(identical with an authentic specimen[33]) δ 1.7 (m, 4 H, CH_2CH_2), 2.45 (s, 6 H, $ArCH_3$), 4.0 (m, 4 H, OCH_2), and 7.60 (AB quartet, Δ_{AB} = 29 Hz, J_{AB} = 8 Hz, 8 H, p-C_6H_4).

Tribenzylamine and Acetyl *p*-Toluenesulfonate.—Solutions of acetyl *p*-toluenesulfonate (8.7 g, 75% pure, 30 mmol) in ether (100 ml) and tribenzylamine (11.7 g, 40 mmol) in ether were mixed at room temperature. An immediate white precipitate was deposited and the reaction mixture left at room temperature for 24 hr. The crystalline material was filtered and dried, mp 202–203°. It was identified as the tosylate salt of tribenzylamine: yield, 13.2 g (96%); ν_{max} 1600, 750, 700, and 690 cm^{-1}; nmr δ 2.40 (s, 3 H $ArCH_3$), 4.31 (d, J = 5 Hz, 6 H, $ArCH_2N$), 7.3 (m, 15 H, Ar), and 7.70 (AB quartet J_{AB} = 8 Hz, 4 H, p-C_6H_4).

Anal. Calcd for $C_{28}H_{29}NO_3S$: C, 73.5; H, 5.95; N, 3.06; S, 6.99. Found: C, 73.41; H, 6.20; N, 2.78; S, 6.72.

The identity was confirmed by synthesis of the salt from *p*-toluenesulfonic acid and tribenzylamine, mp 204–205°, mmp (with product) 202–203°.

Trimethylamine and Acetyl Methanesulfonate.—To a solution of acetyl methanesulfonate (3.32 g, 24 mmol) in ether (100 ml) was added at room temperature an excess of trimethylamine (5 ml). After standing for some minutes the resulting white precipitate was filtered off and recrystallized from acetonitrile, mp 204–205°. It was identified as the methanesulfonate salt of trimethylamine by comparison with an authentic sample prepare from methanesulfonic acid, mp 204–206°, mmp 204°, yield 3.8 g (97%).

The residual ether solution was now evaporated to dryness under high vacuum. The resulting oil appeared to be polymerized ketene: yield, 800 mg (79%); ν_{max} 1790, and 1830 cm^{-1} [(C=O (saturated), C=O (anhydride)]; nmr δ 2.25 (s, CH_2).

Triethylamine and Acetyl Methanesulfonate in the Presence of 1-(*N*-Morpholino)isobut-1-ene (26).—A solution of acetyl methanesulfonate (4.14 g, 30 mmol) in ether (25 ml) was added dropwise at room temperature to a solution of triethylamine (3.0 g, 30 mmol) and 1-(*N*-morpholino)isobut-1-ene (26) (4.2 g, 30 mmol) in 50 ml of ether. The reaction mixture was kept at room temperature for 2 hr and the precipitated sulfonate salt of triethylamine was filtered off. The solution was evaporated to dryness under reduced pressure leaving a colorless oil, yield 3.43 g (62%). The oil was distilled under reduced pressure collecting two compounds: 3-morpholino-2,2-dimethylcyclobutanone[30] (27) [bp 64° (0.1 mm); ν_{max} 1780 cm^{-1} (cyclobutane C=O); nmr δ 1.17, 1.21, (s, 6 H, CH_3), 2.12 (s, 2 H, $COCH_2$), 2.45 (m, 4 H, NCH_2), 2.92 (s, 1 H, NCH), and 3.70 (m, 4 H, OCH_2)] and 1-morpholino-4-methylpent-1-ene-3-one[30] (28) {bp 110–112° (0.1 mm); ν_{max} 1640 cm^{-1} (N–C=C); nmr δ 1.08 [d, J = 7 Hz, 6 H, $CH(CH_3)_2$], 2.5 (s,[7] J = 7 Hz, 1 H, $CH(CH_3)_2$], 3.32 (m, 4 H, NCH_2), 3.70 (m, 4 H, OCH_2), and 6.38 (AB quartet, Δ_{AB} = 136.5 Hz, J_{AB} = 13 Hz, 2 H, NCH=CH)}.

Registry No.—**8a**, 19859-09-7; **8b**, 26923-81-9; **9a**, 19859-06-4; **9b**, 19859-00-8; **9c**, 19859-11-1; **10a**, 26923-85-3; **10b**, 26923-86-4; **11a**, 26923-87-5; **11c**, 26923-88-6; **13a**, 19859-10-0; **13b**, 26923-90-0; **16**, 19859-07-5; **17**, 26923-92-2; **18**, 26923-93-3; **20a**, 26923-94-4; **20b**, 26923-95-5; **21a**, 26923-96-6; **21b**, 26923-97-7; **24**, 26923-98-9; **27**, 2618-48-6; **28**, 2618-47-5; **29**, 26924-01-6; **30**, 26924-02-7; **32**, 26924-03-8; *n*-butyl tosylate, 778-28-9; *n*-propyl tosylate, 599-91-7; benzyl acetate, 140-11-4; isopropyl tosylate, 2307-69-9; butane-1,4-diol bistosylate, 4724-56-5; tribenzylamine (tosylate salt), 26924-09-4.

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[33] N. Frydmann and Y. Mazur, unpublished results.

