Hydrogen Bonding in Organic Synthesis.   Part 8.† Reactions of 2-Nitropropane in the Presence of Tetraethylammonium Fluoride.   The Interaction of the Nitro-group with Fluoride

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Fluoride ions are capable of encouraging the tautomerisation of 2-nitropropane by forming a strong hydrogen bond to the aci-hydroxy-proton.   Tetraethylammonium fluoride–2-nitropropane solvates are convenient sources of the 2-nitropropane anion as demonstrated by their efficient reactions with benzyl halides (to give aldehydes and C-alkylated nitropropanes), and Michael acceptors.   Prolonged exposure of 2-nitropropane to fluorides results in hydrolysis of the nitroalkane.   Explanations are suggested for the previously reported transformation of nitro-ketones in the presence of fluorides and for the reactions of potassium fluoride with highly acidic nitro-compounds.

REACTION systems containing both nitro-compounds and fluoride ions have provided some surprises in the past. Yoshikoshi reported that fluorides were capable of catalysing Michael additions to nitroalkenes which could not be carried out by using such a powerful base as sodium hydride.[1] Furthermore, he observed that, in the presence of fluoride ions, some of his nitro-dione Michael adducts were transformed to triones or to oxo-furans. Ostaszynski reported that potassium fluoride

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[1] T. Yanami, M. Kato, and A. Yoshikoshi, *J.C.S. Chem. Comm.*, 1975, 726.

underwent proton transfer with nitro-ketones and dinitro-compounds to form double salts.[2] Although these nitro-compounds are especially acidic, many of them have pK_a values no higher than those of simple carboxylic acids which do not undergo proton transfer with fluoride.[3-6]

Fluoride ions are perhaps the most powerful of H-bond electron donors and their ability to form strong hydrogen bonds has been demonstrated on several occasions.[3-7] Primary and secondary nitro-compounds in themselves, possess a site for H-bonding to fluoride (the hydrogen directly attached to the nitro-carbon) and through tautomerisation possess a particularly powerful H-bond electron acceptor site (the N-hydroxy-hydrogen). In view of this and because of the ability of fluoride ions to encourage the tautomerisation of other active methylene compounds,[8,9] we decided to investigate the interaction of the nitro-group with fluoride for 2-nitropropane. Some selected fluoride-assisted reactions of 2-nitro-propane have been looked at, where H-bond activation of the nitroalkane provides an interesting and often superior alternative to more conventional methods.

The Fluoride-assisted Tautomerisation of 2-Nitro-propane.—When an aqueous solution of tetraethyl-ammonium fluoride is evaporated in the presence of an
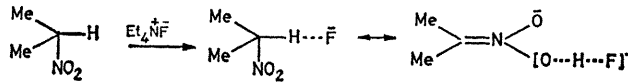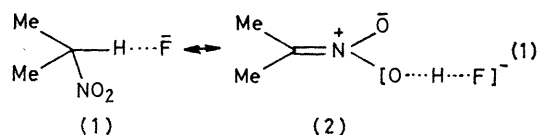

excess of 2-nitropropane, a viscous yellow liquid is produced which contains both 2-nitropropane and its *aci*-tautomer as shown by [1]H n.m.r. spectroscopy. Details of the [1]H n.m.r. spectrum of this system and of 2-nitropropane itself (for comparison purposes) are given in Table 1. The downfield shift in the CH reson-ance suggests H-bonding between fluoride and both 2-nitropropane tautomers [equation (1)]. The shift of the single methyl resonance of (2) compares favourably with that observed (1.90 p.p.m.) for the *aci*-anion of 2-nitropropane.[10] The relative amounts of (1) and (2) depend on the concentration of fluoride. For example, for a fluoride : 2-nitropropane mole ratio of *ca.* 3 : 1 (dimethylformamide solution), the equilibrium at room temperature lies almost entirely in favour of (2), whereas a solution containing a 1 : 2 mole ratio shows only *ca.* 20% of (2) under the same conditions. It should be pointed out, however, that traces of water, which in-evitably are present in these solutions, must effect the actual amount of available fluoride.

