

## NOTES.

*The Kinetics of Alkyl-Oxygen Fission in Ester Hydrolysis.*  
*Part IV.\* tert.-Butyl Formate in Aqueous Acetone.*

By V. R. STIMSON.

[Reprint Order No. 6393.]

THE rate of the acid-catalysed hydrolysis of *tert.*-butyl formate is proportional to the concentrations of both ester and acid catalyst. A plot of rate against acid concentration shows that no uncatalysed reaction of comparable rate occurs. A small rise in  $k_1$  (ca. 5% from 30 to 70% reaction) found during the reaction is attributed to autocatalysis by the formic acid produced. The value of  $\log_{10} 10^6 k_1 / C_A$  (sec.<sup>-1</sup>) is 5.47 at 100° in 60% acetone. This represents a rate 22 times that of *tert.*-butyl benzoate and 2 : 4 : 6-trimethylbenzoate and comparable with that of ethyl and methyl formate;  $k_1 / C_A$  for these two esters is  $2.2 \times 10^{-1}$  and  $2.0 \times 10^{-1}$  sec.<sup>-1</sup>, respectively (calc. from the results at 25° of Newling and Hinshelwood, *J.*, 1936, 1357), and for *tert.*-butyl formate  $3.0 \times 10^{-1}$  sec.<sup>-1</sup> (calc.).

The Arrhenius equation is accurately followed, the activation energy being  $16.3 \pm 0.5$  kcal./mole and  $\log_{10} A$  (sec.<sup>-1</sup>) 9.04. The value of  $E$  is quite different from that found for *tert.*-butyl benzoate and 2 : 4 : 6-trimethylbenzoate (ca. 30 kcal./mole; Parts I, *J.*, 1954, 2848; II, *J.*, 1955, 2010; and III \*), for which mechanism  $A_{AL}1$  has been suggested, but is almost identical with that found for methyl and ethyl formate (15.6 kcal./mole; Newling and Hinshelwood, *loc. cit.*), and lies within the range of values (15—17 kcal./mole, cf. Part I) generally found for hydrolysis of methyl and ethyl esters of aliphatic acids which are hydrolysed by mechanism  $A_{AC}2$ . Hence it is suggested that

\* Part III, *J.*, 1955, 2673.

the acid hydrolysis of *tert.*-butyl formate occurs largely if not wholly by mechanism  $A_{AC}2$  and that a transition in mechanism from  $A_{AL}1$  to  $A_{AC}2$  occurs in the series 2 : 4 : 6-trimethylbenzoate, benzoate, acetate, and formate, between the benzoate and formate for the *tert.*-butyl ester.

The result is that expected from an analysis (as in Part III) of rates of hydrolysis of formates by  $A_{AC}2$  and *tert.*-butyl esters by  $A_{AL}1$ , and agrees with the observation that diphenylmethyl formate undergoes acyl-oxygen fission (Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686) even though diphenylmethyl shows strong electron-releasing properties in  $S_N$  reactions.

*First-order rate constants ( $k_1$ ) for hydrolysis of tert.-butyl formate in 60% acetone.*

( $C_A$  and  $C_E$  are the concentrations of hydrochloric acid and ester respectively.)

Temp.	$10^2 C_A$ (mole/l.)	$10^2 C_E$ (mole/l.)	$10^3 k_1$ (min. <sup>-1</sup> )	$k_1/C_A$ (min. <sup>-1</sup> ) l. mole <sup>-1</sup>	Temp.	$10^2 C_A$ (mole/l.)	$10^2 C_E$ (mole/l.)	$10^3 k_1$ (min. <sup>-1</sup> )	$k_1/C_A$ (min. <sup>-1</sup> ) l. mole <sup>-1</sup>
97.1°	0.30	1.53	45	15.0	84.4	0.17	1.90	11.3	6.6
"	0.28	1.93	41	14.6	80.3	0.79	1.73	41	5.2
"	0.28	2.00	42	14.8	73.4	0.82	1.56	28.0	3.4
"	0.15	1.67	22.4	14.5	72.3	0.17	1.62	4.9	2.9
"	0.13	1.43	19.7	15.3					

*Experimental.—Preparation of tert.-butyl formate.* (a) Samples prepared by Bateman and Hughes's method (*J.*, 1940, 935) contained small amounts (up to 10%) of free acid. (b) A mixture of dried, fractionated *tert.*-butyl alcohol (m. p. 24.5—25.0°; 25 ml.) and formic acid ("AnalaR," anhyd.; 25 ml.) after standing overnight was quickly distilled, 15 ml. of b. p. <90° being collected, which on fractionation through an 8-in. column packed with Fenske helices gave 3 g. of product having b. p. 76°/680 mm. and containing 85% of ester (calc. from the acid produced on complete hydrolysis) and <1% of free acid, which values were unchanged on redistillation. Hydrolysis produced a reducing substance (0.88 mol. as formic acid by permanganate titration; Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., 1944, p. 361). *tert.*-Butyl alcohol did not interfere with the estimation. The analysis (Found: C, 58.3; H, 11.0. Calc. for  $C_6H_{10}O_2$ : C, 58.7; H, 9.9%) is of the right order.

