quinoline *N*-oxide[13] cautiously. The mixture was then heated under reflux for 15 min and poured slowly over crushed ice. The mixture was made strongly basic with a KOH solution. The aqueous layer was extracted with ether, and the ether extracts were dried (K_2CO_3) and concentrated to give a brown solid. This solid was dissolved in low-boiling petroleum ether and basic alumina was added. Stirring for 10 min followed by filtration gave a yellow filtrate which upon concentration gave 17.3 g (78%) of crude 2-chloro-3-methylquinoline (**3**, X = Cl). Recrystallization from hexane gave white needles, mp 82–84° (lit.[9] mp 89–90°).

2-Bromo-3-methylquinoline (3, X = Br).—A mixture of 5.00 g (0.031 mol) of **3** (X = O) and 12.70 g (0.045 mol) of phosphorus oxybromide was stirred at 140° for 3 hr. After this time the mixture was poured onto 200 g of crushed ice and subsequently extracted with both 600 ml of methylene chloride and water. When solution was complete, the layers were separated and the aqueous layer was extracted with 150 ml of methylene chloride. The combined organic layers were washed with 150 ml of water, dried ($MgSO_4$), filtered, and concentrated to yield **3** (X = Br) as a tan solid that weighed, after drying, 5.78 g (83%). The solid was recrystallized once from hexane to afford an analytical sample that melted at 96–97°: pmr (CF_3COOH) δ 8.42 (s, 1 H, 4-quin), 7.87–8.33 (m, 4 H, ArH), and 2.52 ppm (s, 3 H, CH_3).

Anal. Calcd for $C_{10}H_8BrN$: C, 54.07; H, 3.64; N, 6.31. Found: C, 54.41; H, 3.58; N, 6.36.

2-Chloro-3-methylquinoline Hydrochloride (3, X = Cl·HCl).—2-Chloro-3-methylquinoline (**3**, X = Cl) was taken up in ether and anhydrous HCl was bubbled into the solution until precipitation was complete. The solid was removed by filtration and dried to give **3** (X = Cl) hydrochloride: mp 215–218°; pmr ($CDCl_3$) δ 8.99 (s, 1 H, 4-quin), 9.63–7.61 (m, 4 H, ArH), and 2.74 ppm (s, 3 H, CH_3).

Anal. Calcd for $C_{10}H_9Cl_2N$: C, 56.11; H, 4.24; N, 6.54. Found: C, 56.34; H, 4.05; N, 6.61.

2-Iodo-3-methylquinoline (3, X = I).—To a stirred mixture of 24.0 g (0.112 mol) of **3** (X = Cl, HCl) in 600 ml of methyl ethyl ketone (MEK) was added 60 ml of a saturated aqueous solution of sodium iodide. The solution was heated under reflux for 24 hr. The solvent was removed by distillation, and excess water was added. The brown solid which precipitated was treated with saturated aqueous sodium bicarbonate and ether. The aqueous layer was extracted with chloroform and the combined organic phases were washed with aqueous sodium bisulfite, dried ($MgSO_4$), filtered, and concentrated to yield a light red oil that solidified upon the addition of hexane. Recrystallization of the solid from hexane gave 19.4 g (60%) of **3** (X = I) as long needles, mp 87–89°, pmr (CH_2Cl_2) δ 7.88–7.25 (m, 5 H, ArH) and 2.52 ppm (s, 3 H, CH_3).

Anal. Calcd for $C_{10}H_8IN$: C, 44.64; H, 3.00; N, 5.21. Found: C, 44.56; H, 2.82; N, 5.13.

2-Chloro-3-bromomethylquinoline (1, X = Cl).—To a solution of 14.7 g (0.082 mol) of **3** (X = Cl) in 300 ml of dry CCl_4 was added 14.8 g (0.082 mol) of *N*-bromosuccinimide (NBS) along with 0.1 g of dibenzoyl peroxide. The mixture was heated with a 100-W lamp and reflux was continued for 11 hr. After this time the mixture was filtered, and the solvent was evaporated to afford 20.0 g (95%) of a white solid, which on recrystallization from hexane gave **1** (X = Cl) as white needles, mp 121–125°, pmr ($CDCl_3$) δ 8.21–7.54 (m, 5 H, quin) and 4.69 ppm (s, 2 H, CH_2).