Details of the i.r. spectrum of a solution of tetraethyl-ammonium fluoride and 2-nitropropane containing

[2] A. Ostaszynski, J. Wielgat, and T. Urbanski, *Tetrahedron*, 1969, **25**, 1929.
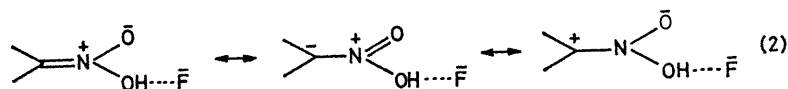[3] J. H. Clark and J. Emsley, *J.C.S. Dalton*, 1973, 2154.
[4] J. H. Clark and J. Emsley, *J.C.S. Dalton*, 1974, 1125.
[5] J. H. Clark and J. M. Miller, *J. Amer. Chem. Soc.*, 1977, **99**, 498.
[6] J. Emsley and O. P. A. Hoyte, *J.C.S. Dalton*, 1976, 2219.

mostly (2) are given in Table 2. The band at $1\,550$ cm^{-1} is almost certainly due to asymmetric stretching of the nitro-group in (1), its intensity being considerably lower than that in 2-nitropropane. The sharp band at $1\,500$

TABLE 1

The effect of added fluoride on the [1]H n.m.r. of 2-nitro-propane *

δ(Me) 1.56 (doublet)	1.55 (doublet)	1.88 (singlet)
δ(CH) 4.71 (multiplet)	4.86 (multiplet)	
δ(OH)		*ca.* 6.4? (singlet, broad)

* DMF solution.

cm^{-1} is tentatively assigned to C=N stretching in (2). Although the C=N band in oximes and imines occurs in the $1\,680$—$1\,620$ cm^{-1} range, its position in (2) is not unreasonable when one considers the suggested overall range of C=N stretching frequencies, $1\,680$—$1\,510$ cm^{-1}.[11]

TABLE 2

I.r. spectra (600—4 000 cm^{-1})

2-Nitro-propane in DMF solution.^{a} (liquid film)	2-Nitro-propane with excess Et$_4$NF in DMF solution ^{a} (liquid film)	2-Nitro-propane *aci*-anion ^{b}	Assignment
3 600—2 600s, br			OH stretch $\bar{\text{F}} \cdots$ HOH and $\bar{\text{F}} \cdots$ HO$_2$N=CMe$_2$ (?)
3 015s			⎱CH$_3$ and CH
2 960ms			⎰stretch
2 920m			
		1 605s	ν_s(C=N)?
1 550vs	1 550m		ν_s(NO$_2$)asym.
	1 500m		ν_s(C=N)?
1 470ms	1 470w		ν_b(CH$_3$)asym.
1 455 (sh)			
1 405ms	1 410m		
1 380m	1 380w		⎱ν_b(CH$_3$)sym.
1 365ms			⎰
1 320m	1 250w	1 295s	ν_s(NO$_2$)sym.
	1 180s	1 168vs	ν_s(NO$_2$)asym.
1 180w			
1 145w		1 153vs	
1 110s		1 070m	
		943m	
860w			ν_s(C–N)

^{a} Bands due to DMF have been eliminated. ^{b} Ref. 11.

The lower frequency could be explained in terms of nitrogen attaining greater polar character as a result of resonance of the type illustrated below [equation (2)]. The bands at $1\,250$ and $1\,180$ cm^{-1} are tentatively

[7] J. S. Martin and F. Y. Fujiwara, *Canad. J. Chem.*, 1971, **49**, 3071.
[8] J. H. Clark and J. M. Miller, *J.C.S. Chem. Comm.*, 1977, 64.
[9] J. H. Clark and J. M. Miller, *J.C.S. Perkin I*, 1977, 1743.
[10] A. A. Griswald and P. S. Starcher, *J. Org. Chem.*, 1965, **30**, 1687.
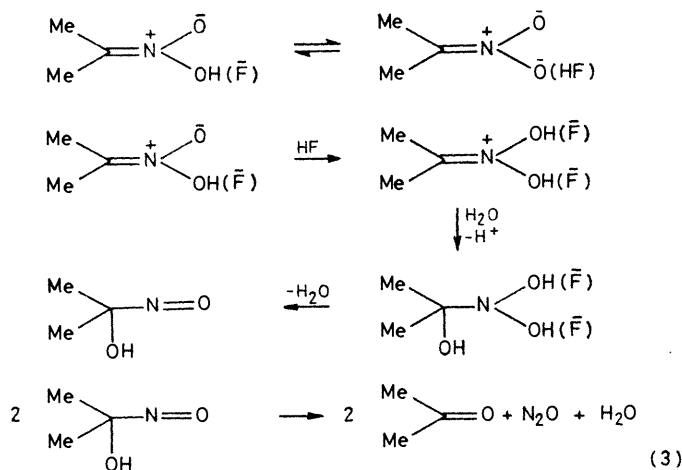[11] H. Feuer, C. Savides, and C. N. R. Rao, *Spectrochimica Acta*, 1963, **19**, 431.

