Ethylation of Aliphatic Ketones on Electroreduction in Tetraethylammonium Fluoroborate–Liquid Ammonia Solutions

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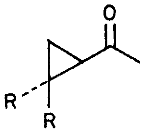
The reduction of acetylcyclopropane and pentan-2-one by electrogenerated solvated electrons in liquid ammonia in the presence of butyltrimethylammonium fluoroborate, or several other tetra-alkylammonium salts, gives the same products as when lithium metal is used as the source of solvated electrons, but when the electroreduction is performed in the presence of tetraethylammonium fluoroborate the major products are tertiary alcohols, $R^1R^2C(OH)Et$. Tributylethylammonium fluoroborate also functions as an ethylating agent, but not as a butylating agent. These results are rationalised on the basis of the stability of Et_4N^+ and Bu_3EtN^+ towards solvated electrons, and the instability of the other tetra-alkylammonium cations under these conditions.

THE mechanism of the reductive ring cleavage of acetylcyclopropanes by metal–ammonia solutions has been extensively studied in recent years.[1,2] While substituent effects upon the direction of ring cleavage indicate that a carbanionic species is involved in the cleavage step, it was not possible to say categorically whether such a species was formed by the addition of one or two electrons to the carbonyl group, although both groups of workers have assumed the latter. An obvious extension to the previous work was to study the reductive cleavage of acetylcyclopropanes electrochemically, preferably in liquid ammonia, in the hope that electroanalytical methods and controlled potential electrolysis might lead to a conclusion regarding the number of electrons which are added to the carbonyl group before ring cleavage occurs. The use of liquid ammonia as the solvent in electrochemical reductions has already been investigated extensively by Bard and his co-workers,[3] who have demonstrated the unique aprotic properties of this solvent.

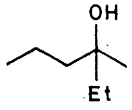
Unfortunately however, the main objective of the study was thwarted by the fact that acetylcyclopropanes are not electroactive within the cathodic range available using solutions of tetra-alkylammonium salts in liquid ammonia. The cathodic limit is set by the discharge of electrons from the cathode into the solution, sometimes accompanied by amalgamation of the tetra-alkylammonium cation if mercury is the cathode material used.[4] We therefore had to be content with preparative electroreductions at potentials beyond the electron discharge potential. At these potentials reduction of the substrate could either be direct, *i.e.* electron transfer at the electrode, or, perhaps more likely, indirect, *i.e.* by solvated electrons.

We initially used butyltrimethylammonium fluoroborate as the supporting electrolyte since this was the most soluble (1M) of a series of tetra-alkylammonium salts which we had investigated. It appears that, with the exception of tetraethylammonium fluoroborate, the most soluble tetra-alkylammonium fluoroborates in ammonia are those with three of the alkyl groups identical, *e.g.* $BuMe_3N^+$, Bu_3MeN^+, Bu_3EtN^+; when all the alkyl groups are identical the solubility is in general rather low.

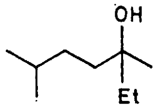
Using 0.1M-butyltrimethylammonium fluoroborate in ammonia, the reduction of acetylcyclopropane (I) and 1-acetyl-2,2-dimethylcyclopropane (II) using both controlled current and controlled potential conditions gave the same products as when lithium in ammonia is used, *viz.* pentan-2-one and pentan-2-ol from (I), and 5-methylhexan-2-one and 4,4-dimethylpentan-2-one (after chromic acid oxidation of the ketone–alcohol mixture) from (II). In the latter case the ratio of the two ketones was also the same as that observed for a lithium–ammonia reduction.[1] This suggests that the species undergoing ring cleavage in the electrochemical system is the same as that involved in the lithium–ammonia system.



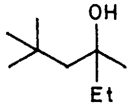
(I) R = H
(II) R = CH_3



(III)



(IV)



(V)

With this supporting electrolyte it was observed that the solvated electrons discharged from the mercury cathode were not stable (a blue colour was only observed close to the electrode even in the absence of ketone), and a grey solid amalgam was deposited at the mercury cathode.

