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# **960.** *The Interaction of Alkylbenzenes with Excess of Friedel–Crafts Acetylating Agent.*

By G. Baddeley and E. Wrench.

This reaction, in methylene chloride, at 20° gives mainly *p*-alkylacetophenones. After removal of the solvent under reduced pressure, raising the temperature of the reaction mixture to about 70° effects further reaction, including dehydrogenation of the alkyl substituent and acetylation of the resulting styrene derivative.

Aryl ketones having bulky *oo′*-substituents, *e.g.*, methyl groups, can be acylated by the Friedel–Crafts method; thus mesitylene and durene can be diacylated. Further, aromatic compounds such as *p*-ethylphenol and 5-*m*-xylenol, which have groups which greatly facilitate electrophilic substitution, readily undergo nuclear diacylation.[1] A different type of acylation of aromatic ketones is exemplified by the action of acetic anhydride–boron fluoride complex on acetophenone: acetoacetophenone is formed. On the other hand, acylation of alkylbenzene at room temperature and in the presence of aluminium chloride effects only monoacylation; further reaction occurs only at raised temperatures (about 70°) and may involve three or more competitive reactions: (i) The acylating agent may undergo self-condensation; thus an acetylating agent gives acetylacetone and other products. (ii) The aromatic component may be dealkylated; thus small amounts of acetophenone are among the products of the action of excess of acetylating agent on *p*-*n*-propyl- and *p*-*n*-butyl-acetophenone. (iii) The acetylating agent may dehydrogenate the alkyl substituent, giving an aldehyde and a styrene derivative which undergoes acylation of the ethylenic group; thus the action of excess of acetylating agent on ethylbenzene gives 4-*p*-acetylphenylbut-3-en-2-one:

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_3 + AcCl,AlCl_3 \longrightarrow \mathit{p}\text{-}CH_3{\cdot}CH_2{\cdot}C_6H_4Ac,AlCl_3 + HCl}$$

$$\Big\downarrow \mathrm{AcCl,AlCl_3}$$

$$\mathrm{\mathit{p}\text{-}CH_3{\cdot}CH{\cdot}C_6H_4Ac,AlCl_3 + AlCl_4^- + CH_3{\cdot}CHO \longrightarrow \mathit{p}\text{-}CH_2{:}CH{\cdot}C_6H_4Ac,AlCl_3 + HCl + CH_3{\cdot}CHO,AlCl_3}$$

$$\Big\downarrow \mathrm{AcCl,AlCl_3}$$

$$\mathrm{\mathit{p}\text{-}Cl_3Al,Ac{\cdot}CH{:}CH{\cdot}C_6H_4Ac,AlCl_3 + HCl}$$

$$\Big\downarrow \mathrm{H_2O}$$

$$\mathrm{\mathit{p}\text{-}Ac{\cdot}CH{:}CH{\cdot}C_6H_4Ac}$$

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[1] Von Auwers and Schornstein, *Fortschr. Chem. Phys.*, 1924—26, **18**, 76.

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The reaction of excess of an acetylating agent with indane and tetralin has been reported;[2] we now describe its reaction with *m*-ethylacetophenone and a number of alkylbenzenes.

The products and yields (±5%) are listed in the Table. Where the yields do not total 100, non-volatile material was also obtained. The structures of the olefinic diketones were determined by conventional methods. In experiments 1, 2, 3, 5, and 7 the acetylphenyl group was sufficiently polarisable, even though its acetyl group was in combination with aluminium chloride, to provide an electromeric release of electrons which enabled acetylation to occur at the terminal carbon atom of the styrene system. Acetylation at the carbon atom adjacent to the ring occurred in experiments 4 and 6.

| Exp. | Reactant | Products | |
|---|---|---|---|
| 1 | Ph·CH$_2$·CH$_3$ | $p$-C$_6$H$_4$Ac·C$_2$H$_5$ (60%) | $p$-C$_6$H$_4$Ac·CH:CHAc (10%) |
| 2 | Ph·CH$_2$·CH$_2$·CH$_3$ | $p$-C$_6$H$_4$Ac·C$_3$H$_7$ (40%) | $p$-C$_6$H$_4$Ac·CH:CHMeAc (15%) |
| 3 | Ph·CHMe$_2$ | $p$-C$_6$H$_4$Ac·CHMe$_2$ (70%) | $p$-C$_6$H$_4$Ac·CMe:CHAc (10%) |
| 4 | Ph·CH$_2$·CH$_2$Et | $p$-C$_6$H$_4$Ac·C$_4$H$_{10}$ (55%) | $p$-C$_6$H$_4$Ac·CAc:CHEt (35%) |
| 5 | Ph·CHMeEt | $p$-C$_6$H$_4$Ac·CHMeEt (30%) | $p$-C$_6$H$_4$Ac·CMe:CMeAc (25%) |
| 6 | Ph·CH$_2$·CHMe$_2$ | $p$-C$_6$H$_4$Ac·CH$_2$·CHMe$_2$ (50%) | $p$-C$_6$H$_4$Ac·CAc:CMe$_2$ (15%) |
| 7 | $m$-C$_6$H$_4$Ac·C$_2$H$_5$ | $m$-C$_6$H$_4$Ac·C$_2$H$_5$ (60%) | $m$-C$_6$H$_4$Ac·CH:CHAc (30%) |
| | PhR (R = H, Me, Bu$^t$) | $p$-C$_6$H$_4$Ac·R (70%) | |