assigned to the symmetric and asymmetric NO_2 stretching vibrations, these values falling close to those assigned to the same vibrations in the 2-nitropropane *aci*-anion (1 295 and 1 168 cm^{-1} respectively).[11] Bands due to HF_2^- which would occur had a significant amount of proton transfer taken place in the solution, are not readily apparent in our spectrum.

Fluoride-assisted Hydrolysis of 2-Nitropropane.—On refluxing a solution of tetraethylammonium fluoride (hydrated) in an excess of 2-nitropropane over a long period, some 90% of the 2-nitropropane decomposed

studied the interaction of KF with a series of strong organic acids and concluded that the double potassium salts are formed by compound with pK_a values less than 7. A number of reports since then, however, have shown that no such decomposition occurs in a variety of fluoride–carboxylic acid systems [3-6] where the acids have pK_a values of less than 7. We suggest that the proton transfer observed in fluoride–nitro-compound systems is primarily a feature of the nitro-group. The *aci*-form of a nitro-compound, the formation of which is encouraged by the presence of fluoride ions, is a powerful

$$\text{(2)}$$

to acetone, with a corresponding increase in the amount of water in the system. Aqueous tetrabutylammonium fluoride and caesium fluoride (run in the presence of a small amount of dibenzo-18-crown-6 to assist solubilization) were also found to catalyse this decomposition.

The transformation of primary or secondary nitro-compounds to aldehydes or ketones is known as the Nef
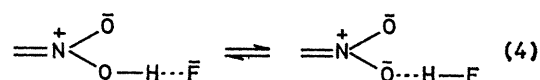
H-bond electron acceptor, that is, a very strong H-bonding acid.

On H-bonding to fluoride, there will be a tendency to undergo proton transfer because the acidity of the electron acceptor (the *aci*-form of 2-nitropropane) is probably comparable to that of the electron donor-H (FH) in this system. The interesting feature of fluoride systems is that despite the surprisingly low acidity of HF in water, HF is generally a very strong acid and most organic compounds are weaker acids than HF. As a result, fluoride can H-bond to a wide variety of protic organic compounds without significant amounts of proton transfer occurring. Where the organic is especially acidic such as for nitro-ketones and di-nitroalkanes, proton transfer with $\bar{F}$ may be close to 100% whereas for the less acidic mononitroalkanes it may only be a partial process [equation (4)]. Should the nitro-group be capable of enhancing the formation of HF in systems containing fluoride ions, it may be capable of doing so by other than a fluoride-assisted tautomerisation mechanism. In order to test this hypothesis we turned our attention to a tertiary nitro-compound which cannot form an *aci*-tautomer. An aqueous dimethylformamide (or dioxan) solution of tetrabutylammonium fluoride was evaporated in the

$$\text{(3)}$$

reaction.[12] It is difficult to envisage a mechanism for the decomposition of 2-nitropropane to acetone in our systems without involving an acid-catalysed hydrolysis of the *aci*-tautomer. It becomes necessary, therefore, to explain the acidic properties of our systems and to do this we should reconsider the H-bond formed between fluoride and the *aci*-form of 2-nitropropane. We suggest that partial proton transfer occurs *via* the H-bond leading to the formation of small amounts of HF which should be capable of behaving as the required acid catalyst in the manner outlined below [equation (3)].

The generation of HF in systems containing fluoride ions and a nitro-compound is not without precedent. Ostaszynski *et al.* found that ethyl nitroacetate, nitro-ketones with a CH_2NO_2 group, and *gem*-dinitroalkanes react with potassium fluoride to form double salts composed of KHF_2 and the nitro-compound.[2] The authors

$$\text{(4)}$$

presence of nitrobenzene. After a short while, the solution became deep blue in colour and, on separation, the fluoride was found to have decomposed, almost entirely, to tributylamine and tetrabutylammonium hydrogen bifluoride, the nitrobenzene being recovered unchanged. The significant enhancement in the rate of decomposition of the fluoride in the presence of nitro-benzene suggests that the latter is acting as a base by removing HF from the fluoride. The basicity of the nitro-group has been established in a series of articles.[13-15] We may be forming a complex such as (3) stabilised by
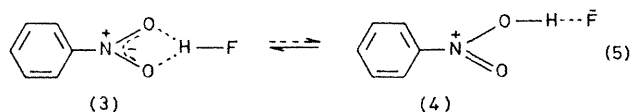
[12] W. E. Noland, *Chem. Rev.*, 1955, **55**, 137.
[13] J. C. D. Brand, *J. Chem. Soc.*, 1950, 997.

