Hydrogen Bonding in Organic Synthesis. Part 7.† Intermolecular Self-condensation of Some Enolisable Ketones in the Presence of Fluoride

By **James H. Clark** and **Jack M. Miller,*** Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1

A number of enolisable ketones undergo intermolecular self-condensation and cyclisation in the presence of fluoride. Fluoride encourages the enolisation of ketones, thereby providing an hydroxylic electron-acceptor site capable of forming strong H-bonds with the fluoride anion. The reactions of the H-bond-activated ketones are usually characteristic of enolate anions: aldol-type condensations and Michael reactions are observed.

RECENT investigations of hydrogen-bond-assisted reactions have shown that the use of fluorides can provide fast and efficient routes to a number of organic condensation products.[1-6] Fluoride anion acts as an electron source in H-bonds with a wide variety of protic organic compounds. The resulting anionic solvates can behave as a source of highly reactive organic nucleophiles under essentially neutral conditions.[2] Hydrogen bonds between fluoride anion and a number of hydroxylic organic compounds are particularly strong,[2,7] and we decided to investigate the possibility of strong H-bonding between fluoride and the enol forms of some enolisable ketones. It soon became apparent that many of these systems afforded self-condensation products by H-bond-assisted enolisation and dehydration.

Self-condensation of β-Diketones.—Few examples of the self-condensation of β-diketones are known. Heptane-2,4,6-trione self-condenses under carefully controlled conditions, in a reaction that is pH-sensitive.[8] Heikel has reported that pentane-2,4-dione gives some self-condensation product on refluxing for a long period with aqueous hydroxide.[9] He suggested that the product

† Part 6, ref. 13.

[1] J. H. Clark and J. M. Miller, *J.C.S. Chem. Comm.*, 1976, 229.

[2] J. H. Clark and J. M. Miller, *J. Amer. Chem. Soc.*, 1977, **99**, 498.

[3] J. H. Clark and J. M. Miller, *J.C.S. Chem. Comm.*, 1977, 64.

[4] J. H. Clark, H. L. Holland, and J. M. Miller, *Tetrahedron Letters*, 1976, 3361.

[5] J. H. Clark and J. M. Miller, *Tetrahedron Letters*, 1977, 599.

[6] J. H. Clark and J. Emsley, *J.C.S. Dalton*, 1975, 2129.

[7] J. H. Clark and J. Emsley, *J.C.S. Dalton*, 1973, 2154; 1974, 1127.

[8] J. R. Bethell and P. Maitland, *J. Chem. Soc.*, 1962, 3751.

[9] A. Heikel, *Suomen Kem.*, 1935, **8B**, 33 (*Chem. Abs.*, 1936, **30**, 438).

might be 2'-hydroxy-4',6'-dimethylacetophenone; however, Blaise obtained no self-condensation product on treating pentane-2,4-dione with base.[10] Attempts to effect the self-condensation of other β-diketones have failed.[11]

Pentane-2,4-dione is converted from 80% enol (in the pure liquid) to 100% enol on shaking with potassium fluoride–dimethylformamide (KF–DMF) at room temperature. The enolisation is accompanied by considerable broadening of the enolic CH peak in the ¹H n.m.r. spectrum. In the presence of KF alone, the ¹H n.m.r. spectrum shows pentane-2,4-dione as $86(\pm2)\%$ enol, whereas the presence of DMF alone appears to reduce the proportion of enol. This suggests that DMF is essential to the fluoride-assisted enolisation of the diketone, which may be a result of the small but significant

i.r. spectra for the existence of HF either in the solvate or in solutions of any of the fluorides in pentane-2,4-dione or in pentane-2,4-dione–DMF, which rules out the possibility of proton transfer.

On refluxing the KF–DMF–pentane-2,4-dione mixture, the β-diketone undergoes quantitative intermolecular self-condensation to produce 2'-hydroxy-4',6'-dimethylacetophenone. 1-Phenylpentane-2,4-dione was also converted entirely into the enol form on treatment with KF–DMF and underwent subsequent intermolecular self-condensation on refluxing to provide 4'-benzyl-2'-hydroxy-6'-methyl-3'-phenylacetophenone.

