

431. Reaction of Indane and Tetralin with Excess of Acetylating Agent.

By G. BADDELEY, E. WRENCH, and (in part) R. WILLIAMSON.

5-Acetylundane and 6-acetyltetralin, the products of Friedel-Crafts acetylation at room temperature, react readily with acetylating agent above 70°; they provide (a) 2:5- (I) and 2:6-diacetylundane (II), and (b) 6:3-diacetyl-1:2-dihydronaphthalene (VI) respectively. 4-*p*-Acetylphenylbut-3-en-2-one (V) has been prepared by acetylation of *p*-acetylstyrene, and its ultra-violet absorption spectrum has been compared with the spectra of (I), (II), and (VI).

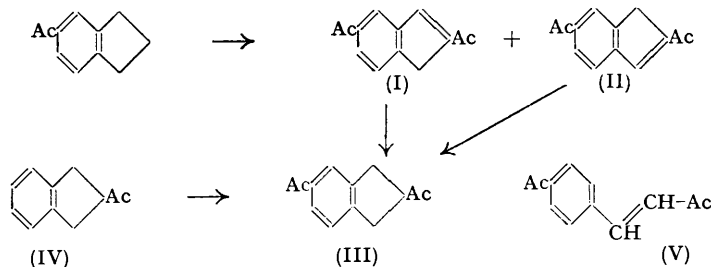
The mechanism of interaction of acylating agent and alicyclic hydrocarbon is discussed and applied to the acylation of 5-acetylundane, 6-acetyltetralin, 9:10-dihydroanthracene, and cyclohexane.

INDANE and tetralin are readily acetylated by acetyl chloride or acetic anhydride in the presence of aluminium chloride; the products, 5-acetylundane (von Braun, Kirschbaum, and Schumann, *Ber.*, 1920, **53**, 1155) and 6-acetyltetralin (Barbot, *Bull. Soc. chim.*, 1930, **47**, 1314) respectively, like all aryl ketones in which mesomeric interaction of aryl and carbonyl groups is not inhibited by bulky substituents in the *o*- and *o'*-positions, cannot be acetylated further in the aromatic ring, nor are they affected by fusion with excess of aluminium chloride at temperatures up to 170°. These considerations, together with the knowledge that acetylating agents react with aliphatic and alicyclic hydrocarbons, made it appear possible that reaction of acetylating agent with the non-aromatic rings of the above ketones could be enforced; this has been realised.

Tetralin was gradually added to a mixture of acetyl chloride (3 mol.) and aluminium chloride (4 mol. as AlCl₃) in ethylene dichloride at room temperature; after 6-acetyltetralin had been formed further ready evolution of hydrogen chloride occurred only above 70°. Solvent was removed under reduced pressure and the residue, after 2 hours at 100°, gave 3:6-diacetyl-1:2-dihydronaphthalene (VI). When applied to indane this procedure gave a mixture of 2:5- (I) and 2:6-diacetylundane (II). In the presence of solvent, these products are also obtained after reaction for 2 hours at 75° or for several days at room temperature.

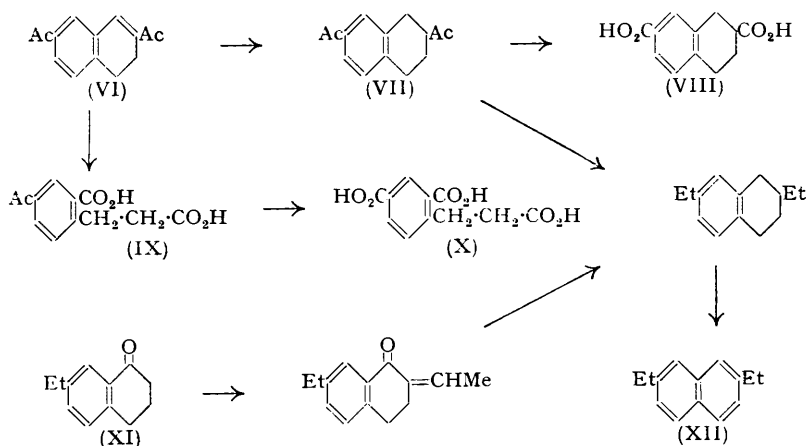
In ethanolic sodium ethoxide, (I) isomerised to (II), and catalytic hydrogenation of each gave 2:5-diacetylundane (III), identical with the product of acetylation of 2-acetylundane (IV). The identity of the two, isomeric diacetylundanes is established by a comparison of their absorption spectra with those of 4-*p*-acetylphenylbuten-2-one (V), benzylideneacetone, and 4-acetylstyrene (XIII), as recorded in the Table. The absorption spectrum of 3:6-diacetyl-1:2-dihydronaphthalene (VI) is similar to that of (I). The constitution of (VI) was established (a) by conversion into 2:7-diacetyl-1:2:3:4-tetrahydronaphthal-

ene (VII) (no absorption at 300 m μ), followed by oxidation with selenium dioxide to tetralin-2 : 7-dicarboxylic acid (VIII) or reduction and dehydrogenation to 2 : 7-diethyl-