[14] J. C. D. Brand, W. C. Homing, and M. B. Thomley, *J. Chem. Soc.*, 1952, 1374.
[15] R. J. Gillespie and C. Solomons, *J. Chem. Soc.*, 1957, **1796**.

H-bonding, in our systems. The very high acidity of protonated nitrobenzene will mean that the equilibrium [equation (5)] should lie almost entirely in favour of (3).

This is supported by ^{1}H n.m.r. spectroscopy which does not show any peaks characteristic of protonated nitro-benzene [15] but there is a marked downfield shift (ca. 0.1 p.p.m.) in the position of the meta and para ring hydrogens suggesting a small change in the electron

out under rigorously anhydrous conditions, nitro-trans-formations may not have occurred at all.

Reactions of Benzyl Halides with 2-Nitropropane in the Presence of Tetraethylammonium Fluoride (TEAF).— Alkylation of the salts of nitro-compounds usually occurs as oxygen-alkylation producing an unstable nitronic ester which breaks down into an oxime and a carbonyl compound and may, in fact, serve as a means of preparing aldehydes and ketones.[17,18] There are instances, however, when carbon-alkylation results, particularly when o- and p-nitrobenzyl chloride is used as the alkylating agent.[19,20] The remarkable depend-ence of such alkylations on the alkylating agent and

density of the ring in the H-bond electron donor on bonding to HF as might be expected. The u.v. spectrum of a solution of nitrobenzene in chloroform containing tetrabutylammonium hydrogen bifluoride appears to show a weak broad band centred between the major absorption band of nitrobenzene (270 nm) and that of protonated nitrobenzene (365 nm),[13] which is not un-reasonable for a species such as (3). The intensity of this bond is highly dependent on the concentration of the bifluoride.*
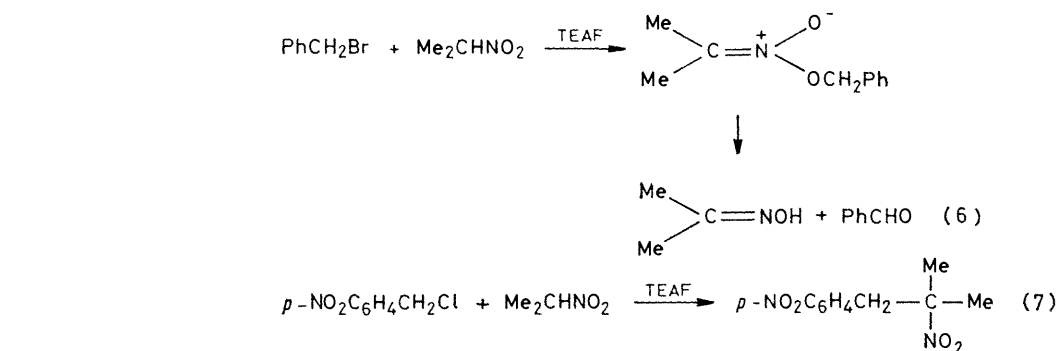
A further example of the interaction of nitro-groups with fluoride is found in the interesting and important transformation of Michael adducts, formed by the fluoride-catalysed reaction of cyclohexane-1,3-diones with nitroalkenes, to triones and to oxofurans on pro-longed treatment with KF–xylene, reported recently by Yoshikoshi.[1] We suggest that these transformations may be explained by a mechanism similar to that proposed here [equation (3)]. Ring-closure to oxo-furans is comparable to the previously reported fluoride-catalysed cyclisation of diones.[16] It is of interest to note that the water produced in the aldol condensation stage is necessary for the hydrolysis of the aci-nitro-intermediate; when no ring closure could occur, the formation of the trione product required a considerably longer period of time [1] and had the reaction been carried

also on the leaving group [21] has been the subject of much attention in the literature.[22,23]