The acetophenones presumably arise from initial aldol condensation and dehydration, followed by intramolecular ring closure with elimination of a second molecule of water. For pentane-2,4-dione, ring closure may occur at
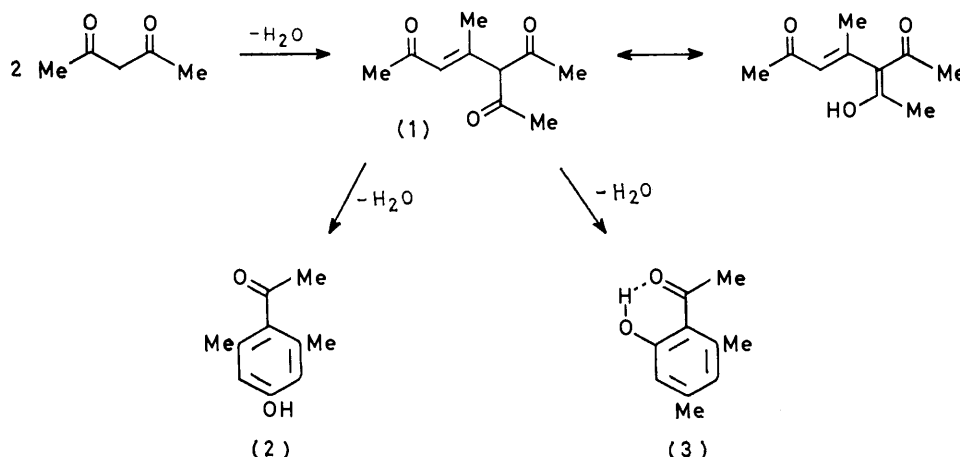
SCHEME 1

solubility of KF in DMF, although the ability of DMF to provide a more ' reactive ' fluoride anion by cation solvation cannot be discounted. It appeared that studies with the soluble tetra-alkylammonium fluorides might provide a clearer picture of the interaction of the fluoride anion with pentane-2,4-dione.

The stable, non-hygroscopic, crystalline monosolvate $Bu^n_4N^+[F \cdots HO\cdot CMe\dot{:}CH\cdot COMe]^-$ may be prepared readily by evaporating to dryness an aqueous solution of the fluoride in the presence of an excess of pentane-2,4-dione. The ¹⁹F n.m.r. spectrum of this solvate shows a doublet (J 2.27 Hz) at -50 °C in $CDCl_3$ solution, similar to that observed for the very strongly H-bonded hydrogendifluoride anion;[12] the ¹H n.m.r. spectrum shows that the β-diketone is totally enolised and the ¹³C n.m.r. spectrum shows the enolic olefinic carbon signals $ca.$ 20 p.p.m. upfield relative to pure pentane-2,4-dione.* All these observations are consistent with strong H-bonding between the fluoride anion and the enol hydroxylic proton. There is no evidence from ¹H or ¹⁹F n.m.r. or

two different positions, leading to two possible isomers (Scheme 1), whereas for 1-phenylpentane-2,4-dione the initial intermolecular condensation may occur in two different ways (condensation at MeCO or at $PhCH_2CO$), and each of the two possible intermediates (4) and (5) may cyclise in four different ways (Scheme 2).

The self-condensation of pentane-2,4-dione gives exclusively the 2'-hydroxy-isomer (3). If we assume that the ring closure occurs by attack of $^-CO\cdot CH_2^-$ on the most distant carbonyl group followed by reprotonation and elimination of water (as, for example, in the Robinson cyclisation of hexane-2,5-dione[14]) there seem to be three reasons for the formation of (3) only. First, of the three possible positions at which proton abstraction to form $^-CO\cdot CH_2^-$ can occur, two will result in the compound (3). Secondly, the enol tautomer of (1) (the formation of which should be encouraged by the presence of fluoride) is capable of stabilising the carbanion $=C(OH)\cdot CH_2^-$ by delocalisation onto two carbonyl groups. Finally, the formation of (3) should be encouraged by the production of a six-membered chelate ring by intramolecular H-

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* Details of the preparation and properties of this solvate are given elsewhere.[13]

[10] E. E. Blaise, Compt. rend., 1914, **158**, 708.

[11] W. J. Houlihan and A. T. Nielsen, Org. Reactions, 1968, **16**, 1.

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

[13] J. H. Clark and J. M. Miller, J.C.S. Perkin I, 1977, 1743.

[14] R. M. Acheson and R. Robinson, J. Chem. Soc., 1952, 1127.

bonding between the carbonyl and the 2'-hydroxy-group.