## EXPERIMENTAL

*Procedure.*—Alkylbenzene was added to a cooled mixture of aluminium chloride (5 mols.) and acetyl chloride (3 mols.) in methylene chloride. When the ready reaction providing hydrogen chloride and 4-alkylphenyl methyl ketone had subsided the solvent was volatilised under reduced pressure and the temperature of the residue was raised until further reaction occurred. When evolution of hydrogen chloride was essentially complete, the mixture was decomposed with ice and dilute hydrochloric acid, and the organic product was extracted with chloroform, dried (K$_2$CO$_3$), and fractionally distilled under reduced pressure.

(i) *Ethylbenzene.* This (20 g.), after reaction at 110° for 2 hours, gave 4-ethylacetophenone (17·5 g.) (semicarbazone m. p. and mixed m. p. 153—154°), and 4-*p*-acetylphenylbut-3-en-2-one[2] (4 g.), b. p. 190—210°/15 mm. The latter crystallised from light petroleum in radiating needles, m. p. and mixed m. p. 107°, $\lambda_{\text{max.}}$ 2950 Å ($\varepsilon$ 29,500). It gave: (*a*) terephthalic acid, m. p. 210° (dimethyl ester, m. p. and mixed m. p. 92°), on oxidation with dilute nitric acid (*d* 1·2) at 180°; (*b*) *p*-acetylbenzoic acid,[3] m. p. 205° (methyl ester,[4] m. p. 92°; 2 : 4-dinitrophenylhydrazone, m. p. 278°), on oxidation with aqueous permanganate at 0°; and (*c*) 4-*p*-acetylphenylbutan-2-one, m. p. and mixed m. p. 28°, on catalytic hydrogenation.

(ii) n-*Propylbenzene.* This (36 g.), similarly treated, gave 4-*n*-propylacetophenone (20 g.), b. p. 84—88°/0·5 mm. (oxime, m. p. and mixed m. p. 43—44°), and 4-*p*-acetylphenyl-3-methylbut-3-en-2-one (8 g.), b. p. 135—145°/0·5 mm. The latter was purified *via* its *disemicarbazone*, needles, m. p. 274—275° (decomp.) (from dilute acetic acid) (Found: C, 57·4; H, 6·2; N, 26·6. C$_{15}$H$_{20}$O$_2$N$_6$ requires C, 57·0; H, 6·3; N, 26·6%), and separated from light petroleum in radiating needles, m. p. 120°, $\lambda_{\text{max.}}$ 2900 Å ($\varepsilon$ 34,520) (Found: C, 77·0; H, 6·9. C$_{13}$H$_{14}$O$_2$ requires C, 77·2; H, 6·9%). It gave terephthalic acid and *p*-acetylbenzoic acid by oxidation with dilute nitric acid and permanganate respectively. 4-*p*-Acetylphenyl-3-methylbut-3-en-2-one was also obtained by the action of excess of acetylating agent on 4-*n*-propylacetophenone at 90—100°.

(iii) iso*Propylbenzene.* This (80 g.), after reaction at 60—70° for 2 hr., gave acetophenone (1 g.) (semicarbazone, m. p. and mixed m. p. 202°), 4-*iso*propylacetophenone (74 g.), b. p. 120—125°/12 mm. (oxime, m. p. and mixed m. p. 70°), and 4-p-*acetylphenylpent*-3-*en*-2-*one* 10 g.), b. p. 117—120°/0·02 mm., radiating needles, m. p. 56° (from light petroleum) (Found: C, 77·6; H, 7·0. C$_{13}$H$_{14}$O$_2$ requires C, 77·2; H, 6·9%), $\lambda_{\text{max.}}$ 2850 Å ($\varepsilon$ 13,720). The *bis*-2 : 4-*dinitrophenylhydrazone* separated from nitrobenzene in dark red needles, m. p. 276° (Found: C, 53·3;

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[2] Baddeley, Wrench, and Williamson, *J.*, 1953, 2110.
[3] Ingle, *Ber.*, 1894, **27**, 2507.
[4] Meyer, *Annalen*, 1883, **219**, 264.