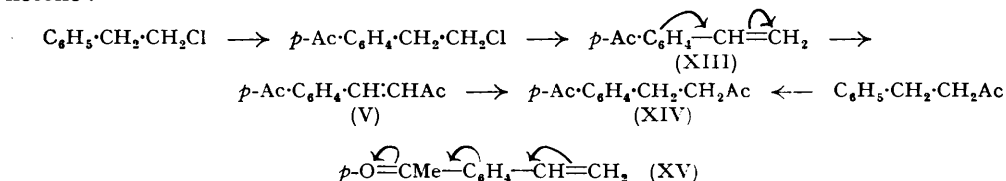


naphthalene (XII), and (b) by oxidation successively with permanganate and hypochlorite to the acids (IX) and (X). An authentic sample of (XII) was prepared from 7-ethyl-1-tetralone (XI).

	$\lambda_{\max.}$ (Å)	ϵ	$\lambda_{\max.}$ (Å)	ϵ
2 : 6-Diacetylandene (II)	3050	25,800	—	—
2 : 5- " (I)	2950	22,000	2550	23,000
2 : 5-Diacetylandene (III)	—	—	2550	13,400
4-Acetylstyrene (XIII)	2800	21,500	—	—
Benzylideneacetone	2860	23,440	—	—
4- <i>p</i> -Acetylphenylbut-3-en-2-one (V)	2950	29,500	—	—
3 : 6-Diacetyl-1 : 2-dihydronaphthalene (VI)	3000	16,600	2600	32,500
2 : 7-Diacetyl-1 : 2 : 3 : 4-tetrahydronaphthalene (VII) ...	—	—	2500	12,000

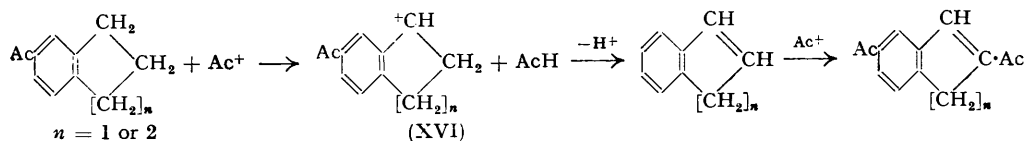


4-*p*-Acetylphenylbut-3-en-2-one (V), which was needed for comparison, could not be obtained by acetylation of benzylideneacetone or styrene; the former was not acetylated and the latter was polymerised (Bachmann *et al.*, *J. Org. Chem.*, 1947, 12, 108). It was readily prepared by acetylation of acetylstyrene, which was obtained by acetylation of 2-phenylethyl chloride under carefully selected conditions (see Experimental section) and subsequent dehydrochlorination with triethanolamine. Its structure was established by catalytic hydrogenation to a dihydro-derivative which is 2-*p*-acetylphenylethyl methyl ketone (XIV) since it is identical with the product of acetylation of methyl 2-phenylethyl ketone :



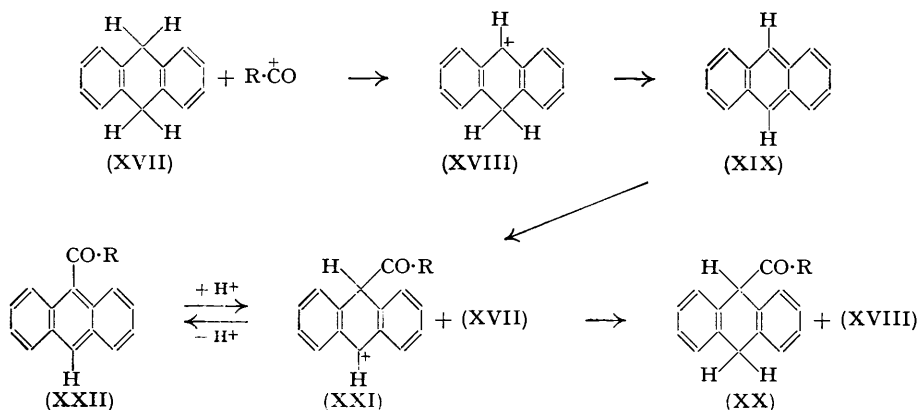
It is noteworthy that the acetyl group of *p*-acetylstyrene lowers the electron density at the vinyl group (as shown in XV) sufficiently to prevent polymerisation in the presence of acetylating agent, while, at the same time, the *p*-acetylphenyl group is sufficiently polarisable to provide an electromeric release of electrons (shown in XIII) which enables acetylation to occur at the terminal carbon atom.