In the case of 1-phenylpentane-2,4-dione, the picture

orientation in structure (6), especially when one compares the ¹H n.m.r. spectrum with that of compound (3) (see Table). Secondly, the ¹H n.m.r. spectrum shows the
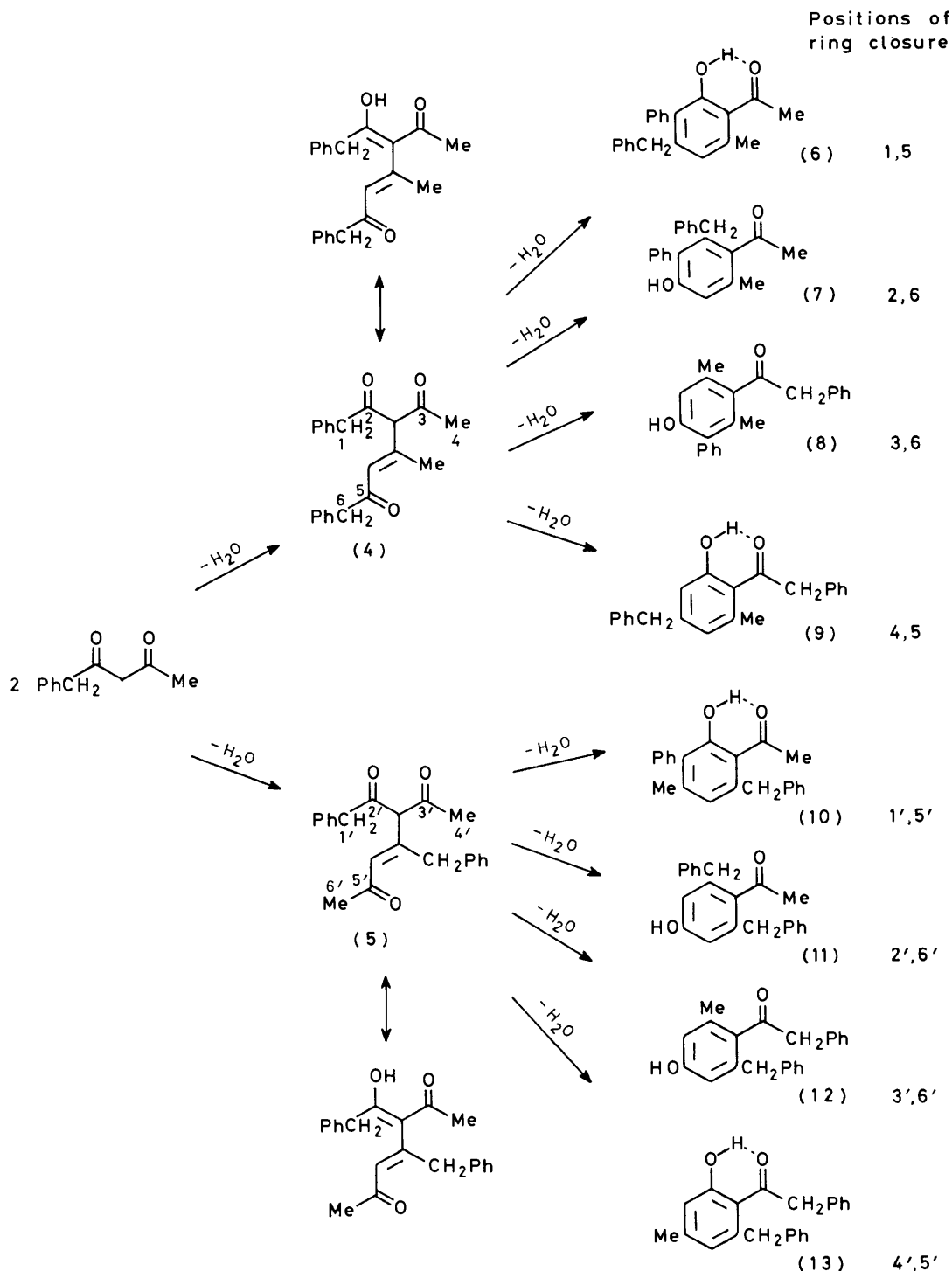
SCHEME 2
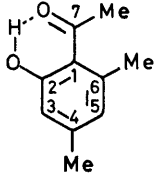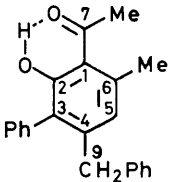
is more complex. The evidence in favour of (6) being the sole product is as follows. First, there are two methyl signals in the ¹H n.m.r. spectrum, and their position and the changes induced by a shift reagent point towards the

presence of one benzylic methylene and two phenyl groups. We can now rule out structures (9)—(13) and possibly (8). Thirdly, the relatively small change in the position of the one CH signal on adding shift reagent

suggests that this proton is not adjacent to an hydroxy-group. Finally, the low-field position of the hydroxy-signal, closely similar to that of the OH in (3), together with the observed low concentration dependence, strongly suggests a hydroxy-group *ortho* to the MeCO group. Structures (7) and (8) can now be ruled out, leaving only (6). The ^{1}H and ^{13}C n.m.r. spectra of (6)

possible to carry out heteronuclear condensations of the H-bond-activated enol form of the diketone with halogenoalkanes without formation of significant amounts of self-condensation product by carrying out such reactions in the absence of DMF, simply using an excess of diketone as solvent. Thus pentane-2,4-dione reacts with 1,3-dibromopropane in the presence of KF to form the

