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Deacylations and Syntheses of Some 9-Acylfluorenes

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Deacylations of substituted 9-acetyl-, 9-propionyl-, 9-benzoyl-fluorene, and 9-fluorenyl 9-methyl-9-fluorenyl ketones were studied; the reactivity of deacylation was enhanced by the substitution of the 9-hydrogen atom on 9-acetylfluorene. The reaction of 9-acetylfluorene with ethyl nitrate afforded 9-*aci*-nitrofluorene.

Deacylation promoted by a base has been known already to occur in the active methylene to which an acyl group is attached. In fluorene derivatives, 9-benzoylfluorene (**1**) gave fluorene (**2**) and benzoic acid,[1] and 9-chloro-9-acetylfluorene (**3**) afforded 9,9′-bifluorenyl (**4**).[2] The present work deals with the deacylation of 9-acylfluorenes in order to clarify the reactivities on the 9-carbon atom of fluorenes.

Deacetylation of 9-acetylfluorene (**5**)[3] yielded **2** and ethyl acetate; the yield of **2** increased (28—96%) with the increase of base concentration (1—20%) and with the extension of the reaction time (1—10 h). The deacetylation may be explained by the nucleophilic attack of ethoxide anion on the cationic carbon atom of carbonyl in **5** to form the intermediary carbanion (A) as the reverse-Claisen-type condensation (Scheme 1).

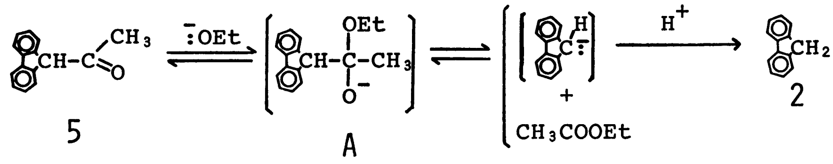
The deacylation of some 9-acylfluorenes was carried out as shown in Table 1. The substituent effect in the deacylation of 9-propionyl- (**6**),[4] 2-ethyl-9-acetyl- (**7**), and 2-bromo-9-acetylfluorene (**8**) was observed to be less significant in comparison with that of **5**. The reaction of 9,9-dibenzoylfluorene (**9**)[5] with base afforded **1**, which was further converted to **2** by debenzoylation.

The elimination was accelerated remarkably in the deacetylation of **3**, 9-methyl- (**10**),[6] and 9-hydroxy-9-acetylfluorene (**11**).[7] The ethoxide anion may be able to attack on the two positions of **5**, that is, the 9-carbon and the carbonyl carbon atoms. The 9-acetylfluoren-9-ide anion would be stabilized by resonance as enolate anion and **5** is less reactive under these conditions. The substitution on the 9-position of **5** prevents the attack on this position and results in the significant formation of the elimination product.

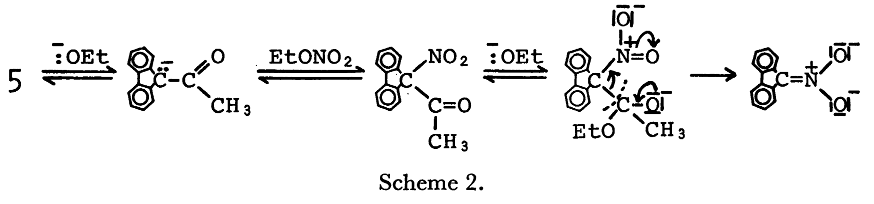
The reaction of **5** with ethyl nitrate in the presence of sodium ethoxide gave pure 9-*aci*-nitrofluorene[8] in good yield. The ethoxide anion removes a proton from the 9-position on the **5**. The resulting carbanion may afford the intermediary 9-nitro-9-acetylfluorene by an attack of ethyl nitrate, and this was converted to 9-*aci*-nitrofluorene by the action of a second ethoxide anion and by the tautomeric effect of the nitro group (Scheme 2).

The deacetylation of the substrate containing an electron-attracting group proceeds more readily than that having an electron-releasing group. Actually, the progress of the deacylations for **3** and also for **10** was followed by means of gas chromatography; the **10** still remained in a considerable amount (37%) at the reaction step in which all the **3** had been consumed. Chloride **3** gave 9,9′-bifluorenylidene (46%) and **4** (trace), and the ethylene was reduced to **4** under similar conditions.

