spectrum *m/e* (rel intensity) 203 (29), 91 (100), 71 (20), and 43 (44).

Anal. Calcd for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.40; H, 8.91.

The Benzylation of 2-Heptanone (23).—Solutions of lithium enolates were prepared from the ketone **23**, the enol acetate **24**, or the silyl enol ether **30** (contains 84% $\Delta^{1,2}$ and 16% $\Delta^{2,3}$ isomers) by the methods previously described. The results of the benzylation reactions are summarized in eq K and L. For small scale reactions the crude alkylated products were mixed with a weighed amount of internal standard (hexadecane) and analyzed by glpc (silicone gum SE-52 on Chromosorb P). The retention times of the various components follow: ketone **23**, 3.4 min; benzyl bromide, 8.4 min; ketone **26**, 19.6 min; hexadecane, 20.6 min; ketone **27**, 22.2 min; ketone **29b**, 34.0 min; and ketone **28**, 37.6 min. The glpc apparatus was calibrated with known mixtures of authentic samples and collected (glpc) samples of products from representative reactions were identified with authentic samples by comparison of glpc retention times and ir spectra. In certain of the alkylation experiments a third dialkylated product, thought to be **29a**, was also detected (retention time, 37.0 min on a glpc column packed with silicone gum SE-52 Chromosorb P). On a glpc column packed with silicone fluid no. 710 on Chromosorb P, retention times were for **29b**, 34.0 min; **29a**, 36.4 min; and **28**, 38.8 min. The nmr spectra (CCl_4) of collected samples containing this component **29a** had an additional singlet at δ 1.75 ($COCH_3$). Although we did not obtain a sufficient amount of this ketone **29a** for complete characterization, the spectra of a collected sample are consistent with the structure assigned: ir (CCl_4) 1705 (C=O) and 1355 cm^{-1} (CH_3CO); mass spectrum *m/e* (rel intensity), 203 (28), 147 (46), 91 (65), and 43 (100).

In a preparative reaction performed in dilute solution where alkylation was relatively slow, the enolate from 11.06 g (87 mmol) of 2-heptanone (**23**) and 116 mmol of lithium diisopropylamide was allowed to react for 2.5 hr at 25° with 17.5 g (102 mmol) of benzyl bromide in 500 ml of 1,2-dimethoxyethane. Distillation of the crude product separated 5.6 g of forerun [bp 32° (60 mm) to 95° (8 mm), mainly 2-heptanone], 8.0 g (41%) of monobenzylated products [bp 70–80° (0.08 mm), $n^{25}D$ 1.4912–1.5071, primarily ketone **26**], and 3.3 g (12%) of a mixture of dibenzylated ketones **28** and **29b** [bp 131–138° (0.08 mm), $n^{25}D$ 1.5203–1.5281].

Registry No.—**1**, 583-60-8; **3**, 946-33-8; **5a**, 29478-32-8; **5b**, 29478-33-9; *cis*-**8**, 29478-34-0; *trans*-**8**, 29478-35-1; **9**, 1206-21-9; **10**, 29478-36-2; **11**, 29494-41-5; **20**, 29494-42-6; **21**, 7382-10-7; **22**, 7382-11-8; **26**, 29494-51-7; **27**, 6047-99-0; **28**, 29494-45-9; **29a**, 29494-46-0; **29b**, 29494-47-1; **35**, 29478-38-4; **36**, 29494-48-2; 1,1-dibenzyloxycyclohexane, 29494-49-3; 2-methyl-6-benzalcyclohexanone, 29494-50-6; *trans*-1-phenyl-1-octen-3-one, 29478-39-5; 3-benzal-2-heptanone, 10225-39-5; 1,5-diphenyl-3-pentanone, 5396-91-8.

Notes

A Comparison of Various Tetraalkylammonium Salts as Supporting Electrolytes in Organic Electrochemical Reactions[1]