Reaction of the tetraethylammonium fluoride–2-nitro-propane monosolvate (see Experimental section) with benzyl halides ($PhCH_2X$ and Ph_2CHX, X = Cl, Br, or I; PhCH=CHCH$_2$Cl and m-NO$_2$C$_6$H$_4$CH$_2$Cl) over mole-cular sieves, occurs smoothly and efficiently to produce carbonyl compounds, C-alkylated 2-nitropropanes (with p-NO$_2$C$_6$H$_4$CH$_2$Cl), or mixtures of both (with p-NO$_2$C$_6$H$_4$-CH$_2$X, X = Br or I; and o-NO$_2$C$_6$H$_4$CH$_2$Cl). Equations (6) and (7) illustrate the formation of carbonyl com-pounds and C-alkylated products for benzyl bromide and p-nitrobenzyl chloride. Advantages over the con-ventional process involving the lithium or sodium salts of 2-nitropropane include brevity and operational simplicity. Reactions employing the metal salts of 2-nitropropane may require a lengthy and tedious initial preparation of the salt.[21] The reactions we attempted are summarised in Table 3.

It is interesting to note that where mixtures of C-alkylated product and carbonyl compound occur, the proportion of the former would seem to be somewhat higher in our system than in those involving 2-nitro-propane salts, especially in the case of o-nitrobenzyl chloride. This is in agreement with the previously reported alkylations of β-dicarbonyl compounds using

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* The concentration of available HF is dependent on the degree of dissociation of the bifluoride which is dependent on the concentration of bifluoride.

[16] J. H. Clark and J. M. Miller, *J.C.S. Perkin I*, 1977, 2063.
[17] S. V. Lieberman, *J. Amer. Chem. Soc.*, 1955, **77**, 1114.
[18] H. B. Hass and M. L. Bender, *Org. Synth.*, 1950, **30**, 99.
[19] L. Weister and R. W. Halmkamp, *J. Amer. Chem. Soc.*, 1945, **67**, 1167.

[20] H. B. Hass and M. L. Bender, *J. Amer. Chem. Soc.*, 1949, **71**, 1767, 3482.
[21] N. Kornblum and P. Pink, *Tetrahedron*, 1963, **19**, 17.
[22] N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *J. Amer. Chem. Soc.*, 1967, **89**, 725.
[23] R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, 1964, **86**, 3904.

TEAF and alkyl iodides where O-alkylation was effectively inhibited.[8,9] This tendency to produce the C-alkylated product is probably a result of shielding of the oxygen in the ambient nucleophile by the H-bonded fluoride and possibly by additional shielding by the large cation.

Michael Additions of Fluoride-activated 2-Nitropropane. —A number of Michael additions have been shown to be accelerated by the presence of fluoride ions [1,2,24—29] although there are relatively few examples employing tetra-alkylammonium fluorides as catalysts [25,26] and

TABLE 3

Nature of reaction of YC_6H_4–$CH(Z)X$ with 2-nitropropane in the presence of tetraethylammonium fluoride [a]

Y	Z	X	Reaction conditions	O-Alkylation, (%)	C-Alkylation, (%)
H	H	Cl	Reflux/4 h	75	0
H	H	Br	RT */10 min	85	0
H	H	I	RT/10 min	90	0
H	Ph	Cl	Reflux/1 h	72	0
H	Ph	Br	RT/10 min	87	0
H	Ph	I	RT/10 min	82	0
p-NO$_2$	H	Cl [b,c]	RT/20 h	0	75
p-NO$_2$	H	Br [c]	RT/4 h	65	24
p-NO$_2$	H	I [c]	RT/<1 h	85 [d]	10
o-NO$_2$	H	Cl [b]	RT/12 h	15 [d]	82
m-NO$_2$	H	Cl [b]	RT/24 h	73 [d]	0

* RT = room temp.

[a] All yields refer to pure products isolated except for the runs employing the p-nitrobromide and iodide; here the yields are by [1]H n.m.r. and are *ca.* 5—15% higher than the yields of pure p-nitrobenzaldehyde and 2-methyl-2-nitro-1-(p-nitrophenyl)propane isolated. [b] Using the sodium salt of 2-nitropropane in an excess of 2-nitropropane the following product yields were recorded: p-NO$_2$, 83% C-alkylated, 1% aldehyde (1 h/80 °C); o-NO$_2$, 46% C-alkylated, 30% aldehyde (18 h/25 °C); m-NO$_2$, 73% aldehyde (15 min/80 °C) (H. B. Hass and M. L. Bender, *J. Amer. Chem. Soc.*, 1949, 71, 3482). [c] Using the lithium salt of 2-nitropropane in DMF the following product yields were recorded: chloride, 95% C-alkylated, 1% aldehyde (20 h/−16 °C); bromide, 16% C-alkylated, 50% aldehyde (4 h/−19 °C); iodide, 7% C-alkylated, 67% aldehyde (2 h/−18 °C).[22] [d] Present as the free aldehyde and as the condensation product with 2-nitropropane.[12] The 2-methyl-2-nitro-1-(nitrophenyl)propanol products could be quantitatively reconverted to the aldehydes by short treatment with base.

