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PRELIMINARY NOTE

# A Modified Synthesis of Fluorinated 1,3-Diketones

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SUMMARY

The reinvestigation of acylation reactions of fluorinated aryl methylketones with ethyl esters at 0°C afforded fluorinated 1,3-diketones in excellent yields.

The chemistry of fluorinated 1,3-diketones has been extensively pursued [1-4] and their uses as ligands [5, 6] and intermediates [4] in various synthetic processes have been reported. In connection with our extensive work on fluorinated 1,3-diketones [2-4], we observed that the yields obtained by method of Adams et al. [8] were not entirely satisfactory. Further, it was noticed that when a 2,5-disubstituted aryl-ketone was used (viz. 2-chloro-5-fluoro-), the reaction tended to be violent during the addition of the ester.

We are now reporting a modified synthetic method for preparing these compounds at a low temperature and with enhanced yields. The experimental procedure adopted in our laboratory is outlined below.

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The fluoroaryl methylketones were prepared as reported earlier[2-4], commercial grade sodamide (Fluka) was used; other chemicals were dried and purified before use. The glass apparatus were dried and calcium chloride drying tubes used for protection against atmospheric moisture.

A mixture of sodamide (2M) and absolute ether (50 ml), in a three neck rb flask (500 ml) fitted with a reflux condenser, a dropping funnel and a mercury seal stirrer, was cooled in an ice bath. To this was added the fluoroaryl methylketone (1M) in absolute ether (50 ml) followed by a slow addition of the ethyl ester (1.5 M) in absolute ether (50 ml) with stirring. The cooling and stirring was continued for an hour after the addition. The ice bath was removed and the reaction mixture stirred overnight. It

TABLE 1
Fluorinated 1,3-Diketones, $ArCOCH_2COR$, prepared.

$$ArCOCH_3 + RCOOC_2H_5 \xrightarrow[0^oC]{NaNH_2 \text{ in ether at}} ArCOCH_2COR$$

| S.No. | Substituent in Ar | R | Yield (%) | Ref. |
|---|---|---|---|---|
| 1 | 4-F | $C_2F_5$ | 60 | 3 |
| 2 | 2-Cl, 5-F | Me | 68 | 2 |
| 3 | 3-Cl, 4-F | $CF_3$ | 57 | 2 |
| 4 | 2-Cl, 4-F | $CF_3$ | 62 | 2 |
| 5 | 2,5-DiF | $C_2F_5$ | 60 | 3 |
| 6 | 2,4-DiF | Me | 58 | 3 |
| 7 | 2,4-DiF | $CF_3$ | 63 | 3 |
| 8 | 4-F, 3-OMe | $C_2F_5$ | 61 | 3 |

was refluxed for 2-4 hrs and the solvent removed under reduced pressure. The sodium salt of the diketone, so obtained, was dissolved in ice (300 g) and the free 1,3-diketone generated by treating with hydrochloric acid. It was extracted with ether and purified by distillation and recrystallization. The physical properties were identical to those reported previously.

The 1,3-diketones prepared and their yields are given in Table 1.

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