Since we had found that solvated electrons were much more stable in the presence of tetraethylammonium fluoroborate, and that there was no amalgam formation at a mercury cathode, we also performed reductions using this salt as the supporting electrolyte. Using 0.1M-tetraethylammonium fluoroborate in ammonia and controlled current conditions with either a mercury or platinum cathode, reduction of acetylcyclopropane (I)

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[1] A. J. Bellamy, E. A. Campbell, and I. R. Hall, *J.C.S. Perkin II*, 1974, 1347.

[2] W. G. Dauben and R. E. Wolf, *J. Org. Chem.*, (*a*) 1970, **35**, 374; (*b*) *ibid.*, p. 2361.

[3] A. Demortier and A. J. Bard, *J. Amer. Chem. Soc.*, 1973, **95**, 3495; W. H. Smith and A. J. Bard, *ibid.*, 1975, **97**, 5203, 6491; I. Vantires, W. H. Smith, and A. J. Bard, *J. Electrochem. Soc.*, 1975, **122**, 894.

[4] H. A. Laitinen and C. J. Nyman, *J. Amer. Chem. Soc.*, 1948, **70**, 3002.

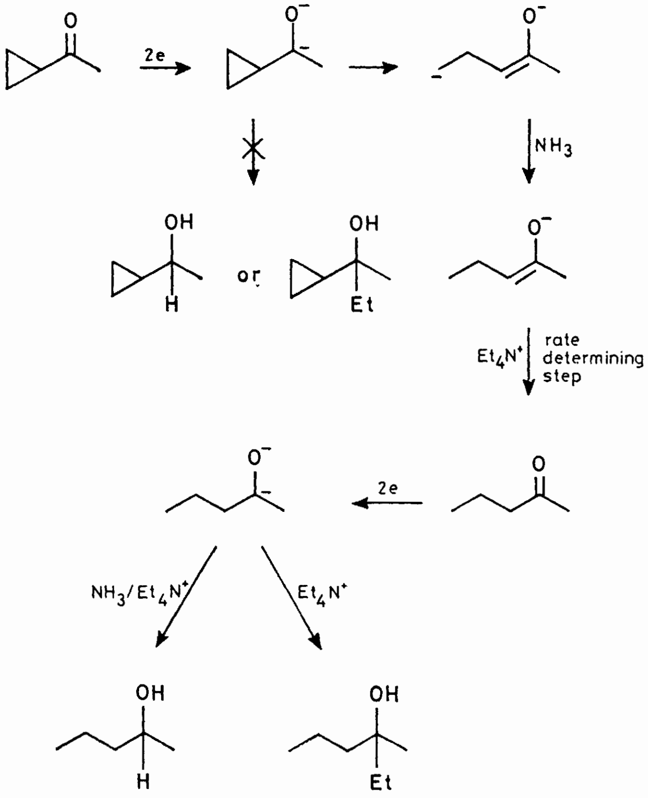
now gave 3-methylhexan-3-ol (III) as the major product (70—75% yield), with minor amounts of pentan-2-one and pentan-2-ol. The reduction of pentan-2-one under the same conditions also gave 3-methylhexan-3-ol and pentan-2-ol. The reduction of 1-acetyl-2,2-dimethylcyclopropane (II) gave a mixture of two tertiary alcohols 3,6-dimethylheptan-3-ol (IV) and 3,5,5-trimethylhexan-3-ol (V), the former predominating, with minor amounts of the two ketones which were formed when the electrolysis was performed in the presence of butyltrimethylammonium fluoroborate; clearly (IV) and (V) were derived from these ketones in the same way that (III) was derived from pentan-2-one.

A more detailed examination of the electroreduction of acetylcyclopropane in the presence of tetraethylammonium fluoroborate showed that the solution remained colourless until two electron equivalents of current had been passed, when it became blue, and that no 3-methylhexan-3-ol or pentan-2-ol was formed until all the acetylcyclopropane had been consumed (see Experimental section); this coincided with the solution turning blue and represents 100% current efficiency for the reduction of acetylcyclopropane to pentan-2-one.