Interaction of excess of acetylating agent and 5-acetylundane or 6-acetyltetralin is best represented by the scheme :



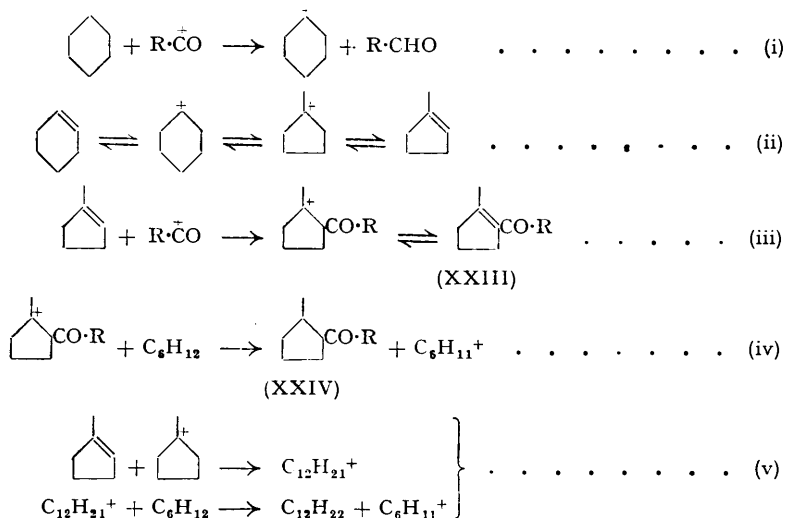
Loss of hydride ion to acetyl cation occurs at a methylene group adjacent to the benzene ring since, in this way, resonance stabilisation of the resulting carbonium ion (XVI) is best effected. This stabilising effect requires release of electrons from the benzene ring and, therefore, the methylene group in the *meta*-position to the acetyl group is the one affected. The subsequent steps are self-explanatory. (XVI; $n = 2$), unlike the cyclohexyl cation (see below), does not rearrange; this difference is probably due to spread of the positive charge into the aromatic ring. When $n = 1$, the product, 2 : 5-diacetylundane, readily affords the 2 : 6-isomer by migration of a proton.

Direct acylation of a methylene group seems to occur in 9 : 10-dihydroanthracene (XVII) since the 9-acyl derivative (XX) is obtained. In fact, the reaction is best represented by the annexed scheme in which reaction is initiated by transfer of hydride ion from (XVII) to acyl cation, a ready process as the charge on (XVIII) is spread over two benzene rings, and formation of anthracene (XIX). A chain reaction then ensues : (XIX) affords 9-acetylanthracene (XXII) which, as the cation (XXI), is reduced to (XX) by gain of hydride ion from (XVII). This scheme is supported by the fact (see Experimental section) that a mixture of (XVII), (XXII), and aluminium chloride affords (XIX) and (XX).



These considerations can, by suitable modification, be applied to the acylation of aliphatic and alicyclic hydrocarbons. The following scheme, in which the hydrocarbon is cyclohexane, is analogous to that for reaction of alkyl cation with saturated hydrocarbons (Schmerling, "Catalytic Reactions of Hydrocarbons—Ionic Mechanism," Symposium No. 24, Sept, 1952, New Jersey). Reaction (i) accounts for the formation of aldehyde (cf. Nenitzescu *et al.*, *Annalen*, 1931, **491**, 189; *Ber.*, 1932, **65**, 1449) and, like (iv), involves transfer of hydride ion. Reaction (ii) represents interconversion of cyclohexene and 1-methylcyclopentene (Adkins and Roebuck, *J. Amer. Chem. Soc.*, 1948, **70**, 4041) and includes the same isomerisation of cycloalkyl cations as occurs in the interconversion of cyclohexane and methylcyclopentane (Pines, Abraham, and Ipatieff, *ibid.*, 1948, **70**, 1742).

