THE FRIEDEL-CRAFTS ACYLATION REACTION AND ITS APPLICATION TO POLYCYCLIC AROMATIC HYDROCARBONS

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I. Introduction

In the past the Friedel–Crafts ketone synthesis has generally been regarded more as a branch of the related alkylation reaction than as a separate topic. The essential difference between the two reactions—the amount of catalyst required—had been recognized but largely ignored. It is the purpose of this article to discuss the acylation reaction on its own merits and to review its general features with emphasis on the developments of the last twelve years.

In Sections II and III, which deal with the mechanism and special features of the acylation reaction, no attempt at a comprehensive bibliography is made, but only leading references are given. In Section IV, which comprises a discussion of the acylation reactions of ten polycyclic aromatic hydrocarbons and tables of results, a complete literature coverage is attempted.

For the purposes of this review the term "acylation" is interpreted as the direct formation of compounds containing one carbonyl group attached to the aromatic system. This definition includes the formation of ketones, carboxal-

dehydes, carboxylic acids, and amides, and does not include the related (but indirect) Gattermann aldehyde synthesis, the Houben–Fischer ketone synthesis, nor the formation of diketones, etc. Further, the acylations only of the unsubstituted polycyclic hydrocarbons are discussed, in order to set a limit.

The names and numbering systems used are those of *Chemical Abstracts*.

II. The Mechanism of the Friedel–Crafts Acylation Reaction[1]

In general terms the Friedel–Crafts acylation reaction involves three reactants—a hydrocarbon, an acyl component, and a catalyst. The overall reaction is, for example,

$$ArH + RCOCl + AlCl_3 \rightarrow ArCOR \cdot AlCl_3 + HCl$$

The finer points of the mechanism of the reaction, beyond the initial stage, still remain to be solved. It is generally agreed that the first stage is the interaction of the acid halide with aluminum halide giving an addition compound, which is the *potential* acylating agent.

$$RCOX + AlX_3 \rightarrow RCOX \cdot AlX_3$$

This adduct is alternatively considered to be an oxonium complex, $RC(X)=\overset{\oplus}{O}-\overset{\ominus}{AlX_3}$ (25, 134, 343) or $[RC(X)=\overset{\oplus}{O}-\overset{\ominus}{AlX_2}-\overset{\oplus}{O}=C(X)R]^{\oplus}AlX_4^{\ominus}$ (267), or an ion-pair $[RCO]^{\oplus}[AlX_4]^{\ominus}$. A degree of ionization has been experimentally established (25, 145, 146, 147, 255, 256, 329). The acyl cation so produced is accepted by many authors as the *actual* acylating agent in Friedel–Crafts reactions (25, 104, 140, 147, 236, 237, 338). Evidence has recently been obtained (25) that the cation is present only in traces in a particular system, and the addition compound was consequently represented as

$$RC(X)=\overset{\oplus}{O}-\overset{\ominus}{AlX_3} \rightleftharpoons RCO^{\oplus} + AlX_4^{\ominus}$$

The fact that 2,4,6-tribromobenzoyl halide reacts with such hydrocarbons as *m*-xylene and benzene (25), in the presence of aluminum halide, was considered to provide evidence that the acylating agent is here not the sterically hindered oxonium complex, but the acylium ion.

The postulate that the attacking agent in aromatic acylations is the acyl cation has recently been attacked (66). It is known that the acylation of toluene results in the practically exclusive formation of the *p*-isomer (337). The conclusion drawn was that some intermediate must be involved in the substitution stage of larger steric requirements than the acylium ion, which would be expected to yield some *o*-isomer as well. The implication of this appears to be that substitution proceeds rather by a bimolecular nucleophilic attack (S_N2 type) of the aromatic component on the acyl halide–aluminum halide adduct. Such a mechanism would then be analogous to the mechanism of the benzylation of benzene, i.e., in a related Friedel–Crafts alkylation reaction (67, 70).

Moreover, in certain acylating systems, such as acetyl perchlorate (76, 77, 78)

[1] For earlier reviews and data see references 134, 147, 202, 398, 409, and 411.

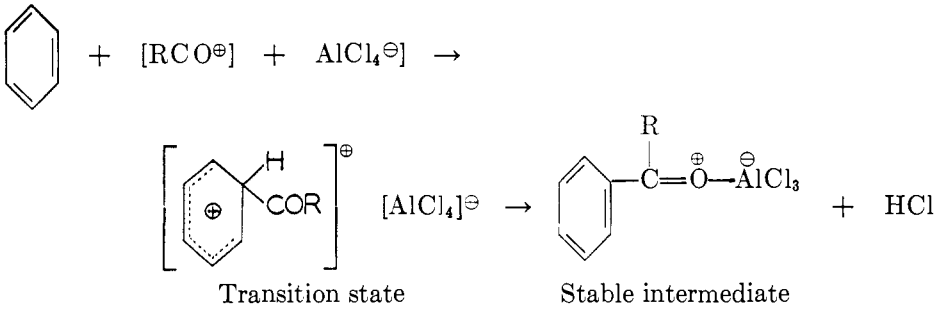
and aromatic hydrocarbons, in which the presence of acyl cations is not doubted, the idea that acylation proceeds exclusively by the simple ionic mechanism seems to break down (81, 408). Such a reagent is capable of giving excellent yields of acylated product with very reactive aromatics such as anisole or mesitylene, but is far less effective with toluene, and gives only poor yields with benzene. On the other hand, the acyl chloride–aluminum chloride reagent gives good yields of ketone under mild conditions not only with benzene but with deactivated molecules such as chlorobenzene. Two explanations have been offered for this apparent anomaly. The first (79, 80, 81) states that the low concentration of ions normally present in acylating systems in hydrocarbon solvents may be appreciably increased, when aluminum chloride is used, by contact with Friedel–Crafts complexes, the so-called "red oils," which are known to be present under similar conditions. These complexes, shown to be of the type $R^{\oplus}[AlX_4 \cdot nAlX_3]^{\ominus}$, are believed to provide a suitable environment for the production of ionic intermediates (69, 72). The second explanation (408) suggests that acylation by means of acyl chloride and aluminum chloride may take place by either of two mechanisms, the ionic (*I*) and the nucleophilic substitution (*S*) mechanisms,[2] depending on the reactivity of the aromatic substrate. With a reactive aromatic substance acylation would occur by both processes simultaneously; acylation of less activated hydrocarbons (e.g., toluene) would proceed to a larger extent by substitution (*S*), and in the case of benzene exclusively so, i.e., the acyl cations undoubtedly present are insufficiently reactive to account for the rapid acylation of unreactive compounds. A duality of mechanism for the Friedel–Crafts acylation reaction had been envisaged earlier (80) and does seem to offer an attractive working hypothesis.

It was observed (25) that 2,4,6-trimethylbenzoyl chloride does not react under normal (i.e., aluminum chloride-catalyzed) conditions with benzene, or even with *m*- or *p*-xylene, but does with anisole. This seemingly abnormal result was explained on the assumption that the aluminum chloride complex in this case was completely ionized, giving the trimethylbenzoylium ion, for which great stability (and low reactivity) is to be expected, owing to the electron-releasing alkyl groups (408). It does seem unnecessary, however, to postulate complete ionization, even in this favorable case. It is more likely that this is a case of substitution (*S*) being suppressed owing to steric hindrance in the addition complex; the ionic reaction can still proceed, but owing to the low reactivity of the ion, the rate of reaction becomes observable only with the highly reactive anisole. A further conclusion is that normal Friedel–Crafts acylation of alkyl-substituted benzene derivatives must occur predominantly by the substitution (*S*) reaction, particularly when the acyl halide employed possesses electron-releasing substituents (190). Some further results observed with 2,4,6-tribromobenzoyl chloride (25) deserve comment. The rates of reaction with *m*-xylene, *p*-xylene, benzene, and naphthalene were observed to decrease in the stated sequence. The order of reactivity of the first three substances is probably normal, since toluene is acetylated more rapidly than benzene (295, 333, 334). The po-

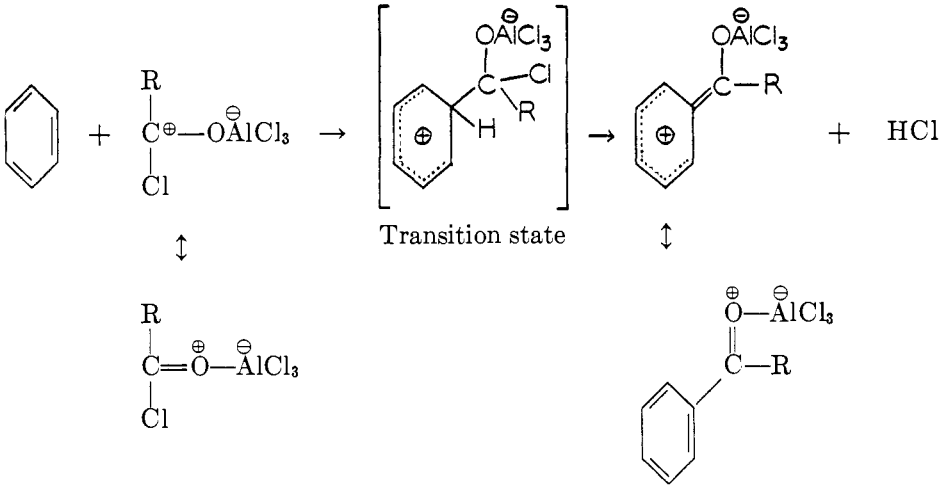
[2] Subsequent conclusions are independent of the precise nature of this substitution reaction.

sition of naphthalene in this sequence is definitely abnormal however, since it is acetylated much more rapidly than benzene (333, 334). It has been suggested that in this system the acylating agent is the tribromobenzoyl cation (see above); further evidence for this is supplied by the observation (25) that acylation occurs in the α-position of naphthalene. It seems likely that the bulky aluminum chloride complex, the agent in the alternative substitution (S) reaction, would seek out the sterically more accessible β-position (see Section IV,A). Furthermore, normal acylations in carbon disulfide under conditions most exactly duplicating those of the present experiment usually give α- and β-isomers in the approximate ratio of 3:2 (32). It follows that the usual high reactivity of naphthalene in acylation reactions is due predominantly to substitution by the S type of mechanism (190). It had previously been concluded (408) that acylation of benzene occurs solely by the substitution (S) mechanism. In the present case acylation by the ionic mechanism can occur not only with benzene but with the less reactive naphthalene, because of the unusually high reactivity of the cation, due to the substituent bromine atoms. The two types of mechanism may be formulated as follows:

Ionic mechanism (I):



Substitution mechanism (S):



The ionic (*I*) mechanism is that previously postulated (347, 423); the substitution (*S*) mechanism is written as a bimolecular nucleophilic attack by the hydrocarbon on the oxonium complex.

The undoubted activation of the acyl halide by means of the catalyst leaves untouched the question of whether the aromatic hydrocarbon is also activated in some manner by means of the catalyst (237, 349), as for instance in the "proton theory of activation" (409). It has, however, been shown that the complexes most likely to be produced in these systems, e.g., $C_6H_6 \cdot Al_2Br_6$, do not play any significant role in Friedel–Crafts reactions (70, 71).

Quite a different type of mechanism has also been proposed (234), which has received some support (199, 302). The initial step proposed is the formation of an enol derivative, e.g., with acetyl chloride, $CH_2{=}CCl{-}OAlCl_2$, since one mole of hydrogen chloride was found to be evolved from a solution in carbon disulfide with one mole of aluminum chloride. The resultant product was successfully condensed with benzene to give a 65 per cent yield of acetophenone. However, since the initial formation of the enol complex takes four days, such an intermediate cannot be of significance in normal Friedel–Crafts reactions.

Mechanisms of other types have been proposed, but they may be dismissed since they are not founded on experimental evidence (238, 252, 387).

Conclusions: (*1*) Normal Friedel–Crafts acylation reactions with aromatic substances of a wide range of reactivity probably proceed primarily by a novel type of substitution mechanism (*S*). (*2*) Ionic substitution becomes important only under special circumstances, when (*a*) a sterically hindered acyl halide is used, or (*b*) a sterically hindered position, e.g., the 9-anthryl position, is being substituted.

III. General Features of the Friedel–Crafts Acylation Reaction

A. The catalyst

The use of aluminum chloride as a Friedel–Crafts catalyst has been the subject of excellent monographs (259, 409), and prominence will therefore be given to more recent investigations. Aluminum chloride is most generally used, because it undoubtedly is the cheapest of the most efficient catalysts in this reaction. The purity of the aluminum chloride itself may have a considerable influence on the yield of product (54, 356, 409, 424). The cause is very likely the presence of trace elements, e.g., a particular grade of aluminum chloride was found to be much more active than could be accounted for by its ferric chloride content alone, and its greater activity was thought to be due partly to the titanium chloride it contains (409). Admixture of ferric chloride to aluminum chloride was stated to result in decreased yields (356), which rose on increasing the amount of ferric chloride to a maximum at 50 mole per cent, and then again decreased. Later investigators (289) found the activity to increase steadily with increasing mole per cent of ferric chloride to a maximum at greater than 50 mole per cent. The mixed catalysts were found, however, to yield less ketone per mole of total metal chloride than did the pure aluminum chloride.

The addition of a trace of water to a reaction mixture may moderate otherwise violent reactions, such as the action of nitrophthalic acid on toluene (306, 369). More often, however, the addition of water appears to activate the catalyst. In one investigation of the acetylation of naphthalene in carbon disulfide (172, 371), a drop of water was added to start the reaction. In other investigations (277, 278, 431) it was observed that a little water added to anhydrous aluminum chloride caused considerable improvements in yield. It should be realized, of course, that in practice perfectly anhydrous conditions for the Friedel–Crafts reaction are rarely obtained. It has been claimed that aluminum chloride containing neither moisture nor hydrogen chloride (deriving from partial hydrolysis) may be found to be entirely useless as a catalyst (409). This is very unlikely. The activating influence of water on aluminum halides was explained (148) by the formation of hydrates of the type $[AlX_3OH]^{\ominus}H^{\oplus}$, which can act as powerful proton sources; such acids would be expected to behave in a similar manner to other proton acids, which can act as Friedel–Crafts catalysts.

It has been known for a long time that stoichiometric amounts of aluminum chloride are required for complete utilization of the acyl component (47, 409). The equations may be written as follows (97, 202, 205, 235, 326):

$$RCOCl + AlCl_3 \rightarrow RCOCl \cdot AlCl_3 \quad \text{(a)}$$

$$(RCO)_2O + 3AlCl_3 \rightarrow 2RCOCl \cdot AlCl_3 + AlOCl \quad \text{(b)}$$

$$RCOOH + 2AlCl_3 \rightarrow RCOCl \cdot AlCl_3 + AlOCl + HCl \quad \text{(c)}$$

$$RCOOR' + 2AlCl_3 \rightarrow RCOCl \cdot AlCl_3 + AlOCl + R'Cl \quad \text{(d)}$$

In practice a ratio (number of moles of catalyst to number of moles of acyl component) of 1.1 has been found optimum for reaction (a) (202), at least 3 for reaction (b) (201), at least 2 for reaction (c) (204), and 2.2 for reaction (d) (328).