In the reduction of pentan-2-one, the formation of 3-methylhexan-3-ol decreased when the concentration of tetraethylammonium fluoroborate was lowered to 0.02M, and was completely suppressed when ethanol (0.1M) was added. Under normal conditions the solution remained colourless until two electron equivalents of current had been passed.

The mechanism shown in the Scheme accounts for the above observations concerning the formation of ethylated products. The addition of two electrons to the carbonyl group of acetylcyclopropane must be followed by a fast cleavage reaction since no 1-cyclopropylethanol or 2-cyclopropylbutan-2-ol is formed. The intermediate carbanion–enolate anion would be expected to be monoprotonated at C(5) by the solvent, but the enolate anion is not sufficiently basic to be protonated by ammonia; [2b] protonation at C(2) probably involves the tetraethylammonium cation as a proton source. Since no further reduction occurs until all of the acetylcyclopropane has been consumed and thereafter electrons are discharged from the electrode faster than they are consumed in a further reduction process, protonation of the enolate anion must be the rate-determining process in the Scheme. (The enolate anion would be analysed as pentan-2-one during a sampling experiment.) As free pentan-2-one is generated, further reduction to the corresponding dianion can take place, followed by either protonation by ammonia and/or tetraethylammonium cations to give pentan-2-ol or alkylation by tetraethylammonium cations. A lower concentration of tetraethylammonium fluoroborate or the presence of ethanol would favour the protonation of pentan-2-one dianion and increase the proportion of pentan-2-ol formed.

This mechanistic picture leaves several fundamental questions unanswered: does electron transfer to the carbonyl group occur at the electrode or in solution, or both, and why does the tetraethylammonium cation only function as a proton donor and not as an alkylating agent towards the enolate anion, when it alkylates, and possibly also protonates, pentan-2-one dianion? A further question concerns the difference in behaviour between butyltrimethylammonium and tetraethylammonium cations, and the behaviour of other tetra-alkylammonium cations.



SCHEME

The electrode appears to play an important role in the formation of ethylated products since when reductions of acetylcyclopropane and pentan-2-one in the presence of tetraethylammonium cations were carried out using chemically generated solvated electrons, no 3-methylhexan-3-ol was formed. An obvious difference between butyltrimethylammonium and tetraethylammonium cations is the stability towards solvated electrons. In the case of butyltrimethylammonium cations, there would be a very low concentration of cations close to the electrode surface, but with tetraethylammonium cations, due to their relatively slow reaction with solvated electrons, the concentration in the vicinity of the electrode would be much the same as in the bulk of the solution, with the possibility that the cations could actually be adsorbed at the electrode surface. If electron transfer to the carbonyl group occurs at, or close to, the electrode, then the abundance of tetra-alkylammonium cations in that region might have a fundamental effect upon the course of the subsequent reactions of the carbonyl dianion. The difference in behaviour of the tetraethylammonium cation towards the enolate anion and pentan-2-one dianion may in part be due to the difference in stability of the anions involved, but may also be due to the possibility that reaction of the enolate anion takes place away from the electrode whereas reaction of pentan-2-one dianion takes place close to, or even at, the electrode.

Further support for some of these proposals came from the study of other tetra-alkylammonium salts as supporting electrolytes. We found that for the majority of the tetra-alkylammonium cations studied, they were unstable towards solvated electrons, forming amalgams when a mercury cathode was used, and gave only pentan-2-ol from the reduction of pentan-2-one. Only one other cation resembled the behaviour of the tetraethylammonium cation, *viz.* tributylethylammonium, in that it was relatively stable towards solvated electrons, did not form an amalgam when a mercury cathode was used, and gave more than 80% yield of the ethylated product, 3-methylhexan-3-ol. Interestingly, none of the butylated product, 4-methyloctan-4-ol, was detected. There thus appears to be a correlation between the stability towards solvated electrons and the ability of a tetra-alkylammonium cation to function as an alkylating agent towards pentan-2-one dianion, although we do not understand why cations which are closely related behave so differently (*cf.* Et_4N^+ and Pr_4N^+, Bu_3EtN^+ and Pr_3EtN^+), and why the ethyl group is so special