none involving 2-nitropropane in the presence of tetraethylammonium fluoride.

We have investigated the Michael additions of fluoride-activated 2-nitropropane with four common Michael acceptors. The reactions that have been attempted here are summarised in Table 4 where they are compared to literature examples of the same additions using other bases. It is noteworthy that tetraethylammonium fluoride proves to be an effective catalyst in a variety of solvents when it has been previously reported [2,28,29] that fluoride ion is only effective in polar solvents such as ethanol and reaction in tetrahydrofuran or dioxan does not occur. Although alkali metal and tetra-alkyl-

ammonium fluorides are usually more soluble in protic than in aprotic solvents because of H-bonding, tetra-alkylammonium fluorides are usually soluble in aprotic solvents (especially dimethylformamide) when the solvent contains a quantitative amount of an H-bond electron acceptor and even such weak Michael donors as thiols [26] fall into this class.

EXPERIMENTAL

Instrumentation.—The [1]H n.m.r. spectra were recorded on a Varian A-60 (60 MHz) spectrometer (SiMe$_4$ standard). I.r. spectra were recorded on Perkin-Elmer 237B or Perkin-Elmer 225 spectrometers. Mass spectra were obtained on an A.E.I. MS-30 double-beam mass spectrometer using both the direct probe and interfaced (Watson–Bieman) GC as inlets. U.v. spectra were recorded on a Hitachi–Perkin-Elmer–Coleman 124 double-beam spectrometer using 1-cm path-length quartz cells. A deuterium lamp was used as the source of u.v. light.

Materials.—Tetraethyl- and tetrabutyl-ammonium fluorides were prepared in aqueous solution by neutralisation of the hydroxides (commercial samples in aqueous solution) with 52% hydrofluoric acid. Caesium fluoride was a commercial sample dried at 100 °C *in vacuo* for several hours. Tetraethylammonium fluoride–2-nitropropane monosolvate was prepared by first evaporating an aqueous solution of the fluoride (<80 °C/reduced pressure) to a solid hydrate followed by treatment of the solid with a large excess of the 2-nitropropane and evaporation, with shaking, of the resulting yellow solution under the same conditions, until the [1]H n.m.r. showed a fluoride : 2-nitropropane mole ratio of 1 : 1. Tetrabutylammonium hydrogen bifluoride was prepared by the method of Martin and Fujiwara.[30]

The following benzyl iodides were prepared by reaction of the respective chlorides with NaI in acetone at room temperature in several hours and were isolated in 80—90% yields; benzyl iodide, m.p. 23 °C (lit.,[31] 24.5 °C); diphenyl-iodomethane, m.p. 72 °C; and p-nitrobenzyl iodide, m.p. 125—127 °C (lit.,[21] 127—128 °C). Benzyl bromide, b.p. 198 °C at 760 mmHg (lit.,[31] 201 °C at 760 mmHg), was prepared in 80% yield by refluxing the chloride in an excess of 48% hydrobromic acid for several hours.

2-Nitropropane, NN-dimethylformamide (DMF), tetrahydrofuran, dioxan, and chloroform were commercial samples and were dried over molecular sieves before use. Other materials were commercial samples used as obtained.

Hydrolysis of 2-Nitropropane.—Aqueous tetraethylammonium fluoride (0.01 mol. equiv) was reduced, by brief evaporation, to a solid hydrate and dissolved in an excess of 2-nitropropane (*ca.* 0.05 mol. equiv.). The resulting yellow solution was refluxed, with stirring, over molecular sieves for 16 h at the end of which time sampling and [1]H n.m.r. analysis showed some 90% conversion of the 2-nitropropane into acetone with a large increase in the intensity of the H$_2$O peak. Separation of the mixture confirmed the presence of acetone (m/e 58) and unchanged 2-nitropropane (m/e 89).