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In both polarographic measurements[2a,b] and preparative electrochemical reactions[2a,c–e] with organic substrates, it has become common to use certain tetraalkylammonium salts as supporting electrolytes, especially with aprotic organic solvents such as acetonitrile, dimethylformamide (DMF), hexamethylphosphoramide (HMP), tetrahydrofuran (THF), or 1,2-dimethoxyethane.[3] In such aprotic solvents, electrochemical reductions at a mercury cathode may be performed at highly negative potentials (−2.5 to −2.9 V *vs.* sce), the reduction potential ultimately being limited by the reduction of the quaternary ammonium cation **1** to form an amalgam **2**.[4] Although a variety of tetraalkyl-

$$\underset{\mathbf{1}}{R_4N^+} \xrightarrow[\text{Hg cathode}]{e^-} \underset{\mathbf{2},\ n\,=\,12\text{–}13}{(R_4N)Hg_n}$$

ammonium salts have been prepared and studied,[3,4a,b,5] the salts most commonly used in electrochemical studies have been the readily available tetraethylammonium, tetra-*n*-propylammonium, and tetra-*n*-butylammonium salts, the counterions being iodide, bromide, chloride, perchlorate, and tetrafluoroborate. For polarographic measurements, the selection of a particular supporting electrolyte from among this group of salts is often not critical[6] since these measurements involve very small cell currents and low concentrations of electrolytes. However, the choice becomes more demanding for preparative electrochemical cells. Since relatively high cell currents are involved, it is important to keep the electrical resistance of the cell as low as practical to

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TABLE I

SOLUBILITIES OF TETRAALKYLAMMONIUM SALT ELECTROLYTES AND SPECIFIC RESISTANCES OF THE SOLUTIONS

	Solvent							
	CH_3CN		$CH_3OCH_2CH_2OCH_3$		Tetrahydrofuran		$(CH_3)_2NCHO$	
Electrolyte (mp, °C)	Solubility, g/100 ml of solution (concn, *M*)	Specific resistance, ohm cm (concn, *M*)	Solubility, g/100 ml of solution (concn, *M*)	Specific resistance, ohm cm (concn, *M*)	Solubility, g/100 ml of solution (concn, *M*)	Specific resistance, ohm cm (concn, *M*)	Solubility, g/100 ml of solution (concn, *M*)	Specific resistance, ohm cm (concn*M*)
Et_4NClO_4 (351–352.5 dec)	26 (1.13)	26 (0.60)	(<0.01)		(<0.01)		23 (1.00)	52 (0.60)
$(n\text{-}Pr)_4NClO_4$ (239–240.5)	21 (0.74)	31 (0.60)	(<0.01)		(<0.01)		21 (0.74)	64 (0.60)
$(n\text{-}Bu)_4NClO_4$ (212.5–213.5)	70 (2.05)	37 (0.60)	31 (1.10)	312 (1.0)	50 (1.48)	368 (1.0)	79 (2.29)	77 (0.60)
Et_4NBF_4 (377–378 dec)	37 (1.69)	18 (1.0)	(<0.01)		(<0.01)		27 (1.24)	38 (1.0)
$(n\text{-}Pr)_4NBF_4$ (248–249)	36 (1.32)	23 (1.0)	(<0.01)		(<0.01)		32 (1.17)	51 (1.0)
$(n\text{-}Bu)_4NBF_4$ (162–162.5)	71 (2.21)	31 (1.0)	53 (1.70)	228 (1.0)	65 (2.02)	373 (1.0)	75 (2.34)	69 (1.0)
Et_4NBr (282–287 dec)	7.8 (0.37)		(<0.01)		(<0.01)		4.1 (0.19)	
$(n\text{-}Pr)_4NBr$ (274–281 dec)	29 (1.09)	39 (0.60)	(<0.01)		(<0.01)		18 (0.70)	88 (0.60)
$(n\text{-}Bu)_4NBr$ (119–119.5)	66 (1.99)	48 (0.60)	(<0.1)		4.8 (0.14)		52 (1.57)	106 (0.60)

TABLE II

SPECIFIC RESISTANCES AND LIMITING REDUCTION POTENTIALS FOR TETRAALKYLAMMONIUM SALT SOLUTIONS

	Salt							
	Et_4NBF_4		$(n\text{-}Bu)_4NBF_4$		$(n\text{-}Bu)_4NClO_4$		$(n\text{-}Bu)_4NBr$	
Solvent	Specific resistance, ohm cm (concn, *M*)	Limiting reduction potential, V (*vs.* sce)[a]	Specific resistance, ohm cm (concn, *M*)	Limiting reduction potential, V (*vs.* sce)[a]	Specific resistance, ohm cm (concn, *M*)	Limiting reduction potential, V (*vs.* sce)[a]	Specific resistance, ohm cm (concn, *M*)	Limiting reduction potential, V (*vs.* sce)[a]
Tetrahydrofuran			373 (1.0), 587 (0.50)	−2.75	369 (1.0), 583 (0.50)	−2.90		
1,2-Dimethoxyethane			228 (1.0), 339 (0.50)	−2.75	312 (1.0), 495 (0.50)	−2.85		
Acetonitrile	18 (1.0), 27 (0.50)	−2.70	31 (1.0), 33 (0.50)	−2.74	37 (0.60), 39 (0.50)	−2.77	48 (0.60), 48 (0.50)	−2.76
Dimethylformamide	38 (1.0), 54 (0.50)	−2.72	69 (1.0), 72 (0.50)	−2.80	77 (0.60), 82 (0.50)	−2.85	106 (0.60), 110 (0.50)	−2.80
Hexamethylphosphoramide	538 (0.30)	−2.70[b]	555 (0.50)	−2.90	1125 (0.50)	−2.85	1135 (0.30)	−2.85[b]