Anal. Calcd for $C_{10}H_7BrClN$: C, 46.83; H, 2.75; N, 5.46. Found: C, 46.82; H, 2.90; N, 5.42.

2-Bromo-3-bromomethylquinoline (1, X = Br).—Using the procedure above, 14.22 g (0.064 mol) of **3** (X = Br) and 11.39 g (0.064 mol) of NBS gave 18.65 g (93%) of **1** (X = Br), mp 136–138°, pmr ($CDCl_3$) δ 8.50–7.48 (m, 5 H, ArH) and 4.91 ppm (s, 2 H, CH_2).

Anal. Calcd for $C_{10}H_7Br_2N$: C, 39.90; H, 2.35; N, 4.65. Found: C, 40.20; H, 2.27; N, 4.83.

2-Iodo-3-bromomethylquinoline (1, X = I).—The method above was used to convert 19.4 g (0.072 mol) of **3** (X = I) and 13.3 g (0.072 mol) of NBS to 11.0 g (45%) of **1** (X = I), mp 125–128°, pmr ($CDCl_3$) δ 8.32–7.56 (m, 5 H, quin) and 4.72 ppm (s, 2 H, CH_2).

Anal. Calcd for $C_{10}H_7BrIN$: C, 34.52; H, 2.03; N, 4.02. Found: C, 34.82; H, 2.03; N, 3.89.

3-Bromomethyl-2-quinolone (1, X = O).—The method above converted 5.0 g (0.031 mol) of **3** (X = O) and 5.6 g (0.031 mol) of NBS to 5.4 g (72%) of **1** (X = O), mp 218–219°, pmr (CF_3COOH) δ 8.72–7.68 (m, 4 H, quin) and 4.74 ppm (s, 2 H, CH_2).

Anal. Calcd for $C_{10}H_8BrNO$: C, 50.45; H, 3.38; N, 5.88. Found: C, 50.17; H, 3.34; N, 5.85.

Registry No.—**1** (X = Cl), 35740-82-0; **1** (X = Br), 35740-83-1; **1** (X = I), 35740-84-2; **1** (X = O), 35740-85-3; **3** (X = Br), 35740-86-4; **3** (X = Cl) HCl, 35740-87-5; **3** (X = I), 35820-73-6; 1-propionylisatin, 17529-69-0.

Acknowledgment.—This research was supported in part by Grant CA-12149-01 from the National Cancer Institute of the National Institutes of Health. The authors express their appreciation for this help.

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[13] O. Buchardt, J. Becker, and C. Lohse, *Acta Chem. Scand.*, **19**, 1120 (1965).

Tetraalkylammonium Trifluoromethanesulfonates as Supporting Electrolytes[1]

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The renewed interest in synthetic organic electrochemistry is derived in part from the increased use of nonaqueous and, in particular, aprotic solvents. The use of such solvents is limited, however, by the availability of supporting electrolytes which ionize to give solutions of sufficiently low resistance. This becomes particularly important in bulk electrolyses in which a high solution resistance results in the generation of considerable heat.

Among the most widely used supporting electrolytes in solvents such as acetonitrile, dimethylformamide, methylene dichloride, and tetrahydrofuran are the tetraalkylammonium salts. Their ready availability, ease of purification, and the potential range over which they can be used makes them ideally suited for a variety of electrochemical uses. While the cation determines the solubility, the choice of a specific tetraalkylammonium salt is governed principally by the chemistry of the anion. Unfortunately, the choice of anions is limited. The ease of oxidation of halides to the corresponding halogens, coupled with the high nucleophilicity of the halide ion, severely limits their use as supporting electrolytes. Acetates have been suggested as useful supporting electrolytes, since upon oxidation only ethane and carbon dioxide are generated (*via* the Kolbe reaction). However, it was not found possible to prepare tetraalkylammonium acetates free of acetic acid. House[3] has come to the conclusion that the tetraalkylammonium fluoroborates are the supporting electrolytes of choice, since they are readily prepared and purified, and exhibit the necessary electrochemical properties. Thus, the tetra-*n*-butylammonium salt shows a limiting reduction potential (at mercury) more cathodic than 2.7 V (all potentials are quoted against the sat-

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[1] This work was supported by the National Institutes of Health (Grant AM 14343).