Reaction (iii) suitably represents the acylation of 1-methylcyclopentene. Combination of (iv) with the right-hand side of (iii) illustrates reduction of $\alpha\beta$ -unsaturated ketone by cyclohexane, and several reductions of this type are known; e.g., interaction of cyclohexene, crotonyl chloride, and aluminium chloride in cyclohexane affords saturated ketone, cyclohexyl *n*-propyl ketone (Nenitzescu and Curcaneanu, *Bull. Soc. chim. Romania*, 1939,



1, 133), and an unsaturated ketone (cyclohexenyl propylidene ketone), together with its products of hydrochlorination, in inert solvents (Baddeley, Taylor, and Pickles, *J.*, 1953, 124). This reduction process readily accounts for variation of relative amounts of saturated and unsaturated ketone with experimental procedure; e.g., Telinsky and Tarassowa (*Ber.*, 1932, 65, 1249; *Annalen*, 1934, 508, 115) showed that acetylation of cyclohexane at 18–35° provides mainly (XXIII), whereas, when the temperature is gradually raised to 70°, the product is almost entirely (XXIV).

EXPERIMENTAL

Tetralin and Excess of Acetylating Agent.—(i) *In ethylene chloride.* At room temperature, a mixture of tetralin (16 g.), acetyl chloride (32 g., 2 mol.), and aluminium chloride (56 g., 2 mol.) in ethylene dichloride (40 c.c.) rapidly evolved hydrogen chloride (1 mol.) and gave 6-acetyltetralin. Hydrogen chloride was again rapidly evolved when the mixture was warmed to 70–75° and this reaction was complete after 2 hr. The mixture was worked up in the usual way and gave 6-acetyltetralin (20 g.), b. p. 165–175°/15 mm., and 3 : 6-diacetyl-1 : 2-dihydronaphthalene (VI) (7 g.), b. p. 190–200°/0.12 mm., needles (from light petroleum), m. p. 73–74°, together with unsaturated material of intermediate b. p. These products (20 and 10 g. respectively) were also obtained after reaction for 3 days at 20°. Tetralin (25 g.), acetic anhydride (61 g., 2 mol.), and aluminium chloride (168 g., 4 mol.) in ethylene dichloride at 70–75° gave the same products (14.6 and 13.5 g. respectively).

(ii) *Without solvent.* Tetralin (26 g.) was gradually added to a mixture of aluminium chloride (112 g., 4 mol.) and acetyl chloride (48 g., 3 mol.) in ethylene chloride (75 c.c.). When vigorous reaction at room temperature had ended, the solvent was removed under reduced pressure and the residue heated for 2 hr. at 100°. Only one fraction, b. p. 190–200°/0.12 mm. (18 g.), was obtained and this provided pure (VI) (13 g.).

6-Acetyltetralin and Acetylating Agent (1 mol.).—Since addition of aluminium chloride to a mixture of acetyltetralin and acetyl chloride causes extensive decomposition, the reaction mixture was prepared by adding a molten mixture of the ketone (8.7 g.) and aluminium chloride (10.5 g., 1.5 mol.) to a mixture of acetyl chloride (4.0 g., 1 mol.) and aluminium chloride (10.5 g.). After 2 hr. at 100°, the same two products (5 and 4 g. respectively) were obtained.

Identification of (VI).—(i) This compound (Found: C, 78.7; H, 6.6. C₁₄H₁₄O₂ requires C, 78.7; H, 6.55%) combined with 2 : 4-dinitrophenylhydrazine (2 mol.), affording a bis-2 : 4-