Several samples were made in this way and had purities of 85—90% and gave consistent rate constants. Possible impurities are *tert.*-butyl alcohol, water, and traces of diisobutene which would not be expected to interfere with the kinetics.

The experimental procedure was that described in Parts I and II except that *a* was found from the titre on complete hydrolysis.

The microanalysis was carried out by Dr. W. Zimmermann, of C.S.I.R.O., Melbourne.

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### *Tetracarbonyliron Bisphenylacetylde.*

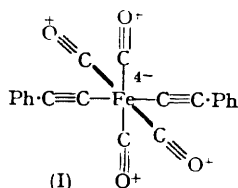
By E. R. H. JONES, P. C. WAILES, and M. C. WHITING.

[Reprint Order No. 6457.]

PRELIMINARY information on war-time German work implied that while iron carbonyl by itself was inert to acetylene under acidic conditions, it did react to some extent when nickel carbonyl was present (see Copenhagen and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold, New York, 1949, pp. 251, 292, 293). Recently Reppe and his colleagues have described much work on metal carbonyl-acetylene reactions, and although the use of acrylic ester as catalyst is said to induce a reaction between acetylene and iron carbonyl, more acrylate being formed, no mention is made of the use of mixed carbonyls (Reppe, *Annalen*, 1953, **582**, 30).

Attempts to effect reaction between iron carbonyl and phenylacetylene under the conditions (aqueous-ethanolic acetic acid at 60—80°) found optimal for nickel carbonyl

(Jones, Shen, and Whiting, *J.*, 1950, 230) proved unsuccessful. Nickel carbonyl was then added to the mixture, an exothermal reaction occurred, and atropic acid was formed; the yield, however, never exceeded that expected from the nickel carbonyl alone, the stoichiometry postulated by Jones, Shen, and Whiting (*J.*, 1951, 766) being assumed to hold. A sparingly soluble, neutral product separated from the mixture in small yield, giving analytical data appropriate for  $C_{20}H_{10}O_4Fe$  or  $C_{20}H_{12}O_4Fe$ . The latter hardly permits rationalisation, but the former suggests structure (I), which is isoelectronic with  $Cr(CO)_6$ ,  $Fe(C\equiv NMe)_4(CN)_2$ , and  $Fe(CN)_6^{4-}$ , possessing a complete 36-electron shell about the central atom, a feature almost invariably associated with great stability



in complexes of the transition metals. This substance was in fact extremely stable; it showed no sign of decomposition at  $220^\circ$ , and it was recovered unchanged after several hours in boiling 20% sulphuric acid. It was, however, readily decomposed by irradiation of its solutions, with the precipitation of ferric oxide; in this it closely resembles ferrocene, which is also otherwise extremely stable. It reacted with alkali, giving a red solution from which some of the original complex could be recovered on acidification. Chromium hexacarbonyl also reacts with alkalis (Rhombberg and Owen, *J. Amer. Chem. Soc.*, 1951, 73, 5904), giving a hydrocarbonyl  $Cr(CO)_5H_2$  which readily disproportionates to the hexacarbonyl.

Several attempts at more rational syntheses of (I), including treatment of iron pentacarbonyl with phenylmagnesium bromide, or of the potassium salt of iron carbonyl hydride with iodophenylacetylene, failed to give recognisable products. There appears to be no close analogy between the complex described above and any of the numerous acetylene-carbonyl complexes reported by Reppe and Vetter (*Annalen*, 1953, 582, 133).

*Experimental.*—Phenylacetylene (7.1 g.), ethanol (20 c.c.), water (1.0 c.c.), and glacial acetic acid (4.2 c.c.) were heated to  $65^\circ$  while a mixture of nickel carbonyl (1.4 g., 1.0 c.c.) and iron pentacarbonyl (5.5 g., 3.8 c.c.), contained under a layer of ethanol in a dropping funnel, was added slowly with stirring. After a short induction period an exothermal reaction began, and the temperature remained at  $60$ – $65^\circ$  without external heating. Heating was then resumed and continued for 2 hr. On cooling of the mixture, the complex separated and after addition of dilute sulphuric acid and ether was collected by filtration; crystallisation from benzene or dilute acetic acid gave fine yellow needles, (0.35 g.) m. p.  $222$ – $222.5^\circ$  (Found: C, 64.5, 64.4; H, 3.1, 3.0; Fe, 15.5.  $C_{20}H_{10}O_4Fe$  requires C, 64.85; H, 2.7; Fe, 15.1.  $C_{20}H_{12}O_4Fe$  requires C, 64.5; H, 3.25; Fe, 15.0%). (Iron was determined on 130 mg. of material, after dissolution in nitric acid, heating for several hours, precipitation as ferric hydroxide, and weighing as the oxide).