[2] NIH Predoctoral Fellow.

[3] H. O. House, E. Feng, and N. P. Peet, *J. Org. Chem.*, **36**, 2371 (1971).

TABLE I

SOLUBILITIES OF TETRAALKYLAMMONIUM SALTS[b]

		DMF		CH_3CN		CH_2Cl_2		THF	
Et_4N^+	$CF_3SO_3^-$	7.2	(2.58)	8.6	(3.1)	8.5	(3.0)	0.2	(0.08)
	ClO_4^{-a}	2.3	(1.00)	2.6	(1.13)				(<0.01)
	BF_4^{-a}	2.7	(1.24)	3.7	(1.69)				(<0.01)
n-Pr_4N^+	$CF_3SO_3^-$	4.9	(1.49)	5.0	(1.49)	4.9	(1.46)	~0.1	(0.03)
	ClO_4^{-a}	2.1	(0.74)	2.1	(0.74)				(<0.01)
	BF_4^{-a}	3.2	(1.17)	3.6	(1.32)				(<0.01)
n-Bu_4N^+	$CF_3SO_3^-$	8.8	(2.25)	9.8	(2.5)	9.6	(2.45)	9.2	(2.35)
	ClO_4^{-a}	7.9	(2.29)	7.0	(2.05)			5.0	(1.46)
	BF_4^{-a}	7.5	(2.34)	7.1	(2.21)			6.5	(2.02)

[a] Reference 3. [b] In g/10 ml (concentration, M).

urated calomel electrode unless otherwise stated) in a variety of aprotic solvents and gives solutions with sufficiently low specific resistances to be suitable for bulk electrolyses.

The principal consideration in choosing a supporting electrolyte, once the electrochemical requirements have been met, is one of inertness toward electrochemically produced intermediates and products. In cathodic reductions where anions and anion radicals are likely intermediates it is to be expected that the tetrafluoroborate anion will be inert. However, in anodic oxidations reactions between tetrafluoroborate and electrochemically generated cations and cation radicals are expected. A chemical analogy is that of the Balz–Schiemann reaction[4] in which the thermal decomposition of an aryl diazonium fluoroborate yields the corresponding aryl fluoride *via* the aryl cation. Similarly, we have found that porphyrin π dications, which are stable in the presence of tetraalkylammonium perchlorates, react with tetrafluoroborates. Clearly then, the tetrafluoroborates do not meet the criteria of chemical inertness during anodic oxidations. This is also true of most of the other supporting electrolytes currently in use, except for those in which the anion is perchlorate. From an electrochemical viewpoint the tetraalkylammonium perchlorates are ideal. They are readily purified, highly soluble in a wide variety of solvents, and the specific resistances and limiting potentials of the resulting solutions are as favorable as those obtained with any other systems. Perchlorate salts suffer from only one disadvantage: since the perchlorate anion is a powerful oxidizing agent, organic perchlorates are frequently, and unpredictably, explosive! We have prepared a number of organic cations by electrochemical methods and have isolated them as their perchlorate salts. The ever-present dangers of such practices were highlighted when it was reported[5] that a recrystallized sample of tetra-n-propylammonium perchlorate exploded upon drying at room temperature!