Since one mole of aluminum chloride is bound as a complex to each mole of ketone produced, the catalyst is in effect being continuously removed from the reaction mixture. The reaction ceases when all the catalyst has been so complexed (402, 409); this is so because the final complex generally possesses very little catalytic activity (25, 134, 319, 412). It is however likely, whenever the final complex is incompletely precipitated, as from nitrobenzene, that a certain equilibrium amount of aluminum chloride is available for further catalysis (see Section IV,A). Consequently, many poor yields quoted in the literature were ascribed to insufficient amounts of catalyst (327). For example, a yield of 50 per cent in the propionylation of benzene with the use of 0.7 mole of aluminum chloride could be increased to 89 per cent by an additional 0.15 mole of catalyst (23). Also, reducing the amount of aluminum chloride in the preparation of benzophenone under certain conditions reduces the yield in almost the same proportion (362). Similarly, the use of low-grade aluminum chloride gave yields of ketone practically proportional to its content of aluminum chloride (200).

Other catalysts (92) for use with acyl halides which have given some measure of success include $AlBr_3$ (130, 229), $CbCl_5$ (129), $TiCl_4$ (124), $ZrCl_4$ (215), $FeBr_3$ (130), $SbBr_3$ (130), Ce (265), $BeCl_2$ (60, 61, 62), P_2O_5 (252, 268, 377), UCl_4, $MbCl_5$, WCl_6 (245), H_2SO_4 (37, 211), Zn (207, 263, 276, 277, 278, 344), $ZnCl_2$ (252, 263, 361), $CuCl_2$ (332), and $HgCl_2$ (332). The first four catalysts mentioned are stated to give yields at least as good as with aluminum chloride, though generally more slowly. The last three catalysts mentioned give good results without the use of solvent, at elevated temperatures. Application of heat is often sufficient to cause reaction between an acyl chloride and especially reactive aromatic substances (131, 319, 409) in the absence of a catalyst.

For use with anhydrides, the following catalysts have been found to be effective: BF_3 (188, 257, 298, 299, 300, 348), HF (158), $ZnCl_2$ (83, 415, 432), H_3PO_4 (323), $SnCl_4$ (74, 75), $SOCl_2$ (435), $(CF_3CO)_2O$ (55), CF_3COOH (56), $HClO_4$ (76, 77, 78, 165), and $AgClO_4$ (79, 103). Both aluminum and zinc chloride proved unsuccessful in the absence of solvent in attempted condensations with phthalic anhydride, with temperatures up to 95°C. (206). Carboxylic acids can be used in conjunction with BF_3 (298, 299, 300), $ZnCl_2$ (317, 318), or P_2O_5 (253).

The Gattermann–Koch synthesis of aldehydes (179) usually employs aluminum chloride with a promoter, such as Cu_2Cl_2, $NiCl_2$, $CoCl_2$, $FeCl_3$, WCl_6, $TiCl_4$ (208, 254). Nickelous chloride gives good yields (254), but titanium tetrachloride is best, as it is highly active even at as low a concentration as 1 per cent (208, 209, 226).

There have been a number of studies comparing yields of ketones under standard conditions with a variety of catalysts. In the acylation of furans the sequence is $SnCl_4 > FeCl_3 > AlCl_3 > TiCl_4$ (93, 106). There are two sequences giving comparisons of catalytic power for a series of chlorides (129, 131), and one for a series of bromides (130), a total of some fifty halides, about ten of which show reasonable activity. The optimum catalyst ratios have been determined for most of these; some do not correspond to theory.

It has been known for some time that the yield falls off rapidly when more than the optimum amount of catalyst is used in acylation reactions (356). This is true for aluminum chloride (356), antimony pentachloride, and tellurium tetrachloride, with an excess of zinc chloride and bismuth trichloride showing a small deleterious effect (131). There are also certain catalysts for which there is an optimum reaction time: aluminum trichloride (95), antimony pentachloride, ferric chloride (131), and titanium tetrachloride (124, 131). The probable reason is self-condensation of the ketone produced; e.g., acetophenone readily affords dypnone under such conditions (95).

The preëminence of aluminum chloride has been suggested (81) to be due to the non-existence of the acid $HAlCl_4$ (68, 355). Likewise the great catalytic power of aluminum bromide (130) may be ascribed to the non-existence of the acid $HAlBr_4$ (143, 164). An alternative explanation is simply that these two catalysts are very powerful Lewis acids (36, 212, 406, 407), and that their addition complexes with acyl halides are therefore highly polarized and very reactive.

B. THE ACYL COMPONENT

The acyl component in the Friedel–Crafts reaction may be any substance which under the influence of a catalyst will give rise to a potential acyl cation or other reactive entity. For the introduction of the acyl group (RCO—) into an aromatic nucleus, the chloride RCOCl is most frequently used. Other reagents—carboxylic acids, esters, and anhydrides—are first converted into RCOX by means of aluminum or other metal halide (205), and then into the reactive complex (see Section II, page 230). It appears that other substances which give rise to aromatic carbonyl compounds in the Friedel–Crafts reaction do so *via* similar reactive intermediates through the agency of the catalyst.

Acyl halides usually behave normally. α,β-Unsaturated acid chlorides generally cannot be used, as they polymerize. Cinnamoyl chloride gives abnormal products with benzene (251) or phenanthrene (191), but successfully acylates more reactive substances, such as aromatic ethers (251, 390, 391), biphenyl (17), anthracene (59), and pyrene (372, 373). The reactivity of the acyl halides has been shown to decrease in the expected order of decreasing atomic weight of the halogens I > Br > Cl > F (94). In the acylation of toluene in the presence of aluminum chloride (288), yields were shown to decrease in the sequence acetyl chloride > benzoyl chloride > 2-ethylbutyryl chloride. With titanium tetrachloride as catalyst (124), yields generally follow the sequence benzoyl chloride > *n*-butyryl chloride > *n*-propionyl chloride > acetyl chloride, i.e., the yields decrease with decreasing chain length.

Either one or both of the acyl residues of an anhydride $(RCO)_2O$ may be utilized, depending on the amount of catalyst supplied (124, 198, 203, 205, 219, 235, 327). Cyclic dicarboxylic acid anhydrides are generally treated so as to give monoacyl derivatives (42). A mixed anhydride, RCOOCOR′, gives a mixture of two ketones, the yield of the ketone with higher molecular weight generally being greater, especially with an excess of aluminum chloride (427).

Carboxylic acids have lately been increasingly used in acylation reactions (124, 204, 235, 286, 287, 317, 318, 326, 395), and the method recommended as the most economical (286). In one set of experiments with aluminum chloride (287), benzene could be condensed with butyric acid, but not with benzoic, phthalic, or oxalic acid.

Acetic anhydride is said to give better yields in the acetylation of bromobenzene (1) but lower yields in the acetylation of toluene (288) than does acetyl chloride. The acetylation of benzene, in the presence of carbon disulfide as solvent, has been shown to give yields decreasing in the order acetyl chloride > acetic anhydride > acetic acid, but with excess benzene as solvent acetyl chloride > acetic acid > acetic anhydride (365). Products have been claimed to be of higher purity when acetic anhydride is used (205, 327).

The use of esters results in both alkylation and acylation (58, 63, 64, 123, 231, 233, 264, 328). Benzene and ethyl acetate, for instance, give both ethylbenzene and acetophenone (244):

$$CH_3COOC_2H_5 + 2C_6H_6 + 2AlCl_3 \rightarrow C_6H_5COCH_3 \cdot AlCl_3 + C_6H_5C_2H_5 + AlOCl + 2HCl$$

Formates are unsuccessful (328). *p*-Nitrophenyl acetate has been found to be nearly as reactive as acetyl chloride in the acetylation of toluene (288). Also, in the benzoylation of toluene, both benzoyl chloride and *p*-nitrophenyl benzoate give better yields than does benzoic anhydride (288).

Ketenes have been successfully used as acylating agents (167, 224, 336, 397, 428), in particular, ketene itself. Like the more common anhydride of acetic acid, ketene presumably is first changed into acetyl chloride in this process (235). Carbon suboxide, which has the ketene-type structure O=C=C=C=O, likewise may be used as an acylating agent (45) in the presence of aluminum chloride or stannic chloride. With benzene a small yield of acetophenone is formed, by way of benzoylacetic acid, together with much polymer.

An aldehyde group may be introduced directly into an aromatic system by the Gattermann–Koch reaction (179), which uses a mixture of carbon monoxide and hydrogen chloride, usually in the presence of aluminum chloride together with an activator (see Section III,A). This reaction fails for the unreactive benzene and chlorobenzene, unless pressure (46, 221) or a good solvent for gases, such as nitrobenzene, is employed (379). The two gases initially combine to give formyl chloride (179, 205, 220), which further reacts to give the complex $[HCO]^{\oplus}[AlCl_4]^{\ominus}$ (202) as the active acylating agent. Alternatively, formic acid may be used in the presence of aluminum chloride (205).

$$\begin{matrix} CO + HCl \\ \qquad\searrow \\ \qquad\quad HCOCl \\ \qquad\nearrow \\ HCOOH \end{matrix} \xrightarrow{AlCl_3} [HCO]^{\oplus}[AlCl_4]^{\ominus} + ArH \rightarrow ArCHO + HCl + AlCl_3$$

A second method for the direct introduction of an aldehyde group into reactive systems uses *N*-methylformanilide in the presence of phosphorus oxychloride (100, 161).

$$C_6H_6 + C_6H_5N(CH_3)CHO \xrightarrow{POCl_3} C_6H_5CHO + C_6H_5NHCH_3$$

Excellent yields have been obtained with very reactive polycyclic hydrocarbons such as anthracene (100, 153, 154) and benzo[*a*]pyrene (157) and fair yields with benz[*a*]anthracene (153) and pyrene (415). Phenanthrene or chrysene do not react (161).

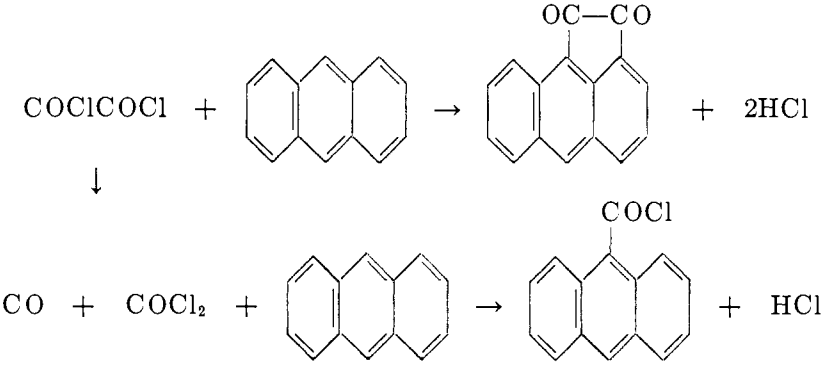
Phosgene reacts with benzene in the presence of aluminum chloride, rapidly giving benzoyl chloride and then, more slowly, benzophenone (2, 4, 5, 170, 171, 430). The relative proportions of the products seem to depend on several factors.

$$C_6H_6 + COCl_2 \rightarrow C_6H_5COCl + HCl$$

$$C_6H_5COCl + C_6H_6 \rightarrow C_6H_5COC_6H_5 + HCl$$

Oxalyl chloride decomposes at a fairly rapid rate into a mixture of phosgene and carbon monoxide in the presence of aluminum chloride (399). When oxalyl chloride is used in a Friedel–Crafts reaction, the nature of the product depends

on the reactivity of the aromatic component. A comparatively unreactive substance, such as benzene, gives only benzoyl chloride and benzophenone (273, 274, 399) and no benzil, whilst highly reactive substances, such as anisole or dimethylaniline, give diketones (400, 401). Alkylated biphenyls may give pheanthraquinones (272). Anthracene gives both 9-anthroic acid, after hydrolysis, and the 1,9-bridged diketone (274).



Carbon dioxide can react with benzene in the presence of aluminum chloride to give benzoic acid and benzophenone (168, 169, 230, 243, 329), the latter deriving presumably from benzoyl chloride formed from the benzoic acid. With more reactive substances (309, 329), such as amines or phenols, zinc or ferric chloride may be substituted as catalysts. The reaction has been stated to fail in the polycyclic field (259), but this is clearly not the case with naphthalene and anthracene (304), though yields are admittedly low.

Carboxylic acid amides may be obtained from carbamyl chlorides (178, 181, 223, 229, 386, 394) or their precursors, isocyanates (180, 222, 269, 270, 394).

$$RN{=}C{=}O + HCl \rightarrow RNHCOCl$$

$$RNHCOCl + C_6H_6 \rightarrow C_6H_5\,CONHR + HCl$$

Dibenzoyl peroxide reacts with benzene at 0°C., in the presence of aluminum chloride, to give a mixture of phenyl benzoate and benzoic acid, almost quantitatively (50, 51, 354). At a higher temperature the reaction proceeds to give benzoic acid, biphenyl, and carbon dioxide (184).

C. THE SOLVENT

A variety of solvents has been used in the Friedel–Crafts ketone synthesis, the most commonly used ones being carbon disulfide and nitrobenzene. These two solvents exemplify the two common types of Friedel–Crafts reactions, heterogeneous and homogeneous. In non-polar solvents, such as carbon disulfide, light petroleum, or carbon tetrachloride, neither aluminum chloride nor its complex with acyl halides is appreciably soluble; the reaction is heterogeneous throughout its course. A polar solvent, such as nitrobenzene, dissolves (and solvates) not only aluminum chloride, but also the acyl chloride–aluminum chloride complex, and usually also the aluminum chloride complex of the re-

sulting ketone (358). Intermediate between these two solvent groups are the chlorinated hydrocarbons, such as ethylene chloride or methylene chloride, which do not appreciably dissolve aluminum chloride (31), but are excellent solvents for the acylating complex and fair solvents for the final ketone complex. It has been shown that solvent power for the aluminum chloride–acetyl chloride complex may be correlated with the dielectric constant of the solvent (19). The consequence of the various solubility relationships in different solvents is discussed further in Sections III,D,1 and IV,A.

The solvent here has two main functions: (*1*) to allow reaction to proceed in a homogeneous medium and to provide a greater catalytic surface area (385), and (*2*) to prevent irreversible side reactions. Thus polycyclic aromatic hydrocarbons tend to undergo rearrangement (127), self-condensation (99, 439, 441, 442), or polymerization (6, 249, 250, 332, 367, 374) with aluminum chloride in the absence of solvent, which does not occur if nitrobenzene is used as a solvent (127, 249, 250). Also, in the absence of solvent, acetyl chloride tends to undergo self-condensation slowly (49). Maleic anhydride is rapidly decomposed by solid aluminum chloride and could not be used in Friedel–Crafts reactions in the absence of solvents (21, 22).

The speed of acetylation of benzene has been reported (105) to decrease in the following solvent sequence: benzene, ligroin, chlorobenzene, bromobenzene, carbon disulfide, nitrobenzene. However, in the presence of undissolved aluminum chloride acetylation is very rapid in nitrobenzene (358), becoming moderate only when the catalyst is dissolved. It seems also that a valid comparison between these solvents was not made, as certain of the reaction mixtures were undoubtedly heterogeneous. In acetylation experiments with a set of non-polar solvents (31), it was observed that cyclohexane, *n*-hexane, and carbon disulfide were each somewhat faster than carbon tetrachloride. It was further noted that the rate of acetylation is much higher with solvents of high dipole moment.

For the acetylation of benzene (365) it is preferable to employ an excess of benzene rather than a solvent such as carbon disulfide. Benzene is also recommended as solvent for reactive polycyclics (216), especially since the tendency for the formation of diketones is reduced (88). *o*-Dichlorobenzene, ether, and tetrachloroethane have also been recommended for use with highly reactive aromatics (19, 258). Ether and nitroparaffins have been recommended (122, 385), since the high concentrations of aluminum chloride obtainable can promote acylation at relatively low temperatures. With nitroparaffins (122) and nitrobenzene (259), however, there are possible explosion hazards, particularly at elevated temperatures. Carbon disulfide has been recommended when alkyl migrations are to be avoided (275, 364), but yields are rarely adequate in this solvent (308). Solvent mixtures have also been employed (19, 31, 162).