In a study of the electron electrode in liquid ammonia, Laitinen and Nyman [4] reported that the cathodic limit was slightly less negative (*ca.* 70 mV) when tetraethylammonium iodide (5×10^{-3}M) was present compared to tetrapropylammonium iodide (5×10^{-3}M). They suggested that in the case of the tetraethylammonium cation, the limit might involve amalgamation of the cation as well as electron dissolution, but in the case of the tetrapropylammonium cation the limit is caused solely by electron dissolution. These observations are obviously at variance with our observations using more concentrated solutions. However, a study [5] of the stability of tetra-alkyl ammonium cations towards solvated electrons in liquid ammonia (formed from potassium) showed that for the series Me_4N^+, Et_4N^+, Pr_4N^+, the tetrapropylammonium cation was the least stable and the tetraethylammonium cation was the most stable; furthermore the cations Et_3MeN^+ and Pr_3MeN^+ were even more unstable than Pr_4N^+ (*cf.* Bu_3MeN^+ *versus* Et_4N^+ *inter alia* in the present work). The tetraethylammonium cation is also reported [6] to be stable in the presence of the conjugate bases of diphenylamine and aniline, but not of diethylamine. Several tetra-alkylammonium amalgams were prepared and studied by Littlehailes and Woodhall; [7] the only difference between the amalgams formed from tetraethylammonium and tetrapropylammonium cations was a slight difference (*ca.* 100 mV) in the potential of the amalgam.

An alternative mechanism for the alkylation reaction which should be considered involves reaction between the radical-anion of pentan-2-one and a tetraethylammonium radical [8] (or amalgam when a mercury cathode is used), giving the tertiary alcohol and triethylamine. Although the tetraethylammonium cation is not visibly reduced when there is sufficient reducible material present to consume all of the solvated electrons being discharged from the electrode, in the latter half of an acetylcyclopropane electrolysis when the solution is blue due to an excess of solvated electrons, other effects would not be so readily detected. Thus the conditions obtaining at this stage may be sufficient for the simultaneous production of the pentan-2-one radical-anion and the tetraethylammonium radical, assuming that the cation of the latter is reducible under these conditions. However, during the electrolysis of pentan-2-one, an excess of electrons does not exist until all the pentan-2-one has been consumed, and yet the tertiary alcohol is still formed. We therefore do not feel, on the basis of the existing evidence, that this mode of reaction is important.

In the course of studying the electrochemical reduction of other substrates, *i.e.* benzophenone, benzoycyclopropane, acetophenone, diphenylacetylene, *cis*-stilbene, and oct-4-yne, in liquid ammonia,[9] we have looked for alkylation of other radical-anions and dianions when tetraethylammonium fluoroborate was used as the supporting electrolyte, but have found no evidence for such behaviour. In view of the widespread use of tetraethylammonium salts as supporting electrolytes in aprotic solvents, it is perhaps surprising that alkylation by the supporting electrolyte has not been observed more often, but if the alkylation reported here is relatively slow, then it may be that only ammonia, with its greater stability towards reduced species with respect to protonation,[3] would allow such a reaction to compete effectively with protonation. The only related example in the literature we are aware of is the formation of 9-butylanthracene when anthracene is reduced electrochemically in the molten salt, tetrabutylammonium nitrate, at 150 °C.[10] It is thought that this product results from alkylation of an anthracene anion by the tetrabutylammonium cation.[11] However, Shono and his co-workers have recently obtained results similar to those reported here, in that alkylation, particularly ethylation, of ketones occurs when the latter are electrochemically reduced at carbon in anhydrous dimethylformamide containing tetra-alkylammonium salts.[12]

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[5] D. A. Hazelhurst, A. K. Holliday, and G. Pass, *J. Chem. Soc.*, 1956, 4653; see also E. Grovenstein, jun., and R. W. Stevenson, *J. Amer. Chem. Soc.*, 1959, **81**, 4850.