Such considerations have prompted us to look for a cation which possesses the nonnucleophilic and low coordinating power of perchlorates but lacks its oxidizing properties. Since nucleophilicity is associated with conjugate bases of strong acids, our attention was drawn to trifluoromethanesulfonic acid, the strongest Brønsted acid known.[6] The stability of the trifluoromethanesulfonate anion is illustrated by the observation that methyl trifluoromethanesulfonate is 10^4 times more reactive toward acetolysis than methyl p-toluenesulfonate.[7] Moreover, studies on the trifluoromethanesulfonate anion show it to be a very poor ligand.[8]

Treatment of aqueous solutions of tetraalkylammonium bromides or hydroxides with trifluoromethanesulfonic acid gives a precipitate of the corresponding trifluoromethanesulfonate salt. Recrystallization from a variety of aprotic solvents, followed by drying at elevated temperatures, yields the pure, anhydrous, solvent-free product. The salts have solubilities (Table I) which in every case are comparable to those of the corresponding tetrafluoroborates or perchlorates. Furthermore, the specific resistances of solutions of these salts are very similar (Table II) to those of the perchlorates and tetrafluoroborates. Finally, the limiting anodic and cathodic potentials for the solutions (Table III) are, where they can be compared directly, essentially the same as for the perchlorates and tetrafluoroborates. These potentials are limited in the cathodic direction by the reduction of the tetraalkylammonium cation (forming an amalgam at mercury[9]) in all the solvents examined except methylene dichloride, which is itself reduced at a potential of -1.8 V. The limiting anodic potential is determined by oxidation of the solvent, which occurs at 3.0 V for acetonitrile and 1.8 V for both DMF and CH_2Cl_2. We have used these tetraalkylammonium trifluoromethanesulfonates as supporting electrolytes for a variety of anodic and cathodic cyclic voltametric studies as well as for controlled potential bulk electrolyses, and find that they are comparable in every respect to their perchlorate or tetrafluoroborate counterparts, with the exceptions that the trifluoromethanesulfonate anion is nonoxidizing and does not react with highly oxidized substrates.

The obvious advantages of using the trifluoromethanesulfonates over the perchlorates necessitates their economical preparation, and, while the neutralization of the appropriate tetraalkylammonium hydroxide, or methathesis of the bromides, by trifluoromethanesulfonic acids presents a simple and efficient preparation, the use of a preformed tetraalkylammonium cation adds considerably to the expense of the final product. Esters of trifluoromethanesulfonic acid are

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(4) H. Suschitzky, *Advan. Fluorine Chem.*, **4**, 1 (1965).

(5) R. H. Felton, personal communication. This sample of tetra-n-propylammonium perchlorate was prepared from the corresponding hydroxide and perchloric acid. The product was thoroughly washed with water and recrystallized from ethanol. The recrystallized sample (100 g) was placed in a plastic desiccator, attached directly to a vacuum pump, evacuated to 10^{-4} Torr, and left at room temperature. After some time, while still attached to the pump, the sample exploded and blew the top off the desiccator.

(6) T. Gramstad, *Tidsskr. Kjemi, Bergv. Met.*, **19**, 62 (1959).

(7) A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*, **90**, 1598 (1968).

(8) A. Scott, and H. Taube, *Inorg. Chem.*, **10**, 62 (1971).

(9) J. D. Littlehailes and B. J. Woodhall, *Chem. Commun.*, 665 (1967).

TABLE II.—SPECIFIC RESISTANCES FOR TETRAALKYLAMMONIUM SALTS[b]

	DMF		CH_3CN		CH_2Cl		THF	
$Et_4N^+CF_3SO_3^-$	47.4	(1.0)	23.6	(1.0)	75.0	(1.0)		
	63	(0.5)	32.7	(0.5)	145	(0.5)		
	121	(0.2)	57.5	(0.2)	414	(0.2)		
	205	(0.1)	96.6	(0.1)	9.6	(0.1)		
$Et_4N^+ClO_4^-$[a]	52	(0.6)	26	(0.6)				
$Et_4N^+BF_4^-$[a]	38	(1.0)	18	(1.0)				
	54	(0.5)	27	(0.5)				
$Pr_4N^+CF_3SO_3^-$	67.6	(1.0)	32	(1.0)	89.3	(1.0)		
	78	(0.5)	38	(0.5)	152	(0.5)		
	137	(0.2)	64.3	(0.2)	388	(0.2)		
	232	(0.1)	108	(0.1)	840	(0.1)		
$Pr_4N^+ClO_4^-$[a]	64	(0.6)	31	(0.60)				
$Pr_4N^+BF_4^-$[a]	51	(1.0)	23	(1.0)				
$Bu_4N^+CF_3SO_3^-$	93	(1.0)	43.4	(1.0)	139	(1.0)	322	(1.0)
	89	(0.5)	44.4	(0.5)	185	(0.5)	478	(0.5)
	146	(0.2)	77.2	(0.2)	409	(0.2)	1285	(0.2)
	246	(0.1)	121	(0.1)	841	(0.1)	3080	(0.1)
$Bu_4N^+ClO_4^-$[a]	77	(0.6)	37	(0.6)			369	(1.0)
	82	(0.5)	39	(0.5)			583	(0.5)
$Bu_4N^+BF_4^-$[a]	69	(1.0)	31	(1.0)			373	(1.0)
	72	(0.5)	33	(0.5)			587	(0.5)