Mixed Sulfonic–Carboxylic Anhydrides. III.[1]
Reactions with Aromatic Ethers and Aromatic Hydrocarbons

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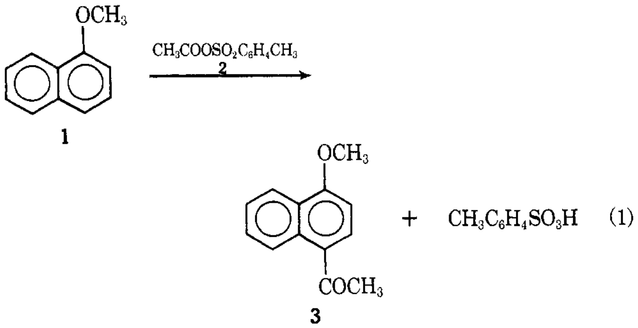
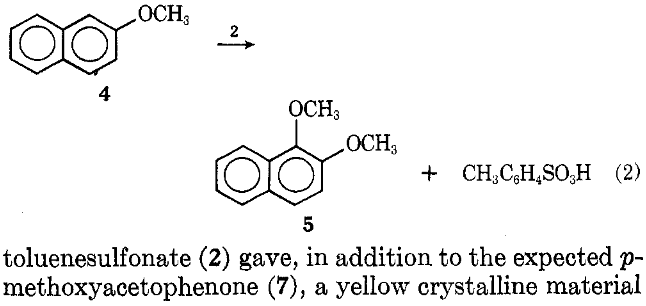
Received September 22, 1969

Mixed sulfonic–carboxylic anhydrides are shown to react with aromatic ethers. The products isolated depend upon the reaction conditions. When these are mild, the monoacylated aromatic ethers are formed but under more vigorous conditions these latter undergo self-condensation to the respective dypnones or triphenylbenzenes. Reaction with aromatic hydrocarbons is slow but the reaction with 9,10-dihydroanthracene effects aromatization in good yield, a reaction shown not to be of the ionic type of mechanisms usually associated with mixed anhydride reactions.

Previous publications in this series have demonstrated the reactive nature of mixed sulfonic–carboxylic anhydrides[1,2] as acylating agents. Aliphatic ethers were shown to undergo facile cleavage following initial acylation of the ether oxygen atom,[1] and thus it was of interest to examine the behavior of these reagents toward aromatic ethers.

With aromatic ethers the reaction was swift and comparatively clean. Thus reaction at room temperature of 1-methoxynaphthalene (1) with acetyl *p*-toluenesulfonate (2) in acetonitrile gave exclusively the 4-acetyl isomer 3 in 82% yield (eq 1), while under similar conditions 2-methoxynaphthalene (4) gave a 65% yield of the 1-acetyl isomer 5 (eq 2).





With the smaller, less hindered molecules, anisole and phenetole, reaction could be made to proceed further. Thus anisole 6 refluxed in acetonitrile with acetyl *p*-toluenesulfonate (2) gave, in addition to the expected *p*-methoxyacetophenone (7), a yellow crystalline material

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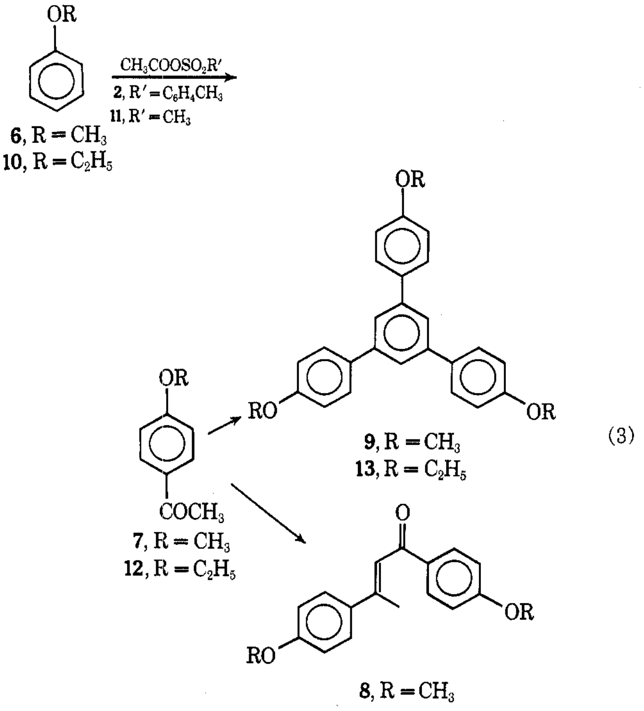
* To whom correspondence should be addressed.

[1] Paper II in this series: M. H. Karger and Y. Mazur, *J. Org. Chem.*, **36**, 532 (1971).