2114 Reaction of Indane and Tetralin with Acetylating Agents.

dinitrophenylhydrazone, red prisms (from nitrobenzene), decomp. 270° (Found: C, 54.5; H, 3.8; N, 19.6. $C_{26}H_{22}O_8N_8$ requires C, 54.4; H, 3.8; N, 19.5%). (ii) The compound (VI) (10.7 g.) in ethanol over Raney nickel absorbed hydrogen (1 mol.), giving 2 : 7-*diacetyltetralin* (VII) (9.5 g.), b. p. 180—190°/0.3 mm., plates (from light petroleum), m. p. 52—53° (Found: C, 77.6; H, 7.9. $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.4%), which formed a *bis*-2 : 4-*dinitrophenylhydrazone*, orange rods (from nitrobenzene), decomp. 246° (Found: C, 54.8; H, 4.3; N, 19.9. $C_{26}H_{24}O_8N_8$ requires C, 54.2; H, 4.2; N, 19.45%). A mixture of (VII) (2.5 g.), selenium dioxide (2.5 g.), water (0.5 c.c.), and dioxan (35 c.c.) was refluxed for 4 hr.; the organic product was isolated and oxidised with hydrogen peroxide (30%; 20 c.c.) and aqueous sodium hydroxide (8%; 30 c.c.); acidification gave *tetralin*-2 : 7-*dicarboxylic acid* (VIII) (0.5 g.), m. p. 260° (decomp.) (Found: C, 65.6; H, 6.05%; equiv., 105. $C_{12}H_{12}O_4$ requires C, 65.4; H, 5.45%; equiv., 110). The acid (VIII) (1.5 g.) and palladised charcoal (30%; 0.8 g.) at 270° gave naphthalene and hydrogen (2 mol.). (iii) A mixture of (VII) (6.0 g.), amalgamated zinc (80 g.), and hydrochloric acid (*d* 1.6; 350 c.c.) was refluxed for 19 hr. and gave 2 : 7-*diethyltetralin* (2.2 g.), b. p. 150—155°/15 mm. (Found: C, 89.4; H, 10.65. $C_{14}H_{20}$ requires C, 89.4; H, 10.6%), which was dehydrogenated over palladised charcoal at 270° to 2 : 7-*diethylnaphthalene*; the *picrate*, m. p. and mixed m. p. (see below) 77—78°, crystallised from ethanol in orange needles (Found: C, 58.0; H, 4.8; N, 10.0. $C_{20}H_{23}O_7N_3$ requires C, 58.0; H, 4.6; N, 10.1%). (iv) Finely powdered (VI) (0.5 g.), shaken for 3 hr. with ice-cold aqueous potassium permanganate (1.0 g. in 25 c.c.), gave β -4-*acetyl-2-carboxyphenylpropionic acid* (IX) as radiating needles, m. p. 218—220° (from water) (Found: C, 61.5; H, 5.3%; equiv., 118. $C_{12}H_{12}O_5$ requires C, 61.5; H, 5.1%; equiv., 118). Oxidation of (IX) with alkaline hypochlorite at 100° gave β -2 : 4-*dicarboxyphenylpropionic acid*, m. p. 267—268° (Found: C, 55.4; H, 4.2; equiv., 79. Calc. for $C_{11}H_{10}O_6$: C, 55.4; H, 4.2%; equiv., 79); Zinke and Franke (*Annalen*, 1897, 293, 168) give the m. p. as 265—266°.

Authentic 2 : 7-Diethylnaphthalene.— β -*p*-Ethylbenzoylpropionic acid was obtained by interaction of ethylbenzene, succinic anhydride, and aluminium chloride in ethylene chloride and afforded 7-ethyl-1-tetralone (Bachmann and Edgerton, *J. Amer. Chem. Soc.*, 1940, 62, 2222; Krollpfeiffer, *Ber.*, 1923, 56, 626). The product (19 g.) together with acetaldehyde (10 g., 2 mol.) at 0° was subjected for 3 hr. to a stream of dry hydrogen chloride and, after storage overnight, gave 7-ethyl-2-ethylidene-1-tetralone (17 g.), b. p. 180—185°/12 mm. (Found: C, 84.3; H, 7.8. $C_{14}H_{15}O$ requires C, 84.0; H, 8.0%). Hydrogenation over Raney nickel gave 2 : 7-diethyl-1-tetralone, b. p. 165—170°/12 mm. [*semicarbazone*, m. p. 198—199° (Found: N, 15.9. $C_{15}H_{21}ON_3$ requires N, 16.3%)], and 2 : 7-diethylnaphthalene was obtained by Clemmensen reduction.

Indane and Excess of Acetylating Agent.—(i) *In ethylene chloride at 20°*. Indane (24 g.) was added to a solution of aluminium chloride (84 g.) and acetyl chloride (48 g.) in solvent (60 c.c.); after 3 days at 20°, the mixture gave 5-acetylintane (9.3 g.), b. p. 110—120°/0.1 mm., and a mixture of 2 : 5- (I) and 2 : 6-diacetylintane (II) (10.7 g.), b. p. 180—190°/0.1 mm., which melted over a wide range.