[a] Reference 3. [b] In ohm cm (concentration, *M*).

TABLE III.—LIMITING ANODIC AND CATHODIC POTENTIALS FOR TETRAALKYLAMMONIUM SALTS[a]

	DMF			CH_3CN			CH_2Cl_2			THF		
	Pt^+	Pt^-	Hg^-	Pt^+	Pt^-	Hg^-	Pt^+	Pt^-	Hg^-	Pt^+	Pt^-	lg^-
$Et_4N^+CF_3SO_3^-$	1.8	−2.2	−2.65	3.0	−2.5	−2.8	1.8	−1.6	−1.7			
$Et_4N^+ClO_4^-$[b]	1.6	−2.1	−3.0			−2.8						
$Et_4N^+BF_4$[c]			−2.72			−2.70						
$Pr_4N^+CF_3SO_3^-$	1.85	−2.3	−2.7	3.0	−2.4	−2.6	1.8	−1.7	−1.8			
$Bu_4N^+CF_3SO_3^-$	1.8	−2.3	−2.8	3.0	−2.1	−2.7	1.8	−1.8	−1.9	1.6	−2.2	−3.2
$Bu_4N^+ClO_4^-$	1.5[b]	−2.5[b]	−3.0[b]			−2.77[c]	1.8[b]	−1.7[b]	−1.9[b]			−2.9[c]
$Bu_4N^+BF_4^-$[c]			−2.80			−2.74						−2.75

[a] The potentials are measured against $Ag/AgCl^+$ except in *b* and *c* (where the reference electrode is SCE) SCE is +242 mV and Ag/AgCl +197 mV *vs.* the hydrogen electrode. [b] C. K. Mann, "Electro-analytical Chemistry," A. J. Bard, Ed., Arnold, London, 1969, p 57. [c] Reference 3.

powerful alkylating agents,[10] which suggested that the treatment of such an ester with a tertiary amine should give directly the tetraalkylammonium salt. This proved to be the case, and our standard method for the preparation of these salts now follows this route.

Experimental Section[11]

Tetraethylammonium Trifluoromethanesulfonate.—To 50 g (34 mmol) of a 10% solution of tetraethylammonium hydroxide in water was added 5 g (33 mmol) of trifluoromethylsulfonic acid. The solution was stirred for 30 min and then taken down to dryness on a rotary evaporator to give a quantitative yield of the crude salt, mp 140°. Three recrystallizations from THF gave 6.0 g (65%) of $Et_4NCF_3SO_3$: mp (after drying under vacuum) 160–161°; ir (CH_2Cl_2) no OH absorption, bands at 1250, 1228 (sh), 1162, and 1035 cm^{-1}; nmr ($CHCl_3$) δ 1.39 (12 H, t, $J = 7$ Hz), 3.44 (8 H, q, $J = 7$ Hz).

Anal. Calcd for $C_9H_{20}F_3NO_3S$: C, 38.70; H, 7.23; N, 5.01; S, 11.48. Found: C, 38.97; H, 7.40; N, 5.17; S, 12.01.