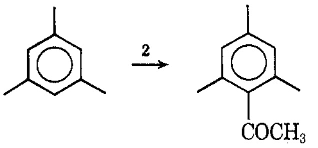
[2] M. H. Karger and Y. Mazur, *J. Amer. Chem. Soc.*, **90**, 3878 (1968); *cf.* C. G. Overberger and E. Sarlo, *ibid.*, **85**, 2446 (1963).

identified as the dypnone (**8**). More concentrated solutions of the two reagents gave, however, the triphenylbenzene, **9**, with none of the dypnone being isolated. A precisely similar result was observed with phenetole (**10**) and acetyl methanesulfonate (**11**) which gave the expected 4-acetylphenetole (**12**) as the major product under all conditions, but only the triphenylbenzene, **13**, in the absence of solvent. Thus, in dilute solution we witness a condensation of two molecules, but in concentrated solution three molecules condense with cyclization to the aromatic derivative. Such condensations are readily rationalized since initial acylation by mixed anhydride results in the release of 1 mol of sulfonic acid. The use of sulfonic acid ion-exchange resin to effect self-condensation of acetophenones is well known[3] as is the mineral acid catalyzed condensation of acetophenones to their respective 1,3,5-triarylbenzenes.[4] The formation of the two condensation products appears far more rapid and effective with mixed anhydride than by either of these two methods.[5]



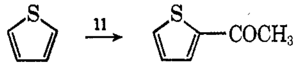
(3)

The reaction of acyl halides with aromatic hydrocarbons is well known and extensively documented.[6] This reaction is, however, invariably performed in the presence of Lewis acid, a procedure which may have inherent disadvantages, particularly of inter- or intramolecular alkyl group migration. While milder catalysts such as mineral acids or polyphosphoric acid have in some cases been used effectively, weaker acids such as the alkanesulfonic acids have been less successful. Acylations with carboxylic acids in the presence of trifluoroacetic anhydride have been successfully employed under mild conditions.[7] The high reactivity of mixed sulfonic–carboxylic anhydrides led us to investigate their reactions with aromatic hydrocarbons in the hope that acylation could be effected under mild conditions without the need of added catalyst. Reaction with aromatic hydrocarbons proved less straightforward and much slower than with aromatic ethers. Only polymethylbenzenes, while requiring forcing conditions, tended to react to give the nuclear acylated product alone. Thus mesitylene gave the monoacetyl product in 64% yield after treatment with mixed anhydride at 100° for 24 hr (eq 4). Xylenes, toluene, and naphthalene gave, under similar conditions, mostly unchanged starting material. What reaction there was resulted in complex mixtures of acetylated products which were not separated. Benzene itself under maximally vigorous conditions failed to react at all. Thus nuclear acylation on a benzene nucleus by mixed anhydride requires considerable activation by attached alkyl group.[7a]



$+ \ CH_3C_6H_4SO_3H$ (4)

Thiophene was readily acylated in 69% yield, the reaction proceeding exothermically at room temperature (eq 5). Reaction with furan was uncontrollable giving polymeric material, a consequence of the acid sensitivity of furan derivatives.[7b] Diphenyl ether gave no



$+ \ CH_3SO_3H$ (5)

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(3) N. B. Lorrete, *J. Org. Chem.*, **22**, 347 (1967), who found that acetophenone, for example, when maintained at 70–75° for 246 hr over Dowex 50 sulfonic acid ion-exchange resin gave 24% dypnone and 10% 1,3,5-triphenylbenzene.

(4) R. E. Lyle, E. J. Dewitt, N. M. Nichols, and W. Cleland, *J. Amer. Chem. Soc.*, **75**, 5959 (1953), and references cited therein. *p*-Methoxyacetophenone in a solution of hydrogen chloride in ethanol maintained at room temperature for 4 months gave a 54% yield of the triphenylbenzene. The yield at the end of 34 days was 2%.

(5) A likely reason for this appears to us the possibility that initial reaction to give the acetophenone is followed by attack by unreacted mixed anhydride to give the enol acetate, which rapidly reacts with unreacted acetophenone to give the dypnone. This latter by reaction with a second mole of enol acetate gives ultimately the triphenylbenzene. This explains the usually observed yield of acetylated aromatic ether as being no greater than 50%. That methanesulfonic acid is the sole agent of the condensations is unlikely. When we took an equimolar mixture of acetophenone and methanesulfonic acid and maintained the mixture overnight at room temperature, the acetophenone was recovered unchanged to the extent of 90%. Only traces of other material were observed to be present.

(6) P. Gore, "Friedel-Crafts and Related Reactions," G. Olah, Ed., Interscience, New York, N. Y., 1964, p 1, and references therein.

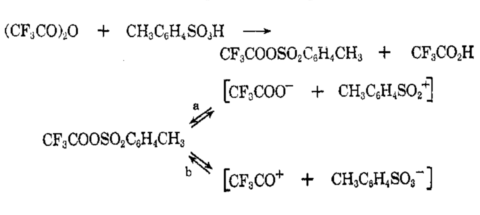
(7) (a) E. J. Bourne, M. Stacey, J. C. Tatlow, and J. M. Tedder, *J. Chem. Soc.*, 718 (1951). This reaction is thought to proceed *via* an initial equilibration between the carboxylic acid and trifluoroacetic anhydride. The resulting mixed anhydride can itself then dissociate to the trifluoroacetate ion and the acyl cation, which species acts as the effective acylating agent. Since mixed sulfonic–carboxylic anhydrides can participate in analogous equilibria (see ref 2) they should undergo similar reactions to those observed toward aromatic nuclei by carboxylic acid–trifluoroacetic anhydride mixtures.