^{1}H N.m.r. and ^{13}C n.m.r. chemical shifts of 2'-hydroxyacetophenones

δ_H	δ_H ^{a}
2.23 (3 H, s, Me-4)	2.36 (3 H, s, Me-4)
2.53 (3 H, s, Me-6)	2.80 (3 H, s, Me-6)
2.59 (3 H, s, Me-7)	3.27 (3 H, s, Me-7)
6.48 (1 H, s, H-5)	6.65 (1 H, s, H-6)
6.59 (1 H, s, H-3)	7.02 (1 H, s, H-3)
12.36br (1 H, s, OH)	14.24br (1 H, s, OH)

δ_C	
21.484 (Me-4)	
24.467 (Me-6)	
33.109 (Me-7)	
116.797 (C-3)	
119.292 (C-4)	
124.526 (C-5)	
139.620 (C-6)	
146.133 (C-1)	
163.783 (C-2)	
205.414 (C-7)	

δ_H	δ_H ^{a}
2.53 (3 H, s, Me-6)	2.87 (3 H, s, Me-6)
2.64 (3 H, s, Me-7)	3.48 (3 H, s, Me-7)
3.69 (2 H, s, H$_2$-9)	3.73 (2 H, s, H$_2$-9)
6.53 (1 H, s, H-5)	6.73 (1 H, s, H-5)
7.18 (10 H, m, Ph)	7.18 (10 H, m, Ph)
12.5br (1 H, s, OH)	15.3br (1 H, s, OH)

δ_C	
24.101 (Me-6)	128.482 (Ph)
33.170 (Me-7)	128.908 (Ph)
39.378 (C-9)	130.308 (Ph)
119.710 (C-4)	139.520 (C-6)
124.584 (C-5)	141.711 (C-3)
126.109 (Ph)	146.220 (C-1)
127.509 (Ph)	162.895 (C-2)
128.361 (Ph)	205.712 (C-7)

^{a} After addition of a deuteriated europium(III) shift reagent.

and (3) (see Table) and the mass spectra (see Experimental section) are entirely consistent with the proposed structures.

In Scheme 2, cyclisation would be expected to occur between positions 1 and 5 [intermediate (4)] or 1' and 5' [intermediate (5)]. In (5), the benzylic protons on C-1' are more acidic than those on C-4' or -6'; in (4), the benzylic protons on C-1 are more acidic than those on C-4 and those on C-6, the latter being due to delocalisation in the enol form of (4) [1,5-ring closure will also be preferred over 2,6- or 3,6- because of the added stability of the six-membered chelate ring in the product (6)].

The *exclusive* formation of the product (6) from 1,5-ring closure is puzzling. Both (6) and (10) would be expected to have enhanced stability due to intramolecular H-bonding, and the mechanistic differences between the pathways leading to the intermediates (4) and (5) and between 1,5- and 1',5'-ring closures seem trivial. However, in the absence of a more obvious reason one must assume either that the formation of (4) is much preferred to that of (5), or that the former intermediate cyclises much more readily.

In the absence of DMF the formation of (3) proceeded only very slowly [for pentane-2,4-dione with KF alone, less than 5% conversion into (3) was observed after 16 h at reflux temperature]. This suggested that it might be

diketone (14) and 3-acetyl-2-methyldihydropyran (*ca.* 4 : 5 molar ratio). Less than 1% of self-condensation product was found after work-up.

(14)

(15)
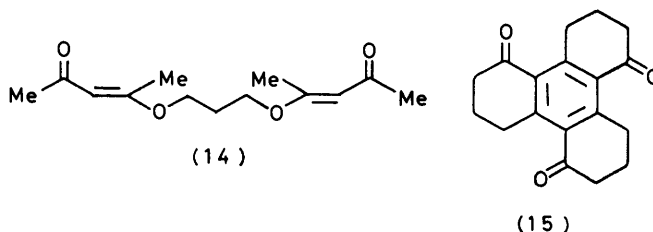
Cyclohexane-1,3-dione undergoes rapid and efficient self-condensation in the presence of KF–DMF to provide polycyclic trione isomers such as (15). Addition of the β-diketone to KF–DMF at room temperature causes considerable warming of the mixture, indicative of a strong H-bond. This is confirmed by the appreciable shift (>1 000 cm^{-1}) in the enolic OH stretching frequency.

Cyclohexane-1,3-dione has been observed previously to undergo intermolecular self-condensation in the presence of hydrogencarbonate at pH 6 to produce 5-oxo-6-(4-oxocyclohexyl)hexanoic acid;[15] a more similar re-

[15] K. Conrow, *J. Org. Chem.*, 1966, **31**, 1050; H. Steller, E. Sienhold, E. Klauke, and M. Coenen, *Chem. Ber.*, 1953, **86**, 1308.

action to ours is the self-condensation of cyclohexanone in the presence of sodium ethoxide to produce dodeca-hydrotriphenylene.[16]

Self-condensation of Butane-2,3-dione.—The self-condensation of α-diketones is not a new reaction; previous examples, including that of butane-2,3-dione, have been reported.[11] On refluxing butane-2,3-dione with KF–DMF, the diketone was quantitatively converted into the intermolecular self-condensation product 2,5-dimethyl-1,4-benzoquinone.