Tetra-*n*-propylammonium Trifluoromethanesulfonate. Method A.—A solution of 100 g (0.375 mol) of tetra-*n*-propylammonium bromide in 200 ml of water was rapidly stirred while 57.4 g (0.376 mol) of trifluoromethanesulfonic acid was slowly added. The solution was cooled to room temperature and filtered, and the product was washed with water. This gave 115 g (91%) of the crude salt, mp 149–163°. Recrystallization from methylene dichloride–benzene gave 101.2 g (80%) of $(n\text{-}Pr)_4NCF_3SO_3$ as clear plates: mp (after drying under vacuum) 164.5–165.5°; ir (CH_2Cl_2) no OH absorption, bands at 1238, 1223, 1155, and 1031 cm^{-1}; nmr (CH_2Cl_2) δ 1.1 (12 H, t, $J = 7$ Hz), 1.5–2.1 (8 H, m), and 3.1–3.35 (8 H, m).

Anal. Calcd for $C_{13}H_{28}F_3NO_3S$: C, 46.55; H, 8.41; N, 4.18; S, 9.50. Found: C, 46.75; H, 8.44; N, 4.22; S, 9.59.

Method B. Trifluoromethanesulfonic Anhydride.—A well-mixed suspension of 60 g (0.40 mol) of trifluoromethanesulfonic acid and 60 g (0.42 mol) of phosphorus pentoxide was allowed to stand at room temperature for 1 hr. The volatile product was then distilled, at 12 mm, into a Dry Ice–acetone trap, giving 46 g (87%) of the anhydride which was used without further purification.

A solution of 10 g (35.5 mmol) of trifluoromethanesulfonic anhydride and 45 mol of dry methylene dichloride was stirred and cooled in an ice bath. Dry pyridine (2.80 g, 35.5 mmol) was slowly added while the temperature was maintained below 10°, dry *n*-propanol (2.13 g, 35.5 mmol) was then slowly added, and the mixture was filtered. The filtrate, containing the propyl trifluoromethanesulfonate, was cooled in an ice bath and 5.1 g (35.6 mmol) of tri-*n*-propylamine (purified by distillation from naphthyl isocyanate) was slowly added. The solution was taken down to dryness. The residue was dissolved in the minimum of hot water and allowed to stand at 0° until crystallization was complete. The product, 8.9 g (75%), was collected by filtration; recrystallization gave a product identical with that described above.

Tetra-*n*-butylammonium Trifluoromethanesulfonate. Method A.—A solution of 9.7 g (30 mmol) of $(n\text{-}Bu)_4NBr$ in 30 ml of water was rapidly stirred while 4.5 g (30 mmol) of trifluoromethanesulfonic acid was slowly added. After cooling to room temperature the mixture was filtered and the product was washed with water to give 8.82 g (75%) of the crude salt, mp 109–111°. The filtrate was extracted with methylene dichloride to give a further 2.68 g (23%) of the salt, mp 100–104°. The combined solids were twice recrystallized from methylene dichloride–ether to give 10.72 g (91%) of $(n\text{-}Bu)_4NCF_3SO_3$: mp (after drying

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(10) R. L. Hansen, *J. Org. Chem.*, **30**, 4322 (1965).

(11) Melting points are uncorrected. Nmr spectra were recorded at 60 MHz with tetramethylsilane as internal reference.

under vacuum) 111–112.5°; ir (CH_2Cl_2) no OH absorption, bands at 1235, 1220, 1154, and 1031 cm^{-1}; nmr ($CHCl_3$) δ 1.0–1.25 (12 H, m), 1.4–2.1 (16 H, m), and 3.15–3.65 (8 H, m).

Anal. Calcd for $C_{17}H_{36}F_3NO_3S$: C, 52.15; H, 9.27; N, 3.58; S, 8.19. Found: C, 52.17; H, 9.23; N, 3.65; S, 8.38.

Method B.—A solution of 10 g (35.5 mmol) of trifluoromethanesulfonic anhydride and 45 ml of methylene dichloride was stirred and cooled in an ice bath. Dry pyridine (2.80 g, 35.5 mmol) was slowly added while the temperature was maintained below 10°. Dry *n*-butyl alcohol (2.63 g, 35.5 mmol) was then slowly added and the mixture was filtered. The filtrate, containing the butyl trifluoromethanesulfonate, was cooled in an ice bath and 6.58 g (35.5 mmol) of tri-*n*-butylamine (purified by distillation from naphthyl isocyanate) was slowly added. The solution was taken down to dryness and the solid was triturated with ether. The ethereal solution was filtered and taken down to dryness, and the product was recrystallized as above to give 6.9 g (50%).