D. FACTORS INFLUENCING THE POSITION OF SUBSTITUTION IN POLYCYCLIC SYSTEMS

1. Solvent

Monosubstituted benzene derivatives are acylated predominantly in the para position, and this has been explained (48, 66) as being due to an attacking

reagent of large steric requirements. On the other hand, acylation of polycyclic aromatic systems seems abnormal (because orientation of substitution depends to a large extent on the solvent employed). Naphthalene, for instance, nitrates exclusively in the more reactive α-position, but gives in Friedel–Crafts acylations a mixture of the α- and β-ketones; in solvents such as ethylene dichloride the α-isomer is obtained almost exclusively, and in nitrobenzene solution the β-isomer is formed predominantly. Other solvents give mixtures of ketones in between these two extremes. The explanation usually given for this anomaly (19, 42, 104, 152) is that the acyl chloride–aluminum chloride adduct gives in the presence of nitrobenzene a bulky complex, e.g., of the type $RC(X)=OAlCl_3 \cdot O_2NC_6H_5$, which acts as the acylating agent and finds easier spatial accommodation in the β-position than in the α-position, which is sterically hindered by the hydrogen atom in the peri position. Support for this is found in the observation that the precipitated complex formed between β-naphthyl methyl ketone and aluminum chloride incorporates one mole of nitrobenzene (358). Similar bulky complexes are believed to be the cause of the appreciable β-substitution of naphthalene in the presence of excess acyl halide (19). There is little doubt that these complexes are capable of being formed under the usual reaction conditions. There is, however, a number of facts which this theory cannot explain. (*a*) Anthracene may be benzoylated by means of aluminum chloride and excess benzoyl chloride in nitrobenzene solution at $-10°C.$, when the meso (or 9-) isomer is formed in 79 per cent yield (262). Here there is evidence for rapid acylation at a sterically inaccessible position in the presence of nitrobenzene. (*b*) Pyrene may be acylated in excellent yields in nitrobenzene at its most reactive position, the 3-position (which is of the α-naphthyl type) (12, 433). (*c*) An increase in temperature should result in increased substitution at the more sterically hindered position, whatever the solvent. There is strong evidence (Sections IV,A and IV,B) that the opposite is the case, certainly in naphthalene and in anthracene. This strongly suggests an analogy with certain well-known reversible systems such as occurs in the sulfonation of naphthalene. In subsequent sections it is shown that reversibility is an all-important feature in the Friedel–Crafts reaction in polycyclic hydrocarbons, and that it is capable of explaining satisfactorily the so-called "abnormal" substitution reactions of these systems. Briefly, acylation may be considered a reversible process in which the relative proportion of possible isomers is determined mainly by the duration of the reaction and by the solubilities of the ketone complexes in the solvent employed. How important a factor reversibility may be with benzene derivatives cannot be decided at the present time. That it does occur there is no doubt; for example, in the phthaloylation of chlorobenzene (130, 202) an improvement of yield is observed when the hydrogen chloride produced is swept out as it is formed, thus shifting an equilibrium in favor of the ketone.

Other theories concerning the role of the solvent will be discussed in Section IV,A.

2. Ratio of catalyst to acyl component

The optimum ratio R (of the number of moles of catalyst to the number of moles of acyl component) for complete conversion into the acyl halide–aluminum

halide complex has already been discussed. It is usually found that such a ratio, e.g., $R = 1$ for acyl chlorides, gives in practice a maximum total yield. A value for $R < 1$ will lower the overall yield because not all the acyl halide can be utilized. If $R > 1$ it will promote further reactions, e.g., of the ketone with itself to give chalcones (*cf.* Section III,A). In addition to its effect on the total yield the ratio R has a profound effect on the course of substitution. For instance, in the acetylation of naphthalene in ethylene chloride (19) a lowering of R from 1 to 0.5 lowers the content of α-isomer from 98 per cent to 60 per cent. The theory of a bulky complex in this case appears wholly acceptable. Further, with $R = 1$, β-chloropropionyl chloride substitutes mainly in the β-position of naphthalene, and with $R = 2.2$ mainly in the α-position (246, 294). No satisfactory explanation has been offered for such cases.

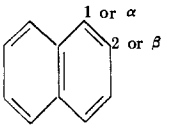
The orientation of the acetylation of anthracene is very dependent on R (*cf.* table 4). Thus with $R = 2$ (in carbon disulfide) or $R = 0.3$ (in benzene) the 9-position is substituted, with $R = 1$ (in benzene or nitrobenzene) the 2-position, and with $R = 1.5$ (in nitrobenzene) the 1-position is favored. The influence of R on the substitution of other polycyclic hydrocarbons has been little investigated.

3. Addition sequence

The order in which the reactants are brought into contact with each other is often highly important, particularly with very reactive hydrocarbons. The method which has been used most frequently involves addition of the catalyst to a mixture of the hydrocarbon and acyl component. This is clearly an unsatisfactory procedure, for instance with naphthalene, where one or another isomer may be formed. Before complete addition of the catalyst $R < 1$ and considerable β-substitution results (19). A different procedure, known as Perrier's (340, 341, 342), involves final addition of the hydrocarbon to the preformed acyl chloride–catalyst adduct. It is the method most generally recommended for good yields and for elimination of side reactions. In a systematic investigation of the different addition procedures, it was observed (32) that best yields and purest isomers are obtained by Perrier's sequence, or one in which a mixture of hydrocarbon and acyl chloride is added to a suspension of the catalyst (during the early part of which reaction $R > 1$). Another frequently used addition sequence (57, 280), based on a presumed activation of the hydrocarbon by the catalyst, involves the final addition of the acyl component. Yields by this method are very rarely satisfactory, and usually mixtures of isomers are obtained.

IV. The Acylation of Polycyclic Aromatic Hydrocarbons

A. NAPHTHALENE



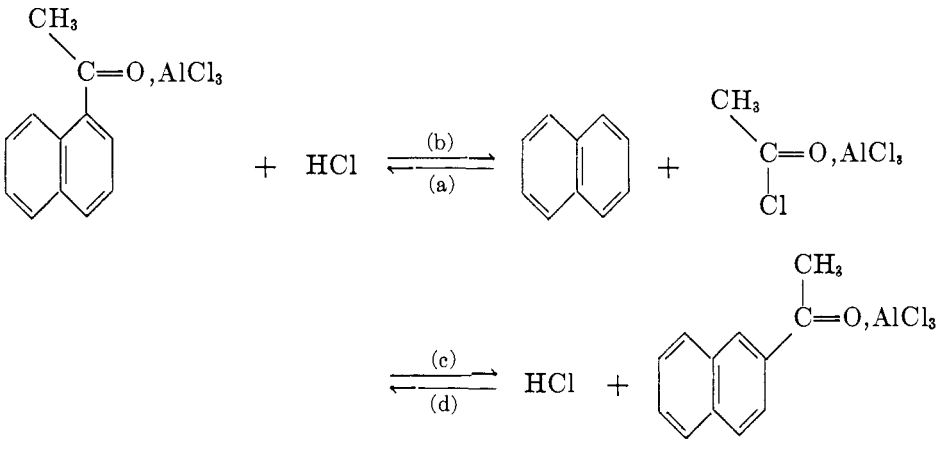
Naphthalene

In most acylations with napthalene a mixture of the two isomers is obtained. Nearly pure α-isomer may be obtained by use of $R = 1$ and a solvent such as ethylene chloride, methylene chloride, or chloroform, from which the ketone complex precipitates rapidly. In one set of comparable experiments (31) on the acetylation of napthalene, a wide variation of isomer content was observed in the various solvents: chloroform or ethylene chloride (91 per cent α-isomer), tetrachloroethane (88 per cent α-isomer), bromobenzene and chlorobenzene (85 per cent α-isomer), *p*-chlorotoluene (80 per cent α-isomer), *o*-dichlorobenzene (70 per cent α-isomer), carbon disulfide, carbon tetrachloride, *n*-hexane, and cyclohexane (65 per cent α-isomer), nitromethane (35 per cent α-isomer), *o*-nitrotoluene (30 per cent α-isomer), and nitrobenzene (25 per cent α-isomer); benzene is usually similar to *o*-dichlorobenzene. This solvent sequence is a general one, denoting the ease with which "normal" substitution of the aromatic hydrocarbon is achieved under the usual Friedel–Crafts conditions. The only exceptions appear to be in the phthaloylation of naphthalene (141), where the ratio of isomers is stated to be sensibly constant for a range of solvents (but where the method of analysis employed was not accurate), and in the Friedel–Crafts acylation of pyrene, where there is no variation in the orientation of substitution.

The solvent effect on substitution in naphthalene has been the subject of much speculation (19, 42, 104, 105, 152, 358), and it is generally believed that the preferred entry in the usually less reactive β-position in solvents such as nitrobenzene is due to the formation of a bulky complex involving acyl chloride, aluminum chloride, and nitrobenzene, which finds better steric accommodation in the β-position of naphthalene. Another effect of such complex formation would be a reduction of the electron demand and hence of the reactivity of the reagent, as compared with the unsolvated addition complex (19). It is difficult to understand on this theory alone why in nitrobenzene benzoyl chloride gives a mixture of isomers containing 68 per cent of the α-isomer, under the same conditions that acetyl chloride gives a mixture containing only 34 per cent of the α-isomer.

A different explanation has recently been proposed, *viz.*, that the relative proportions of the two isomers in acylation reactions of naphthalene depend solely on the dipole moment of the solvent (31). If this postulate is reinterpreted, i.e., that the governing factor is the degree of association of the reactive complex with polar solvent molecules, the conclusion is fundamentally the same as the above; as the postulate is stated, however, it is not in any way self-consistent.

An alternative explanation is now proposed, that the Friedel–Crafts acylation reaction of reactive hydrocarbons is a reversible process. For instance, in the acetylation of naphthalene in ethylene chloride solution (19), the α-ketone is first formed, rapidly, but is precipitated as its aluminum chloride complex. Further reaction is here prevented and the product is nearly pure α-isomer. In nitrobenzene solution, however, precipitation of a complex occurs rarely, and deacylation of the α-isomer may proceed, to be followed by slower reacylation in the β-position.



On this basis the proportion of β-isomer should increase the longer the reaction period, the higher the temperature, and the smaller the proportion of precipitated product. This would mean that reactions (a) and (b) are postulated to be faster than (c) and (d). Ultimate equilibrium amounts of α- and β-isomers would be governed by the electronic and steric behavior of the two substituent positions and the reagents, and would not depend on the mechanisms involved. It is unlikely that true equilibrium is ever achieved, because of irreversible destruction of the ketones and because the hydrogen chloride necessary for the reverse processes (b) and (d) is slowly being eliminated; while hydrogen chloride is still being produced the system may be considered active. It is significant that the actual solubility at 20°C. of hydrogen chloride in nitrobenzene (330) is four times that in ethylene dichloride (210), and would be increased still further in the former solvent owing to the presence of highly polar substances.

As has been indicated in Section III,D,1, the proportion of α-isomer should increase with rise in temperature if the steric hindrance theory is correct. On the other hand, the proportion of the β-isomer is expected to increase with rise in temperature, according to the present theory. Increases in the proportion of the β-isomers have been reported for acylations of naphthalene with acetyl chloride (91, 361), succinic anhydride (185, 186, 187), and phthalic anhydride (141, 206, 429), but also denied for acetylation (114, 280, 285), but in no case was information given about the absolute quantities of the isomers obtained. Fortunately, the appropriate data are available (19). In the acetylation of naphthalene there is an increase in the content of the β-isomer over the temperature range 35–120°C., but as the overall yield decreases also, the change in α:β ratio may be due in part to a readier decomposition of the α-naphthyl ketone (19). And indeed the actual *amount* of β-isomer formed shows no significant increase. Similar data are available for the benzoylation of naphthalene. At 35°C. a 75 per cent yield of mixed ketone is obtained, containing 32 per cent of the β-isomer; at 150°C. only 54 per cent of mixed ketone is obtained, containing 62 per cent of the β-isomer. There has been an increase of the β-isomer

from 24 per cent to 33 per cent actual yield. In this case self-condensation of the ketone produced is likely to be negligible, and it is suggested that a genuine increase in the yield of the β-isomer is a general phenomenon, which is often difficult to observe because of concurrent side reactions.

Further information may be obtained from recent acylation experiments (252) in which the hydrogen chloride produced is continuously removed from the reaction mixture. Under these conditions the reverse reactions (b) and (d) would be suppressed (though probably not eliminated). It was found that an increase in temperature here produced a slight *decrease* in the per cent of β-isomer both in acetylation and in benzoylation. Summarizing, it is likely that the predominant β-acylation of naphthalene in nitrobenzene medium is due to a primary attack in the α-position by an attacking agent of low steric requirements, followed by a rearrangement to the more stable β-isomer, involving deacylation and resynthesis (possibly accompanied by some independent attack) by means of a reagent of considerable steric requirements.

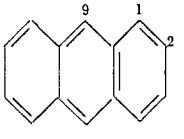
Such isomerizations may be considered to be related to well-known cases in the aromatic and heterocyclic fields (24, 33, 136, 247, 301, 346). These appear to occur only with specially reactive aromatic positions.

The observed proportion of the α-isomer in mixtures of alkyl naphthyl ketones is said to decrease with an increase in chain length of the acyl group (28), from 50 per cent of the α-isomer in acetylation to 20 per cent in stearoylation.

The competitive rates of acetylation of naphthalene and benzene have recently been investigated, and the former found to react at a far greater rate. The experiment, however, involved free aluminum chloride and the unsatisfactory solvent, carbon disulfide (333, 334). In a homogeneous reaction between naphthalene and phthalic anhydride in the presence of 13 moles of benzene (141) a 91 per cent yield of mixed naphthoylbenzoic acids was obtained. On the assumption that the whole of the 9 per cent loss involved conversion to benzoylbenzoic acid, the minimum reactivity ratio is seen to be 135:1 in favor of naphthalene. This compares with 7:1 for the bromination of the 1-naphthyl position as against benzene (290).

The data for the Friedel–Crafts acylation reactions of naphthalene have been collected in tables 1–3.