In ethanol the complex showed a broad absorption maximum at  $3300 \text{ \AA}$  ( $\epsilon = 6500$ ) and rising absorption with inflexions at ca. 2320, 2480, 2900, and  $2960 \text{ \AA}$  ( $\epsilon = 22,000, 19,000, 9,000,$  and  $8000$ , respectively); absorption was still appreciable at  $4000 \text{ \AA}$ . In the infrared (Nujol suspension), bands attributable to phenyl groups were observed at 3070, 3030, 1615, 770, 746, and  $688 \text{ cm}^{-1}$  and to  $\cdot C\equiv C\cdot$  and  $\cdot C\equiv O$  (metal carbonyl type) stretching modes at 2070, 2010, and  $1992 \text{ cm}^{-1}$ . Absorption at ca.  $3300 \text{ cm}^{-1}$  (acetylenic CH stretching) was absent.

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*Organosilicon Compounds. Part XVI.\* The Alkaline Hydrolysis  
of Triorganomonosilanes.*

By J. E. BAINES and C. EABORN.

[Reprint Order No. 6474.]

THE theoretical significance of the kinetics of the alkaline hydrolysis of organosilicon hydrides (Price, *J. Amer. Chem. Soc.*, 1947, **69**, 2600; Gilman and Dunn, *ibid.*, 1951, **73**, 3404; Gilman, Dunn, and Hammond, *ibid.*, p. 4499; Kaplan and Wilzbach, *ibid.*, 1952, **74**, 6152; 1955, **77**, 1297) and the value of the reaction for indicating the steric effects of substituents on ease of nucleophilic substitution at silicon (*e.g.*, West, *ibid.*, 1954, **76**, 6015) prompt us to record some fragmentary observations on the reactions of triorganomonosilanes with aqueous-alcoholic alkalis.

*Salt Effects.*—Although Price (*loc. cit.*) states that the specific rate constant,  $k_s (= k_1/[\text{OH}^-]$ , where  $k_1$  is the observed first-order rate constant), for alkaline solvolysis in aqueous alcohol is independent of the concentration of alkali it appears from his results that there is a considerable salt effect. For the solvolysis of triethylsilane (*ca.* 0.07M) in 94.5 vol.-% ethanol-water (s.g. 0.8180 at 60° F) at 34.9° we have examined the effect of varying the sodium hydroxide concentration and of adding sodium iodide or perchlorate. Good first-order kinetics during a run are observed for the whole range of salt concentration, but Table 1 shows that  $k_s$  falls markedly as the salt concentration is raised. At a given

TABLE 1.

[NaOH] (M) .....	0.0497	0.0740	0.100	0.201	0.100	0.302	0.201
Added salt .....	—	—	—	—	NaI	—	NaI
[Added salt] (M) .....	—	—	—	—	0.102	—	0.102
[Total salt] (M) .....	0.0497	0.0740	0.100	0.201	0.202	0.302	0.303
$k_s$ (min. <sup>-1</sup> mole <sup>-1</sup> l.) .....	0.124	0.117	0.110	0.094	0.092	0.081	0.082
[NaOH] (M) .....	0.201	0.403	0.201	0.804	0.201	1.126	
Added salt .....	NaClO <sub>4</sub>	—	NaI	—	NaI	—	
[Added salt] (M) .....	0.098	—	0.203	—	0.600	—	
[Total salt] (M) .....	0.299	0.403	0.404	0.804	0.801	1.126	
$k_s$ (min. <sup>-1</sup> mole <sup>-1</sup> l.) .....	0.082	0.076	0.075	0.054	0.51	0.043	

salt concentration,  $k_s$  is independent of which sodium salts are present, and thus disturbance of the equilibrium,  $\text{HO}^- + \text{EtOH} \rightleftharpoons \text{EtO}^- + \text{H}_2\text{O}$ , by added hydroxide ion is not a major factor.

The straight line,  $\log k_s = -0.79 - 0.55 \mu^{\frac{1}{2}}$  ( $\mu$  = ionic strength), fits the data excellently.

The solvolysis of triethylsilane is faster with potassium hydroxide than with sodium hydroxide in the range studied ( $[\text{KOH}] = 0.2\text{--}1.1\text{M}$ ), increasingly so as the alkali concentration is raised; at an alkali concentration of 1.125M the reaction is 1.35 times as fast with potassium hydroxide as with sodium hydroxide. The line,  $\log k_s = -0.87 - 0.34 \mu^{\frac{1}{2}}$ , fits the data shown in Table 2.