Purification of Solvents.—Methylene dichloride was refluxed for 24 hr over, and distilled from, calcium hydride under argon, and stored over 3A and 5A molecular sieves. The specific resistance was 1.44 × 10^6 ohm cm.

Acetonitrile was refluxed for 2 days over, and then distilled from, calcium hydride (10 g/l.) under argon. This distillate was then twice distilled from P_2O_5 (5 g/l.) under argon and stored over 3A molecular sieves. The specific resistance was 9.9 × 10^5 ohm cm.

Dimethylformamide (spectra grade, Eastman) was stored over 4A molecular sieves. The specific resistance was 5.67 × 10^5 ohm cm.

Tetrahydrofuran was refluxed over and distilled from sodium–potassium alloy under argon.

Solubility Measurements.—Mixtures of the purified solvents and an excess of the salt (pulverized and dried under vacuum at 50°) were heated until most of the salt had dissolved and then held at 28° until equilibrium was reached. Three separate aliquots of the supernatant liquid were then taken down to dryness and dried to constant weight under vacuum.

Specific Resistance Measurements.—Measurements were made using an Industrial Instruments conductivity cell with platinized platinum electrodes. The cell constant (0.098) was determined using 0.100 and 0.010 *M* aqueous solutions of KCl. Solutions were protected from the atmosphere and immersed in an oil bath maintained at 25.0°. The resistances were measured on a Serfass conductivity bridge, Model RCM 15, at a frequency of 1 KHz.

Measurements of Limiting Anodic and Cathodic Potentials.—A mercury drop (25.1 mm^2), hanging from the end of a capillary, was used for the cathodic measurements against mercury, and a platinum disc (7.1 mm^2) was used for the anodic and cathodic measurements against platinum. The reference electrode consisted of a long, thin (0.4 × 15 cm) tube with a cracked tip at the bottom. This tube was filled with the solvent and supporting electrolyte under investigation, and the aqueous reference electrode was isolated *via* a KCl–agar bridge placed in it. The counter electrode was in every case a small platinum sphere. Readings were taken using an M. I. Associates polarographic instrument with a Tetronics oscilloscope for the display. The limiting potential was taken to be that voltage at which dI/dV equalled 5 × 10^{-6} A V^{-1}.

Registry No.—$Et_4NCF_3SO_3$, 35895-69-3; (n-Pr)$_4NCF_3SO_3$, 35925-48-5; (n-Bu)$_4NCF_3SO_3$, 35895-70-6; Et_4NBF_4, 429-06-1.

Synthesis of the Housefly Sex Attractant

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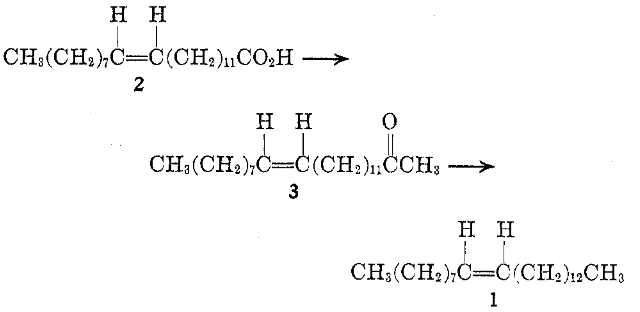
The isolation, identification, and one synthesis of the sex attractant, (*Z*)-9-tricosene (1), of the housefly (*Musca domestica* L.) were recently reported.[1] We described here a very efficient synthesis of 1 from readily available starting materials.

Erucic acid (2)[2] was converted into ketone 3 by the action of 2 equiv of methyllithium.[3] Huang-Minlon reduction[4] of 3 gave 1 in an overall yield of 85%. This



$$\underset{\mathbf{2}}{\mathrm{CH_3(CH_2)_7\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}(CH_2)_{11}CO_2H}} \longrightarrow$$

$$\underset{\mathbf{3}}{\mathrm{CH_3(CH_2)_7\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}(CH_2)_{11}\overset{O}{\overset{\|}{C}}CH_3}} \longrightarrow$$

$$\underset{\mathbf{1}}{\mathrm{CH_3(CH_2)_7\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}(CH_2)_{12}CH_3}}$$

process is easily adaptable to large-scale preparations and requires no expensive reagents.