B. ANTHRACENE



Anthracene

A large number of substitution reactions have shown that the 9(or meso)-position of anthracene is easily the most reactive one, and this is borne out by

uncatalyzed Friedel–Crafts reactions (266, 274, 320, 388). Meso-substituted compounds are obtained otherwise only under very mild Friedel–Crafts conditions, i.e., at low temperatures and with the avoidance of an excess of catalyst, and with carbon disulfide or benzene as solvent. Under other than specially mild conditions only 1- and 2-acyl isomers have been isolated. Further, 9-anthryl methyl ketone was able to be converted under Friedel–Crafts conditions into mixtures of 1- and 2-anthryl methyl ketones (32, 73, 227, 242, 275, 284), e.g, in 64 per cent yield to the 1-isomer by treatment at 40°C. with 1.3 equivalents of aluminum chloride and 3.7 equivalents of aluminum chloride in nitrobenzene solution, or in 68 per cent yield to the 2-isomer, using one equivalent of catalyst only (32). The suggestion was therefore made (73, 275) that in the acetylation of anthracene the 9-position is first attacked, with subsequent migration of the acetyl group to the positions of the outer ring. This view is confirmed by the isolation of the 9-anthryl isomer in 55 per cent yield after 3.5 hr. from a reaction which after 17 hr. gave only the 1- and 2-isomers (191). The question arises whether the normal substitution of anthracene in the outer rings in nitrobenzene solution occurs *via* the 9-isomer or whether a bulky complex is formed which prevents such attack and allows substitution only in the outer rings. The former is likely to be the case, since under specially mild conditions, by conducting a benzoylation of anthracene at −10°C. for 5 min. in nitrobenzene solution, a 79 per cent yield of the 9-isomer could be isolated (262). Likewise, anthracene could be substituted in the 9-position in 52 per cent yield by means of cinnamoyl chloride in nitrobenzene solution (191), isolation being facilitated in this case by ready precipitation of the ketone complex. Under these conditions it is most unlikely that a large attacking reagent is involved. It should be noted that of the two outer positions of anthracene the 1-position is the one substituted to a greater extent in nitrobenzene solution, a result which is in contrast to the case of naphthalene. Relevant to the concept of a deacylation–reacylation process is the smooth conversion (32) of 9-anthryl methyl ketone to 9-anthryl phenyl ketone under conditions identical with the preparation of the latter substance (115), and the ready deacylation under acid-catalyzed conditions of a number of acyl derivatives of very reactive aromatic positions (7, 115, 119, 176, 191, 248, 262, 281, 378).

In a particular benzoylation experiment (276, 340, 341, 342) a mixture of three isomeric anthryl phenyl ketones was obtained, one undoubtedly the 9-isomer, and two others melting at 75°C. and 208°C. However, 1- and 2-anthryl phenyl ketones have been synthesized unambiguously (420) and found to melt at 141°C. and 187°C., respectively.

Acetylation of anthracene in the presence of 12 moles of benzene (191), giving a 71 per cent yield of 9-anthryl isomer, points to a reactivity of that position in excess of thirty times that of benzene. Since, however, only a trace of acetophenone could be detected in this reaction, the reactivity ratio must be considerably higher.

Results of Friedel–Crafts reactions with anthracene are found in table 4.

TABLE 1

The acetylation of naphthalene

Acyl Component[a]	Catalyst[a]	Solvent	Sequence[b]	Temperature	Product[c]	Yield	References
				°C.		*per cent*	
CH_3COCl (0.5)	$AlCl_3$ (1)	CS_2	a	<15	$\alpha + \beta$	30	(352, 403)
CH_3COCl (0.5)	$AlCl_3$ (1)	CS_2	b	0	α (pure)	35	(128)
CH_3COCl (0.5)	$AlCl_3$ (1)	CS_2	b	0	α (44) β (56)	45	(280)
CH_3COCl (0.5)	$AlCl_3$ (1)	CS_2	b	0	α (pure)	60–80	(32, 91)
CH_3COCl (0.5)	$AlCl_3$ (1)	CS_2	b	0	α, β (>30)	?	(160)
CH_3COCl (1)	$AlCl_3$ (1)	CS_2	a	Reflux	$\alpha + \beta$	15	(345, 360)
CH_3COCl (1)	$AlCl_3$ (1)	CS_2	b	Room temperature, reflux	$\alpha + \beta$	45	(422)
CH_3COCl (1)	$AlCl_3$ (1)	CS_2	c	Room temperature	$\alpha + \beta$	Good	(340)
CH_3COCl (1?)	$AlCl_3$ (1?)	CS_2	d	?	α	?	(32, 113, 315)
CH_3COCl (1)	$AlCl_3$ (1)	CS_2	?	0	α	?	(172)
CH_3COCl (1)	$AlCl_3$ (1.04)	CS_2	a	0 or 30	α (53) β (47)	70–78[d]	(32)
CH_3COCl (1)	$AlCl_3$ (1.04)	CS_2	b	0 or 30	α (60) β (40)	89[d]	(32)
CH_3COCl (1)	$AlCl_3$ (1.04)	CS_2	c	30	α (62) β (38)	71[d]	(31, 32)
CH_3COCl (1)	$AlCl_3$ (1.04)	CS_2	d	0 or 30	α (65) β (35)	80–92[d]	(32)
CH_3COCl (1)	$AlCl_3$ (1.2)	CS_2	c	Reflux	$\alpha > \beta$	40	(32)
CH_3COCl (1.3)	$AlCl_3$ (0.96)	CS_2	b	Room temperature	α (56) β (44)	35	(280)
CH_3COCl (1.3)	$AlCl_3$ (0.96) H_2O (trace)	CS_2	b	Room temperature	α	?	(172)
CH_3COCl (1.4)	$AlCl_3$ (1.04)	CS_2	c	30	α (65) β (35)	20	(31)
CH_3COCl (1.4)	$AlCl_3$ (1.2)	CS_2	b	Reflux	α (66) β (33)	37–45	(345)
CH_3COCl (1.5)	$AlCl_3$ (1.5)	CS_2	d	−50	α (41) β (53)	36	(285)
CH_3COCl (1.5)	$AlCl_3$ (1.5)	CS_2	d	18	α (45) β (55)	?	(285)
CH_3COCl (1.6)	$AlCl_3$ (1.2)	CS_2	b	0	α (65) β (35)	?	(404)

CH_3COCl (1.6)	$AlCl_3$ (1.4)	CS_2	a	−40 to −50	α (59) β (41)	30	(280)
CH_3COCl (1.6)	$AlCl_3$ (1.4)	CS_2	a	−5 to 0	α (61) β (39)	67	(280)
CH_3COCl (1.6)	$AlCl_3$ (1.4)	CS_2	a	10 to 20	α (49) β (51)	64	(280)
CH_3COCl (1.6)	$AlCl_3$ (1.4)	CS_2	a	45	α (55) β (65)	70	(280)
CH_3COCl (1.6)	$AlCl_3$ (1.5)	CS_2	a	?	α (50) β (50)	?	(280)
CH_3COCl (1.6)	$AlCl_3$ (3)	CS_2	a	?	α (64) β (36)	?	(280)
CH_3COCl (1.6)	$AlCl_3$ (4)	CS_2	a	?	α (60) β (40)	?	(280)
CH_3COCl (1.6)	$AlCl_3$ (4.5)	CS_2	a	?	α (68) β (32)	?	(280)
CH_3COCl (1.6)	$AlCl_3$ (5)	CS_2	a	?	α (55) β (45)	?	(280)
CH_3COCl (1.6)	$AlCl_3$ (6)	CS_2	a	?	α (67) β (33)	?	(280)
CH_3COCl (2)	$AlCl_3$ (1)	CS_2	b	0	α (mainly)	43	(311)
CH_3COCl (2)	$AlCl_3$ (1.7)	CS_2	a	0	α (>40)	91	(279)
CH_3COCl (excess)	$AlCl_3$ (?)	CS_2	?	Cool	β (mainly)	Good	(114)
CH_3COCl (?)	$AlCl_3$ (?)	CS_2	?	−15	α (70) β (30)	?	(160)
CH_3COCl (?)	$AlCl_3$ (?)	CS_2	?	13	α	30	(436)
CH_3COCl (?)	$AlCl_3$ (?)	CS_2	?	?	α (mainly)	?	(350)
CH_3COCl (?)	$AlCl_3$ (?)	CS_2	?	?	α + β (mainly)	?	(361)
CH_3COCl (?)	$AlCl_3$ (?)	CS_2	?	?	α + β	?	(315)
CH_3COCl (?)	$AlCl_3$ (?)	CS_2	?	0 to 50	α (60) β (40)	ca. 75	(366)
CH_3COCl (1)	$AlCl_3$ (1)	CH_2Cl_2	c	35	α (pure)	95	(18, 20)
CH_3COCl (1)	$AlCl_3$ (1)	$CHCl_3$	d	30–35	α (90) β (10)	54	(31)
CH_3COCl (1)	$AlCl_3$ (1)	$CHCl_3$	c	30–35	α (99) β (1)	54	(31)
CH_3COCl (2)	$AlCl_3$ (2)	$CHCl_3$	c	30–35	α (99) β (1)	90	(31)
CH_3COCl (1)	$AlCl_3$ (1.04)	CCl_4	c or d	30	α (68) β (32)	75[d]	(31)
CH_3COCl (?)	$AlCl_3$ (?)	C_2H_5Cl	?	?	α	?	(105)
CH_3COCl (1)	$AlCl_3$ (1)	C_2H_5Br	c	35	α	75	(18, 20)

TABLE 1—*Continued*

Acyl Component[a]	Catalyst[a]	Solvent	Sequence[b]	Temperature	Product[c]	Yield	References
				°C.		*per cent*	
CH_3COCl (1)	$AlCl_3$ (1)	$(CH_2Cl)_2$	c	35	α (pure)	95	(18, 20)
CH_3COCl (1)	$AlCl_3$ (1)	$(CH_2Cl)_2$	c	35	α (98) β (2)	93	(19)
CH_3COCl (1)	$AlCl_3$ (1)	$(CH_2Cl)_2$	c	35	α (98) β (2)	90	(389)
CH_3COCl (1)	$AlCl_3$ (1.04)	$(CH_2Cl)_2$	c	30	α (pure)	88	(31, 32)
CH_3COCl (1)	$AlCl_3$ (1.04)	$(CH_2Cl)_2$	a	30	α (84) β (16)	49	(32)
CH_3COCl (1)	$AlCl_3$ (1.04)	$(CH_2Cl)_2$	b	30	α (80) β (20)	85[d]	(32)
CH_3COCl (1)	$AlCl_3$ (1.04)	$(CH_2Cl)_2$	d	30	α (91) β (9)	88[d]	(31, 32)
CH_3COCl (2)	$AlCl_3$ (1)	$(CH_2Cl)_2$	c	35	α (60) β (40)	76	(19)
CH_3COCl (2)	$AlCl_3$ (2)	$(CH_2Cl)_2$	c	35	α (98) β (2)	93	(19)
CH_3COCl (1)	$AlCl_3$ (1)	$(CH_2Br)_2$	c	35	α	74	(18, 20)
CH_3COCl (1)	$AlCl_3$ (1)	$(CHCl_2)_2$	c	30–35	α (95) β (5)	78	(31)
CH_3COCl (1)	$AlCl_3$ (1)	$(CHCl_2)_2$	c	35	α	75	(18, 20)
CH_3COCl (1)	$AlCl_3$ (1)	$(CHCl_2)_2$	d	35	α (88) β (12)	85	(31)
CH_3COCl (1.6)	$AlCl_3$ (1)	Light petroleum	b	Room temperature, reflux	α + β	?	(339)
CH_3COCl (?)	$AlCl_3$ (?)	Light petroleum	?	?	α (50) β (50)	?	(105, 404)
CH_3COCl (1)	$AlCl_3$ (1.04)	*n*-Hexane	c or d	30	α (65) β (35)	88[d]	(31)
CH_3COCl (1)	$AlCl_3$ (1.04)	Cyclohexane	c or d	30	α (68) β (32)	88[d]	(31)
CH_3COCl (1)	$AlCl_3$ (1.04)	CH_3NO_2	c or d	30–35	α (35) β (65)	54	(31)
CH_3COCl (1)	$AlCl_3$ (1.1)	C_6H_6	b	10–13	α	40	(404)
CH_3COCl (1)	$AlCl_3$ (1.1)	C_6H_6	f	?	α (50) β (50)	40	(358)
CH_3COCl (0.95)	$AlCl_3$ (1.04)	C_6H_5Cl	d	30	α (85) β (15)	84	(32)

CH_3COCl (1)	$AlCl_3$ (1)	C_6H_5Cl	d	30–35	α (85) β (15)	82	(31)
CH_3COCl (1)	$AlCl_3$ (1.05)	C_6H_5Cl	b	5	α (66) β (34)	41	(252)
CH_3COCl (1.4)	$AlCl_3$ (1.04)	C_6H_5Cl	a or b	20–80	α (65) β (35)	66[d]	(32)
CH_3COCl (1.4)	$AlCl_3$ (1.04)	C_6H_5Cl	c	20–80 or 30–35	α (90) β (10)	83[d]	(31, 32)
CH_3COCl (1.4)	$AlCl_3$ (1.04)	C_6H_5Cl	d	0, 30, 50, or 80	α (75) β (25)	70–88[d]	(32)
CH_3COCl (1.4)	$AlCl_3$ (3.1)	C_6H_5Cl	d	30	α (85) β (15)	92	(32)
CH_3COCl (1.6)	$AlCl_3$ (1.2)	C_6H_5Cl	b	0	α (42) β (58)	?	(404)
CH_3COCl (2)	$AlCl_3$ (2.1)	C_6H_5Cl	d	30	α (85) β (15)	86	(32)
CH_3COCl (5)	$AlCl_3$ (1.04)	C_6H_5Cl	d	0 or 30	α (60) β (40)	42–50	(32)
CH_3COCl (?)	$AlCl_3$ (?)	C_6H_5Cl	?	?	α	?	(105)
CH_3COCl (1)	$AlCl_3$ (1)	C_6H_5Br	d	30–35	α (86) β (14)	73	(31)
CH_3COCl (?)	$AlCl_3$ (?)	C_6H_5Br	?	?	α (mainly)	?	(105)
CH_3COCl (1)	$AlCl_3$ (1)	o-$C_6H_4Cl_2$	d	30–35	α (70) β (30)	66	(31)
CH_3COCl (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	35	α (34) β (66)	82	(19)
CH_3COCl (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	100	α (25) β (75)	76	(19)
CH_3COCl (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	120	α (19) β (81)	70	(19)
CH_3COCl (1)	$AlCl_3$ (1.04)	$C_6H_5NO_2$	a	−5 to 0, or 30	α (24) β (76)	32–51	(32)
CH_3COCl (1)	$AlCl_3$ (1.04)	$C_6H_5NO_2$	b	−5 to 0, or 30	α (28) β (72)	57–64	(32)
CH_3COCl (1)	$AlCl_3$ (1.04)	$C_6H_5NO_2$	c	−5 to 0, or 30	α (31) β (69)	55–78	(31, 32)
CH_3COCl (1)	$AlCl_3$ (1.04)	$C_6H_5NO_2$	d	−5 to 0, or 30	α (27) β (73)	54–90	(31, 32)
CH_3COCl (1)	$AlCl_3$ (1.05)	$C_6H_5NO_2$	b	−5	α (26)[e] β (74)	77	(252)