TABLE 2.

[KOH] (M) .....	0.200	0.280	0.375	0.563	0.750	1.126
$k_s$ (min. <sup>-1</sup> mole <sup>-1</sup> l.) .....	0.096	0.90	0.82	0.071	0.068	0.058

Clearly the salt effects must be considered when rates of alkaline hydrolysis are used to compare reactivities of various organosilicon hydrides. The magnitude of the salt effect, the dependence of  $\log k$  on  $\mu^{\frac{1}{2}}$  and not on  $\mu$ , and the higher rates with potassium than with sodium hydroxide (which suggest that activities should be used in place of concentrations) fit a hypothetical reaction between a negative ion and an entity having a partial fractional positive charge rather than a reaction between an ion and a neutral molecule. The nature

of the transition state is fairly well understood (Kaplan and Wilzbach, *loc. cit.*) but seems to offer no explanation of our results.

*Formation of the Silanol Anion.*—Aryldimethylsilanes are more reactive than trialkylsilanes in alkaline hydrolysis, and for rate studies lower concentrations of alkali have to be used, so that the organosilane is present in large excess. Under these conditions the first-order plot based on the evolved hydrogen shows a continuous curvature in the direction of falling rate. That this is due to formation of the aryldimethylsilanol (which removes hydroxide or ethoxide ion by formation of the silanol anion, *e.g.*,  $\text{Me}_2\text{ArSiOH} + \text{OH}^- \rightleftharpoons \text{Me}_2\text{ArSiO}^- + \text{H}_2\text{O}$ ) was shown by adding the appropriate silanol; this caused a marked fall in the initial rate and led to a first-order plot closer to a straight line. The magnitude of the effect is shown in Table 3, approximate initial first-order rate constants being listed.

TABLE 3.

Ar	Ph		<i>p</i> -Me·C <sub>6</sub> H <sub>4</sub>	
[KOH] (M) .....	0·0153	0·0153	0·0186	0·0186
[ArMe <sub>2</sub> SiH] (M) .....	0·051	0·051	0·082	0·061
[ArMe <sub>2</sub> SiOH] (M) .....	—	0·058	—	0·056
<i>k</i> <sub>1</sub> (min. <sup>-1</sup> ) .....	0·097	0·043	0·063	0·040

The first-order plots are curved even for trialkylsilanes when these are present initially in few-fold excess over the alkali (*e.g.*, in the reaction of 0·24M-triethylsilane with 0·07M-sodium hydroxide).

*Reactivities of Triorganosilanes.*—The rates of solvolysis of several trialkylsilanes in 94·5 vol.-% ethanol-water containing 1·120M-sodium hydroxide are shown in Table 4, along with the constants of the Arrhenius equation,  $k_1 = A \exp(-E/RT)$ .

TABLE 4.

R	Et	Pr <sup>n</sup>	Bu <sup>n</sup>	Bu <sup>t</sup>	Pr <sup>t</sup>
<i>k</i> <sub>1</sub> (min. <sup>-1</sup> ) at 34·9° .....	0·0633	0·0253	0·0174	0·00261	0·00139
<i>k</i> <sub>1</sub> (min. <sup>-1</sup> ) at 23·3° .....	0·226	0·00855	0·00587	0·00852	0·00431
<i>E</i> (kcal./mole) .....	15·9	16·8	16·8	17·3	18·1
log <i>A</i> * .....	10·1	10·3	10·2	9·7	10·0
Relative rates (34·9°) .....	100	40	27	4·1	2·2

\* Calc. for time in min.

The order of decreasing reactivity of the trialkylsilanes is that of increasing electron release in the radical R, which is known to lead to a fall in rate (see below), but probably steric hindrance is mainly responsible for the sequence observed. It is surprising that the reactivities of *triisobutyl*- and *triisopropyl*-silane are so close since distinctly greater steric hindrance would be expected for nucleophilic attack on the latter compound.

While accurate comparison is impossible, dimethylphenylsilane appears to be roughly 50 times as reactive as triethylsilane, and thus (using Price's figures, *loc. cit.*) about 14 times as reactive as dimethyl-*n*-propylsilane. Dimethyl-*p*-tolyl- is less reactive than dimethylphenylsilane, so that electron supply towards silicon slows the solvolysis, as found for triarylsilanes in moist piperidine (Gilman and Dunn, *loc. cit.*).

We thank Imperial Chemical Industries Ltd., Nobel Division, for a maintenance grant to one of us (J. E. B.).

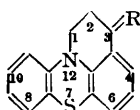
### Reactions with Girard Reagents.