[a] The voltage at which the actual residual current exceeds by a factor of three the value obtained by extrapolating the line defined by the residual current readings in the region −0.5 to −1.5 V. Unless otherwise noted all solutions used for polarographic measurement were 0.50 *M* in the ammonium salt. [b] The concentration of the ammonium salt was 0.30 *M*.

avoid a large voltage drop across the cell and the associated liberation of excessive heat as the electrolysis proceeds. Furthermore, the substantial amounts of these electrolytes required in preparative electrolyses make it prudent to select salts which both are easily prepared and/or purified and are relatively economical.

To provide a basis for selecting supporting electrolytes from among the easily accessible ammonium salts, we have prepared and/or purified the commonly used salts and have determined the solubilities of these salts in the aprotic solvents frequently used in electrochemical reactions. In those cases where the salts were soluble in useful concentrations, the specific resistances of the solutions were also determined. For those solvent–electrolyte solutions which appeared most useful for electrochemical preparations, the specific resistances were measured at two different concentrations and the background reduction potentials for the solutions were measured. These data are summarized in Tables I and II.

Experimental Section[7]

Preparation of the Tetrafluoroborates. A. Tetra-*n*-butylammonium Tetrafluoroborate.—A solution of 8.4 g (25 mmol) of $(n\text{-}Bu)_4NBr$ (Eastman) in a minimum volume of H_2O (*ca.* 18 ml) was treated with 3.6 ml (*ca.* 26 mmol) of aqueous 48–50% HBF_4 (Allied Chemical). The resulting mixture was stirred at 25° for 1 min and then the crystalline salt was collected on a filter, washed with H_2O until the washings were neutral, and dried. The crude salt (6.3 g or 79%, mp 155–157°) was recrystallized three times from EtOAc–pentane mixtures to separate 6.0 g (75%) of $(n\text{-}Bu)_4NBF_4$ as white needles: mp (after drying) 162–162.5° (lit. mp 153–155°,[8a] 161.8°,[8b] 166°[5b]); ir ($CHCl_3$) no OH, NH, or C=O absorption in 3- and 6-μ regions: uv (95%

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[7] All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with a Perkin-Elmer Model 237 or Model 257 infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Cary Model 14 or a Perkin-Elmer Model 202 recording spectrophotometer. The nmr spectra were determined at 60 Mc with a Varian Model A-60 or Model T-60 nmr spectrometer. The chemical shift values are expressed in δ values (parts per million) relative to a tetramethylsilane internal standard.

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EtOH) weak end absorption (ϵ 1.6 at 205 mμ); nmr ($CDCl_3$) δ 3.0–3.5 (8 H, m, CH_2N), 1.2–2.0 (16 H, m, CH_2), and 0.8–1.2 (12 H, m, CH_3).

B. Tetra-*n*-propylammonium Tetrafluoroborate.—Use of the same procedure with 6.7 g (25 mmol) of $(n\text{-Pr})_4NBr$ (Eastman) in *ca*, 13 ml of H_2O yielded 5.1 g (75%) of the crude tetrafluoroborate salt, mp 243–245°. Recrystallization from a MeOH–petroleum ether (bp 30–60°) mixture afforded 4.6 g (65%) of the pure $(n\text{-Pr})_4NBF_4$ as white needles: mp (after drying) 248–249° (lit. mp 239°,[5b] 244–244.5°,[9] 249–250°[8a]); ir ($CHCl_3$) no OH, NH, or C=O absorption in 3- and 6-μ regions; nmr ($CDCl_3$) δ 3.0–3.4 (8 H, m, CH_2N), 1.3–2.1 (8 H, m, CH_2), and 1.03 (12 H, t, J = 7 Hz, CH_3).