[6] W. L. Jolly, *J. Amer. Chem. Soc.*, 1955, **77**, 4958.

[7] J. D. Littlehailes and B. J. Woodhall, *Discuss. Faraday Soc.*, 1968, **45**, 187.

[8] R. K. Quinn and J. J. Lagowski, *J. Phys. Chem.*, 1968, **72**, 1374.

[9] E. M. Abbot and A. J. Bellamy, unpublished work.

[10] G. R. Davies and B. J. Woodhall, *J. Appl. Electrochem.*, 1971, **1**, 137.

[11] See R. Dietz in ' Organic Electrochemistry,' ed. M. M. Baizer, Dekker, New York, 1973, p. 263.

[12] T. Shono, personal communication, and described in a plenary lecture at the 3rd EUCHEM Conference on Organic Electrochemistry, Pitlochry, Scotland, 1977.

EXPERIMENTAL

General Electrolysis Procedure.—The electrolysis cell consisted of two concentric glass cylinders, the outer cylinder forming the cathode compartment and the inner cylinder forming the anode compartment, the two being connected through a medium porosity glass sinter forming the bottom of the inner cylinder. The reference electrode, Pb–0.05M-$Pb(NO_3)_2$, was contained within a glass tube, electrical contact with the catholyte being made *via* a cracked glass seal. The anode was a platinum foil and unless otherwise stated the cathode was a mercury pool.

Liquid ammonia, purified by distillation from sodium, was transferred to the cell as the liquid The cell was thermostatted at −36 °C. Stirring during the electrolysis was achieved either by means of a magnetic stirrer or by bubbling dry nitrogen, saturated with ammonia, through the solution.

After electrolysis, the reference electrode and the anode compartment were removed from the cell and to the catholyte was added an excess of ammonium chloride and ether. The ammonia was then allowed to evaporate, and the ether extract was washed with water and dried ($MgSO_4$). The extract was concentrated to *ca.* 2 ml by distillation through a fractionating column, and the concentrate was analysed by g.l.c. (15% polyethyleneglycol adipate; 70 °C).

Reductions using Butyltrimethylammonium Fluoroborate as the Supporting Electrolyte.—A 0.1M solution of butyltrimethylammonium fluoroborate in liquid ammonia (50 ml) exhibited a cathodic limit at mercury of −1.85 V, the limit being associated with discharge of electrons from the electrode into the solution and the formation of a blue solution close to the electrode During electrolyses beyond the cathodic limit, the mercury pool cathode became covered with a dark grey crust and some of the solid was dispersed into the solution in a finely divided form. Even before the addition of a ketone the blue colour was only observed close to the electrode with the bulk of the solution remaining colourless. The addition of ammonium chloride to the catholyte during work-up caused the grey solid to react vigorously with effervescence, and a clear solution was formed.

(a) *Reduction of acetylcylopropane and pentan*-2-*one.* Electrolysis of acetylcyclopropane (0.042 g, 5×10^{-4} mol) at constant current (100 mA) was stopped after 35 min (210 C; four electron reduction requires 193 C). During the electrolysis the potential of the cathode increased from −2.0 to −2.5 V. The products were pentan-2-one (62%), pentan-2-ol (18%), acetylcyclopropane (19%), and 1-cyclopropylethanol (1%). Electrolysis of pentan-2-one under similar conditions gave pentan-2-ol only.