$$(CF_3CO)_2O + RCO_2H \longrightarrow CF_3CO_2H + CF_3COOCOR$$

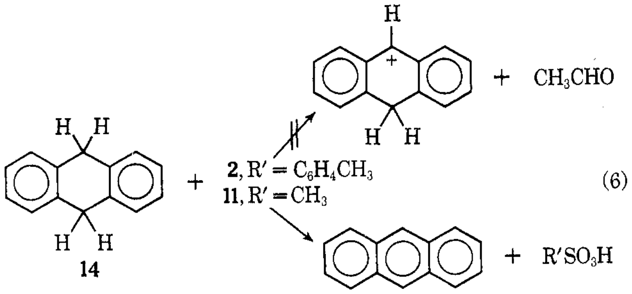
$$CF_3COOCOR \longrightarrow [CF_3COO^- + RCO^+]$$

$$R'SO_2OCOR \longrightarrow [R'SO_2O^- + RCO^+]$$

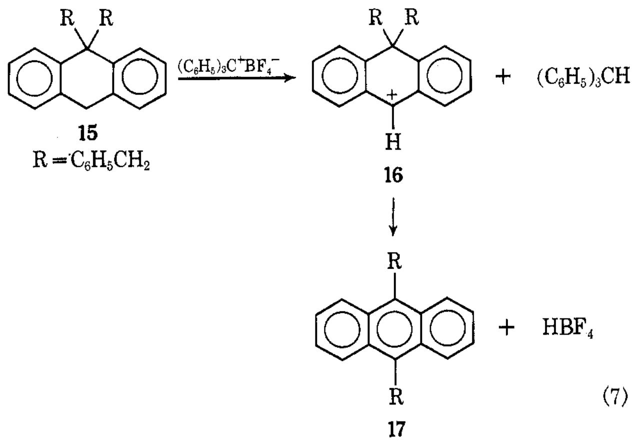
(b) By comparison, acylation of thiophene with trifluoroacetic anhydride and acetic acid required 1 hr at 40–50° to yield 2-acetylthiophene in 50% yield.[7] Furan was acylated at room temperature in 43% yield. From this comparison and that of the acylation of hydrocarbons, the mixed anhydride method of acylation would appear to be more effective than that described by Bourne, *et al.* Interestingly, these workers found that acylations with *p*-toluenesulfonic acid and trifluoroacetic anhydride gave only the sulfone (in 64% yield). In other words equilibrium a predominates over b below.



detectable reaction. Finally, we have briefly examined the reactions of mixed anhydrides with dihydroaromatic compounds exemplified by 9,10-dihydroanthracene. Since mixed anhydrides can conceivably act as good sources of acylium cations which in turn are capable of hydride ion abstraction,[8] we anticipated that 9,10-dihydroanthracene (**14**) and similar compounds might undergo facile dehydrogenation when heated with mixed sulfonic–carboxylic anhydrides in the manner depicted in eq 6.



When acetyl *p*-toluenesulfonate (**2**) and the dihydroanthracene (**14**) were heated in a flask open to the air but protected from moisture, for 2 hr at 130°, and 83% yield of anthracene was indeed obtained. Nmr monitoring of the reaction showed its half-life at 130° to be between 4 and 6 min. The reaction temperature was critical. Thus reaction at 100° for 2 hr or prolonged reflux in acetonitrile gave no trace of aromatized product or of anything other than unchanged starting material. The reaction was, in addition, moderately affected by the presence of air, the yield in the absence of air being little more than one half of that observed in its presence. Finally, in a blank experiment to determine the effect, if any, of the presence of sulfonic acid, the dihydroanthracene (**14**) was heated for 2 hr at 150° in the presence of this acid. Only a trace amount of anthracene was formed. The observation that the reaction began only at the precise temperature for which mixed sulfonic–carboxylic anhydrides have been observed to undergo intramolecular decomposition (probably *via* a free-radical mechanism[9]) cast doubt on the assumed ionic hydride abstraction nature of the reaction. Recent observation has shown that carbonium ions of general type **16** containing substituents R capable of facile migration, undergo aromatization by transannular migration of one of the R[10] groups. When 9,9-dibenzyl-9,10-dihydroanthracene[10] (**15**) was refluxed in acetic acid with triphenylmethyl fluoroborate, a reagent of known hydride abstracting ability,[11] the aromatization was observed to proceed smoothly and the dibenzylanthracene (**17**) was observed among the products, being identified by its uv spectrum which was characteristic of anthracene derivatives (eq 7). When the dihydroanthracene **15** was heated with mixed anhydride under a variety of conditions, however, no trace of anthracene was observed, the only product being recovered starting material (eq 7). This was to us strong evidence against an ionic mechanism in the dihydroanthracene dehydrogenation. Were such a mechanism to hold sway we should have observed the same rearranged product **17** when **15** was heated with mixed anhydride as when it was heated with triphenylmethyl fluoroborate. Thus initiation of the dehydrogenation by hydride abstraction by acylium cation is ruled out. Further evidence against this mechanism was obtained by the observation that diphenylmethane was recovered almost in total after heating at 130° with mixed anhydride, the remainder of the material consisting of nuclear acetylated derivatives. With diphenylmethane, the criteria involved in carbonium ion formation *via* a hydride abstractive process are identical with those of 9,10-dihydroanthracene (**14**) and, while aromatization is a pathway no longer open, we might anticipate the isolation of diphenylmethanol derivatives if indeed hydride abstraction did take place. That such derivatives were not isolated is a further indication that the dehydrogenation reaction under discussion does not involve hydride ion abstraction as its first step. It would therefore appear that the dehydrogenation reaction does not proceed by an ionic mechanism. The nonreaction of tetrahydronaphthalene toward mixed anhydride indicates that the dehydrogenation may be confined to dihydroaromatic systems.