Self-condensation of Cyclohexanone and Cyclopentanone.—The less active monoketones cyclohexanone and cyclopentanone reacted only very slowly in the presence of KF–DMF and appeared to give mixtures of products. We abandoned this method in favour of another involving Bu^n_4NF as the H-bond electron donor. The use of this and of other tetra-alkylammonium fluorides will be discussed later. In the presence of this fluoride and with a simple experimental set-up that allowed continuous removal of water (and unchanged ketone which may be recycled so as to encourage H-bonding between the fluoride and the enolic hydroxy-group of the ketone, cyclohexanone and cyclopentanone underwent rapid and efficient self-condensation (the efficiency of these reactions is assumed on the basis of the amounts of ketone consumed during the reaction) to produce compounds (16) and (17), respectively. These were the only products isolated.

Both compounds have been previously reported as self-condensation products, the former, from treatment of cyclohexanone with sodium in methanol for 75 days,[17] and the latter from the reaction of cyclopentanone with sodium hydride in ethyl acetate which gave acetylcyclopentanone in addition to (17).[18] Whereas (16) arises from the intermolecular condensation of three ketone molecules with loss of only one molecule of water, (17) requires that three ketone molecules condense with loss of two molecules of water. Both reactions probably involve initial H-bond-assisted enolisation followed by Michael addition and subsequent condensation (Scheme 3).

Attempts failed to effect further dehydration of (16) or to provide the cyclopentanone analogue of (16) by reaction with fluoride. It is difficult to explain why (16) should not undergo further reaction under these strongly dehydrating conditions. This seems to be a further example of the peculiar tendency of fluoride to provide only one product even when further reaction might be expected.

The Role of the Fluoride.—The reactions of β-diketones investigated here suggest that fluoride is capable of enolising these ketones, producing H-bonds of the [O · · · H · · · F]⁻ type. This strong H-bond is capable of inducing reactions typical of an enolic anion. All the intermolecular self-condensations described here can be explained in terms of the enolic anion undergoing aldol-type condensation and Michael reaction.

The use of the two different fluorides, KF and Bu^n_4NF, merits comment. In the majority of previous accounts of H-bond-assisted reactions only the alkali metal

fluorides have been employed,[1,2,4-6] although tetra-alkyl-ammonium fluorides have been used as H-bond electron donors in physical investigations.[2,7] Tetra-alkylammonium fluorides are considerably more soluble in most organic solvents and hence facilitate a number of physical measurements. It might also be thought that they would provide more efficient reactions, but in practice their extreme hygroscopic nature and prohibitive cost does not make them an attractive alternative to fluorides
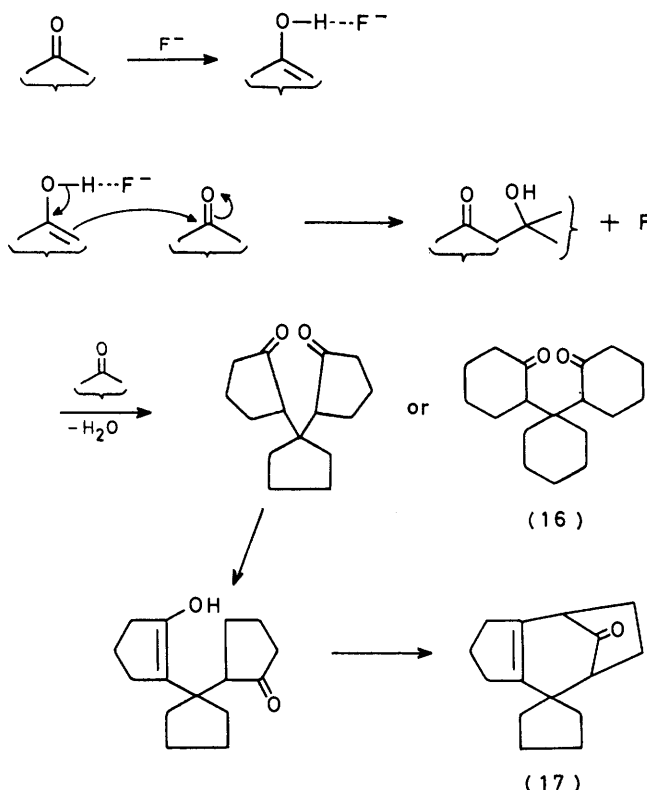
SCHEME 3

such as KF. However, in some instances their disadvantages are outweighed by their ability to provide rapid reaction when the same reaction proceeds only slowly in the presence of alkali metal fluorides, for example, in the self-condensation of cyclohexanone. No effort was made to render the tetra-n-butylammonium fluoride anhydrous before use. The reactivity of the fluoride is such that a concentrated aqueous solution is still a powerful dehydrating reagent and it is sufficient to evaporate this solution in the presence of an excess of the ketone to cause self-condensation of that ketone. Should the enolised ketone be a sufficiently strong H-bond electron acceptor or of sufficiently high b.p., the fluoride can be rendered totally anhydrous by this method (the fluoride forming a strong H-bond to the enolic hydroxy-group