The same solution, when set aside for 16 h at room

[24] E. LeGoff, *J. Amer. Chem. Soc.*, 1962, 84, 3975.

[25] S. Hoz, M. Albeck, and Z. Rappoport, *Synthesis*, 1975, 162·

[26] I. Kuwajima, T. Murafushi, and E. Nakamura, *Synthesis*, 1976, 602.

[27] I. Belsky, *J.C.S. Chem. Comm.*, 1977, 237.

[28] S. Kambe and H. Yasuda, *Bull. Chem. Soc. Japan*, 1966, 39, 2549.

[29] J. M. Patterson and M. W. Barnes, *Bull. Chem. Soc. Japan*, 1969, 40, 2715.

[30] J. S. Martin and F. Y. Fujiwara, *Canad. J. Chem.*, 1971, 49, 3071.

[31] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, Chemical Rubber Company, Ohio, 1976, 57th edn.

temperature showed, by ^{1}H n.m.r. analysis, somewhat less than 10% conversion into acetone, as did a solution containing tetrabutylammonium fluoride instead of the tetraethyl salt.

A mixture of CsF (0.01 mol. equiv.), 2-nitropropane (5 ml), dibenzo-18-crown-6 (100 mg), and a trace of water (ca. 0.005 mol. equiv.) when set aside at room temperature for 48 h showed some 2% conversion into acetone.

Reaction of Nitrobenzene with Tetrabutylammonium Fluoride.—An aqueous solution of tetrabutylammonium fluoride (0.01 mol. equiv.) was briefly concentrated on a water-bath at 80—90 °C under reduced pressure. Nitrobenzene (0.01 mol. equiv.) in DMF (10 ml) was added to the solution which was then evaporated until no further

given in Table 3: benzaldehyde (m/e 106), benzophenone (m/e 182), 2-methyl-2-nitro-1-(p-nitrophenyl)propane, m.p. 66 °C (lit.,[32] 65—66 °C), p-nitrobenzaldehyde, m.p. 103—104 °C (lit.,[31] 106 °C), o-nitrobenzaldehyde, m.p. 41—43 °C (lit.,[31] 43.5—44 °C), m-nitrobenzaldehyde, m.p. 56 °C (lit.,[31] 58 °C), and 2-methyl-2-nitro-1-(o-nitrophenyl)propane, m.p. 56 °C (lit.,[20] 54—55 °C).

The following experimental procedure illustrates the reaction of benzyl halides with 2-nitropropane in the presence of tetraethylammonium fluoride for the specific case of benzyl bromide.

Preparation of Benzaldehyde from Benzyl Bromide.—Tetraethylammonium fluoride–2-nitropropane solvate (0.02 mol. equiv.) was dissolved in an excess of 2-nitropropane

TABLE 4

Michael additions of 2-nitropropane

Tetraethylammonium fluoride catalysis ^{a}

Acceptor	Reaction conditions time (h)/ temp. (°C)	% Yield	Alternate method Catalyst/time (h)/temp. (°C)/ yield (%)	Product ^{b}
CH$_2$=CHCOMe	2/25 ^{c}	95	Triton B/15+/?/69 ^{f}	Me$_2$C(NO$_2$)(CH$_2$)$_2$COMe ^{j}
CH$_2$=CHCO$_2$Me	2/25 ^{d}	78	Basic anionite resin /9/60/ca. 80 ^{g}	Me$_2$C(NO$_2$)(CH$_2$)$_2$CO$_2$Me ^{k}
CH$_2$=CHCO$_2$Et	2/25 ^{e}	79	Bu$_3$P/1.5/25/82 ^{h}	Me$_2$C(NO$_2$)(CH$_2$)$_2$CO$_2$Et ^{l}
PhCH=CHCOPh	4/25 ^{d}	84	CaH$_2$/24/25/85+ ^{i}	Me$_2$C(NO$_2$)CH(Ph)CH$_2$COPh ^{m}