(b) *Reduction of* 1-*acetyl*-2,2-*dimethylcyclopropane.* Electrolysis of 1-acetyl-2,2-dimethylcyclopropane (0.28 g, 2.5×10^{-3} mol) was performed at a controlled potential of −2.0 V. The initial current was *ca.* 60 mA, but the current decreased rapidly as the mercury surface became covered with the grey deposit. The electrolysis was stopped after 575 C had passed (four electron reduction requires 964 C). The products, analysed after oxidation of the initial product mixture in ether with 3M-chromic acid, were 5-methylhexan-2-one (57%), 4,4-dimethylpentan-2-one (26.5%), and 1-acetyl-2,2-dimethylcyclopropane (16.5%). Electrolysis at constant current (50 mA; initial potential −2.0 V; 540 C) gave the same products in 61.3, 28.6, and 10.1% respectively.

Other cathode materials gave the same products: (i) platinum foil (controlled potential −2.7 V; 575 C), 38, 22, and 40% respectively, (ii) lead rod (controlled current 50 mA; 540 C), 50, 43.5, and 6.5% respectively, and (iii) graphite rod (controlled potential −3.3 V; 1 350 C, high background current included), 63.9, 35.0, and 1.1% respectively. In all cases product yields were in excess of 75%.

Reductions using Tetraethylammonium Fluoroborate as the Supporting Electrolyte.—A 0.1M solution of tetraethylammonium fluoroborate in liquid ammonia (50 ml) exhibited a cathodic limit at mercury of −1.9 V. At higher potentials solvated electrons were discharged from the electrode to produce a blue solution. Electrolysis of the above solution at 100 mA for 5 min gave a blue colour which persisted for 10 min. In contrast to the butyltrimethylammonium fluoroborate solution, no grey solid was formed at the mercury surface although it became tarnished.

(a) *Reduction of acetylcyclopropane and pentan*-2-*one.* A solution of acetylcyclopropane (0.084 g, 10^{-3} mol) was electrolysed at constant current (100 mA). The solution remained clear for 35 min (210 C; 2-electron equivalents requires 193 C) and then turned blue. The electrolysis was continued for a further 45 min (480 C; four electron reduction requires 386 C). During the electrolysis the cathode potential remained at *ca.* −2.1 V. The major product was 3-methylhexan-3-ol (70—75% yield), isolated by preparative g.l.c. and identified by comparison with an authentic sample, with minor amounts of pentan-2-one and pentan-2-ol (15—20% combined).

The results of further electrolysis experiments on acetylcyclopropane are given in Table 1.

TABLE 1

Experiment	1	2	3[a]	4[b]	5[c]	6[d]
	Product (%)					
Acetylcyclopropane	0	0	0	5	22	0
Pentan-2-one	37	9	45	75	72	37
Pentan-2-ol	36	29	12	20	6	1
3-Methylhexan-3-ol	27	62	43	0	0	52
No. of coulombs	270	386	386	386	386	386
Overall yield (%)	65	80	62	75	60	76

Unless otherwise stated the following conditions were used: mercury cathode, controlled current 100 mA, 0.1M-Et_4NBF_4, acetylcyclopropane (10^{-3} mol).

[a] Pt electrode. [b] 0.1M-$BuMe_3NBF_4$. [c] 0.1M-$BuMe_3NBF_4$, Pt electrode. [d] 0.05M-Et_4NBF_4, 0.05M-$BuMe_3NBF_4$.

TABLE 2

Experiment	1	2	3[a]	4[b]	5[c]
	Product (%)				
Pentan-2-one	27	0	18	20	56
Pentan-2-ol	63	66	60	80	40
3-Methylhexan-3-ol	10	34	22	0	5
No. of coulombs	135	193	193	135	135
Overall yield (%)	70	70	68	70	60

Unless otherwise stated the following conditions were used: mercury cathode, controlled current 100 mA, 0.1M-Et_4NBF_4, pentan-2-one (10^{-3} mol).

[a] 0.02M-Et_4NBF_4. [b] 0.1M-Et_4NBF_4, 0.1M-EtOH. [c] Pt electrode.