[16] J. Plesek, *Coll. Czech. Chem. Comm.*, 1956, **21**, 368.
[17] S. V. Svetozarskii, K. L. Feller, and E. N. Zil'bemmam, *Zhur. Vsesoyuz. Khim. obshch. im. D. I. Mendeleeva*, 1963, **8**, 113 (*Chem. Abs.*, 1964, **59**, 2788h).
[18] R. M. Acheson, *J. Chem. Soc.*, 1956, 4232.

rather than to water, similar to that observed for other protic organic compounds [2]). Tetra-n-butylammonium fluoride however, does not always provide more rapid ketone self-condensations than alkali metal fluorides. In the case of pentane-2,4-dione for example, the method effective for the self-condensation of cyclohexanone did not provide any acetophenone or indeed any product other than the H-bonded solvate, even after several hours under reduced pressure. This may be because the solvate between the tetra-n-butylammonium fluoride and the diketone is too stable to react under these conditions.

Tetra-alkylammonium fluorides have been used increasingly for various purposes in preparative organic chemistry in the last few years. Other than their use in the cleavage of dimethyl-t-butylsilyl ether,[19] for the fluorination of fluoro-olefins,[20] and for the C-alkylation of β-dicarbonyl compounds,[13] these fluorides have found use in elimination reactions.[21-24] For example, tetra-n-butylammonium fluoride has a remarkable capacity to facilitate intramolecular cyclisations, in particular to allow quantitative conversion of carbamates into substituted hydantoins.[21] We believe that such conversions are examples of H-bond-assisted reactions. We have shown in previous investigations that fluoride is capable of H-bonding to NH groups, thereby providing increased electron density at nitrogen.[2] The present work shows that fluoride is capable of eliminating water and thereby enabling cyclisation to occur. Water is a strong H-bond electron acceptor and we believe that our reactions occur as a result of (a) H-bonding to a suitable electron acceptor site and (b) elimination of a molecule capable of behaving as an H-bond electron acceptor. This reasoning may readily be extended to such eliminations as those described by Pless.[21] Fluoride is capable of H-bonding to the NH groups of carbamates, such as (18), thereby enhancing the electron density at nitrogen; this will facilitate intramolecular condensation by overall elimination of ROH (a strong H-bond electron acceptor) to provide the hydantoin, as was observed (Scheme 4).[21]

(18)
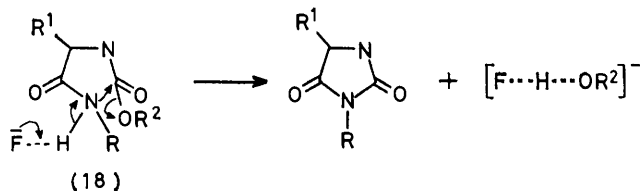
SCHEME 4

EXPERIMENTAL

[1]H N.m.r. spectra were recorded with a Varian A-60 or Bruker WP-60FT (60 MHz) spectrometer. [13]C N.m.r.

* This compound was originally reported to be 3-hydroxy-2,5,7-trimethylcyclohepta-2,4,6-trienone (J. H. Clark and J. M. Miller, *Tetrahedron Letters*, 1977, 139). The acetophenone structure had been discounted on the basis of the reported mass spectrum of this compound in ' Eight Peak Index of Mass Spectra,' 2nd edn., vol. 1, Aldermaston, 1974 [reported spectrum: *m/e* 164 (43), 149 (88), 122 (100), 121 (28), 107 (53), 77 (19), 44 (16), and 28 (23)]. However, an authentic sample of 2'-hydroxy-4',6'-dimethyl-acetophenone was identical with our compound, both samples giving the mass spectrum we report, and the literature spectrum being incorrect.

spectra were recorded with a Bruker WP-60FT (15.08 MHz) spectrometer by using broad-band decoupling facilities. All n.m.r. spectra were obtained for solutions in CDCl₃ with Me₄Si as internal reference. Mass spectra were recorded with an A.E.I. MS-30 double-beam spectrometer. I.r. spectra were recorded with a Perkin-Elmer 237B spectrometer.