By ALEXANDER MACKIE and ANAND L. MISRA.

[Reprint Order No. 6495.]

MACKIE and MISRA (*J.*, 1955, 1281) reported that reaction of 2 : 3-dihydro-3-oxo-1*H*-pyrido[3 : 2 : 1-*kl*]phenothiazine (*Ia*) with Girard reagent "P" (carbohydrazidomethylpyridinium chloride) in presence of absolute ethanol-acetic acid gave two products. One was the expected pyridinium acetylhydrazone-derivative (*Ib*), soluble in water, methanol, and ethanol, insoluble in acetone and non-hydroxylic solvents, and hydrolysed by *N*-hydrochloric acid to the original ketone (*Ia*). The other product (A), was obtained as orange-yellow plates, m. p. 299—300° (decomp.); it was insoluble in water, methanol, ethanol, and acetone, sparingly soluble in chloroform and benzene, very soluble in dioxan, chlorobenzene, and pyridine, and contained no halogen. Although unchanged by boiling concentrated hydrochloric acid or concentrated aqueous potassium hydroxide, it was hydrolysed to the ketone (*Ia*) by refluxing in dioxan with concentrated hydrochloric acid.

It is suggested that the compound has the structure (II) (Found : C, 71.2; H, 4.3; S, 12.2. C<sub>30</sub>H<sub>22</sub>N<sub>4</sub>S<sub>2</sub> requires C, 71.7; H, 4.4; S, 12.7%), and is probably formed by partial hydrolysis

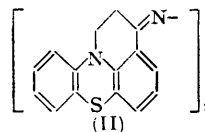


(*Ia*), R = :O

(*Ib*), R = :N·NH·CO·CH<sub>2</sub>·N<sup>+</sup>·C<sub>5</sub>H<sub>5</sub>]Cl<sup>-</sup>

(*Ic*), R = :N·NH·CO·CH<sub>2</sub>·N<sup>+</sup>·Me<sub>3</sub>]Cl<sup>-</sup>

(*Id*), R = :N·NH·COMe



of some of (*Ib*) in ethanol-acetic acid to give the substituted hydrazine, which in turn reacts with unchanged ketone (*Ia*) to give compound (A). This was substantiated by causing equimolecular quantities of (*Ia*) to react with (*Ib*) under similar conditions, whereupon crystals separated from the reaction mixture in small yield, obtained as orange-yellow plates from chlorobenzene, m. p. 295—297° (decomp.) (Found : C, 71.5; H, 4.5%). The structure was further confirmed by the formation of the same product, m. p. 295—297° (decomp.) (Found : C, 70.9; H, 4.3%), by condensation of the ketone (*Ia*) in absolute ethanol-acetic acid with hydrazine sulphate in presence of sodium acetate. The reaction of (*Ia*) with acetohydrazide (Curtius and Hofman, *J. prakt. Chem.*, 1896, 53, 524) under the same conditions as the reaction of (*Ia*) with Girard reagent "P" afforded only the 3-acetohydrazono-2 : 3-dihydro-derivative (*Id*), yellow needles from chlorobenzene, m. p. 258—259° (Found : C, 65.8; H, 4.5. C<sub>17</sub>H<sub>15</sub>ON<sub>3</sub>S requires C, 66.0; H, 4.9%), which was hydrolysed to the ketone (*Ia*) with warm concentrated hydrochloric acid.

Condensation of the ketone (*Ia*) with Girard reagent "T" (carbohydrazidomethyltrimethylammonium chloride) under the same conditions as with reagent "P" gave two compounds, (i) the normal product (*Ic*), yellow stellate needles (turned orange on keeping) from absolute ethanol, m. p. 200° (decomp.) (m. p. lowered on keeping) (Found : C, 55.1; H, 6.0. C<sub>20</sub>H<sub>23</sub>ON<sub>4</sub>ClS, 2H<sub>2</sub>O requires C, 54.7; H, 6.1%); (ii) the compound (A), orange-yellow plates from chlorobenzene, m. p. 295—297° (decomp.) (Found : C, 71.1; H, 4.3%).

The infrared spectra of compounds (*Ib*) and (A) were determined, but owing to the complexity of these molecules, interpretation of the spectra proved difficult. However, one absorption band, with sharp peak, at 1580 cm.<sup>-1</sup>, in the spectrum of compound (A), but absent from that of compound (*Ib*), was very conspicuous. This corresponds to C=C stretching vibrations, and it is known that a direct linkage of an unsaturated group to the nucleus enhances the intensity of this band to such a degree that it becomes more pronounced in the spectrum, thus enabling the detection of conjugation with the rings. Compound (*Ib*) has NH (3450 cm.<sup>-1</sup>) and CO·NH (1668 cm.<sup>-1</sup>) absorption bands, both absent in the spectrum of compound (A). The proposed structure of compound (A) is in agreement with these observations.

