactions performed in aqueous media with tetrahydrofuran as the cosolvent.[8a] The procedure described here for the preparation of tetrafluoroborate salts should be adaptable to the synthesis of other stable arenediazonium salts.

Experimental Section[12]

Preparation of Arenediazonium Tetrafluoroborate Salts. General Procedure. To 1.06 g of boron trifluoride etherate (7.5 mmol) contained in a three-neck round-bottom flask fitted with two addition funnels and a reflux condenser connected to a gas buret was added 5.0 mmol of the aromatic amine in a minimal volume of the anhydrous solvent, usually 10 mL. Prior to addition of the amine, the boron trifluoride etherate was cooled at −15 °C in an ice–acetone bath. If a solid amine–BF_3 complex had formed, additional solvent or ethyl ether was added to produce a homogeneous solution. *tert*-Butyl nitrite (0.618 g, 6.0 mmol) in 5 mL of the same solvent was added dropwise to the rapidly stirred reaction solution over a 10-min period. Following complete addition, the temperature of the reaction solution was maintained at −15 °C for 10 min and then allowed to warm to 5 °C in an ice–water bath over a 20-min period. A crystalline precipitate usually formed during the addition of *tert*-butyl nitrite, and following the 20-min period at 5 °C precipitation was complete. Pentane (40 mL) was then added to the reaction solution, and the solid was suction filtered, washed with cold ether, air-dried, and weighed.

Since boron trifluoride reacts rapidly with *tert*-butyl nitrite under the reaction conditions to form nitrosyl fluoride and since solvent oxidation by nitrosonium salts could be expected to occur, total gas evolution was measured on the closed system by water displacement from a calibrated gas buret. For reactions performed in ether solvents total gas evolution was usually less than 5 mL, and from reactions in methylene chloride less than 1 mL of gas was produced. Decreasing the reaction temperature from −15 to −78 °C did not substantially improve the yield of diazonium salt for reactions performed in ether solvents. Thus, nitrosyl fluoride or the subsequently formed nitrosonium tetrafluoroborate is effectively trapped by the amine under the reaction conditions that are employed.

The use of greater than 1.5 molar equiv of boron trifluoride etherate did not lead to a noticeable improvement in either the yield or the purity of the arenediazonium tetrafluoroborate salt. However, when the amount of $BF_3 \cdot Et_2O$ employed for diazotization was less than or equal to 1.0 molar equiv, water contaminated the tetrafluoroborate salt.

Product Analyses. The solid products obtained by the previous procedure were analyzed by their decomposition temperature[3] and by ^1H NMR spectroscopy. Since the ^1H NMR spectra of only a fractional number of arenediazonium salts have been reported,[9] structural assignments of the benzenediazonium tetrafluoroborate salts are given in Table II. The purities of these salts were determined by use of an internal standard for NMR analysis. Integration of the characteristic absorptions of the diazonium salt and standard provided evidence of 98 ± 2% purity for these salts and the absence of contamination by either water, *tert*-butyl alcohol, or borate esters. ^1H NMR analysis of the reaction solvent after filtration (without use of pentane) showed the presence of water, *tert*-butyl alcohol, and *tert*-butyl borate esters. The IR spectra of selected diazonium tetrafluoroborate salts were also obtained and compared to the spectra of authentic samples.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation for this work.

Registry No.—Boron trifluoride, 7637-07-2; *tert*-butyl nitrite, 540-80-7; nitrosyl fluoride; 7789-25-5.

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Preparation of 1,2-Diketones: Oxidation of Alkynes by Potassium Permanganate in Aqueous Acetone

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Received November 6, 1978

Although the oxidation of alkynes to the corresponding 1,2-diones by potassium permanganate is often considered to be a general reaction, the literature describes only two methods for effecting these transformations. One of them is restricted to alkynes such as stearolic acid,[1] which are soluble in aqueous base, and the other necessitates the use of phase-transfer agents.[2] In this note we wish to report a simple, general method for the oxidation of alkynes to the corresponding 1,2-diones in aqueous acetone solutions (Table I).