Potassium fluoride was a commercial sample dried at 100 °C *in vacuo* for 2 h. Tetra-n-butylammonium fluoride was prepared in aqueous solution by neutralisation of the hydroxide (commercial sample in aqueous solution) with 52% hydrofluoric acid; the solution was briefly concentrated by evaporation on a water-bath at 90 °C before use. Analytical grade *NN*-dimethylformamide was dried over molecular sieves. All the ketones were commercial samples and were used without further treatment except for pentane-2,4-dione, which was distilled immediately before use.

Self-condensation of Pentane-2,4-dione.—A mixture of potassium fluoride (11.62 g, 0.2 mol), pentane-2,4-dione (10.0 g, 0.1 mol) and DMF (40 g) was stirred at room temperature. [1]H N.m.r. analysis showed the presence of 100 ± 1% enol. The mixture was heated at reflux for 16 h, after which [1]H n.m.r. analysis showed no pentane-2,4-dione remaining. The cooled mixture was extracted with diethyl ether; the extract was washed with equal volumes of water (2 ×) and evaporated, and the residue stirred with a large volume of cold water until the water-insoluble product(s) solidified. The solid was filtered off, dried, and recrystallised (2 ×) from pentane, giving pale yellow needles of 2'-hydroxy-4',6'-dimethylacetophenone * (5.25 g, 0.032 mol, 64%), m.p. 55—56 °C (lit.,[25] 57—58 °C) (Found: C, 73.1; H, 7.4. Calc. for $C_{10}H_{12}O_2$: C, 73.2; H, 7.4%), *m/e* 164(41%), 150(9), 149(100), 121(4), 93(5), 91(28), 77(32), and 43(26); $\nu_{max.}$ 1 620 (C=O) and 1 595 cm⁻¹ (C=C) (^{1}H and [13]C n.m.r. data in the Table).

[1]H N.m.r. analysis of a mixture of KF (0.1 mol) and pentane-2,4-dione (0.2 mol) alone at room temperature showed the presence of 86 ± 2% enol. After refluxing this mixture for 16 h, [1]H n.m.r. analysis showed less than 5% reaction. After heating a solution of pentane-2,4-dione (0.1 mol) in DMF (30 g) at reflux for 16 h, [1]H n.m.r. analysis showed no reaction.

Refluxing a mixture of KF (5.81 g, 0.1 mol) and 1-phenyl-pentane-2,4-dione (3.53 g, 0.02 mol) in DMF (20 g) for 16 h, followed by separation similar to that described above gave white crystals of 4'-benzyl-2'-hydroxy-6'-methyl-3'-phenyl-acetophenone (1.63 g, 0.0052 mol, 52%), m.p. 124 °C (from benzene–hexane) (Found: C, 83.55; H, 6.35. $C_{22}H_{20}O_2$ requires C, 83.55; H, 6.35%); $\nu_{max.}$ 1 615 (C=O) and 1 600 cm⁻¹ (C=C); *m/e* 317(12%), 316(49), 302(26), 301(100), 239(5), 182(9), 165(8), and 91(26) (^{1}H and [13]C n.m.r. data in the Table).

Reaction of Pentane-2,4-dione with 1,3-Dibromopropane.—KF (11.62 g, 0.2 mol), pentane-2,4-dione (20.0 g, 0.2 mol), and 1,3-dibromopropane (10.1 g, 0.05 mol) were heated

[19] E. J. Corey and A. Vankateswarlu, *J. Amer. Chem. Soc.*, 1972, **94**, 6190.
[20] W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3091.
[21] J. Pless, *J. Org. Chem.*, 1974, **39**, 2644.
[22] T. H. Chan and W. Mychajlowskij, *Tetrahedron Letters*, 1974, 171.
[23] R. F. Curico and E. M. Dexheimer, *J. Amer. Chem. Soc.*, 1972, **94**, 2868.
[24] J. Hayani, N. Ono, and A. Kaji, *Tetrahedron Letters*, 1968, 1385; 1970, 2727.
[25] K. Auwers, *Ber.*, 1915, **48**, 90.

together at reflux for 3 h; ^{1}H n.m.r. analysis then showed no remaining 1,3-dibromopropane. The cooled mixture was extracted with diethyl ether, and the extract was dried (MgSO$_4$) and evaporated. The residue was extracted with hot pentane and the solution cooled to give crystals of 4,10-*dimethyl-5,9-dioxatridecane-3,10-diene-2,12-dione* (14) (4.32 g, 0.018 mol, 36%), m.p. 72 °C (Found: C, 64.6; H, 8.35. C$_{13}$H$_{20}$O$_4$ requires C, 65.0; H, 8.35%), δ 5.43 (2 H, s, CH), 3.87 (4 H, t, CH$_2$O), 2.3 (2 H, m, CH$_2$), 2.27 (6 H, s, MeCO), and 2.16 (6 H, s, Me); *m/e* 240.