We thank the Council of Scientific and Industrial Research (India) for the award (to A. L. M.) of an Assam Oil Co. Scholarship, Professor F. Bell for helpful criticism, and Dr. L. J. Bellamy, Ministry of Supply, Chemical Inspectorate, for the infrared determinations.

*The Nitration of o-Fluorotoluene.*

By H. SUSCHITZKY.

[Reprint Order No. 6509.]

SCHIEMANN (*Ber.*, 1929, **62**, 1794) and Varma *et al.* (*J. Indian Chem. Soc.*, 1944, **21**, 112) reported that, by nitration of *o*-fluorotoluene with fuming nitric acid, they obtained a mixture of 2-fluoro-5-nitro- (72%) and 2-fluoro-6-nitro-toluene (14%), which they separated by fractional distillation.

This reaction was re-investigated, because the nitro-isomers are useful intermediates for the synthesis of certain heterocyclic structures. The oily nitration product was treated with piperidine or with *cyclohexylamine* to facilitate separation and identification of the products. The nature of the piperidino- and *cyclohexylamino*-compounds suggested the presence of only 2-fluoro-5-nitrotoluene (84%). However, a portion of the nitration product was unaffected by this treatment and yielded, on reduction and benzoylation, 4-benzamido- and 6-benzamido-2-fluorotoluene, the structure of the latter being shown by cyclisation of its nitroso-derivative to a fluoroindazole.

In view of these results (2-fluoro-5-nitro-, 84%; 2-fluoro-4-nitro-, 10%; and 2-fluoro-6-nitro-toluene, 6%), Schiemann's 2-fluoro-6-nitrotoluene must be a mixture of 2-fluoro-6-nitrotoluene (1 part) and 2-fluoro-4-nitrotoluene (*ca.* 2 parts). The yield (20%) in the preparation of 4-fluoroindole-2-carboxylic acid (Allen, Brunton, and Suschitzky, *J.*, 1955, 1283) is therefore raised to 34%.

*Experimental.*—*5-Nitro-2-piperidinotoluene.* The oily mixture of nitro-compounds (29 g.) obtained by nitration of *o*-fluorotoluene (Schiemann, *loc. cit.*) was heated on a water-bath with piperidine (50 c.c.) for 10 hr. and the reaction mixture was then added to concentrated hydrochloric acid (200 c.c.) cooled by a freezing mixture. An oily layer separated which was repeatedly extracted with chloroform. The acidic layer on dilution with water afforded yellow needles of *5-nitro-2-piperidinotoluene*, m. p. 48° (from benzene) (33.5 g., corresponding to 84% of 2-fluoro-5-nitrotoluene) (Found: C, 65.5; H, 7.3; N, 12.4.  $C_{12}H_{16}O_2N_2$  requires C, 65.5; H, 7.3; N, 12.7%).

*2-cyclohexylamino-5-nitrotoluene.* Warming of the nitration product (34 g.) with *cyclohexylamine* (65 g.) on a water-bath (12 hr.) followed by treatment with concentrated hydrochloric acid (180 c.c.) and removal of an oily layer as described above, yielded *2-cyclohexylamino-5-nitrotoluene* as yellow needles, m. p. 93° (ethanol) (44.4 g., corresponding to 82% of 2-fluoro-5-nitrotoluene) (Found: C, 66.4; H, 7.6; N, 11.9.  $C_{13}H_{18}O_2N_2$  requires C, 66.6; H, 7.7; N, 11.9%).

*6-Benzamido-2-fluorotoluene.* A portion of the oil (5 g.) obtained from both the above preparations was reduced with stannous chloride (30 g.) dissolved in a mixture of concentrated hydrochloric acid (85 g.) and ethanol (20 c.c.). Benzoylation of the purified reduction product (7.1 g.) (steam distillation) gave a white solid which was fractionately crystallised from a minimum of boiling ethanol. The insoluble portion could be cyclised to a fluoro-indazole (see below) and was, therefore, *6-benzamido-2-fluorotoluene* (2.6 g.), m. p. 158—159° (needles from ethanol) (Found: C, 73.8; H, 5.3; N, 6.3.  $C_{14}H_{12}ONF$  requires C, 73.8; H, 5.1; N, 6.0%).

*4-Benzamido-2-fluorotoluene.* From the mother-liquors of the above fractionation *4-benzamido-2-fluorotoluene* separated as white plates (4.3 g.), m. p. 124—128° (m. p. 127—128° after chromatography from benzene on alumina). The product did not depress the m. p. of a sample prepared from authentic 4-amino-2-fluorotoluene (Schmelkes and Rubin, *J.*, *Amer. Chem. Soc.*, 1944, **66**, 1631) (Found: C, 73.6; H, 5.0; N, 5.9.  $C_{14}H_{12}ONF$  requires C, 73.8; H, 5.1; N, 6.0%).