(ii) *In absence of solvent*. The same fractions (8 and 7 g. respectively) were obtained after addition of indane (24 g.) to acetic anhydride (61 g., 3 mol.) and aluminium chloride (168 g., 6 mol.) in ethylene chloride (120 c.c.), removal of solvent under reduced pressure and heating of the residue for 2 hr. at 100°. These two fractions (7 and 15 g. respectively) were obtained by addition of indane (24 g.) to acetyl chloride (48 g.) and aluminium chloride (84 g.) and heating at 100° for 2 hr.

Identification of (I) and (II). (i) Mixtures of (I) and (II) were fractionally crystallised from ethanol and afforded 2 : 6-*diacetylintane* (II) as small plates, m. p. 161—163° (Found: C, 78.2; H, 6.1. $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.0%), and the more soluble 2 : 5-*isomer* (I) as rods, m. p. 106—108° (Found: C, 77.8; H, 6.0%).

(ii) Both slowly decolorised aqueous permanganate and bromine in carbon tetrachloride and absorbed hydrogen (1 mol.), to provide 2 : 5-*diacetylintane* (III) (Found: C, 77.8; H, 6.8. $C_{13}H_{14}O_2$ requires C, 77.5; H, 6.9%). This was obtained in poor yield by interaction of 2-acetylintane (IV) (Perkin, *J.*, 1894, 241) (5 g.), aluminium chloride (13 g.), and acetyl chloride (3.1 g.). (iii) Addition of ethanolic sodium ethoxide to (I) gave a deep-red solution and addition of hydrochloric acid precipitated a solid from which (II) was obtained by crystallisation from ethanol. (iv) The identity of (I) and (II) was established by comparison of their absorption spectra with those of 4-*p*-acetylphenylbuten-2-one (V), *p*-acetylstyrene (XIII), and benzylideneacetone.

2-p-Acetylphenylethyl Chloride.—A solution of acetyl chloride (16 g., 2 mol.) and aluminium

chloride (15 g., 1.1 mol.) in ethylene chloride was added to 2-phenylethyl chloride (13.5 g.) in ethylene chloride. Reaction was complete in a few minutes and gave the required chloride (14 g.), b. p. 168°/15 mm. The 2 : 4-dinitrophenylhydrazone separated from ethanol in orange-yellow needles, m. p. 184° (Found : C, 52.5; H, 4.6; N, 15.2; Cl, 9.7. $C_{16}H_{16}O_4N_4Cl$ requires C, 53.0; H, 4.2; N, 15.4; Cl, 9.8%).

p-Acetylstyrene (XIII).—This compound (6 g.), b. p. 110°/12 mm., was obtained by steam-distillation of the above chloride (10 g.), triethanolamine (100 c.c.), and water (50 c.c.); it separated from light petroleum in needles, m. p. 33° (Found : C, 81.7; H, 6.9. $C_{10}H_{10}O$ requires C, 82.1; H, 6.9%), and afforded *p*-ethylacetophenone (semicarbazone, m. p. and mixed m. p. 153°) by hydrogenation.

4-*p*-Acetylphenylbut-3-en-2-one (V).—The ketone (XIII) (1.3 g.) was gradually added to a mixture of acetyl chloride (1.0 g.) and excess of aluminium chloride in methylene chloride. Reaction was instantaneous and gave (V) (1.4 g.), as pale yellow plates, m. p. 103° (Found : C, 76.6; H, 6.2. $C_{12}H_{12}O_2$ requires C, 76.5; H, 6.5%), from light petroleum. Hydrogenation gave 4-*p*-acetylphenylbutan-2-one (XIV), b. p. 150°/0.15 mm., which was identified by its bis-2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 272° (Found : C, 52.2; H, 4.4; N, 20.0. $C_{24}H_{22}O_8N_8$ requires C, 52.5; H, 4.0; N, 20.4%). Authentic (XIV) was prepared by addition of methyl 2-phenylethyl ketone (7.5 g.), obtained by hydrogenation of benzylideneacetone, to a mixture of acetyl chloride (4 g.) and aluminium chloride (15 g.) in methylene chloride.

Interaction of 9 : 10-Dihydroanthracene, 9-Benzoylanthracene, and Aluminium Chloride.—The reactants (0.7, 1.0, and 0.5 g. respectively) were brought together in carbon disulphide and set aside for 24 hr. Chromatographic separation of the products in benzene on alumina gave anthracene and 9-benzoyl-9 : 10-dihydroanthracene.