The filtrate, after several coolings to remove the bulk of the product (14), was evaporated then the residue was distilled to give 3-*acetyl-2,3-dihydro-2-methylpyran* (2.80 g, 0.02 mol, 40%), b.p. 175—178 °C at 760 mmHg; n_D^{24} 1.5023 (Found: C, 68.3; H, 8.6. C$_8$H$_{12}$O$_2$ requires C, 68.6; H, 8.6%); δ$_H$ 3.98 (2 H, t, CH$_2$O), 2.2 (4 H, m, CH$_2$), 2.20 (3 H, s, MeCO), and 2.15 (3 H, s, Me); δ$_C$ 191.294 (C=O), 110.223 (:C–O), 100.485 (:C·COMe), 66.584 (OCH$_2$), 29.457 (*Me*CO), 22.823 (CH$_2$), 21.971 (CH$_2$), and 21.058 (Me); ν$_{max.}$ 1 745 (C=O) and 1 590 cm^{-1} (C=C); *m/e* 140.

Self-condensation of Cyclohexane-1,3-dione.—A mixture of KF (5.81 g, 0.1 mol) and cyclohexane-1,3-dione (11.3 g, 0.1 mol) in DMF (30 g) was heated at reflux for 1 h; ^{1}H n.m.r. analysis then showed no starting material. The mixture was extracted with diethyl ether, and the extracts were washed several times with water, dried (MgSO)$_4$, and evaporated to give a reddish residue which on cooling afforded a solid product. Recrystallisation from ethanol gave a mixture of isomeric hexahydrotriphenylenetriones (6.5 g, 0.023 mol, 69%), m.p. 54 °C (Found: C, 77.4; H, 6.35. C$_{18}$H$_{18}$O$_3$ requires C, 77.0; H, 6.4%); ν$_{max.}$ 1 720 (C=O), 1 650 (C=O of enol?), and 1 605 cm^{-1} (C=C); *m/e* 282(28%), 254(33), 240(28), 239(31), 110(17), 86(72), 84(100), and 82(50).

Self-condensation of Butane-2,3-dione.—A mixture of KF (11.6 g, 0.2 mol) and butane-2,3-dione (4.3 g, 0.05 mol) in DMF (30 g) was heated at reflux for 16 h, after which ^{1}H

n.m.r. analysis showed no starting material. The cooled mixture was extracted with diethyl ether, and the extracts were washed several times with water, dried (MgSO$_4$), and evaporated. Cooling the residue provided a solid which on recrystallisation from chloroform gave yellow crystals of 2,5-dimethyl-1,4-benzoquinone (2.04 g, 0.015 mol, 60%), m.p. 123—125 °C (lit., 124—125 °C); δ 6.53 (2 H, s, CH) and 2.05 (6 H, s, CH$_3$); *m/e* 136.

Self-condensation of Cyclohexanone and Cyclopentanone.—A mixture of tetra-n-butylammonium fluoride (20 g, in concentrated aqueous solution) and cyclohexanone (50 g, 0.51 mol) was heated on a water-bath at 100 °C for 1 h, then at 100 °C under reduced pressure for 1 h, so as to remove the water produced and unchanged cyclohexanone. The mixture was then stirred with water (200 ml) for 1 h. The solid product was filtered off, washed with cold water, dried in *vacuo*, and recrystallised from ethanol to give fine white needles of 2,2'-cyclohexylidenedi(cyclohexanone) (16) (8.4 g, 0.03 mol, 18%), m.p. 179—180 °C (lit.,[17] 182 °C) (Found: C, 78.5; H, 10.25. Calc. for C$_{18}$H$_{28}$O$_2$: C, 78.25; H, 10.15%); ν$_{max.}$ 1 715 cm^{-1} (C=O); *m/e* 276 (7%), 258(13), 179(100), 178(95), 81(83), 79(22), 67(30), and 55(21). Extraction of the water–cyclohexanone mixture trapped during the reaction with ether gave cyclohexanone (39.5 g, 0.40 mol, 79%), *m/e* 98.

Cyclopentanone (50 g, 0.59 mol) and tetra-n-butylammonium fluoride, treated similarly, gave, after passage through a silica column (benzene), spiro[cyclopentane-1,2'-tricyclo[6.2.1.0^{3,7}]undec3(7)en]-1,1'-one (17) (7.3 g, 0.034 mol, 17%), m.p. 86 °C (lit.,[18] 84—85 °C); ν$_{max.}$ 1 715 (C=O) and 1 645 cm^{-1} (C=C); *m/e* 216(100%) 150(38), 149(34), 93(47), 91(25), 79(27), 71(21), and 67(23).