*4-Fluoroindazole.* *6-Benzamido-2-fluorotoluene* (2 g.) was nitrosated (4.5 hr.) in a mixture of glacial acetic acid (12 c.c.) and acetic anhydride (10 c.c.). When the product, obtained by pouring the reaction mixture on to crushed ice, was crystallised from cold acetic anhydride the *N-nitroso-compound* (2 g.) separated, m. p. 65° (decomp.) (Found: N, 11.2.  $C_{14}H_{11}O_2N_2F$  requires N, 10.7%). A solution of this compound (2 g.) in benzene (20 c.c.; sodium-dried) was kept at room temperature for two days; the solid, obtained by extracting the benzene

layer with concentrated hydrochloric acid followed by basification with ammonia solution, was steam-distilled and yielded 4-fluoroinadazole as white needles, m. p. 130—131° (ethanol) (Found : C, 61.7; H, 3.3; N, 20.3.  $C_7H_5N_2F$  requires C, 61.8; H, 3.7; N, 20.6%).

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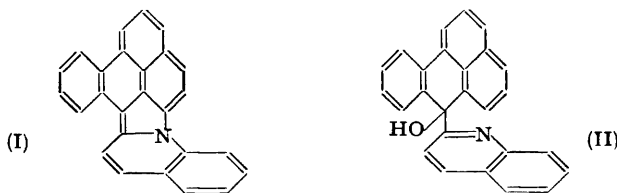
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### *Decomposition of Quinaldic and mesoBenzanthrone-3-carboxylic Acids in the Presence of mesoBenzanthrone.*

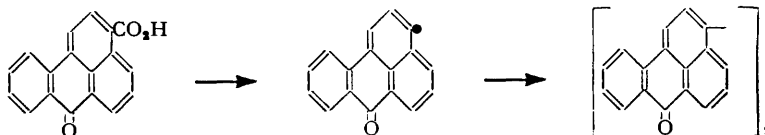
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THE thermal decomposition of quinaldic acid affords the 2-quinolyl anion and this reacts with quinoline to form 2:2'-diquinolyl (Brown and Hammick, *J.*, 1949, 173). It was of interest to investigate the same decomposition in the presence of *meso*benzanthrone which is known to undergo substitution by anions *ortho* and *para* to the carbonyl group (Bradley, *J.*, 1948, 1175). The reaction did not take the expected course but there resulted a crystalline product,  $C_{26}H_{15}N$ , which appeared to be a pyrrocoline derivative (I). It is possible that the first product of the reaction is 2-(7-hydroxy-7-benzanthryl)quinoline (II) which then undergoes cyclisation with loss of water. The expected products, 4- or 6-2'-quinolyl*meso*benzanthrone, were not encountered.



*meso*Benzanthrone-3-carboxylic acid is readily decarboxylated when heated in quinoline with copper powder (Backhouse and Bradley, *J.*, 1955, 849), but the kinetics of the reaction have not been investigated. When the acid is decomposed in the presence of *meso*benzanthrone, di-3-*meso*benzanthranyl is formed. This product might result by (a) the formation of 3-*meso*benzanthranyl radicals which then unite or (b) the formation of 3-*meso*benzanthranyl anions which then attack free *meso*benzanthrone. Direct substitution by anions at the 3-position of *meso*benzanthrone, though possible in theory, has not been previously observed in practice, and for this reason a radical mechanism appears to be the more probable.



**Experimental.**—*Quinaldic acid and meso*benzanthrone. A mixture of quinaldic acid (5 g.) and *meso*benzanthrone (25 g.) was heated for 2 hr. at 180°. The product was dissolved in hot benzene (400 c.c.); a residue (0.055 g.) remained. On being cooled the brown solution gave *meso*benzanthrone (17 g.), and an additional amount (7.3 g.) of less pure material (*A*) separated when the mother-liquor was concentrated to 50 c.c. The mother liquor from the concentrated solution was then extracted with hydrochloric acid. After being made alkaline and steam-distilled the acid solution afforded quinoline (2.2 c.c.) and non-volatile, brown needles (0.05 g.) of 2:2'-diquinolyl, m. p. 183—190° (m. p.s below 300° are corrected) (picrate, m. p. 213—213.5°). Brown and Hammick record m. p. 192.5—193.5° and m. p. 211—212° for the base and picrate, respectively. The residue (0.6 g.) which remained on evaporation of the acid-washed