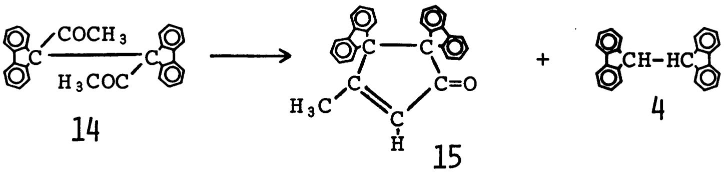
The reactivity of the carbonyl group in 9-*t*-butyl-9-acetylfluorene (**12**) is hindered by the bulky substituent



Scheme 1.



Scheme 2.



Scheme 3.

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TABLE 1. CHARACTERIZATION AND DEACYLATION OF 9-ACYLFLUORENES

Compound	Characterization		Deacylation	
	^{1}H-NMR chemical shift$^{a)}$ δ(ppm); J (Hz)	ν(C=O) on IR spectrum (cm^{-1})	Fluorene %	Recovd %
5	1.60 ($-CH_3$); 4.78 (>CH–)	1698	42 (**2**)	45
6	0.78 ($-CH_3$, J=6.3); 1.75($-CH_2-$); 4.64 (>CH–)	1700	42 (**2**)	38
7	1.26 ($-CH_3$, J=6.0); 1.46 ($-COCH_3$); 2.67 ($-CH_2-$); 4.59 (>CH–)	1701	45 (2-Ethyl-)	45
8	1.65 ($-CH_3$); 4.75 (>CH–)	1698	55 (2-Bromo-)$^{b)}$	
9		1680	23(**1**); 26(**2**)	
1	5.37 (>CH–)	1681	66 (**2**)	26
10	1.37 ($-CH_3$); 1.57 ($-COCH_3$)	1702	94 (9-Methyl-)	trace
11	1.54 ($-CH_3$); 4.78 (–OH)	1700	96 (9-Hydroxy-)	trace
12	0.99 ($-CH_3$); 1.36 ($-COCH_3$)	1699	34 (9-*t*-Butyl-)	57
13	2.19 ($-CH_3$); 2.87 ($-CH_2-$, J=4.8); 4.45 (>CH–)	1707		99

a) Measured in $CDCl_3$ or CCl_4. b) In addition, 2-bromo-9-acetyl-9-hydroxyfluorene (2%, mp 154—155 °C, IR: (OH) 3460; (C=O) 1704 cm^{-1}) and 2,2′-dibromo-9,9′-diacetyl-9 9′-bifluorenyl (0.3%, mp 238—240 °C, IR: (C=O) 1705 cm^{-1}) were isolated.

TABLE 2. CHARACTERIZATION AND DEACYLATION OF 9-ACYLFLUORENES

Compound	Characterization		Deacylation	
	^{1}H-NMR chemical shift δ (ppm) (Solvent)	ν (C=O) on IR spectrum (cm^{-1})	Time h	Products (%)
16	1.78 ($-CH_3$); 4.52 (>CH–) (Pyridine-d_5)	1700	1	**2** (31); **17** (10); **18** (31); 9-Methylfluorene (9); Recovd (42)
16			10	**2** (58); **17**(22); **18** (30); 9-Methylfluorene (41)
18	1.69 ($-CH_3$); 1.04 ($-CH_3$, J=7.0 Hz);3.97 ($-CH_2-$) (CCl_4)	1721	10	9-Methylfluorene (18); **17** (14); Recovd (67)
19	3.63 ($-CH_3$); 4.71 (>CH–) (CCl_4)	1729	10	**2** (8); **20** (57); Ethyl ester of **20** (10)

from the approach of an attacking ethoxide ion, therefore, the yield of 9-*t*-butylfluorene[9] decreased. No deacetylation was observed in the cases of 9-acetonylfluorene (**13**)[10] and 2-acetylfluorene.[11] This finding shows that deacylation occurs when the acyl group is attached directly to the active 9-position of fluorenes. The anomalous lower field (2.19 ppm) of the methyl chemical shift of **13** compared with that (1.60 ppm) of **5** is ascribed to the predominant conformation of **13** and **5**; the mobile methyl group of **13** may be located further away from the shield zone of the aromatic rings than that of **5**.

The reaction of 9,9′-diacetyl-9,9′-bifluorenyl (**14**)[2] afforded dehydrate compound **15** accompanied by **4** (Scheme 3); **15** would be formed by the intramolecular aldol-type condensation.