An electrolysis of acetylcyclopropane (2×10^{-3} mol) in 0.1M-tetraethylammonium fluoroborate solution (100 ml) at 100 mA which was sampled periodically gave the following analyses: (number of coulombs passed; % acetylcyclopropane, % pentan-2-one, % pentan-2-ol, % 3-methylhexan-3-ol) (i) 318; 13, 87, 0, 0, (ii) 390 (two electron equivalents); 0, 100, 0, 0, (iii) 456; 0, 91, 3, 6, (iv) 648; 0, 24, 19, 57, and (v) 750; 0, 0, 30, 70.

The results of electrolysis experiments on pentan-2-one are given in Table 2. The solution did not turn blue until *ca.* 193 C (two electron equivalents) had been passed.

(b) *Reduction of* 1-*acetyl*-2,2-*dimethylcyclopropane*. Electrolysis of 1-acetyl-2,2-dimethylcyclopropane (0.28 g, 2.5×10^{-3} mol) was performed at a controlled current current of 50 mA for 3 h (540 C; four-electron reduction requires 965 C). During the electrolysis the cathode potential increased from -2.5 to -2.9 V. The major products were 3,6-dimethylheptan-3-ol and 3,5,5-trimethylhexan-3-ol, the former predominating, which were isolated by preparative g.l.c. and identified by comparison with authentic samples. Smaller amounts of 1-acetyl-2,2-dimethylcyclopropane, 5-methylhexan-2-one, and 4,4-dimethylpentan-2-one were also isolated (after chromic acid oxidation).

Butyltrimethylammonium Fluoroborate.—Butyltrimethylammonium bromide was prepared from an ethanolic solution of trimethylamine and 1-bromobutane. The addition of a slight excess of 40% aqueous fluoroboric acid to a saturated aqueous solution of the bromide gave the solid fluoroborate which was filtered off. The filtrate was concentrated and addition of ethanol–ether precipitated more fluoroborate. Recrystallisation from ethanol gave the pure *salt*, m.p. 191—193 °C (Found: C, 41.65; H, 8.85; N, 6.8. $C_7H_{18}BF_4N$ requires C, 41.4; H, 8.85; N, 6.9%).

Tetraethylammonium Fluoroborate.—A 40% aqueous solution of fluoroboric acid (37.5 ml) was added to a 25% aqueous solution of tetraethylammonium hydroxide (100 ml) and the fluoroborate separated out. After filtration more fluoroborate was isolated by adding ethanol–ether to the concentrated filtrate. Recrystallisation from aqueous ethanol gave the pure salt, m.p. >300 °C.

1-*Acetyl*-2,2-*dimethylcyclopropane*.—This was prepared from trimethylsulphoxonium iodide and mesityl oxide following the procedure of Roberts *et al.*[13]

Synthesis of Authentic Tertiary Alcohols.—Reaction of ethylmagnesium bromide [from magnesium (0.166 g atom) and ethyl bromide (0.184 mol)] in ether with the appropriate ketone (0.16 mol) gave (i) 3-methylhexan-3-ol (75%; b.p. 140 °C; from pentan-2-one), $\nu_{max.}$ (film) 3 400 cm^{-1}; *m/e* (70 eV) (no parent ion), 101 ($P - CH_3$), 87 ($P - C_2H_5$), 73 ($P - C_3H_7$), (low eV) 98 ($P - H_2O$); (ii) 3, 6-dimethylheptan-3-ol (80%; b.p. 170 °C; from 5-methylhexan-2-one), $\nu_{max.}$ (film) 3 400 cm^{-1}, *m/e* (70 eV) (no parent ion) 129.128 705 ($P - CH_3$; $C_8H_{17}O$ requires 129.127 933), 115.112 072 ($P - C_2H_5$; $C_7H_{15}O$ requires 115.112 284), 73.065 375 ($P - C_5H_{11}$; C_4H_9O requires 73.065 336), (low eV) 126 ($P - H_2O$); (iii) 3,5,5-trimethylhexan-3-ol (76%; b.p. 148 °C; from 4,4-dimethylpentan-2-one), $\nu_{max.}$ (film) 3 400 cm^{-1}, *m/e* [as for (ii)]. The structures of all three alcohols were further supported by ^1H and ^{13}C n.m.r. spectroscopy, including the use of Eu(fod)$_3$ shift reagent.