Experimental Section

General experimental details, followed in this paper, have been given in part II of this series.[1]

1-Methoxynaphthalene (1) and Acetyl *p*-Toluenesulfonate (2).—A mixture of 1-methoxynaphthalene (**1**) (6.0 g, 37.8 mmol) and acetyl *p*-toluenesulfonate (**2**) (12 g, 75% pure, 42 mmol) in acetonitrile was kept at room temperature for 24 hr. Work-up in the usual manner gave a dark oil with a single major component on tlc (25% ether–hexane on silica), yield 6.2 g, 82%. This component was readily purified by column chromatography (Woelm alumina, activity grade I) and identified as 4-acetyl-1-methoxynaphthalene (**3**): mp 68–70° (lit.[12e] 70–71°); ir (Nujol mull) ν_{max} 1670, 1580, 840, 825, and 765 cm^{-1}; nmr δ 2.55 (s, 3 H, $ArCOCH_3$), 3.80 (s, 3 H, CH_3), 7.0 (AB quartet, Δ_{AB} = 75 Hz, J_{AB} = 8 Hz, 2 H, 1,2,3,4-substituted OC_6H_2), and 7.34–8.7 (16-line multiplet, 4 H, OC_6H_4). Comparison of the nmr spectra of the pure compound and of the crude oil showed the latter to contain not less than 90% of the former.

2-Methoxynaphthalene (4) and Acetyl *p*-Toluenesulfonate (2).

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[8] I. Tabushi, K. Fujita, and R. Oda, *Tetrahedron Lett.*, 4247, 5455 (1968).

[9] M. H. Karger and Y. Mazur, *J. Org. Chem.*, **36**, 528 (1971).

[10] A. L. J. Beckwith, W. B. Renfrow, A. Renfrow, and J. K. Teubner, *Tetrahedron Lett.*, 3463 (1968). Thus 9,9-dibenzyl-9,10-dihydro-10-hydroxyanthracene (**14**) ($R = CH_2C_6H_5$) when refluxed in acetic acid for 12 hr afforded 9,10-dibenzylanthracene (**16**) ($R = CH_2C_6H_5$) in 60% yield (eq 6).

[11] W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 2773 (1959).

[12] (a) C. R. Noller and R. Adams, *J. Amer. Chem. Soc.*, **46**, 1893 (1924); (b) E. C. Dodds, R. L. Huang, W. Lawson, and R. Robinson, *Proc. Roy. Soc., Ser. B*, **140**, 470 (1953); (c) W. Schneider and F. Seabach, *Chem. Ber.*, **54B**, 2298 (1921); (d) K. Fries, *ibid.*, **54**, 712 (1921); (e) W. Schneider and F. Kunau, *ibid.*, **54B**, 2304 (1921); (f) J. R. Johnson and G. E. May, *Org. Syn.*, **18**, 1 (1938); (g) A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1001 (1957).

—A mixture of 2-methoxynaphthalene (4) (2.0 g, 12.6 mmol) and excess acetyl *p*-toluenesulfonate (2) (10 g, 47 mmol) in acetonitrile was kept for 24 hr at room temperature. Work-up in the usual manner gave a pale yellow oil. To an ether solution of this oil was added pentane until the point of crystallization was reached, when the solution was cooled, depositing colorless needles of 1-acetyl-2-methoxynaphthalene (5), mp 50–54°. Recrystallization from ether–pentane gave pure material: mp 59–60° (lit.[12d] 59–60°); yield, 1.6 g (65%). The mother liquor (0.36 g) contained mostly 1-acetyl-2-methoxynaphthalene (5) as shown on tlc (5% ether–pentane on silica): ir (Nujol mull) ν_{max} 1690, 1620, 1600, 840, 820, and 740 cm^{-1}; nmr δ 2.60 (s, 3 H, ArCOCH$_3$), 3.85 (s, 3 H, OCH$_3$), and 7.45 (m, 5 H, Ar).

Anisole (6) and Acetyl Sulfonates 2. A.—A mixture of anisole (6) (4.7 g, 47.2 mmol) and acetyl *p*-toluenesulfonate (2) (13.0 g, 75% pure, 47.2 mmol) was refluxed for 48 hr in acetonitrile (25 ml). The reaction mixture was worked up in the usual manner leaving a pale yellow oil, yield 5.3 g (77%). A sample of the product (4.0 g) was distilled under reduced pressure collecting two fractions: *p*-methoxyacetophenone (7) {bp 105° (1 mm) [lit.[12a] 139° (15 mm)]; yield 1.15 g; ir ν_{max} 1660 (ArCO), 1600 (ArC=C), and 840 cm^{-1} (2 adjacent free H); nmr δ 2.51 (s, 3 H, ArCOCH$_3$), 3.83 (s, 3 H, OCH$_3$), and 7.40 (AB quartet, Δ_{AB} = 60 Hz, J_{AB} = 8.5 Hz, 4 H, *p*-C$_6$H$_4$)} and a yellow solid [bp 210–220° (1 mm); yield 2.4 g]. The yellow solid was dissolved in ether and cooled, collecting pale yellow crystals of 1,3-bis-*p*-methoxybut-3-ene-1-one (8): mp 93–94° (lit.[12b] 96°); uv λ_{max} 325 mμ (ϵ 23,700); ir (Nujol mull) ν_{max} 1650 (C=C-C=O), 1600 (Ar C=C), 810 and 830 cm^{-1} (2 adjacent free H); nmr δ 2.55 (d, J = 1.5 Hz, 3 H, C=CCH$_3$), 3.85 (s, 3 H, OCH$_3$), 3.87 (s, 3 H, OCH$_3$), and 6.8–8.1 [m, 9 H, *p*-C$_6$H$_4$ (2), C=CH-C=O)]. The mother liquor (*ca.* 1.7 g) was complex, tlc (20% ether–pentane on silica) showing eight spots.