TABLE 1—*Concluded*

Acyl Component [a]	Catalyst [a]	Solvent	Sequence [b]	Temperature	Product [c]	Yield	References
				°C.		*per cent*	
CH_3COCl (1)	$AlCl_3$ (1.05)	$C_6H_5NO_2$	b	5, 10, or 25	α (28)[e] β (72)	60–67	(252)
CH_3COCl (1)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	b	8–10	β	88	(404)
CH_3COCl (1.05)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	Cool	β (mainly)	30–50	(350)
CH_3COCl (1.05)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	f	6–10	β (mainly)	88	(358)
CH_3COCl (1.05)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	f	6–10	α (21) β (79)	75	(32)
CH_3COCl (1.1)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	b	−5 to 0	α (mainly)	85	(271)
CH_3COCl (1.6)	$AlCl_3$ (1.2)	$C_6H_5NO_2$	b	0	α (11) β (89)	?	(404)
CH_3COCl (?)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	−5 to −3	β (mainly)	56 (crude)	(311)
CH_3COCl (?)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	e	?	β (mainly)	53	(405)
CH_3COCl (?)	$AlCl_3$ (?)	$C_6H_5NO_2$	?	≤10	β (pure)	?	(83, 105, 358, 366, 438)
CH_3COCl (?)	$AlCl_3$ (?)	$C_6H_6NO_2$	?	8–10	β	25	(436)
CH_3COCl (1)	$AlCl_3$ (1)	*p*-$CH_2C_6H_4Cl$	d	30–35	α (80) β (20)	82	(31)
CH_3COCl (1)	$AlCl_3$ (1.04)	*o*-$CH_3C_6H_4NO_2$	c or d	30–35	α (30) β (70)	71–75	(31)
CH_3COCl (1)	$AlCl_3$ (1)	$(CH_2Cl)_2$[f]	c	35	α (40) β (60)	70	(19)
CH_3COCl (1)	$AlCl_3$ (1)	$(CH_2Cl)_2$[g]	c	35	α (29) β (71)	88	(19)
CH_3COCl (1)	$AlCl_3$ (1)	$(CH_2Cl)_2$[h]	c	35	α (40) β (60)	82	(19)
CH_3COCl (1)	$AlCl_3$ (2)	$(CH_2Cl)_2$[h]	c	35	α (98) β (2)	87	(19)
CH_3COCl (1)	$AlCl_3$ (1)	C_6H_6[h]	f	10–13	β (mainly)	59	(358)
CH_3COCl (1)	$AlCl_3$ (1)	C_6H_6[i]	f	10–13	α + β	49	(358)
CH_3COCl (1)	$AlCl_3$ (1.04)	CCl_4[g]	c or d	30	α (25) β (75)	66–68	(31)
CH_3COCl (1)	$AlCl_3$ (1.04)	CCl_4[j]	c or d	30	α (45) β (55)	47–61	(31)
CH_3COCl (1)	$AlCl_3$ (1.04)	CCl_4[k]	c or d	30	α (60) β (40)	64–71	(31)
CH_3COCl (1)	$AlCl_3$ (1.04)	CCl_4[l]	c or d	30	α (60) β (40)	75	(31)

CH_3COCl (3.2)	$AlCl_3$ (1.9)		a	Room temperature	α (52) β (48)	58 (crude)	(280)
CH_3COCl (40)	$AlCl_3$ (1.04)		c	30	α (65) β (35)	57	(31)
$(CH_3CO)_2O$ (?)	$AlCl_3$ (?)	CS_2	?	−15	α (70) β (30)	?	(160, 361)
$(CH_3CO)_2O$ (1)	$AlCl_3$ (2)	$(CH_2Cl)_2$	c	35	α (98) β (2)	60	(19)
$(CH_3CO)_2O$ (1)	$AlCl_3$ (2.1)	$(CH_2Cl)_2$	c	35–50	α (pure)	59	(18, 20)
$(CH_3CO)_2O$ (0.5)	$AlCl_3$ (1.1)	C_6H_6	b	10–13	α	35	(404)
$(CH_3CO)_2O$ (1)	$AlCl_3$ (1.1)	C_6H_6	f	18–25	α + β	35	(358)
$(CH_3CO)_2O$ (0.5)	$AlCl_3$ (1.6)	C_6H_5Cl	d	30	α (80) β (20)	58	(32)
$(CH_3CO)_2O$ (1)	$AlCl_3$ (3.1)	C_6H_5Cl	d	30	α (72) β (28)	65	(32)
$(CH_3CO)_2O$ (0.5)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	b	8–10	β	22–29	(404)
$(CH_3CO)_2O$ (1)	$AlCl_3$ (1.4)	$C_6H_5NO_2$	f	22–29	β	23	(358)
$(CH_3CO)_2O$ (0.4)	$AlCl_3$ (0.8)		b	Heated	α + β	?	(361)
$(CH_3CO)_2O$ (1)	HF (excess)			50–60	α + β (mainly)	29	(158)
Tetraacetylglucopyranyl chloride (0.016)	$AlCl_3$ (0.09)		b	80–90	α	23	(225)
$CH_2{=}C{=}O$ (excess)	$AlCl_3$ (?)	CS_2	a	0	α + β	20–37	(224)
$CH_2{=}C{=}O$ (excess)	$AlCl_3$ (1.5)	CS_2	e	0	α + β (trace)	35	(428)

(a) Figures in parentheses in these columns refer to molar equivalents of reagents used, based on 1 mole-equivalent of the hydrocarbon component.

(b) a = final addition of the acyl component;
b = final addition of the catalyst;
c = final addition of the hydrocarbon;
d = addition of a mixture of the acyl component and the hydrocarbon to the catalyst;
e = addition of a mixture of the acyl component and the catalyst to the hydrocarbon;
f = addition of the catalyst to part of the mixture of the acyl component and hydrocarbon, followed by addition of the remaining part of the latter;
g = admixture of the reaction components;
h = hydrogen chloride is passed through the mixture of the other components in the solvent.

(c) Figures in parentheses refer to percentages of the isomers obtained.

(d) Allowing for recovered naphthalene.

(e) Conducted in a system being continuously exhausted of the gases evolved.

(f) Additional component: benzoyl chloride (1 mole).

(g) Additional component: nitromesitylene (1 mole).

(h) Additional component: nitrobenzene (1 mole).

(i) Additional component: nitrobenzene (1 mole) added near the end of the reaction.

(j) Additional component: *p*-chloronitrobenzene (1 mole).

(k) Additional component: *m*-chloronitrobenzene (1 mole).

(l) Additional component: *o*-chloronitrobenzene (1 mole).

TABLE 2

Aliphatic acylations of naphthalene

Acyl Component [a]	Catalyst [a]	Solvent	Sequence [b]	Temperature	Product [c]	Yield	References
				°C.		*per cent*	
CH_3CH_2COCl (0.8)	$AlCl_3$ (2.2)	CS_2	b	Reflux	α (mainly)	22	(311)
CH_3CH_2COCl (1)	$AlCl_3$ (1)	CS_2	a	Reflux	α (50) β (50)	70	(360)
CH_3CH_2COCl (?)	$AlCl_3$ (?)	CS_2	b	0	α	60–80	(90, 91)
CH_3CH_2COCl (?)	$AlCl_3$ (?)	CS_2	d	?	α + β	?	(113)
CH_3CH_2COCl (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β	54	(84)
CH_3CH_2COCl (1.1)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	b	−5 to −3	β (mainly)	57	(311)
$CH_3(CH_2)_2COCl$ (1)	$AlCl_3$ (1)	CS_2	a	Reflux	α (50) β (50)	75	(360)
$CH_3(CH_2)_2COCl$ (?)	$AlCl_3$ (?)	CS_2	b	0	α	60–80	(90, 91)
$CH_3(CH_2)_2COCl$ (?)	$AlCl_3$ (?)	CS_2	d	?	α + β	?	(113)
$CH_3(CH_2)_2COCl$ (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	?	β (mainly)	?	(107)
$CH_3(CH_2)_2COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β?	62	(84)
$CH_3(CH_2)_2COCl$ (?)	$AlCl_3$ (?)		g	80 or 180	α (mainly)	?	(107)
$(CH_3)_2CHCOCl$ (1)	$AlCl_3$ (1)	CS_2	a	Reflux	α (mainly) + β	67	(360)
$CH_3(CH_2)_2COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β?	63	(84)
$(CH_3)_2CHCH_2COCl$ (1)	$AlCl_3$ (1)	CS_2	a	Reflux	α + β	?	(360)
$(CH_3)_2CHCH_2COCl$ (?)	$AlCl_3$ (?)	CS_2	b	0	α	60–80	(90, 91)
$CH_3(CH_2)_4COCl$ (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	−5	β (mainly)	49	(425)
$CH_3(CH_2)_4COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β?	64	(84)
$CH_3(CH_2)_6COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β?	?	(84)
$CH_3(CH_2)_6COCl$ (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	−5	β (mainly)	58	(425)
$CH_3(CH_2)_6COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β?	64	(84)
$CH_3(CH_2)_6COCl$ (1.1)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	b	−5	β	50	(28)
$CH_3(CH_2)_7COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β?	59	(84)
$CH_3(CH_2)_8COCl$ (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	−5	β (mainly)	51	(425)
$CH_3(CH_2)_8COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β	63	(28, 84)
$CH_3(CH_2)_8COCl$ (1.1)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	b	−5	β	54	(28)
$CH_3(CH_2)_9COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β	58	(28, 84)
$CH_3(CH_2)_{10}COCl$ (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	−5	β (mainly)	52	(425)
$CH_3(CH_2)_{10}COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β	47	(28, 84)
$CH_3(CH_2)_{10}COCl$ (1.1)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	b	−5	β	60	(28)
$CH_3(CH_2)_{12}COCl$ (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	−5	β (mainly)	50	(425)
$CH_3(CH_2)_{12}COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β?	60	(84)

$CH_3(CH_2)_{14}COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β?	?	(84)
$CH_3(CH_2)_{16}COCl$ (1)	$AlCl_3$ (1)	CS_2	b	0	α + β	83	(305)
$CH_3(CH_2)_{16}COCl$ (1)	$AlCl_3$ (1.1)	CS_2	b	?	α (80) β (20)	31	(381)
$CH_3(CH_2)_{16}COCl$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	−5 to 0	β	?	(84)
$CH_3(CH_2)_{16}COCl$ (1.1)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	b	−5	β	74	(28)
$ClCH_2COCl$ (1.2)	$AlCl_3$ (1.1)	CS_2	b	Cool	α + β	81	(310, 350)
$ClCH_2COCl$ (0.5)	P_2O_5 (0.02)		g	150–180	α (84), β (16)	78	(377)
$Cl(CH_2)_2COCl$ (1)	$AlCl_3$ (1)	CS_2	b	0	β	27	(246)
$Cl(CH_2)_2COCl$ (1)	$AlCl_3$ (2.2)	CS_2	e	Room temperature	α	?	(294)
$CH_3CH(Cl)CH_2COCl$ (1)	$AlCl_3$ (2.2)	CS_2	e	Room temperature	α	?	(294)
$C_6H_5CH_2COCl$ (1)	$AlCl_3$ (1.6)	CS_2	b	Room temperature	α + β	77	(193, 363)
$C_6H_5CH_2COCl$ (1)	$AlCl_3$ (2)	CS_2	b	0	α + β (mainly)	47	(120)
$(C_6H_5)_2CHCOCl$ (?)	$AlCl_3$ (?)	CS_2	?	?	α	?	(296)
CO_2 (excess)	$AlCl_3$ (0.96)	CS_2	a	30–35	α	8	(304)
$(COCl)_2$ (2.5)	$AlCl_3$ (1.4)	CS_2	b	0	α (66) β (33)	80 (crude)	(274)
$(COBr)_2$ (1)	$AlCl_3$ (2)	CS_2	b	Cool	α (mainly)	?	(401)
NH_2COCl (0.5)	$AlCl_3$ (0.2)	CS_2	b	Cool	α (mainly)	Nearly quantitative	(181, 182)
HCNO (1)	$AlCl_3$ (0.32)	CS_2	h	Cool	α	Good	(180, 394)
KCNO (1.3)	$AlCl_3$ (1.3)	CS_2	h	Room temperature	α	?	(222)
C_6H_5CNO (1.3)	$AlCl_3$ (1.3)	CS_2	g	Room temperature	α?	?	(270)
n-$C_8H_{16}OOCCOCl$ (1)	$AlCl_3$ (?)		g	Warm	?	?	(359)
Maleic anhydride (1)	$AlCl_3$ (2.1)	CH_2Cl_2 or $(CHCl_2)_2$	e	Room temperature?	α (33) β (66)	73 (crude)	(22)
Maleic anhydride (0.67)	$AlCl_3$ (1.3)	C_6H_6	b	<20, 80	α (60)[d] β (40, crude)	70–80	(52)
Maleic anhydride (0.67)	$AlCl_3$ (1.3)	C_6H_6	b	<20, 60–70	α[d]	?	(331)
Maleic anhydride (1.1)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	b	<15	α	35	(197, 228)
Succinic anhydride (0.19)	$AlCl_3$ (0.16)	CS_2	g	50–60	β (mainly)	5 (crude)	(53)
Succinic anhydride (0.2)	$AlCl_3$ (0.17)	CS_2	g	50–60	β (mainly)	Nearly quantitative	(261)
Succinic anhydride (?)	$AlCl_3$ (?)	CS_2 or C_6H_6	e	Cold	α (50) β (50)	?	(185, 186, 187)
Succinic anhydride (1)	$AlCl_3$ (2)	$(CHCl_2)_2$	b	Room temperature	β	74	(353)
Succinic anhydride (0.6)	$AlCl_3$ (1.2)	$C_6H_5NO_2$	d	Cold	α (54) β (46)	65	(15, 150, 213, 325)
Succinic anhydride (0.6)	$AlCl_3$ (1.2)	$C_6H_5NO_2$	d	0–10	α (51) β (49)	78	(59)

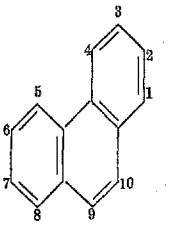
TABLE 2—*Concluded*

Acyl Component[a]	Catalyst[a]	Solvent	Sequence[b]	Temperature	Product[c]	Yield	References
				°C.		*per cent*	
Succinic anhydride (0.64)	$AlCl_3$ (1.3)	$C_6H_5NO_2$	d	0	α (56) β (44)	80	(166)
Succinic anhydride (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	c	0, room temperature	α	?	(353)
Succinic anhydride (1.1)	$AlCl_3$ (1.2)	$C_6H_5NO_2$	b	Cold	β (43) β (57)	83	(135, 163)
Succinic anhydride (1.1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	10	α	?	(232)
Succinic anhydride (1.1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	10	β	?	(228)
Succinic anhydride (?)	HF (excess)		g	Heated	Tar		(158)
2-Methylsuccinic anhydride (0.57)	$AlCl_3$ (1.2)	$C_6H_5NO_2$	d	Cold	α (51) β (49)	55	(213)
2-Ethyl-2-methylsuccinic anhydride (0.45)	$AlCl_3$ (1.2)	$C_6H_5NO_2$	d	Cold	α	49	(29)
2,2-Dimethylsuccinic anhydride (0.52)	$AlCl_3$ (1.2)	$C_6H_5NO_2$	b	0, room temperature	α (60) β (40)	60	(384)
2,3-Dimethylsuccinic anhydride (?)	$AlCl_3$ (?)	$C_6H_5NO_2$	?	?	α + β	17	(150)
Cyclopentene-1,2-dicarboxylic anhydride (0.79)	$AlCl_3$ (1.6)	$C_6H_5NO_2$	b	0	α + β	?	(382, 383)
Cyclopentene-1-carboxylic-1-acetic acid anhydride (0.7)	$AlCl_3$ (1.2)	$C_6H_5NO_2$	d	0, room temperature	α (72) β (28)	13	(382, 383)

[a][b][c] See footnotes (a), (b), and (c) of table 1.

[d] This is a cyclized product (22).