Experimental Section[5]

(*Z*)-Tricos-14-en-2-one (3).—To a 10.7-g (31.3 mmol) quantity of erucic acid (2) (Columbia Organic Chemicals) in dry ether (200 ml) containing *o*-phenanthroline (5 mg) was added 31.5 ml (63.0 mmol) of 2.00 *M* methyllithium in hexane (Lithcoa), at a rate such that gas evolution was moderate. The reddish-brown reaction mixture was stirred for 30 min and quenched by cautiously adding 10% NaOH (100 ml), saturated $NaHCO_3$ (10 ml), and saturated $(NH_4)_2SO_4$ (10 ml). The phases were separated and the aqueous phase was extracted with ether (3 × 100 ml). The combined organic phases were dried ($MgSO_4$), concentrated, and distilled to give 9.77 g (93.3%) of ketone **3**: bp 140° (0.10 mm); n^{23}D 1.4572; ir (CCl_4) 3015 (olefinic CH), 1725 cm^{-1} (C=O); nmr (CCl_4) δ 0.88–2.50 (m, 42 H, all protons except olefinic; CH_3 s at δ 2.00), 5.27 [t, *J* (apparent) ≅ 4.5 Hz, 2 H, olefinic]; mass spectrum (70 eV) showed M·$^+$ at *m/e* 336; vpc (3% SE-30, 8 ft × 0.125 in., 250°, 50 ml/min) showed one peak.

Anal. Calcd for $C_{23}H_{44}O$: C, 82.07; H, 13.18. Found: C, 82.04; H, 13.30.

(*Z*)-9-Tricosene (1).—To a solution of 3.1 g (47 mmol) of 85% KOH in diethylene glycol (30 ml) was added 4.77 g (14.1 mmol) of ketone **3** and 2.0 g (40 mmol) of 85% hydrazine hydrate. The reaction mixture was heated at 140° until the water had been removed and then at 193° for 4 hr. The cooled reaction mixture was poured into ice–water (150 ml), neutralized with 6 *N* HCl, and extracted with pentane (5 × 100 ml). The combined extracts were dried ($MgSO_4$), concentrated, and distilled to give 4.55 g (88.8%) of olefin **1**: bp 170–172° (0.5 mm); n^{23}D 1.4532 [lit.[1] bp 157–158° (0.1 mm); n^{26}D 1.4517]; ir (CCl_4) 3015 cm^{-1} (olefinic CH); nmr (CCl_4) δ 0.67–2.25 (m, 44 H, all protons except olefinic; $CH_2CH{=}CHCH_2$ m, at δ 1.98), 5.25 [t, *J* (apparent) ≅ 4.5 Hz, 2 H, vinyl]; mass spectrum (70 eV) showed M·$^+$ at *m/e* 322; vpc (3% SE-30, 8 ft × 0.125 in., 250°, 50 ml/min) showed one peak.

Anal. Calcd for $C_{23}H_{46}$: C, 85.63; H, 14.37. Found: C, 85.75; H, 14.30.

Registry No.—**1**, 27519-02-4; **3**, 36706-99-7.

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[1] D. A. Carlson, M. S. Mayer, D. L. Silhacek, J. D. James, M. Beroza, and B. A. Bierl, *Science*, **174**, 76 (1971).

[2] Eurcic acid is available commercially, or it can be isolated from rapeseed oil: C. R. Noller and R. H. Talbot, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 258.

[3] M. J. Jorgenson, *Org. React.*, **18**, 1 (1970).

[4] Huang-Minlon, *J. Amer. Chem. Soc.*, **68**, 2487 (1946).

[5] Microanalyses were performed by Alfred Bernhardt Microanalytisches Laboritorium, Elbach über Engleskirchen, Mülheim (Ruhr), West Germany.