B.—A mixture of anisole (6) (11.0 g, 90 mmol) and acetyl methanesulfonate (11) (15 g, 90 mmol) were kept at room temperature for 16 hr. After an initial induction time of 2 or 3 min, the temperature of the reaction mixture rose considerably, indicating an exothermic reaction. The deep yellow reaction mixture was poured into chloroform–bicarbonate solution and worked up in the usual manner to yield a deep red oil (14.0 g). The oil was then distilled under reduced pressure collecting *p*-methoxyacetophenone (7), yield 7.0 g (46%), bp 86° (0.3 mm), identified by comparison of its ir and nmr spectra with the sample previously obtained. The residual dark oil (7.0 g) was placed on a Kieselgel column and eluted with 25% ether–hexane to afford, as the only product, a pale yellow crystalline material, recrystallized from ether, mp 140–142°. It was identified as 1,3,5-tri(*p*-methoxyphenyl)benzene (9) (lit.[12c] mp 142°), yield 5.4 g (77% column recovery, 41% overall yield).

Acetyl Methanesulfonate (2) and Phenetole (10). A.—A mixture of phenetole (10) (10.0 g, 82 mmol) and acetyl methanesulfonate (11) (11.3 g, 82 mmol) were kept at room temperature for 16 hr. The dark brown reaction mixture was then poured into chloroform–bicarbonate solution and worked up in the usual manner. The resultant deep red oil (12 g) was distilled under reduced pressure to afford 4-acetylphenetole (12), bp 97° (1 mm), which solidified on standing and was recrystallized from ether as pale yellow prisms: mp 34–36° (lit.[1] mp 36–37°); yield 6.7 g (49%); ir ν_{max} 1680, 1600, 1580, 1270, and 850 cm^{-1}; nmr δ 1.40 (t, J = 7.5 Hz, 3 H, CH$_2$CH$_3$), 2.50 (s, 3 H, ArCOCH$_3$), 4.07 (q, J = 7.5 Hz, 2 H, CH$_2$CH$_3$), and 7.32 (AB quartet, Δ_{AB} = 62 Hz, J_{AB} = 8 Hz, 4 H, *p*-C$_6$H$_4$).

The nonvolatile residue from the distillation (4.8 g) was shown on tlc (20% ether–hexane on silica) to contain, as a major component, a uv active compound running as a single spot. Accordingly, this residue, a black viscous oil, was placed on a Kieselgel column and eluted with 20% ether–hexane. A single component was collected, running as a single spot on tlc, identical with the uv active material initially observed. It was purified by recrystallization from hexane to give colorless needles, mp 60–61°, yield 3.4 g (71% column recovery, 24% overall yield). It was identified as 1,3,5-tri(*p*-ethoxyphenyl)benzene (13): ir ν_{max} 1610, 1250, 840, 830, and 705 cm^{-1}; uv (in ether) λ_{max} 267 nm (ϵ 77,300); nmr δ 1.40 (t, J = 8 Hz, OCH$_2$CH$_3$), 4.04 (t, J = 8 Hz, 6 H, OCH$_2$CH$_3$), 7.30 (AB quartet, Δ_{AB} = 38 Hz, J_{AB} = 8 Hz, 12 H, *p*-C$_6$H$_4$), and 7.63 (s, 3 H, all *m*-C$_6$H$_3$); mass spectrum *m/e* 438 (M$^+$), 410 (M$^+$ − 28), 382 (M$^+$ − 56), and 354 (M$^+$ − 84).

Anal. Calcd for C$_{30}$H$_{30}$O$_3$: C, 82.16; H, 6.90. Found. C, 82.07; H, 7.07.

B.—Phenetole (10) (10.0 g, 82 mmol) in acetonitrile (25 ml) was mixed with acetyl methanesulfonate (11) (11.3 g, 82 mmol). After 4 hr at room temperature no reaction was detectable, the ir of the mixture being unchanged. The mixture was refluxed for 90 min when it had turned a deep red. The infrared spectrum of the crude solution showed no mixed anhydride remaining. It was poured into chloroform–bicarbonate and worked up in the usual manner to yield a red-brown oil (11.7 g). Distillation under reduced pressure gave 4-acetylphenetole (12), bp 83° (0.04 mm), yield 5.2 g (52%).

Benzene and Acetyl *p*-Toluenesulfonate (2). A.—Acetyl *p*-toluenesulfonate (13.0 g) was refluxed in benzene (50 ml) for 18 hr. Work-up in the usual manner gave only *p*-toluenesulfonic anhydride.

B.—Acetyl *p*-toluenesulfonate in an excess of benzene was heated in a sealed tube at 130° for 2 hr. Work-up in the usual manner gave only *p*-toluenesulfonic anhydride.