C. PHENANTHRENE

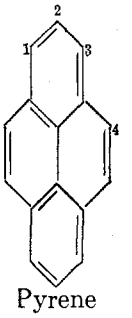


Phenanthrene

In Friedel–Crafts reactions the 2- and 3-positions are favored, i.e., the β-type positions, even in carbon disulfide suspension, though in better yields in the presence of nitrobenzene. Meso-substitution has been reported for the acetylation of phenanthrene (426), the product obtained melting at 123°C. However, 9-phenanthryl methyl ketone synthesized unambiguously was found to melt at 75°C. (312). From a comparison of physical constants of the ketones and of several derivatives, it is likely that the specimen of the earlier workers (426) was a molecular compound of the 9- and 2-isomers. The general formation of the 2- and 3-isomers was regarded as a remarkable anomaly (312), yet this is in accord with the general substitution pattern of polycyclic aromatic hydrocarbons in Friedel–Crafts reactions. A high yield of an authentic 9-isomer has never been obtained in a Friedel–Crafts reaction. However, under conditions of easy isolation of the ketone complex reasonable yields of 1-phenanthryl phenyl ketone may be obtained in the benzoylation of phenanthrene (9, 10, 191). In nitrobenzene the reaction product consists largely of the 3-isomer, lesser amounts of the 1- and 2-isomers being formed. Evidence has also been obtained for a slow conversion of 3-phenanthryl methyl ketone into 2-phenanthryl methyl ketone under Friedel–Crafts conditions (191). Circumstantial evidence exists therefore for an initial substitution of phenanthrene predominantly in the 1-position (and possibly the 9-position), followed by isomerization to the more stable 2- and 3-positions, with the ultimate accumulation of the 2-isomer. Treatment of 9-phenanthryl methyl ketone under Friedel–Crafts conditions, with aluminum chloride or bromide, failed to show any isomerization (314). Possibly in this case a high concentration of hydrogen halide is required for effective isomerization.

Table 5 details results obtained in Friedel–Crafts reactions with phenanthrene.

D. PYRENE



Pyrene

TABLE 3

Aromatic acylations of naphthalene

Acyl Component[a]	Catalyst[a]	Solvent	Sequence[b]	Temperature	Product[c]	Yield	References
				°C.		*per cent*	
C_6H_5COCl (1)	$AlCl_3$ (1)	CS_2	a	Reflux	α (50) β (50)	43	(360)
C_6H_5COCl (1)	$AlCl_3$ (1)	CS_2	c	Room temperature	α (mainly) + β	78	(149)
C_6H_5COCl (1)	$AlCl_3$ (1)	CS_2	d	Low	α (mainly) + β	65	(142)
C_6H_5COCl (1)	$AlCl_3$ (1)	CS_2	d	47	α (80) β (20)	90	(142)
C_6H_5COCl (1.1)	$AlCl_3$ (1.1)	CS_2	c	Room temperature, 50	α (85) β (15)	93	(307)
C_6H_5COCl (?)	$AlCl_3$ (?)	CS_2	b	0	α	60–80	(90, 91)
C_6H_5COCl (1)	$AlCl_3$ (1)	$(CH_2Cl)_2$	c	35	α (96) β (4)	86	(18, 19, 20)
C_6H_5COCl (2)	$AlCl_3$ (1)	$(CH_2Cl)_2$	c	35	α (60) β (40)	60	(19)
C_6H_5COCl (2)	$AlCl_3$ (2)	$(CH_2Cl)_2$	c	35	α (96) β (4)	86	(19)
C_6H_5COCl (0.22)	$AlCl_3$ (0.24)	C_6H_5Cl	c	45–50	α (75) β (25)	71	(252)
C_6H_5COCl (1)	$AlCl_3$ (1.05)	C_6H_5Cl	c	80	α (68) β (32)	82	(252)
C_6H_5COCl (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	35	α (68) β (32)	75	(19)
C_6H_5COCl (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	150	α (38) β (62)	54	(19)
C_6H_5COCl (1)	$AlCl_3$ (1.05)	$C_6H_5NO_2$	c	5	α (72)[d] β (28)	64	(252)
C_6H_5COCl (1)	$AlCl_3$ (1.05)	$C_6H_5NO_2$	c	10	α (73)[d] β (27)	68	(252)
C_6H_5COCl (1)	$AlCl_3$ (1.05)	$C_6H_5NO_2$	b	2–3	α (69)[d] β (31)	40	(252)
C_6H_5COCl (1)	$AlCl_3$ (1.05)	$C_6H_5NO_2$	c	60	α (50) β (50)	65	(96)
C_6H_5COCl (1)	$AlCl_3$ (3.6)	$C_6H_5NO_2$	b	8–12	β	19	(437)
C_6H_5COCl (?)	$AlCl_3$ (?)	$C_6H_5NO_2$	?	?	β (mainly)	?	(107)
C_6H_5COCl (1)	$AlCl_3$ (1)	$(CH_2Cl)_2$[e]	c	35	α (70) β (30)	80	(19)

C_6H_5COCl (1)	$AlCl_3$ (2)	$(CH_2Cl)_2$[e]	c	35	α (96) β (4)	85	(19)
C_6H_5COCl (1)	$AlCl_3$ (1)	$(CH_2Cl)_2$[f]	c	35	α (90) β (10)	80	(19)
C_6H_5COCl (?)	$AlCl_3$ (?)[g]	Various	?	80 or 180	α (mainly)	?	(107)
C_6H_5COCl (?)			g	Reflux	α	?	(320)
C_6H_5COCl (<1)	Zn, or Fe (?)		b	170–180	α (mainly) + β	70	(207)
C_6H_5COCl (0.018)	P_2O_5 (0.02)		g	200–220	α (69) β (31)	56	(252)
C_6H_5COCl (0.25)	P_2O_5 (trace)		g	200	α (mainly)	90	(108)
C_6H_5COCl (?)	P_2O_5 (trace)		b	170–200	α + β	90	(98)
C_6H_5COCl (?)	P_2O_5 (trace)			180–200	α (80) β (20)	?	(268)
C_6H_5COCl (0.73)	PCl_5 (?)		b	?	α (mainly) + β	82	(207)
C_6H_5COCl (0.36)	$AlCl_3$ (0.1)		b	150	α (trace) + β (mainly)	?	(361, 396)
C_6H_5COCl (?)	$AlCl_3$ (?)			170	α + β (mainly)	85	(357)
C_6H_5COCl (0.25)	$ZnCl_2$ (0.03)		g	95–98	α (75) β (25)	57	(252)
C_6H_5COCl (0.36)	$ZnCl_2$ (0.19)			125	α + β	?	(361)
C_6H_5COCl (1)	$ZnCl_2$ (1)			130–140	α (44) β (56)	45	(263)
C_6H_5COCl (0.35)	$CuCl_2$ (trace)			Boiled	α	47	(332)
C_6H_5COCl (0.35)	$HgCl_2$ (trace)			Boiled	α	26	(332)
$(C_6H_5CO)_2O$ (1)	BF_3 (3)	CCl_4	c	Room temperature	α (mainly) + β	4	(188)
$(C_6H_5CO)_2O$ (1)	BF_3 (3)	$C_6H_5NO_2$	c	Room temperature	α + β (trace)	60	(188)
C_6H_5COOH (1)	BF_3 (?)	$C_6H_5NO_2$	?	Room temperature			(188)
C_6H_5COOH (?)	P_2O_5 (?)			200–220	α + β	33	(253)
C_6H_5COOH (excess)	PCl_5 (excess)		b	?	α + β	?	(207)
o-$CH_3C_6H_4COCl$ (?)	$AlCl_3$ (?)	CS_2	?	0	α	?	(375)
m-$CH_3C_6H_4COCl$ (?)	$AlCl_3$ (?)	CS_2	?	0	α	80	(293, 375)
p-$CH_3C_6H_4COCl$ (?)	$AlCl_3$ (?)	CS_2	?	0	α	?	(293, 375)
o-ClC_6H_4COCl (?)	$AlCl_3$ (?)	CS_2	b	?	α?	?	(376)
m-ClC_6H_4COCl (0.9)	$AlCl_3$ (1.2)	?	b	0, room temperature	α + β	73	(89, 376)
p-ClC_6H_4COCl (0.9)	$AlCl_3$ (1.2)	CCl_4	b	0	α (mainly) + β	?	(89, 324, 376)
2,4,6-$Br_3C_6H_2COCl$ (0.5)	$AlCl_3$ (0.75)	CS_2	c	18	α	?	(25)
p-$CH_3OC_6H_4COCl$ (1)	$AlCl_3$ (2.3)	$(CH_2Cl)_2$	c	Room temperature	α	85	(19)
m-$O_2NC_6H_4COCl$ (1)	$AlCl_3$ (4.1)	$(CH_2Cl)_2$	c	Room temperature	α	90	(25)
p-$C_6H_5C_6H_4COCl$ (1)	$AlCl_3$ (1)	CS_2	g	Room temperature, reflux	α	60	(375)
1-Naphthoyl chloride (1)	Zn (trace)		b	Boiled	α	16	(207)
1-Naphthoic acid (0.95)	P_2O_5 (?)			200–220	α + β	35	(253)
2-Naphthoyl chloride (0.67)	$AlCl_3$ (1.1)	$(CH_2Cl)_2$	c	50	α	52	(18, 20)

TABLE 3—*Concluded*

Acyl Component[a]	Catalyst[a]	Solvent	Sequence[b]	Temperature	Product[c]	Yield	References
				°C.		*per cent*	
2-Naphthoyl chloride (1)	Zn (trace)		b	Boiled	$\alpha + \beta$	56	(207)
2-Naphthoic acid (?)	P_2O_5 (?)			200–220	β?	?	(253)
Anthraquinone-1-carboxylic acid chloride (0.67)	$AlCl_3$ (0.82)	$C_6H_5NO_2$	g	Room temperature	α?	33	(376)
Anthraquinone-2-carboxylic acid chloride (0.67)	$AlCl_3$ (0.9)	$C_6H_5NO_2$	g	75–80	$\alpha + \beta$ (trace)	25	(375)
Pyridine-2-carboxylic acid chloride (0.5)	$AlCl_3$ (1.9)	CS_2	g	Reflux	β	Good	(183)
Pyridine-3-carboxylic acid chloride (?)	$AlCl_3$ (?)	CS_2	g	Reflux	?	Low	(144, 434)
Phthalic anhydride (0.19)	$AlCl_3$ (0.16)	CS_2	g	50–60	β	?	(53)
Phthalic anhydride (0.43)	$AlCl_3$ (1.8)	CS_2	b	Reflux	α	30	(174, 189)
Phthalic anhydride (0.87)	$AlCl_3$ (0.96)	CS_2	g	Warmed	α (mainly) + β	53	(195)
Phthalic anhydride (0.87)	$AlCl_3$ (1)	CS_2	b	Reflux	$\alpha + \beta$ (trace)	33	(195)
Phthalic anhydride (0.9)	$AlCl_3$ (1.9)	CS_2	c	Reflux	α (mainly)	?	(413)
Phthalic anhydride (0.95)	$AlCl_3$ (2.1)	CS_2	b or d?	0–20	α (63) β (37)	16	(141)
Phthalic anhydride (0.95)	$AlCl_3$ (2.1)	CS_2	b or d?	20–46	α (ca. 75) β (ca. 25)	33	(141)
Phthalic anhydride (1)	$AlCl_3$ (2.2)	CS_2	?	0, 5, or 15	α (mainly) + β	92–95	(206)
Phthalic anhydride (?)	$AlCl_3$ (?)	$(CH_2Cl)_2$	?	10	α (mainly)	84	(155)
Phthalic anhydride (0.8)	$AlCl_3$ (1.8)	$(CHCl_2)_2$	b	Reflux	α (mainly) + β	?	(177)
Phthalic anhydride (0.95)	$AlCl_3$ (2.1)	$(CHCl_2)_2$	b or d?	0–20 or 20–45	α (68) β (32)	93	(141)
Phthalic anhydride (1)	$AlCl_3$ (2.2)	$(CHCl_2)_2$	c	28	$\alpha + \beta$ (mainly)	>34	(30, 410)
Phthalic anhydride (0.67)	$AlCl_3$ (1.5)	C_6H_6	b	Room temperature, or 75	α (mainly) + β	97	(219, 421)
Phthalic anhydride (0.67)	$AlCl_3$ (1.5)	C_6H_6	b	Room temperature	α (78) β (22)	88	(297)
Phthalic anhydride (0.67)	$AlCl_3$ (1.5)	C_6H_6	g	75	α	?	(217)
Phthalic anhydride (0.95)	$AlCl_3$ (2.1)	C_6H_6	b or d?	0–20	α (69) β (31)	89	(141)
Phthalic anhydride (0.95)	$AlCl_3$ (2.1)	C_6H_6	b or d?	20–80	α (>50) β (<50)	91	(141)
Phthalic anhydride (1)	$AlCl_3$ (1)	C_6H_6	b	Room temperature	$\alpha + \beta$	?	(429)
Phthalic anhydride (1)	$AlCl_3$ (2.2)	C_6H_6	?	0, 5, or 15	α (mainly) + β	92–98	(206)
Phthalic anhydride (0.95)	$AlCl_3$ (2.1)	o-$C_6H_4Cl_2$	b or d?	0–20	α (62) β (38)	91	(141)
Phthalic anhydride (1)	$AlCl_3$ (2.2)	o-$C_6H_4Cl_2$	?	0, 5, or 15	α (mainly) + β	98	(206)

Phthalic anhydride (1)	$AlCl_3$ (2.2)	*o*-$C_6H_4Cl_2$	?	−5	$\alpha + \beta$ (trace)	94	(206)
Phthalic anhydride (1)	$AlCl_3$ (2.2)	*o*-$C_6H_4Cl_2$	?	40	$\alpha + \beta$	97	(206)
Phthalic anhydride (1)	$AlCl_3$ (2.2)	*o*-$C_6H_4Cl_2$	?	?	α (mainly) + β	?	(241)
Phthalic anhydride (0.67)	$AlCl_3$ (1.5)	$C_6H_5NO_2$	b	30–40	β	31	(437)
Phthalic anhydride (0.95)	$AlCl_3$ (2.1)	$C_6H_5NO_2$	b or d?	20	α (81) β (19)	28	(141)
Phthalic anhydride (0.95)	$AlCl_3$ (2.1)	$C_6H_5NO_2$	b or d?	40	α (74) β (26)	49	(141)
Phthalic anhydride (0.95)	$AlCl_3$ (2.1)	$C_6H_5NO_2$	b or d?	60	α (73) β (27)	52	(141)
Phthalic anhydride (0.35)	$AlCl_3$ (0.49)		b	100	α	0.5	(3)
Phthalic anhydride (0.9)	$AlCl_3$ (1.8)		c	40–60, 90–100	?	?	(316)
Phthalic anhydride (1)	$AlCl_3$ (2)		g	5–8	?	Good	(316)
3,6-Dichlorophthalic anhydride (0.42)	$AlCl_3$ (1.2)	CS_2	b	Reflux	α (?)	28	(196)
4,5-Dichlorophthalic anhydride (0.42)	$AlCl_3$ (1.2)	CS_2	b	Room temperature	α (?)	?	(417)
3,4,5,6-Tetrachlorophthalic anhydride (0.45)	$AlCl_3$ (1)	CS_2	b	Reflux	α	78	(196)
Isophthalyl chloride (0.46)	$AlCl_3$ (1.9)	CS_2	b	Room temperature	$\alpha\alpha$	89 (crude)	(370)
Terephthalyl chloride (0.46)	$AlCl_3$ (1.9)	CS_2	b	Room temperature	$\alpha\alpha$	93 (crude)	(370)
Diphenic acid anhydride (0.24)	$AlCl_3$ (1)	C_6H_6	b	Room temperature	β	?	(35)
Naphthalene-1,2-dicarboxylic acid anhydride (0.62)	$AlCl_3$ (1.6)	CS_2	b	Reflux	$\alpha + \beta$	37	(418)
Naphthalene-2,3-dicarboxylic acid anhydride (0.67)	$AlCl_3$ (1.7)	CS_2	b	Boiled	α (mainly) + β	34	(419)
Pyromellitic anhydride (0.42)	$AlCl_3$ (1.4)	C_5H_5N	b	25, 50–60	$\alpha\alpha$ (mainly)	63 (crude)	(111)
Pyridine-2,3-dicarboxylic acid anhydride (0.86)	$AlCl_3$ (2.5)	C_6H_6	b	Reflux	$\alpha + \beta$ (mainly)	22	(239, 240)
Benzothiophene-2,3-dicarboxylic acid anhydride (0.33)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	25	$\alpha + \beta$	92	(291)

[a][b][c] See footnotes (a), (b), and (c) of table 1.