Attempted Ethylation of Acetylcyclopropane and Pentan-2-*one using Chemically Generated Solvated Electrons*.—(i) *Sodium*. Acetylcyclopropane (10^{-3} mol) in a 1M solution of tetraethylammonium fluoroborate in liquid ammonia was reduced using sodium (10^{-2} g atom). The reaction mixture was worked up as described for the electrochemical reductions after 1.5 h. Analysis of the product mixture, after oxidation by chromic acid, by g.l.c. indicated the presence of pentan-2-one and acetylcyclopropane in the ratio 1 : 2; there was no peak corresponding to 3-methylhexan-3-ol.

A similar reduction of pentan-2-one (10^{-3} mol) gave only pentan-2-ol.

(ii) *Lithium*. Acetylcyclopropane (10^{-3} mol) was reduced during 1.5 h using lithium (10^{-2} g atom) in a solution of tetraethylammonium chloride (1.1×10^{-2} mol) in liquid ammonia (50 ml). Analysis of the product mixture, after oxidation, by g.l.c. showed only pentan-2-one and acetylcyclopropane.

(iii) *Potassium*. Potassium (2.5×10^{-3} g atom) was added to a solution of pentan-2-one (10^{-3} mol) in a 1M solution of tetraethylammonium chloride in liquid ammonia (25 ml), and a blue solution was formed. The blue colour disappeared after 30 min and a white suspension remained. The reaction mixture was worked up after 1 h and subsequent analysis by g.l.c. showed only pentan-2-one and pentan-2-ol.

Attempted Electrolytic Alkylation of Pentan-2-*one using Other Supporting Electrolytes*.—Pentan-2-one (10^{-3} mol) in a solution of the supporting electrolyte in liquid ammonia was reduced using a mercury pool cathode at constant current (100 mA) for 30 min (180 C; two electron reduction requires 193 C).

The supporting electrolytes which were investigated were tetramethylammonium fluoroborate, diethyldimethylammonium iodide, triethylmethylammonium iodide, tributylmethylammonium fluoroborate, ethyltripropylammonium fluoroborate, tributylethylammonium fluoroborate, and tetrapropylammonium fluoroborate. The concentration of supporting electrolyte used was 0.1M except in the cases of tetramethylammonium (*ca.* 0.02M), tributylmethylammonium (*ca.* 0.075M), and tetrapropylammonium fluoroborates (*ca.* 0.02M), which were used as saturated solutions. The iodides were avoided where possible due to the formation of the explosive nitrogen tri-iodide at the anode during electrolysis; when the iodides were used, the nitrogen tri-iodide was decomposed with an aqueous sodium sulphite solution.

Solvated electrons were observed beyond the cathodic limit in all cases except that of tetramethylammonium fluoroborate when only amalgam formation occurred. In this latter case, a platinum cathode was used instead of mercury. Tetrapropylammonium fluoroborate gave a slightly larger cathodic range (-2.0 V) at mercury than the other supporting electrolytes; a reduction wave for the ketones was observed just before the limit in this case.

In all cases except one, the supporting electrolytes exhibited similar behaviour to butyltrimethylammonium fluoroborate; the solvated electrons were rapidly destroyed and a grey solid was usually deposited on the mercury. Pentan-2-ol was the only reduction product in these cases. However, when tributylethylammonium fluoroborate was used the solvated electrons were more stable, although less so than in the tetraethylammonium case as shown by the length of time taken for a solution resulting from electrolysis at 100 mA for 5 min (in the absence of ketone) to decolorise. In this case the electrolysis solution and the mercury surface remained very clean during the reduction and a high yield of ethylated product (>80%) was obtained, but there was no evidence for butylation. A similar result was obtained on reduction of acetylcyclopropane.

The presence or absence of alkylated products in the above reductions was confirmed by synthesis of the authentic tertiary alcohols and g.l.c. analysis.

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[13] R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, 1967, **89**, 1404.