Mesitylene and Acetyl *p*-Toluenesulfonate (2).—Mesitylene (1.20 g, 10 mmol) was heated with acetyl *p*-toluenesulfonate (2.4 g, 11.2 mmol) at 100° for 4 hr, when reaction was judged from the absence of starting material in the nmr to be complete. Work-up in the usual manner gave a brownish oil which was distilled under reduced pressure, collecting acetomesitylene: bp 80° (2.0 mm) [lit. 90° (3 mm)]; yield, 1.1 g (64%); ir ν_{max} 1690 (ArC=O), 1600 (ArC=C), and 855 cm^{-1} (one free hydrogen atom); nmr δ 2.20 (s, 6 H, OCH$_3$), 2.26 (s, 3 H, *p*-CH$_3$), 2.46 (s, 3 H, ArCOCH$_3$), and 6.85 (s, 2 H, ArH).

Acetyl Methanesulfonate (11) and Thiophene.—Acetyl methanesulfonate (11) (13.0 g, 94 mmol) was slowly added to thiophene (15.9 g, 190 mmol). An exothermic reaction ensued, and the reaction mixture was kept at room temperature for 2 hr before being worked up in the usual manner to yield a reddish oil (12.3 g). This oil was distilled under reduced pressure collecting colorless 2-acetylthiophene: bp 60–62° (0.1 mm) [lit.[12f] 89–91 (3 mm)]; yield, 8.1 g (69%); ir ν_{max} 1670 cm^{-1}; nmr δ 2.51 (s, 3 H, ArCOCH$_3$), 7.10 (m, 1 H, SCHCH–), and 7.62 (m, 2 H, SCHCHCH=).

9,10-Dihydroanthracene (14) and Acetyl *p*-Toluenesulfonate (2). A.—9,10-Dihydroanthracene (14) (2.5 g, 14 mmol) was heated with a large excess of acetyl *p*-toluenesulfonate (2) (9.8 g, 45 mmol) in an open flask protected from moisture at 130° for 2 hr. Work-up in the usual manner gave a solid residue (2.05 g, 83%). Recrystallization from ether gave yellow-green crystals, mp 202–205°, mmp (with anthracene) 204°. The crude material was shown on tlc to run as a single spot with identical R_f value as anthracene. The nmr spectrum contained only a characteristic ten-line multiplet between δ 7.2 and 8.5 with no trace of the two singlets at δ 3.90 and 7.20 associated with 9,10-dihydroanthracene (14).

B.—The reaction A above was repeated in an nmr tube on a small scale, the tube being maintained at 130° and the singlet at δ 3.90 (aliphatic CH$_2$) from the starting material being rescanned and integrated at 2-min intervals. The intensity of this line was observed to decrease rapidly, the estimated half-life of the reaction being 4–6 min. After 45 min the line remained only as a weak shoulder and the full spectrum of the reaction product was identical with that of anthracene.

C.—The reaction A repeated at 100° for 2 hr gave only recovered starting material. Similarly when repeated under reflux in acetonitrile (25 ml) for 12 hr only recovered starting material in 83% yield was obtained.

D.—Identical reactions were carried out by heating two samples of 2.5 g of dihydroanthracene (14) with 3.3 g of mixed anhydride 2 at 130° for 2 hr, (a) under nitrogen, and (b) under dry air. Identical work-up procedures gave, in the latter case, a 52% yield and, in the former case, a 30% yield of recovered solid. The two products contained exactly the same proportion of anthracene (16) (57%) and 9,10-dihydroanthracene (14) (43%) as estimated by nmr integration measurements.

E.—In a blank experiment 9,10-dihydroanthracene (14) (4.0 g, 22.4 mmol) and *p*-toluenesulfonic acid (2) (1.0 g, 5.8 mmol) were heated at 150° for 2 hr. Work-up in the usual manner gave a solid product (2.3 g, 58%) whose composition, as estimated from the nmr spectrum, was, 9,10-dihydroanthracene (14) (94%) and anthracene (6%).

Acetyl Methanesulfonate (11) and 9,10-Dihydroanthracene (14).—Acetyl methanesulfonate (11) (2.8 g, 20 mmol) and 9,10-dihydroanthracene (14) (1.76 g, 9.8 mmol) were heated in a sealed tube at 130° for 2 hr. Work-up in the usual manner gave a solid (1.2 g, 69%) containing equal proportions of starting material and anthracene as estimated from nmr and tlc.

Acetyl Methanesulfonate (11) and 9,9-Dibenzyl-9,10-dihydroanthracene (15). A.—Acetyl methanesulfonate (11) (1.3 g. 9.4 mmol) was heated with the dibenzyldihydroanthracene (15) (500 mg, 1.4 mmol) at 130° for 2 hr. Work-up in the usual manner (but with chloroform as solvent) gave a dark solid whose nmr showed the presence of only starting material.

B.—Repeat of reaction A (2.6 g of mixed anhydride + 360 mg of reagent) in refluxing acetic acid (10 ml) for 30 min gave again only recovered starting material (280 mg).