[d] The hydrogen chloride formed was removed continuously by suction.

[e] Additional component: nitrobenzene (1 mole).

[f] Additional component: *m*-dinitrobenzene (1 mole).

[g] Or other catalysts, *viz.*, zinc chloride, ferric chloride, phosphorus pentoxide.

TABLE 4

Acylations of anthracene

Acyl Component[a]	Catalyst[a]	Solvent	Sequence[b]	Temperature	Product[c]	Yield	References
				°C.		*per cent*	
CH_3COCl (1)	$AlCl_3$ (1.8)	CS_2	b	Room temperature	9-	26	(175)
CH_3COCl (1)	$AlCl_3$ (2)	CS_2	b	−5 to 0	9-	28	(32)
CH_3COCl (3)	$AlCl_3$ (3)	C_6H_6	b	0–10	1- + 2-	?	(227, 242, 282)
CH_3COCl (3)	$AlCl_3$ (3)	C_6H_6	b	0–5	2- (mainly)	?	(83)
CH_3COCl (3)	$AlCl_3$ (3)	C_6H_6	b	0[d]	9-	55	(191)
CH_3COCl (3)	$AlCl_3$ (3)	C_6H_6	b	0[e]	1- (84) 2- (16)	40	(191)
CH_3COCl (6)	$AlCl_3$ (2)	C_6H_6	b	−5 to 0, 10	9-	Very good	(227, 242, 283)
CH_3COCl (6)	$AlCl_3$ (2)	C_6H_5	b	−5 to 0	9-	57–60	(303)
CH_3COCl (6)	$AlCl_3$ (2)	C_6H_6	b	−5 to 0	9-	71	(59)
CH_3COCl (excess)	$AlCl_3$ (2)	C_6H_6	b	−5 to 0, 10	9-	Very good	(227, 242, 283)
CH_3COCl (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	10–15	1- (trace) 2- (mainly)	?	(227. 242. 282)
CH_3COCl (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	10–15	2-	38	(32)
CH_3COCl (2)	$AlCl_3$ (3)	$C_6H_5NO_2$	b	10–15	1- (mainly) 2- (trace)	?	(227, 242, 282)
CH_3COCl (2)	$AlCl_3$ (3)	$C_6H_5NO_2$	c	10–15	1-	64	(32, 59)
CH_3CH_2COCl (excess)	$AlCl_3$ (?)	C_6H_5	b	−5 to 0	9-	?	(227, 242, 282)
CH_3CH_2COCl (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	b	10–15	1- (trace) 2- (mainly)	?	(227. 242, 282, 420)
$C_6H_5CH_2COCl$ (0.92)	$AlCl_3$ (1)	CS_2	b	Cold	2-	Fair	(87)
$C_6H_5CH{=}CHCOCl$ (1)	$AlCl_3$ (4)	CS_2	b	13–15	9-	90	(59)
$C_6H_5CH{=}CHCOCl$ (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	5–10	9-	52	(59)
$C_6H_5N(CH_3)CHO$ (2)	$POCl_3$ (1.8)	*o*-$C_6H_4Cl_2$	c	90–95	9-	77–84	(154)
$C_5H_5N(CH_3)CHO$ (2)	$POCl_3$ (1.8)	*o*-$C_6H_4Cl_2$	c	90–95	9-	92	(153)
CO_2 (excess)	$AlCl_3$ (0.66)	CS_2	b	30	9-?	6	(304)
$(COCl)_2$ (3.5)	$AlCl_3$ (2)	CS_2	b	0	9-	24	(274)
$(COCl)_2$ (1)		$C_6H_5NO_2$	g	120–240	9-	67	(266, 388)
$(COCl)_2$ (3.5)			g	<160	9-	30	(274)
$COCl_2$ (1)			a	180–200	9-	Low	(34, 194)
NH_2COCl (1)	$AlCl_3$ (1)	$(CHCl_2)_2$	g	80	9-?	95	(394)
Maleic anhydride (0.9)	$AlCl_3$ (2)	C_6H_6	b	Room temperature, 60–70	9-[f]	44	(331)
Succinic anhydride (1)	$AlCl_3$ (1)	CH_2Cl_2	b	0	1- 2- (trace) 9-	?	(368)

Succinic anhydride (?)	$AlCl_3$ (?)	C_6H_6	?	?	9-[g]	?	(42)
Succinic anhydride (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	Room temperature	1- + 2-	43	(292)
Succinic anhydride (1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	5–10	1- + 2- (mainly)	10–13	(40, 121, 163)
Succinic anhydride (1)	$AlCl_3$ (2.3)	$C_6H_5NO_2$	c	5–10	2-	22	(159)
C_6H_5COCl (1)	$AlCl_3$ (1)	CS_2	c	ca. 40	1-, 2-, and 9-	?	(340, 341, 342)
C_6H_5COCl (1)	$AlCl_3$ (2)	CS_2	b	Room temperature	Mixture	50	(276, 340)
C_6H_5COCl (1)	$AlCl_3$ (1)[h]	CS_2	b	Warmed	1- (trace) 2- (trace) 9-	28	(277, 278)
C_6H_5COCl (5)	$AlCl_3$ (2)	$C_6H_5NO_2$	a	−10	9-	79	(262)
C_6H_5COCl (1.4)	Zn (0.08)	CS_2	b	Reflux	9-	78	(276, 277, 278)
C_6H_5COCl (0.35)	$HgCl_2$ (trace)			Boiled	1- + 2-	?	(332)
C_6H_5COCl (2)		$C_6H_5NO_2$	g	Reflux	9-	Nearly quantitative[i]	(320)
$(C_6H_5CO)_2O$ (1.6)	$AlCl_3$ (2.2)	CS_2	a	Room temperature, reflux	9-	79	(115)
Anthraquinone-2-carboxylic acid chloride (2.4)	$AlCl_3$ (4)	1,3,5-$C_6H_3Cl_3$	g	100	2- + 9-	?	(133)
Phthalic anhydride (0.67)	$AlCl_3$ (1.5)	C_6H_6	b	Room temperature	9-	Very good	(218, 219)
Phthalic anhydride (0.67)	$AlCl_3$ (1.5)	C_6H_6	g	Room temperature	9-?	?	(217)

[a][b][c] See footnotes (a), (b), and (c) of table 1.

[d] Reaction time 2.5 hr.

[e] Reaction time 20 hr.

[f] Stated to be the maleic anhydride adduct of anthracene (368), since the melting point and that of the methyl ester correspond.

[g] β-9-(9,10-Dihydroanthroyl)propionic acid.

[h] The catalyst contained water equivalent to 0.1 mole.

[i] This could not be confirmed (83).

TABLE 5

Acylations of phenanthrene

Acyl Component[a]	Catalyst[a]	Solvent	Sequence[b]	Temperature	Product[c]	Yield	References
				°C.		*per cent*	
CH_3COCl (1.3)	$AlCl_3$ (1.3)	CS_2	b	<20	9-[d]	?	(426)
CH_3COCl (1.3)	$AlCl_3$ (1.3)	CS_2	b	<20	2- + 3-	5–10	(312)
CH_3COCl (1.4)	$AlCl_3$ (2.2)	$C_6H_5NO_2$	a	25[e]	2- (19)) 3- (81	80	(191, 312)
CH_3COCl (1.4)	$AlCl_3$ (2.2)	$C_6H_5NO_2$	a	25[f]	2- (34) 3- (66)	76	(191)
CH_3COCl (1.4)	$AlCl_3$ (2.2)	$C_6H_5NO_2$	a	25	2- (trace) 3- (mainly)	65	(8)
CH_3COCl (1.3)	$SnCl_4$ (?)	CS_2	b	<20	2- + 3-.	<5	(312)
CH_3COBr (1.3)	$AlCl_3$ (1.3)	CS_2	b	<20	2- + 3-	<5	(312)
$(CH_3CO)_2O$ (?)	$AlCl_3$ (1.3)	CS_2	b	<20	2- + 3-	<5	(312)
$(CH_3CO)_2O$ (?)	HF (excess)		g	50–55	2- (33) 3- (66)	77	(158)
CH_3CH_2COCl (1.4)	$AlCl_3$ (2.1)	$C_6H_5NO_2$	a	0, room temperature	2- (33) 3- (66)	31	(15)
$C_6H_5CH_2COCl$ (0.9)	$AlCl_3$ (1)	CS_2	b?	Cold	*x*-	Very poor	(87)
$(COCl)_2$ (3.4)	$AlCl_3$ (2.0)	CS_2	b	−15	2- (ca. 20) 3- (ca. 80) 9- (trace)	56	(313)
$(COCl)_2$ (3.5)	$AlCl_3$ (?)	CS_2	g	Reflux	Mixture	Nearly quantitative	(274)
$(COCl)_2$ (3.5)		CS_2	g	Reflux	Mixture	Poor	(274)
Succinic anhydride (1.1)	$AlCl_3$ (2.2)	$C_6H_5NO_2$	a	Cool, room temperature	3-, *x*- (trace)	60	(214)
Succinic anhydride (1.1)	$AlCl_3$ (2.2)	$C_6H_5NO_2$	a	Cool	2- (16) 3- (84)	65	(11)
2-Methylsuccinic anhydride (0.9)	$AlCl_3$ (2.2)	$C_6H_5NO_2$	d	0, room temperature	2- (9) 3 (91)	33	(117)
C_6H_5COCl (0.67)	$AlCl_3$ (0.67)	CS_2	b	25	9-	?	(426)
C_6H_5COCl (0.67)	$AlCl_3$ (0.67)	CS_2	b	25	1-	9	(9, 10)
C_6H_5COCl (1)	$AlCl_3$ (1)	CS_2	c	25	1-	8	(9, 10)
C_6H_5COCl (1.2)	$AlCl_3$ (1.2)	CS_2	c	25–30	1-	19	(191)
C_6H_5COCl (?)	$AlCl_3$ (?)	CS_2	c	?	Two products	?	(341, 342)

C_6H_5COCl (1.1)	$AlCl_3$ (2.2)	$C_6H_5NO_2$	a	<0	1- (21) 2- (10) 3- (69)	29	(9, 10)
o-$CH_3C_6H_4COCl$ (0.67)	$AlCl_3$ (0.75)	CS_2	b	0	2- (trace) 3- (trace) 9-	?	(109, 110)
o-$CH_3C_6H_4COCl$ (1)	$AlCl_3$ (2.1)	$C_6H_5NO_2$	a	0	2- (12) 3- (88)	27	(14, 41)
Phthalic anhydride (0.67)	$AlCl_3$ (1.5)	C_6H_6	b	75	Crude mixture	Low	(218)

[a][b][c] See footnotes (a), (b), and (c) of table 1.
[d] This was not confirmed (312). Even from a reaction at −15°C. no 9-isomer could be isolated.
[e] Duration 6 hr.
[f] Duration 17 hr.

TABLE 6

Acylations of pyrene

Acyl Component[a]	Catalyst[a]	Solvent	Sequence[b]	Temperature	Product	Yield	References
				°C.		*per cent*	
CH_3COCl (1.5)	$AlCl_3$ (1.5)	$C_6H_5NO_2$	b	20	3-	72	(137, 138)
$(CH_3CO)_2O$ (8)	$ZnCl_2$ (1.9)	CH_3COOH	g	80–90	3-	90	(83, 415, 416)
$(CH_3CO)_2O$ (1.1)	$AlCl_3$ (2)	$C_6H_5NO_2$	c	0–10	3-	88	(12)
CH_3CH_2COCl (2)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	18–23	3-	82	(139)
$(CH_3CH_2CO)_2O$ (1.1)	$AlCl_3$ (2)	$C_6H_5NO_2$	c	0–10	3-	85	(12)
$(CH_3CH_2CH_2CO)_2O$ (1.1)	$AlCl_3$ (2)	$C_6H_5NO_2$	c	0-10	3-	85	(12)
$[(CH_3)_2CHCO]_2O$ (1.1)	$AlCl_3$ (2)	$C_6H_5NO_2$	c	0–10	3-	82	(12)
$[CH_3CH_2CH(CH_3)CO]_2O$ (1.1)	$AlCl_3$ (2)	$C_6H_5NO_2$	c	0–10	3-[d]	85	(12)
$CH_3CHClCH_2COCl$ (1)	$AlCl_3$ (1.2)	CS_2	b	Room temperature	3-	?	(39, 351)
$C_6H_5CH_2COCl$ (1)	$AlCl_3$ (1)	CS_2	b?	cool	3-	2	(87)
$C_6H_5CH{=}CHCOCl$ (1.3)	$AlCl_3$ (1.1)	C_6H_6	g	20	3-	90	(372, 373, 392)
$C_6H_4N(CH_3)CHO$ (2)	$POCl_3$ (1.8)	*o*-$C_6H_4Cl_2$	c	90–95	3-	54	(415, 416)
$COCl_2$ (?)	$AlCl_3$ (?)	?	?	?	3,3-[e]	?	(393)
NH_2COCl (2)	$AlCl_3$ (1.2)	$C_6H_5NO_2$	b	40–45	3-	?	(393, 394)
$CH_3NHCOCl$ (1.5)	$AlCl_3$ (1.7)	C_6H_6 (or *o*-$C_6H_4Cl_2$)	g	60–70	3-	Nearly quantitative	(223, 394)
KCNO (1.1)	$AlCl_3$ (?)	C_6H_6	h	?	3-	?	(394)
$C_5H_5N(C_2H_5)COCl$ (1.3)	$AlCl_3$ (1.3)	C_6H_5Cl	g	100	3-?	?	(386)
Succinic anhydride (1)	$AlCl_3$ (1.8)	$C_6H_5NO_2$	b	Room temperature	3-	62	(118)
Succinic anhydride (1)	$AlCl_3$ (1.8)	$C_6H_5NO_2$	b	Room temperature	3-	82–87	(13)
Succinic anhydride (1)	$AlCl_3$ (1.8)	$C_6H_5NO_2$	b	Room temperature	3-	90-96	(151, 415, 433)
2-Methylsuccinic anhydride (1)	$AlCl_3$ (1.8)	$C_6H_5NO_2$	b	Room temperature	3-	90	(156, 433)
C_6H_5COCl (1)	$AlCl_3$ (?)	CS_2	b	Boiled	3-	Poor	(375)
C_6H_5COCl (1)	$AlCl_3$ (?)	CS_2	b	Boiled	3-	<50	(392)
C_6H_5COCl (1.3)	$AlCl_3$ (1.2)	$(CH_2Cl)_2$	g	20	3-	90	(372)
C_6H_5COCl (1.1)	$AlCl_3$ (1.5)	C_6H_6	b	<35	3-	92	(415, 416)
C_6H_5COCl (1.3)[f]	$AlCl_3$ (1.1)[g]	C_6H_6[h]	g	20	3-	80	(373, 392)
C_6H_5COCl (excess)	$AlCl_3$ (1.1)	C_6H_6[h]	g	20	3-	Very good	(392)
o-$CH_3C_6H_4COCl$ (?)	$AlCl_3$ (?)	CS_2 or $C_6H_5NO_2$	?	?	3-	Poor	(118)
p-$CH_3C_6H_4COCl$ (1.3)	$AlCl_3$ (1.1)	C_6H_6	g	20	3-	90	(372, 373, 392)
o-ClC_6H_4COCl (1.3)	$AlCl_3$ (1.1)	C_6H_6	g	20	3-	90	(372, 373, 392)
p-BrC_6H_4COCl (1.3)	$AlCl_3$ (1.1)	C_6H_6	g	20	3-	90	(372, 373, 392)
1-Naphthoyl chloride (1.1)	$AlCl_3$ (1.2)	C_6H_6	g	20	3-	80	(372, 392)
2-Naphthoyl chloride (1)	$AlCl_3$ (1)	C_6H_6	g	<50	3-	?	(373)

3-Pyrenoyl chloride (0.56)	$AlCl_3$ (0.5)	CS_2	b	20–25	3-	?	(393)
Phthalic anhydride (1)	$AlCl_3$ (1)	C_6H_6	c	Room temperature	3-	47	(118)
Phthalic anhydride (1)	$AlCl_3$ (1.1)	C_6H_6	b	Room temperature, 50	3-	82	(415, 416)
Phthalic anhydride (0.97)	$AlCl_3$ (2.0)	C_6H_5Cl	b	55-65	3-?	Very good	(260)
3,6-Dichlorophthalic anhydride (1)	$AlCl_3$ (2.2)	C_6H_5Cl	b	55–65	3-?	Very good	(260)

[a][b][c] See footnotes (a) and (b) of table 1.