The same reaction of 9-fluorenyl 9-methyl-9-fluorenyl ketone (**16**) yielded **2**, 9-methylfluorene, 9-methylfluorene-9-carboxylic acid (**17**),[12] and its ethyl ester (**18**),[13] as summarized in Table 2. The ester **18** gave 9-methylfluorene and **17**. Similarly, methyl fluorenyl-9-carboxylate (**19**) yielded **2**, the corresponding carboxylic acid (**20**), and its ethyl ester. The ratio of the yields of these products indicates that **16** cleaves into 9-fluorenide anion and **18**, but not into 9-methylfluoren-9-ide anion and an ester of **20**; this may be attributed to the stability of the 9-fluorenide anion formed, which is greater than that of the methyl derivative.

Experimental

All the melting points are uncorrected. The instruments used in this experiment have been described elsewhere.[11]

Deacylation of 9-Acylfluorene. General Procedure: Sodium metal (1.15 g) was treated with 33 ml of dry ethanol, then 5 mmol of substrate was added, and the mixture was refluxed for 10 h under an atmosphere of dry nitrogen. Upon cooling, the reaction mixture was poured into 150 ml of 3% hydrochloric acid and the resulting precipitate was purified by a combination of alumina-column chromatography, vacuum sublimation, and recrystallization.

Reaction of 14 with Sodium Ethoxide. A 2.070 g portion of **14** was refluxed with 3.4 g of sodium ethoxide in 330 ml of dry benzene for 10 h to give 0.450 g of 3-methyl-4,5-bis(2,2′-biphenylylene)-2-cyclopenten-1-one (**15**), 0.012 g of **4**, and 0.010 g of fluorenone. Mp of **15**: 233.5—234.5 °C. IR: (C=O) 1694 cm^{-1}. Mass: *m/e* 396 (M$^+$), 381, and 352. NMR (benzene-d_6): δ 1.29 (3H, s), 6.47 (1H, s), and 6.65—7.35 (16H, m) ppm. Found: C, 90.96; H, 5.17%. Calcd for $C_{30}H_{20}O$: C, 90.88; H, 5.09%.

Reaction of 5 with Ethyl Nitrate. A soln of 2.08 g of **5**, 1.82 g of ethyl nitrate, and 0.68 g of sodium ethoxide in 20 ml of dry ethanol was refluxed for 2 h. Upon cooling, 100 ml of benzene and 150 ml of water were added to the reaction mixture and the aqueous layer was neutralized with hydrochloric acid to yield 1.53 g of 9-*aci*-nitrofluorene, mp 154 °C (dec). IR: (OH) 2770; (NO_2) 1653, 1441 cm^{-1}.

2-Ethyl-9-acetylfluorene (7). Compd **7** was prepared by means of the same procedure as used for **5** in a 34% yield, bp 142—144 °C/2 Torr (uncorr.). Mass: *m/e* 236 (M^+).

2,4-Dinitrophenylhydrazone, mp 200—202 °C. IR: (NH) 3320; (NO_2) 1614, 1589 cm^{-1}. Found: C, 66.68; H, 4.95; N, 13.58%. Calcd for $C_{23}H_{20}O_4N_4$: C, 66.33; H, 4.84; N, 13.46%.

2-Bromo-9-acetylfluorene (8). The title compd was obtained by the same method as described above, yield 30%, mp 66—67 °C. Mass: *m/e* 288, 286 (M^+), 245, 243, and 207. Found: C, 62.95; H, 3.64%. Calcd for $C_{15}H_{11}OBr$: C, 62.74; H, 3.86%.

*9-*t*-Butyl-9-acetylfluorene (12).* Compd **12** was obtained by a procedure similar to that of **10** in a 39% yield, mp 76.5—77 °C. Mass: *m/e* 264 (M^+), 249, 221, 208, 206, 191, and 165. Found: C, 86.73; H, 7.77%. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63%.

9-Acetonylfluorene (13). This compd was synthesized by the reaction of α-(9-fluorenyl)acetyl chloride with methylmagnesium iodide in the presence of cadmium chloride: yield 58%, mp 62—63 °C (lit,[10] mp 57 °C). Mass: *m/e* 222 (M^+), 179, and 165.

9-Fluorenyl 9-Methyl-9-fluorenyl Ketone (16). To a soln of 9-methyl-9-lithiofluorene (prepared from 0.96 g of lithium chips, 9.4 g of butyl bromide, and 10.3 g of 9-methylfluorene in 100 ml of xylene) was added dropwise 12.0 g of 9-fluorenylcarbonyl chloride in 60 ml of xylene at 0 °C with stirring for 30 min, then the mixture was boiled for 1 h to afford 6.45 g of **16**, mp 226—227.5 °C. Mass: *m/e* 372 (M^+), 179, and 165. Found: C, 90.27; H, 5.57%. Calcd for $C_{28}H_{20}O$: C, 90.29; H, 5.41%.

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