^{a} Donor : acceptor : fluoride mole ratio, usually 1 : 1 : $\frac{1}{2}$. ^{b} Yields of crude isolated product are given. ^{c} THF solvent. ^{d} DMF solvent. ^{e} CHCl$_3$ solvent. ^{f} H. Scheckler, D. L. Ley, and L. Zeldin, *J. Amer. Chem. Soc.*, 1952, **74**, 3664. ^{g} V. I. Isagulyants and E.L. Markosyan, *Doklady Akad. Nauk Arm. S.S.R.*, 1965, **41**, 221 (*Chem. Abs.*, 1962, **64**, 12542). ^{h} D. A. White and M. M. Baizer, *Tetrahedron Letters*, 1973, 3597. ^{i} N. Fishman and S. Zuffanti, *J. Amer. Chem. Soc.*, 1951, **73**, 4466. ^{j} $n_{\rm D}^{22}$ 1.4437 [lit. 1.4444 (20.6 °C)—note f]. ^{k} $n_{\rm D}^{22}$ 1.4401 [lit. 1.4414 (20 °C)—note g]. ^{l} $n_{\rm D}^{23}$ 1.4395 [lit. 1.4383 (25 °C)—U.S. 2,390,918; *Chem. Abs.*, 1946, **40**, 2456]. ^{m} m.p. 149 °C (lit. 146 °C—note i).

ebullition occurred at which time the solution was deep blue in colour.* The cooled viscous liquid was extracted with ether, washed with water ($\times$ 3) to remove the DMF, dried (MgSO$_4$), and evaporated. The residue was shown by ^{1}H n.m.r. analysis and gas chromotography–mass spectrometry to contain nitrobenzene (m/e 123) and tri-n-butylamine (m/e 185). Analysis of the insoluble residue from ether extraction showed mostly tetrabutylammonium hydrogen bifluoride ($\nu_{\rm max.}$ at 2 040, 1 830, 1 460, and 1 230 $\pm$ 5 cm^{-1}).

Reactions of Benzyl Halides with 2-Nitropropane (Table 3).—All reactions were accomplished using the tetraethylammonium fluoride–2-nitropropane solvate and treatment of this solvate with benzyl halide in an excess of 2-nitropropane over 5 Å molecular sieves. Reaction conditions for each run are given in Table 3. The products were generally isolated by standard work-up procedures and were purified by distillation or recrystallisation (as appropriate). Where more than one product was found, the C-alkylated and aldehyde products were separated by column chromatography (basica alumina and benzene).[21] Nitrobenzaldehydes were generally recovered as a mixture of the aldehyde and the condensation product with 2-nitropropane.[21] The 2-methyl-2-nitro-1-(nitrophenyl)propanol products could be quantitatively reconverted into the aldehydes by short treatment with base with little loss in yield. All products were characterised by ^{1}H n.m.r. and mass spectroscopy and had b.p.s or m.p.s consistent with those reported in the literature. The following products were isolated, in yields

* Comparison of the ^{1}H n.m.r. spectrum of this mixture to that of pure nitrobenzene in DMF showed a downfield shift of the *meta* and *para* protons of the former (δ 7.75; Δ ca. 0.1 p.p.m.), the rest of the spectrum being the same.

(10 g) and the solution was stirred at room temperature over molecular sieves. Addition of benzyl bromide (0.01 mol. equiv.) over a 10-minute period provided an exothermic reaction and rapid precipitation of tetraethylammonium bromide. The resulting mixture was diluted with ether, filtered, and the filtrate evaporated. The excess of 2-nitropropane was removed by brief treatment with cold, dilute aqueous sodium hydroxide giving, on separation, benzaldehyde (0.008 5 mol. equiv., 85% recovered).

Reactions of 2-Nitropropane with Michael Acceptors (Table 4).—All reactions were accomplished by stirring the solid hydrate of tetraethylammonium fluoride (prepared by brief evaporation of an aqueous solution) with 2-nitropropane and the Michael acceptor, in the mole ratio 1 : 2 : 2 (10% excess of the acceptor in the case of methyl vinyl ketone), over molecular sieves in DMF, tetrahydrofuran, or CHCl$_3$ (see Table 4) at room temperature. Reactions were monitored by ^{1}H n.m.r. analysis and were stopped on completion (2—4 h). The methods of separation were virtually the same in each case. The mixtures were extracted with ether, the extracts dried (MgSO$_4$) [after aqueous washing ($\times$ 3) of the ether solution for the DMF runs] and evaporated. The products were purified by recrystallisation (for solids) or by column chromatography (silica) and gave ^{1}H n.m.r. and mass spectra consistent with their structure and m.p.s (or refractive indices) consistent with those reported in the literature (Table 4).

^{32} H. B. Bass, E. J. Berry, and M. L. Bender, *J. Amer. Chem. Soc.*, 1949, **71**, 2290.