[d] Cyclized structure, with a possible five-membered ring (39) or six-membered ring (351).

[e] Di-3,3′-pyrenyl ketone.

[f] Alternatively benzoyl bromide.

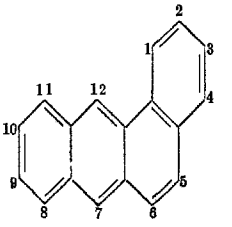
[g] Alternatively ferric chloride.

[h] Alternative solvents: toluene, chlorobenzene, ethylene dichloride

In general, excellent yields are obtained in Friedel–Crafts reactions with pyrene, the 3-position invariably being substituted (table 6). No evidence exists for a tendency to reversible substitution in this hydrocarbon.

A reactivity ratio of pyrene to benzene of >220:1 may be calculated from results of a benzoylation experiment (415),

E. BENZ[*a*]ANTHRACENE



Benz[*a*]anthracene

With ethoxalyl chloride and aluminum chloride in ice-cold nitrobenzene solution, benz[*a*]anthracene gives a 61 per cent yield of the 7-isomer (26). In most other cases (table 7) only very low yields of ketones have been observed. Besides the 7-isomer, the isomers formed in acetylating reactions comprise the 9- and 10-isomers and two (*x*- and *y*-) of unknown orientation (119, 126). These data are in keeping with the idea that the most reactive position is the 7-position, and the most stable ones the unreactive 9-, 10-, *x*-, and *y*-positions. In keeping with this is the observation of an acid-catalyzed deacetylation of

TABLE 7

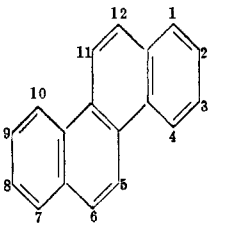
Acylations of benz[a]anthracene

Acyl Component [a]	Catalyst [a]	Solvent	Sequence [b]	Temperature	Product [c]	Yield	References
				°C.		*per cent*	
CH_3COCl (1.1)	$AlCl_3$ (1.9)	$C_6H_5NO_2$	a	Cool	7-	7.5	(126)
$(CH_3CO)_2O$ (1.1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	0	10- (36) *x*- (64)	6	(119)
$(CH_3CO)_2O$ (1.1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	<0	7- (64) 10- (36) *y*- (trace)	13	(119, 126)
$(CH_3CO)_2O$ (1.1)	$AlCl_3$ (1)	$C_6H_5NO_2$	c	Cool, room temperature	9- + 10-	?	(119)
$C_6H_5N(CH_3)CHO$ (2)	$POCl_3$ (1.9)	*o*-$C_6H_4Cl_2$	c	90–95	7-	64	(153)
$(COCl)_2$ (excess)	$AlCl_3$ (1)	CS_2	b	Room temperature, reflux	7-	2	(125)
RNHCOCl (excess)	$AlCl_3$ (?)	CS_2	b	Cool	?	Good	(223, 394)
$C_2H_5OOCCOCl$ (0.9)	$AlCl_3$ (2.2)	$C_6H_5NO_2$	b	0	7-	61	(26)

[a][b][c] See footnotes (a), (b), and (c) of table 1.

7-benz[*a*]anthryl methyl ketone, and its successful isomerization to the 10-ketone by means of one equivalent of aluminum chloride in nitrobenzene solution (119). Quantum-mechanical treatments of benz[*a*]anthracene (27) predict that the least reactive positions are the 9-, 10-, 2-, and 3-positions, i.e., the two β-anthryl and the two β-phenanthryl positions. It is therefore believed that the two unknown ketones were the 2- and 3-isomers, being formed slowly, but stable once formed.

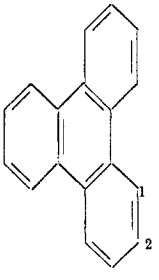
F. CHRYSENE



Chrysene

Friedel–Crafts reagents tend to cause substitution in the 6-position, in agreement with general reactivity studies. Carboxylation by means of oxalyl chloride and aluminum chloride (173, 274) gives solely the 6-carboxylic acid, thus differing from the reaction with phenanthrene (313), which gives a complex mixture. Under somewhat more vigorous reaction conditions, i.e., in nitrobenzene or with $R \sim 0.1$, entry of the substituent can be effected in the 2- and 3-positions. These two positions, therefore, closely resemble the β-positions of phenanthrene. A reactivity ratio >160:1 as compared to benzene may be calculated from data of the reaction of chrysene with phthalic anhydride (44). Results are collected in table 8.

G. TRIPHENYLENE



Triphenylene

TABLE 8

Acylations of chrysene

Acyl Component[a]	Catalyst[a]	Solvent	Sequence[b]	Temperature	Product[c]	Yield	References
				°C.		*per cent*	
CH_3COCl (17)	$AlCl_3$ (1.7)	CS_2	e	Room temperature, 60	2- (88) 6- (12)	55-68 (crude)	(116, 173, 321, 322)
CH_3COCl (17)	$AlCl_3$ (1.7)	CS_2	e	Room temperature, 60	2- (50) 3- (34) 6- (16)	27	(101)
CH_3COCl (?)	$AlCl_3$ (?)	CS_2	?	?	6- ?	?	(83)
CH_3COCl (6)	$AlCl_3$ (1.5)	CS_2	b	Room temperature, 60	6-	74	(41)
CH_3COCl (1)	$AlCl_3$ (1.1)	CH_2Cl_2	c	0, 35–40	6- (pure)	75	(101)
CH_3COCl (2)	$AlCl_3$ (3)	C_6H_6	b	Reflux	6-	?	(414)
CH_3COCl (1)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	c	0, 35–40	2- (39) 3- (38) 6- (28)	23 (crude)	(101)
$CH_3(CH_2)_5COCl$ (1.15)	$AlCl_3$ (1.25)	CH_2Cl_2	c	Room temperature, 35–40	6-	50	(102)
$CH_3(CH_2)_6COCl$ (1.1)	$AlCl_3$ (1.1)	$C_6H_5NO_2$	c	0, 35–40	2- (33) 3- (66)	14	(102)
Cyclohexanoyl chloride (1.2)	$AlCl_3$ (1.2)	$C_6H_5NO_2$	c	0, 35–40	2- (40) 3- (60)	32	(102)
$(COCl)_2$ (3.5)	$AlCl_3$ (0.8)	CS_2	b	0	6-	?	(173, 274)
$(COCl)_2$ (?)				170	6-	Poor	(274)
$CH_3NHCOCl$ (1.5)	$AlCl_3$ (1.7) or $FeCl_3$	C_6H_6 or o-$C_6H_4Cl_2$	g	60–70	?	Very good	(223, 394)
Succinic anhydride (1)	$AlCl_3$ (2)	C_6H_6	b	35–40	6-	30-35	(43)
Succinic anhydride (1)	$AlCl_3$ (2.1)	C_6H_6	g	Room temperature	6-	?	(413)
Succinic anhydride (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	40–80	3- (or 2- ?)	50–55	(43, 116)
Succinic anhydride (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	b	20	3- (or 2- ?), 6- (trace)	6	(116)
Succinic anhydride (1.2)	$AlCl_3$ (2.3)	$C_6H_5NO_2$	b	30	3- (or 2- ?), 6- (trace)	9	(116)
Succinic anhydride (1.2)	$AlCl_3$ (2.3)	$C_6H_5NO_2$	b	45	3- (or 2- ?), 6- (trace)	<6	(116)
Succinic anhydride (1.2)	$AlCl_3$ (2.3)	$C_6H_5NO_2$	b	0	Mixture	?	(116)
C_6H_5COCl (3)	$AlCl_3$ (1.7)	CS_2	a	Room temperature, 60	6-	ca. 70	(173)
C_6H_5COCl (2)	$AlCl_3$ (3)	C_6H_6	b	Reflux	6-	36-42	(414)
Phthalic anhydride (1)	$AlCl_3$ (2.1)	C_6H_6	b	Warmed	6-	?	(414)
Phthalic anhydride (2)	$AlCl_3$ (4)	C_6H_6	b	35–45	6-	Nearly quantitative	(44)

[a] [b] [c] See footnotes (a), (b), and (c) of table 1.

In two cases, acetylation (86) and phthaloylation (112), entry of the acyl group has been shown to be effected in the 2-position. Other substitutions (table 9) have been assumed by analogy to proceed similarly. The β-substitution in triphenylene was regarded as evidence for a strong steric hindrance to the

TABLE 9

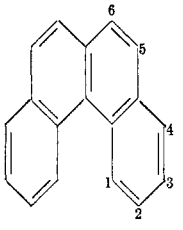
Acylations of triphenylene

Acyl Component [a]	Catalyst [a]	Solvent	Sequence [b]	Temperature	Product	Yield	References
				°C.		*per cent*	
CH_3COCl (17)	$AlCl_3$ (1.7)	CS_2	b	Reflux	2-	51	(86)
CH_3CH_2COCl (18)	$AlCl_3$ (2.4)	CS_2	b	Reflux	2- ?	67	(86)
$COClCOCl$ (2.2)	$AlCl_3$ (2.1)	CS_2	b	0	2-	29	(118)
NH_2COCl (1.5)	$AlCl_3$ (1.7)	C_6H_6	b	60–70	2- ?	98	(223, 380, 394)
Succinic anhydride (1.1)	$AlCl_3$ (1.7)	$C_6H_5NO_2$	b	Room temperature	2- ?	56	(86)
Phthalic anhydride (1.1)	$AlCl_3$ (2.3)	C_6H_6	b	Room temperature	2-	Nearly quantitative	(112)

[a] [b] See footnotes (a) and (b) of table 1.

α-position, which theory predicts as the more reactive. However, acetylation and propionylation were conducted with a large excess of acyl chloride ($R < 0.15$), which would in any case favor an outer position in substitution.

H. BENZO[*c*]PHENANTHRENE



Benzo[*c*]phenanthrene

Acetylation, like other substitutions, proceeds at the 5-position exclusively (table 10).

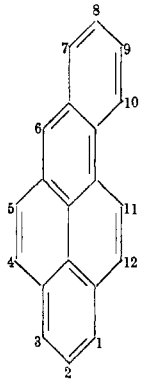
TABLE 10

Acylations of benzo[c]phenanthrene

Acyl Component [a]	Catalyst [a]	Solvent	Sequence [b]	Temperature	Product	Yield	References
						per cent	
CH_3COCl (?)	$AlCl_3$ (?)	?	?	?	Mixture	?	(323)
$(CH_3CO)_2O$ (1)	$AlCl_3$ (2.1)	C_6H_5Cl	b	Room temperature	5-	37	(323)
$(CH_3CO)_2O$ (?)	85% H_3PO_4 (?)	C_6H_6		Reflux	Mixture	?	(323)

[a] [b] See footnotes (a) and (b) of table 1.

I. BENZO[*a*]PYRENE



Benzo[*a*]pyrene

In contrast to normal substitution reactions which give exclusively, and generally in good yield, 6-substituted products, Friedel–Crafts acylations (table 11) give 1-substituted products. This has been described as an anomaly (85, 132). Further, the electrophilic catalyst was said in this case to coördinate with the most reactive position, leaving the next most reactive position open to attack (132); such a process is, however, difficult to visualize. According to the present theory this substitution is not anomalous but in keeping with an initial reversible substitution in the 6-position (a meso position of the anthryl type), followed by irreversible substitution in the more stable 1-position (a 3-pyrenyl type position). The isomer of unknown orientation isolated in an acetylation experiment (432) is probably not the 6-isomer, since nitrobenzene was used as a solvent in its preparation, but the 3-isomer, this position being the one predicted to be next in reactivity (85, 132). Isomerization to a β-type position should not be expected here because positions of the 3-pyrenyl type are stable.

The *N*-methylformanilide method gives a good yield of the 6-aldehyde.

TABLE 11

Acylations of benzo[a]pyrene

Acyl Component[a]	Catalyst[a]	Solvent	Sequence[b]	Temperature	Product[c]	Yield	References
				°C.		*per cent*	
CH_3COCl (20)	$AlCl_3$ (2)[d]	CS_2	c	0	1-	66	(157a, 431)
CH_3COCl (?)	$SnCl_4$ (?)	$C_6H_5NO_2$	?	40	1- (84) *x*- (16)	31	(432)
$(CH_3CO)_2O$ (?)	$ZnCl_2$ (?)	C_6H_6	?	Room temperature	1-	26	(432)
$(CH_3CO)_2O$ (1)	$AlCl_3$ (2)	$C_6H_5NO_2$	a	0	1-	19	(432)
CH_3CH_2COCl (18)	$AlCl_3$ (1.9)	CS_2	c	Room temperature	1-	85	(82)
$C_6H_5N(CH_3)CHO$ (2)	$POCl_3$ (1.8)	*o*-$C_6H_4Cl_2$	g	90–95	6-	90	(157)

[a] [b] [c] See footnotes (a), (b), and (c) of table 1.

[d] With added water.

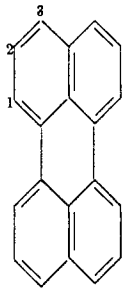
TABLE 12

Acylations of perylene

Acyl Component[a]	Catalyst[a]	Solvent	Sequence (b)	Temperature	Product	Yield	References
						per cent	
NH_2COCl (excess)	$AlCl_3$ (?)	CS_2	b	Cool	?	Good	(223, 394)
$(CH_2COCl)_2$ (0.43)	$AlCl_3$ (1.2)	CS_2	g	Heated	3-	14	(440)
Phthalic anhydride (6.8)	$AlCl_3$ (9.4)		g	170°C.	3- ?	Trace	(440)

[a] [b] See footnotes (a) and (b) of table 1.

J. PERYLENE



Perylene

The 3-position is the most reactive one in this hydrocarbon, and Friedel–Crafts reagents behave normally (table 12). The hydrocarbon is so reactive, however, that further acylation proceeds very readily (409).

V. Conclusions

Introduction of an acyl group into an aromatic system may proceed by either of two mechanisms.

The position of substitution of acyl groups in polycyclic aromatic hydrocarbons is governed by experimental conditions.

Reversibility is an important factor in acylation reactions.

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VI. References

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