C. Tetraethyl Tetrafluoroborate.—Reaction of 5.3 g (25 mmol) of Et_4NBr (Eastman) in *ca.* 8 ml of H_2O with HBF_4 followed by concentration, dilution with Et_2O, and filtration afforded 4.6 g (85%) of the crude tetrafluoroborate salt, mp 375–378° dec. Two recrystallizations from a MeOH–petroleum ether (bp 30–60°) mixture separated 3.7 g (69%) of pure Et_4NBF_4 as white needles: mp (after drying) 377–378° dec (lit. mp 365–367°,[8a] 377–378°[10]); ir (KBr pellet) no OH, NH, or C=O absorption in the 3- and 6-μ regions; nmr (D_2O) δ 3.23 (8 H, q, J = 8 Hz, CH_2N) and 1.28 [12 H, triplet of triplets, J = 8 Hz (H–H) and 2 Hz (N–H)].

Before use in various measurements, each of these tetrafluoroborate salts was pulverized and dried at 80–100° under reduced pressure (0.2–0.3 mm) for 48–96 hr.

Preparation of the Perchlorates. A. Tetra-*n*-butylammonium Perchlorate.—A saturated aqueous solution of 8.4 g (25 mmol) of $(n\text{-Bu})_4NBr$ in 18 ml of H_2O was treated with 2.1 ml (*ca.* 26 mmol) of aqueous 70–72% $HClO_4$ (Baker). After the resulting insoluble perchlorate salt had been collected, washed with cold H_2O, and dried, the yield was 8.0 g (94%), mp 197–199°. Two recrystallizations from an EtOAc–pentane mixture separated 7.6 g (90%) of pure $(n\text{-Bu})_4NClO_4$ as white needles which were dried at 100° under reduced pressure: mp 212.5–213.5° (lit. mp 207–209°,[11a] 212–212.5°,[11b] 213.3–213.6°[11c]); ir ($CHCl_3$) no OH, NH, or C=O absorption in the 3- and 6-μ regions; nmr (pyridine-d_5) δ 3.2–3.7 (8 H, m, CH_2N), 1.2–2.2 (16 H, m, CH_2), and 0.8–1.2 (12 H, m, CH_3).

B. Tetra-*n*-propylammonium Perchlorate.—By the same procedure 6.7 g (25 mmol) of $(n\text{-Pr})_4NBr$ (in *ca.* 13 ml of H_2O) was converted to 6.8 g (94%) of the crude perchlorate salt, mp 232–235°. Recrystallization from aqueous acetone afforded 5.9 g (82%) of the pure $(n\text{-Pr})_4NClO_4$ as white needles which were dried at 100° under reduced pressure: mp 239–240.5° (lit. mp 237–239°[11a]); ir (KBr pellet) no OH, NH, or C=O absorption in the 3- and 6-μ regions; nmr (pyridine-d_5) δ 3.1–3.6 (8 H, m, CH_2N), 1.3–2.2 (8 H, m, CH_2), and 0.95 (12 H, t, J = 7 Hz, CH_3).

C. Tetraethylammonium Perchlorate.—The same procedure was used to convert 5.3 g (25 mmol) of Et_4NBr (in *ca.* 8 ml of H_2O) to 4.7 g (81%) of the crude perchlorate salt, mp 343–344° dec (solution cooled before filtration). Recrystallization from water separated 4.3 g (75%) of the pure Et_4NClO_4 as white needles which were dried at 100° under reduced pressure: mp 351–352.5° dec;[12] ir (KBr pellet) no OH, NH, or C=O absorption in the 3- and 6-μ regions; nmr (pyridine-d_5) δ 3.39 (8 H, q, J = 7.5 Hz, CH_2N) and 1.28 [12 H, triplet of triplets, J = 7.5 Hz (H–H) and 1.9 Hz (N–H)].

Each of the perchlorate salts was pulverized and dried at 80–100° under reduced pressure (0.2–0.3 mm) for 48–96 hr before being used to obtain the measurements summarized in Tables I and II.

Purification of the Tetraalkylammonium Bromides.—Commercial samples of each of the three bromides were dissolved in boiling $CHCl_3$ and then the hot solution was filtered, diluted with petroleum ether (bp 30–60°), and cooled. Each of the crystalline bromides was collected, pulverized, and dried at 100° under reduced pressure (0.2–0.3 mm) for 10 hr. Tetra-*n*-butylammonium bromide was obtained as white prisms: mp 119–119.5° (lit. mp 118°,[8b,13] 122°[5b]); ir (CCl_4) weak, broad absorption at 3380 cm^{-1} (associated OH of H_2O impurity) with no other OH, NH, or C=O absorption in the 3- and 6-μ regions; nmr (CCl_4) δ 3.3–3.8 (8 H, m, CH_2N), 1.3–2.2 (16 H, m, CH_2), and 0.8–1.3 (12 H, m, CH_3); uv (95% EtOH) end absorption (ϵ 400 at 210 mμ).