In order to obtain good yields, it is necessary to maintain an approximately neutral solution. This can be achieved by addition of definite amounts[3] of sodium bicarbonate and magnesium sulfate. The added salts serve as a buffer (pH 7.0–7.5 initially) and neutralize hydroxide ions which are produced during the reduction of permanganate.[4]

Preparation of 8,9-Hexadecanedione. A 2-L Erlenmeyer flask, immersed in a water bath at 25 °C, was charged with reagent grade acetone (1.05 L) and 8-hexadecyne (6 g, 0.027 mol). To this was added a solution of $NaHCO_3$ (1.36 g, 0.0162 mol) and $MgSO_4$ (13.6 g, 0.0552 mol) in water (600 mL). The mixture was stirred with a mechanical stirrer. Powdered potassium permanganate[5] (16.6 g, 0.105 mol) was added in one portion, and the mixture was stirred for 4 h. The unreacted permangante and the precipitated MnO_2 were reduced to soluble Mn^{2+} ions by adding a minimum quantity of $NaNO_2$ (7 g) and 10% H_2SO_4 (70 mL) in small portions. The solution was transferred to a 2-L separating funnel, saturated with NaCl, and extracted with a hexane–ether mixture (1:1, 3 × 200 mL). The organic solvents were removed using a rotary evaporator. The residue was dissolved in ether (50 mL) and extracted with a dilute NaOH solution (5%, 4 × 50 mL) to remove any carboxylic acids present. The ether layer was washed with a saturated solution of NaCl and dried (anhydrous Na_2SO_4), and the solvent was removed in a rotary evaporator. The crude product obtained weighed 6.75 g (98%). The solid, when recrystallized from methanol, gave 8,9-hexadecanedione as yellow plates (5.6 g, 81%): mp 48.5–49.5 °C (lit.[6] 49–50 °C); IR (melt) 2930, 1705, 1475 cm^{-1}; NMR (CCl_4) δ 0.9 (t, 6 H), 1.32 (m, 20 H), 2.67 (t, 4 H).

Acknowledgment. The authors are grateful to the National Research Council of Canada for financial support.

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(3) It was found that the use of approximately 0.9 g of $NaHCO_3$ and 8.5 g of $MgSO_4$ per liter of solution gave good results. The use of excess $NaHCO_3$ promotes oxidation of the solvent.

(4) The yield of dione decreased if the initial pH was allowed to increase to 7.8 or greater or in the absence of either sodium bicarbonate or magnesium sulfate.

(5) A very finely powdered form of potassium permanganate was used. It is available under the trade name Cairox M from the Carus Chemical Co. Inc., La Salle, Ill.

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Table I. Oxidation of Alkynes by Potassium Permanganate[m] in Aqueous Acetone

alkyne	registry no.	reaction time, h	product (yield, %)[a]	registry no.	mp or bp (lit.), °C
5-decyne[b,c]	1942-46-7	4	5,6-decanedione (40)[d]	5579-73-7	60–61/6 torr (90–91/12 torr)[e]
7-tetradecyne[b,f]	35216-11-6	4	7,8-tetradecanedione (69)[g]	6305-47-1	38–39 (38–39)[h]
8-hexadecyne[b,f]	19781-86-3	4	8,9-hexadecanedione (81)[d]	18229-29-3	48.5–49.5 (49–50)[i]
1-phenyl-1-pentyne[b,c]	4250-81-1	1.75	1-phenyl-1,2-pentanedione (77)[g,j]	20895-66-3	
diphenylacetylene[k,c]	501-65-5	3	1,2-diphenyl-1,2-ethanedione (88)[d]	134-81-6	95–96 (95)[l]

[a] The IR and NMR spectra of the products were consistent with the proposed structures. [b] Obtained from the Chemical Samples Co. [c] Molar ratio of alkyne/$KMnO_4$ = 1.85:1. [d] Isolated yield. [e] Reference 7. [f] Molar ratio of alkyne/$KMnO_4$ = 3.9:1. [g] Based on GLC analysis: 224 × 0.6 cm d., 15% silicone gum rubber SE-30 on Chromosorb W 60–80 column. [h] Reference 2. [i] Reference 6. [j] Isolated by use of preparative GLC. [k] Obtained from the Aldrich Chemical Co. [l] Reference 8. [m] Registry no., 7722-64-7.