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H, 3·7; N, 19·5. $C_{25}H_{22}O_6N_8$ requires C, 53·3; H, 3·9; N, 19·9%). Oxidation of the pentenone with permanganate at 0° gave *p*-diacetylbenzene,[5] m. p. 114° (dioxime,[5] m. p. 248—250°); oxidation with dilute nitric acid gave terephthalic acid.

(iv) n-*Butylbenzene*. This (23 g.), after reaction at 80° for 6 hr., gave 4-*n*-butylacetophenone (17 g.), b. p. 140—146°/12 mm. (semicarbazone,[6] m. p. and mixed m. p. 185°), and a fraction, b. p. 145—165°/0·5 mm. (13 g.), which gave a solid which crystallised from light petroleum in *needles*, m. p. 152° (Found: C, 77·8; H, 7·0. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%), $\lambda_{\text{max.}}$ 2500 and 2900 Å (ε 9740 and 9300 respectively), which is probably 3-*p*-acetylphenylhex-3-en-2-one. It gave terephthalic acid and *p*-acetylbenzoic acid when oxidised with dilute nitric acid and permanganate respectively. Ozonolysis in a mixture of acetic acid and ethyl acetate at 0° gave propionaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 155°), and alkali-insoluble material, m. p. 112°, which gave *p*-acetylbenzoic acid by permanganate oxidation.

(v) sec.-*Butylbenzene*. This (26 g.), after reaction at 70° for 5 hr., gave 4-*sec*.-butylacetophenone (10 g.), b. p. 134—136°/14 mm. (semicarbazone,[7] m. p. and mixed m. p. 190°), and 4-p-*acetylphenyl*-3-*methylpent*-3-*en*-2-*one* (10 g.), b. p. 140—150°/0·2 mm., radiating needles, m. p. 162° (from light petroleum) (Found: C, 77·6; H, 7·3. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%), $\lambda_{\text{max.}}$ 2500 and 3000 Å (ε 21,900 and 15,540 respectively) [*bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 180° (decomp.) (from nitrobenzene) (Found: C, 54·0; H, 4·1; N, 19·5. $C_{26}H_{24}O_8N_8$ requires C, 54·2; H, 4·2; N, 19·4%)]. Oxidation of the pentenone with dilute nitric acid and permanganate gave terephthalic acid and *p*-diacetylbenzene respectively.

(vi) iso*Butylbenzene*. This (53 g.), after reaction at 60° for 5 hr., gave 4-*iso*butylacetophenone (36 g.), b. p. 86—90°/0·5 mm. [*semicarbazone*, m. p. 206° (Found: C, 66·5; H, 8·2; N, 18·1. $C_{13}H_{19}ON_3$ requires C, 66·7; H, 8·2; N, 18·0%)], and a pale-green oil (12 g.), b. p. 120—135°/0·03 mm., which slowly darkened in the air. This oil in ethanol at 0° gave mainly 3-p-*acetylphenyl*-4-*methylpent*-3-*en*-2-*one* as a solid which separated from light petroleum in pale yellow needles, m. p. 159—160° (Found: C, 77·4; H, 7·5%), $\lambda_{\text{max.}}$ 2500 and 2950 Å (ε 23,740 and 17,520 respectively) [*bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 190° (decomp.) (Found: C, 54·3; H, 4·7; N, 19·7%)]. This pentenone gave terephthalic acid on oxidation with dilute nitric acid, and *p*-acetylbenzoic acid and acetone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 128°), on oxidation with permanganate.

(vii) m-*Ethylacetophenone and excess of acetylating agent*. Acetyl chloride (32 g.) and 3-ethylacetophenone (28 g.) were added gradually to a cooled suspension of finely powdered aluminium chloride (84 g.) in methylene chloride (100 c.c.). The solvent was volatilised under reduced pressure and the residue was heated at 80° for 2 hr. The mixture was decomposed with ice and dilute hydrochloric acid and gave (i) 3-ethylacetophenone (16 g.), b. p. 117—119°/16 mm. (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 146°), and (ii) 4-m-*acetylphenylbut*-3-*en*-2-*one* (20 g.), b. p. 120—130°/0·1 mm., needles, m. p. 76° (from light petroleum) (Found: C, 76·4; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·5%), $\lambda_{\text{max.}}$ 2450 and 2800 Å (ε 16,440 and 16,700 respectively) [*bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 230° (Found: C, 52·5; H, 3·5; N, 20·1. $C_{24}H_{20}O_8N_8$ requires C, 52·6; H, 3·7; N, 20·4%)]. The butenone gave *iso*phthalic acid (dimethyl ester, m. p. and mixed m. p. 68°) on oxidation with dilute nitric acid, and *m*-acetylbenzoic acid,[8] m. p. 174° (Found: C, 65·7; H, 5·1. Calc. for $C_9H_8O_3$: C, 65·9; H, 4·9%), on oxidation with permanganate.

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MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY. [*Received, July* 19*th*, 1956.]

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