Tetra-*n*-propylammonium bromide was obtained as white prisms: mp 274–281° dec (dependent on rate of heating; lit.[14] mp 252°); ir ($CHCl_3$) broad, weak absorption at 3360 cm^{-1} (assoc OH of H_2O impurity) with no other OH, NH, or C=O absorption in the 3- or 6-μ regions; nmr ($CDCl_3$) δ 3.2–3.7 (8 H, m, CH_2N), 1.4–2.2 (8 H, m, CH_2), and 1.06 (12 H, t, J = 7 Hz, CH_3); uv (95% EtOH) end absorption (ϵ 360 at 210 mμ).

Tetraethylammonium bromide was obtained as white prisms: mp 282–287° dec (dependent on rate of heating; lit.[15] 305° dec); ir ($CHCl_3$) 3370 cm^{-1} (broad, assoc OH of H_2O impurity), no C=O absorption in the 6-μ region; nmr ($CDCl_3$) δ 3.51 (8 H, q, J = 7 Hz, CH_2N) and 1.43 (12 H, triplet of multiplets, J = 7 Hz, CH_3); uv (95% EtOH) end absorption (ϵ 400 at 210 mμ).

Tetra-*n*-butylammonium Acetate.—To 29 ml of a MeOH solution containing 28 mmol of $(n\text{-Bu})_4NOH$ was added 1.65 g (28 mmol) of HOAc. The solution was concentrated under reduced pressure at 25°. The yellow solid which separated upon cooling was collected and recrystallized from 1,2-dimethoxyethane at Dry Ice temperature. The crude $(n\text{-Bu})_4NOAc$ separated as 2.80 g (67%) of fine yellow crystals: mp 75–83°; ir (KBr pellet) 1420 and 1570 cm^{-1} (carboxylate C=O); nmr ($CDCl_3$) δ 3.2–3.6 (8 H, m, CH_2N), 1.96 (3 H, s, CH_3CO), 1.3–2.0 (16 H, m, CH_2), and 0.9–1.2 (12 H, m, CH_3).

All of our attempts to further purify this salt resulted in sufficient decomposition to yield the less soluble acetic acid solvate $(n\text{-Bu})_4NOAc \cdot HOAc$. This material crystallized from benzene as white needles: mp 112.5–114° (lit. mp 113–117°,[16] 116.5–117.5°,[11b] 118°[8b]); ir (KBr pellet) 1675 (broad) and 1390 cm^{-1} (broad, carboxyl and carboxylate C=O); nmr ($CDCl_3$) δ 12.85 (1 H, s, OH), 3.1–3.5 (8 H, m, CH_2N), 1.91 (6, H, s, CH_3CO), 1.2–2.0 (16 H, m, CH_2), and 0.8–1.2 (12 H, m, CH_3).

Purification of Solvents.—Tetrahydrofuran and 1,2-dimethoxyethane were distilled from $LiAlH_4$ immediately before use. Commercial acetonitrile was first distilled from NaH[17] and then redistilled from P_2O_5 to give pure material, bp 80–80.5°, $n^{25}\mathrm{D}$ 1.3440. Sodium (4 g/l.) was dissolved in freshly distilled hexamethylphosphoramide and the pure solvent was distilled from this blue solution under reduced pressure, bp 76.5° (1.4 mm). Because of the continual difficulty we encountered from the presence of dimethylamine when dimethylformamide was distilled at atmospheric pressure,[3] we followed the purification procedure of Brummer[18] in which the DMF was allowed to stand over molecular sieves, type 4A, for several hours and the solvent was then decanted and distilled under reduced pressure, bp 43° (6 mm). The specific resistances of these purified solvents, determined as described subsequently, follow: THF, 2.7 × 10^5 ohm cm; 1,2-dimethoxyethane, 3.5 × 10^6 ohm cm; DMF, 8.0 × 10^5 ohm cm; acetonitrile, 1.5 × 10^6 ohm cm; and HMP, 1.6 × 10^5 ohm cm.

Measurement of Solubilities.—Mixtures of the purified solvents and an excess of each dried, purified salt were stirred in a bath at 25° and 3.00-ml aliquots of the supernatant liquid were removed after periods of 2 and 3 hr. The aliquots were concentrated to dryness under reduced pressure, and the weights of the residual solutes were determined when these weights became constant. The results are summarized in Table I. Since several of the very concentrated solutions were extremely viscous, complete saturation of the solvent may not have been achieved. Because of the difficulty of removing HMP from solutions, the maximum solubility of salts in this solvent were not determined.