benzene solution was chromatographed from benzene on alumina. Two bands resulted, a brown band due to *mesobenzanthrone* and a more mobile, yellow band. Elution of the latter with benzene afforded a solid (0.15 g.) which crystallised from ethanol in yellow needles, m. p. 228—229° [Found: C, 90.5, 90.3; H, 4.4, 4.5; N, 4.0, 4.05%; *M* (Rast),  $346 \pm 30$ .  $C_{26}H_{15}N$  requires C, 91.5; H, 4.4; N, 4.1%; *M*, 341]. More (0.41 g.) of the same *product* was obtained by similar purification of (*A*). It gave a yellow solution (yellow-green fluorescence) in pyridine, unchanged on the further addition of methanolic potassium hydroxide, alone or with sodium dithionite. It was unaffected when heated with potassium hydroxide for 10 min. at 250°. It did not react with methyl iodide, methyl toluene-*p*-sulphonate, or acetic anhydride in benzene. It was insoluble in hydrochloric acid, but dissolved in concentrated sulphuric acid to give a reddish-violet solution which became bluer when heated or kept. Light absorption of a 0.002% solution in alcohol ( $10^{-4} \epsilon$  values in parentheses):  $\lambda_{\max}$ . 211 (4.04), 215 (4.17), 218 (3.43), 220 (3.60), 253 (3.43), 271 (1.88), 290 (3.12), 292 (3.14), 334 (0.88), 351 (0.89), 368 (0.87), 420 (1.95), 440 (2.49), and 468  $m\mu$  (1.57);  $\lambda_{\min}$ . 212 (3.96) 216 (3.35), 219 (3.38), 236 (2.04), 270 (1.87), 275 (1.80), 291 (3.10), 327 (0.84), 342 (0.75), 360 (0.60), 380 (0.59), 429 (1.74), and 456  $m\mu$  (1.12).

*mesoBenzanthrone-3-carboxylic acid and mesobenzanthrone*. Ethyl *mesobenzanthrone-3-carboxylate* [5 g.; m. p. 154° (Found: C, 80.0; H, 4.65. Calc. for  $C_{20}H_{14}O_3$ : C, 79.5; H, 4.6%); Backhouse and Bradley, *loc. cit.*] was refluxed for 3 hr. with 5% aqueous sodium hydroxide (50 c.c.) and alcohol (5 c.c.). Acidification of the resulting solution and crystallisation of the precipitate from nitrobenzene afforded *mesobenzanthrone-3-carboxylic acid* (4.5 g.; m. p. 347—348°) (Found: C, 78.4; H, 3.6. Calc. for  $C_{18}H_{10}O_3$ : C, 78.8; H, 3.6%).

*mesoBenzanthrone-3-carboxylic acid* (3 g.) and *mesobenzanthrone* (15 g.; purified by chromatography on alumina) were heated for 5 hr. at 290—320°. The cooled product was extracted with hot chlorobenzene (300 c.c.), and the extract filtered from a residue (0.18 g.). On being cooled the solution afforded *mesobenzanthrone* (11.22 g.), and more (4.62 g.) separated when the mother-liquor was concentrated to 50 c.c. The remaining solution was chromatographed on alumina. Two bands were formed; one consisted of *mesobenzanthrone* (1.06 g.), the other was orange and less mobile. Elution of the second band with hot chlorobenzene gave a solid (0.09 g.), and this after repeated crystallisation from chlorobenzene afforded yellow prisms, m. p. 421—422° (Found: C, 87.7; H, 4.0. Calc. for  $C_{34}H_{18}O_2$ : C, 89.1; H, 3.9%) not depressed on admixture with authentic 3:3'-*dimesobenzanthronyl* [yellow prisms; m. p. 420—421° (Found: C, 88.3, 88.0; H, 4.0, 3.8. Calc. for  $C_{34}H_{18}O_2$ : C, 89.1; H, 3.9%); Lüttringhaus and Neresheimer (*Annalen*, 1929, 473, 259) record m. p. 412—414°] prepared from 3-bromo*mesobenzanthrone*. The identity of the two samples of 3:3'-*dimesobenzanthronyl* was confirmed by a comparison of the light absorption of their 0.001% solutions in concentrated sulphuric acid. Values of  $10^{-4} \epsilon$  are given in parentheses, those for the product from 3-bromo*mesobenzanthrone* being given first:  $\lambda_{\max}$ . 206 (7.40, 6.95), 247 (6.56, 6.67), 375 (3.73, 3.67), 430 (1.78, 1.79), 543—544 (3.22, 3.44)  $m\mu$ .  $\lambda_{\min}$ . 228 (5.01, 4.95), 279 (0.89, 0.82), 401—402 (1.25, 1.19), 454—455 (0.76, 0.76)  $m\mu$ .

On being heated alone for 5 hr. at 290—320°, *mesobenzanthrone* remained almost unchanged and no 3:3'-*dimesobenzanthronyl* was formed.