Triphenylmethyl Fluoroborate and 9,9-Dibenzyl-9,10-dihydroanthracene (15).—The dihydroanthracene (15) (358 mg, 1.0 mmol) and triphenylmethyl fluoroborate (1.5 g, 3.8 mmol) were refluxed in acetic acid (10 ml) for 30 min when the color of the reaction mixture was observed to change to a deep red from the original yellow. Work-up in the usual manner gave an oil (1.65 g) whose nmr spectrum and tlc showed the absence of starting material and the probable presence of triphenylmethane and triphenylmethanol. The crude oil was placed on a silica column which was then eluted with pentane followed by 5% ether. The first fraction contained triphenylmethane which was recrystallized from hexane to give pure material, mp 92°, mmp 92°, yield 300 mg. Elution with 5% ether gave a glass which could not be crystallized but which was shown to contain 9,10-dibenzylanthracene (17). The glass was purified by precipitation from ether with pentane and sublimation at 300° under reduced pressure (0.01 mm). The resulting glass registered as a single spot on tlc (20% ether–pentane on silica): uv λ_{max} 270 mμ (ϵ 58,000) [lit.[12g] λ_{max} 266 mμ, (ϵ 84,000)]: nmr δ 4.70, 5.0 (m, CH_2Ar), and 7.2 (m, ArH); yield 242 mg (67%).

Diphenylmethane and Acetyl *p*-Toluenesulfonate (2).—Diphenylmethane (2.5 g, 15 mmol) was heated with acetyl *p*-toluenesulfonate (2) (10 g, 47 mmol) at 130° for 2 hr. Work-up in the usual manner gave an oil (2.2 g) whose composition, as judged from the nmr and tlc, was 90% diphenylmethane. The remaining 10% (seven distinct spots on tlc) appeared from the nmr (singlets at δ 2.0, 2.15) to contain some acetylated material.

Registry No.—**1**, 2216-69-5; **2**, 26908-82-7; **4**, 93-04-9; **6**, 100-66-3; **10**, 103-73-1; **11**, 100-06-1; **13**, 7509-23-1; mesitylene, 108-67-8; thiophene, 110-02-1; **14**, 613-31-0; **15**, 26908-83-8; triphenylmethyl fluoroborate, 341-02-6.

Boron Photochemistry. VI. The Possible Role of Bridged Intermediates in the Photolysis of Borate Complexes

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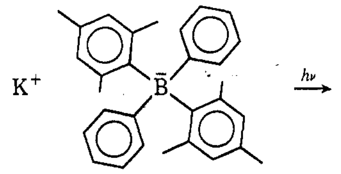
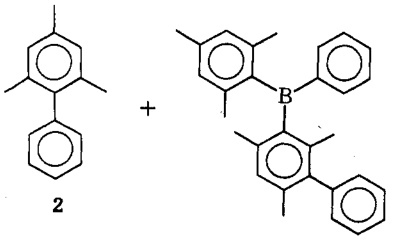
Received July 1, 1970

Several hindered tetraarylborate salts have been synthesized and photolyzed. The unexpected nature of some of the photolysis products has led us to reexamine the photolysis of potassium dimesityldiphenylborate labeled with a deuterium atom in each of the 4-position methyl groups. An examination of the products from the photolysis of this compound has demonstrated that an unusual and unanticipated rearrangement involving a 1,3 shift of a diarylbora group has taken place. A possible mechanism involving bridged intermediates has been proposed to account for this rearrangement.

In a previous publication[1] we discussed the photochemistry of the highly hindered potassium dimesityldiphenylborate (1) in the presence of oxygen to yield 2,4,6-trimethylbiphenyl (2) and (2,4,6-trimethyl-3-biphenylyl)mesitylphenylborane (3).



1



2

3

Three possible routes to 2 were discussed but at that time no attempt was made to distinguish between them. We have now conducted the photolysis of 1 in D_2O–1,2-dimethoxyethane in place of the H_2O–dimethoxyethane used earlier. Previously we considered two primary photochemical processes: (1) the generation of a phenyl radical (R·) by homolytic fission of a phenyl boron bond in the "ate" complex 1; (2) the generation of a mesityl radical by an analogous process. Path a based on process 1 is shown in Scheme I[2] and reveals that in D_2O the 2,4,6-trimethylbiphenyl (2) should contain zero or one D atom/molecule. The deuterium would be located in the mesityl ring since a phenyl radical has attacked the mesityl ring. A similar route, b (not shown), based on process 2, would predict 2,4,6-trimethylbiphenyl (2), which would have a maximum of two D atoms/molecule incorporated into the phenyl ring. A third route, c, which involves the radical pair, 4, of route a is shown in Scheme II. Route c leads to 2,4,6-trimethylbiphenyl (2) containing one deuterium atom per molecule, located on the mesityl ring. Therefore, by examining the position and content of deuterium in the isolated 2, we hoped to be able to determine the route followed by the rearrangement.

2,4,6-Trimethylbiphenyl (2) containing approximately 10% monodeuterated material was obtained experimentally. We were unable to determine the exact ring location of the deuterium label. However, the small extent of incorporation of deuterium is consistent when route a is considered as the major route to 2. Further examination of the proposed routes to 2 reveals a second distinction. Paths a and b yield 2,4,6-tri-

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[1] P. J. Grisdale, B. E. Babb, J. C. Doty, T. H. Regan, D. P. Maier, and J. L. R. Williams, *J. Organometal. Chem.*, **14**, 63 (1968).

[2] The spin state of the biradical **5** is unknown. As a singlet **5** and **6** become canonical structures.