Specific Resistance Measurements.—A conductivity cell, fitted with platinized Pt electrodes and immersed in a 25° bath, was used for all measurements. The cell constant, 1.06 cm^{-1}, for this cell was determined with aqueous 0.100 *M* KCl.[19] The

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resistances were measured with a 1-kHz sine wave signal employing either a General Radio Co. Impedance Comparator, Type 1605-A, or a Serfass Conductivity Bridge, Model RCM15. The specific resistance values for the various electrolyte solutions are summarized in Table I and II.

Polarographic Reduction Potentials.—The background reduction potentials listed in Table II were obtained with a Heath dropping mercury electrode apparatus (Model EUA-19-6) connected to a Heath polarograph module (EUA-19-2), operational amplified (EUA-19-B), amplifier stabilizer (EUA-19-4), and recorder (EU-20V). A Pt wire was employed as an anode and the reference electrode, a Coleman Model 3-512 saturated calomel electrode, was connected to the solution through salt bridges of aqueous 1.0 *M* $NaNO_3$ and 0.5 *M* Et_4NBF_4 in DMF. The limiting background reduction potential for the various solutions was arbitrarily selected to be that voltage at which the actual residual current exceeded by a factor of three, the value obtained by extrapolating the line determined by the residual current readings in the region -0.5 to -1.5 V. To determine the effect of H_2O on these background readings, a portion of each solution was diluted with 5% (by volume) of H_2O (concentration 2.8 *M*) and the readings were repeated. These solutions exhibited an additional polargraphic wave with $E_{1/2}$ values in the range -1.7 to -2.0 V *vs.* sce.

Discussion

Of the various methods[3] which have been employed to prepare the tetraalkylammonium perchlorates and tetrafluoroborates in the laboratory, we consider the reaction of concentrated aqueous solutions of the commercially available tetraalkylammonium bromides with either perchloric acid or tetrafluoroboric acid to be both the most convenient and the most economical. The resulting perchlorates and tetrafluoroborates, which are sparingly soluble in water, were readily collected and then recrystallized from organic solvents and dried to afford the pure salts in good yield. It is often desirable in preparative electrolytic reductions to select a supporting electrolyte whose anion will be oxidized at the anode to produce materials which will not interact with the reduction products formed at the cathode.[20] For this reason the use of tetraalkylammonium bromides as supporting electrolytes is often objectionable because bromine is produced at inert anodes (*e.g.*, Pt or C) and the use of a silver anode (to form AgBr) becomes prohibitively expensive for large-scale preparations. The perchlorate and tetrafluoroborate salts also do not provide the necessary reactants for a discrete anode reaction to form inert products; instead, oxidation of the perchlorate anion or oxidative degradation of the solvent is often observed.[21] Because of these problems, we were led to explore the possibility of preparing a tetraalkylammonium acetate salt as a supporting electrolyte. The acetate anion moiety in such salts would provide the reactant for a Kolbe reaction[22] at the anode to form ethane and carbon dioxide. Although our attempts to obtain crystalline acetates with the tetraethylammonium and tetra-*n*-propylammonium cation were not successful, we were able to obtain a crude sample of tetra-*n*-butylammonium acetate (**3**), mp 75–83°. However, all our efforts to purify this salt **3** resulted in its partial decomposition (presumably in a Hofmann degradation) to form the less soluble complex **4**, mp 112.5–114°, which contained 1 mol of acetic acid per mol of salt. The acetic acid–salt complex **4** has been reported previously[8b,11b,16] but some workers have erroneously referred to it as pure tetra-*n*-butylammonium acetate. We are continuing our search for quaternary ammonium carboxylate salts which will be both readily accessible and easily obtainable in pure form.

$(n\text{-Bu})_4N^+ \ {}^-OCOCH_3$
3

$(n\text{-Bu})_4N^+ \ CH_3CO_2H \cdot CH_3CO_2^-$
4

Among the bromide, perchlorate, and tetrafluoroborate salts which we have examined (Table I), the bromides are distinctly less soluble than the other salts in aprotic solvents, tetra-*n*-butylammonium bromide being the least objectionable in this respect. The solubility properties of the tetrafluoroborates and the corresponding perchlorates are very similar with the tetra-*n*-butylammonium derivatives being more soluble than the lower homologs in both series. At equivalent molar concentrations the specific resistances (Table II) of solutions containing the tetrafluoroborates and the corresponding perchlorates are also very similar. As might be expected with a series of homologous salts, the specific resistance of the solutions increases slightly with an increase in the steric bulk of the quaternary ammonium cation. A much more important factor in determining the specific resistance of these concentrated electrolytic solutions is the solvent used. With the relatively nonpolar solvents, tetrahydrofuran and 1,2-dimethoxyethane [dielectric constants[3] 7.39 (25°) and 3.49 (20°)], the specific resistances of concentrated electrolyte solutions are about ten times the values obtained with solutions in the polar solvents, acetonitrile and dimethylformamide [dielectric constants[3] 37.45 (20°) and 36.7 (25°)]. This is presumably attributable to the higher average degree of aggregation of the concentrated (0.5–1.0 *M*) salt solutions in the nonpolar ethereal solvents. Although hexamethylphosphoramide is a relatively polar solvent [dielectric constant 30 (20°)],[23] concentrated solutions of the quaternary ammonium salts in this solvent are very viscous and the high specific resistance of these solutions is presumably attributable to this fact. Table III illustrates that with less-concentrated solutions of n-Bu_4NBF_4 the specific resistances become more nearly the same in hexamethylphosphoramide and in dimethylformamide. For the more dilute solutions in hexamethylphosphoramide, the resistance values obtained correspond to values obtained in conductance measurements with similar salts.[24]

As indicated in Table II, the reduction potentials at a mercury cathode with these supporting electrolytes are limited to about -2.7 V (*vs.* sce) for the tetraethylammonium salts and about -2.8 to -2.9 V (*vs.* sce) for the tetra-*n*-butylammonium salts. At these potentials reduction of the quaternary ammonium cation **1** to the amalgams begins to occur at a significant rate [$E_{1/2}$ values (*vs.* sce),[4b] -2.8 V for Et_4N^+, and -3.0 V for $(n\text{-Bu})_4N^+$]. The values of these limiting potentials are approximately constant for the various aprotic solvents examined. The deliberate addition of water

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[20] This consideration is true even with divided cells since any inert cell divider which offers a reasonably low electrical resistance will also allow material to diffuse from the anode compartment to the cathode compartment.

[21] (a) For examples, see N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968); (b) R. Brettle and D. Seddon, *J. Chem. Soc. C*, 1153 (1970); (c) K. Koyama, T. Susuki, and S. Tsutsumi, *Tetrahedron*, **23**, 2665 (1967); (d) M. Fleischmann and D. Pletcher, *Tetrahedron Lett.*, 6255 (1968); (e) K. Nyberg, *Chem. Commun.*, 774 (1969).

[22] For a recent review and leading references, see A. K. Vijh and B. E. Conway, *Chem. Rev.*, **67**, 623 (1967).

[23] H. Normant, *Bull. Soc. Chim. Fr.*, 791 (1968).

[24] A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 1892 (1969).

TABLE III

SPECIFIC RESISTANCE VALUES FOR SOLUTIONS OF $(n\text{-Bu})_4NBF_4$

Electrolyte concn, M	Specific resistance at 25°, ohm cm DMF	Specific resistance at 25°, ohm cm HMP
0.5	73	555
0.25	110	608
0.05	382	1780
0.01	1450	5250

(2.8 M) to these solutions resulted in the appearance of a new reduction wave in the potential range -1.7 to -2.0 V (*vs.* sce) which we presume corresponds to the reduction of protons to hydrogen. However, the presence of small amounts of water in these solutions does not significantly change the limiting reduction potentials attainable.[25]

From the foregoing information we concluded that the optimum salts to use as supporting electrolytes in aprotic solvents are the tetra-*n*-butylammonium salts. Only in instances where obtaining the minimum resistance in an electrolyte solution is essential (as in salt bridges to reference electrodes) does there appear to be any advantage offered by the tetraethylammonium salt.

Either the tetrafluoroborate or the perchlorate salt of a particular quaternary ammonium cation offer about the same advantages in terms of solubility and solution resistance. However, except in certain oxidations where the choice of the anion may control the nature of the reaction product,[21e] there are at least two reasons why we believe use of the tetrafluoroborate salts is preferable. In the preparation and purification of these electrolytes we consistently found the tetrafluoroborates to be easier to purify and, especially, to dry than the corresponding perchlorates. Also, we have consistently felt concern about the potential explosive nature of perchlorate salts or of the mixtures of organic materials and perchloric acid which could be formed when these salts are stored or are used as supporting electrolytes. Thus, at least for preparative electrolytic reductions in aprotic solvents, we concluded that the properties and ready availability of tetra-*n*-butylammonium tetrafluoroborate make this salt the supporting electrolyte of choice.

Registry No.—Et_4NClO_4, 2567-83-1; $(n\text{-Pr})_4NClO_4$, 15780-02-6; $(n\text{-Bu})_4NClO_4$, 1923-70-2; Et_4NBF_4, 429-06-1; $(n\text{-Pr})_4NBF_4$, 15553-52-3; $(n\text{-Bu})_4NBF_4$, 429-42-5; Et_4NBr, 71-91-0; $(n\text{-Pr})_4NBr$, 1941-30-6; $(n\text{-Bu})_4NBr$, 1643-19-2; tetra-*n*-butylammonium acetate, 10534-59-5.

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[25] However, small amounts of water may strikingly alter the lifetimes of anions or anion radicals formed as intermediates in electrochemical reductions. See K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K. Roe, *J. Amer. Chem. Soc.*, **92**, 2783 (1970).

The Reaction of Dimethylsulfoxonium Methylide and Griseofulvin

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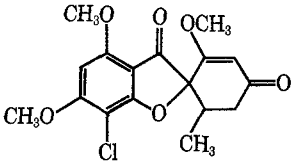
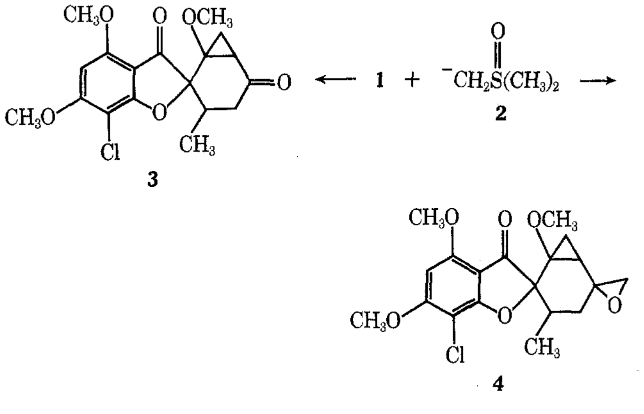
Our finding that the behavior of the β-methoxy-substituted enone system in griseofulvin (1) toward peroxide in base parallels that of enone systems generally in undergoing ready epoxidation[1] prompted us to attempt to introduce the cyclopropyl moiety at position 2′-3′ by allowing 1 to react with dimethylsulfoxonium methylide (2). The latter reagent was first shown by Corey[2] and then by others[3] to react readily with α,β-unsaturated ketones to give the corresponding cyclopropyl ketones.



1

We have found that allowing griseofulvin (1) to react with approximately 1 molar equiv of 2 in dimethyl sulfoxide (DMSO) at room temperature for 20 hr gave a product mixture which could be resolved by partition chromatography into a fraction containing considerable amounts of starting griseofulvin and a new crystalline product. This product melted at 165–175°, showed a band at 5.9 μ in the carbonyl region of the infrared, and an nmr spectrum in chloroform which had as its outstanding feature a new sharp 3-proton singlet at δ 3.13 shifted δ 0.5 upfield from the vinyl OCH_3 signal in griseofulvin. This latter result we attributed to a new OCH_3 group located on a saturated carbon. (The remainder of the chloroform spectrum is given in the Experimental Section. The saturated OCH_3 region in the griseofulvin-containing fraction isolated from the partition chromatogram showed only weak absorption.) The mass spectrum of the product immediately eliminated the cyclopropyl ketone **3** as a possible structure, since it showed a parent ion at m/e 380 corresponding to the introduction of two CH_2 units into the griseofulvin substrate. This was also indicated by its elemental analysis.

The nmr spectrum (60 MHz) of the product in pyridine-d_5 with spin decoupling (done in part at 60 and in part at 100 MHz) permitted its unequivocal formulation as the cyclopropyl epoxide **4**. (Decoupling could not be done in deuterated chloroform because the sample was further transformed during the time required



3

2

4

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[1] H. Newman, *J. Org. Chem.*, **35**, 3990 (1970).

[2] (a) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 867 (1962); (b) *ibid.*, **87**, 1353 (1965).

[3] (a) H. R. Lehmann, H. Muller, and R. Wiechert, *Chem. Ber.*, **98**, 1470 (1965); (b) G. W. Krakower and H. A. VanDine, *J. Org. Chem.*, **31**, 3467 (1966); (c) N. H. Dyson, J. A. Edwards, and J. H. Fried, *Tetrahedron Lett.*, 1841 (1966).