NOTES.

1146. *The Catalytic Action of Anionic Catalysts. Part VII.*[1] *The Reaction of Fluorene with Butyl-lithium.*

By ALWYN G. EVANS and N. H. REES.

WE have previously studied the addition of butyl-lithium to 1,1-diphenylethylene in benzene, and obtained values of 0·18 and unity for the orders in butyl-lithium and olefin, respectively.[2] To find whether the low order in butyl-lithium was independent of the type of reaction involved, we have now studied the reaction in benzene of butyl-lithium with fluorene, to give butane and fluorenyl-lithium. The order in butyl-lithium is again found to be 0·18, and it is unity for fluorene.

Experimental.—Benzene was purified as described earlier.[3] Butyl-lithium in benzene was prepared by the method of Ziegler and Colonius,[4] as modified by Evans and Owen,[5] and it was standardised by estimating the lithium hydroxide formed after hydrolysis. Experience has shown that it was not necessary to use the double-titration method of Gilman and Haubein.[6] Fluorene (B.D.H. pure grade) was purified by the method of Glusker, Stiles, and Yoncoski; [7]

[1] Part VI, Evans and Evans, preceding paper.
[2] Evans and George, *J.*, 1961, 4653.
[3] Evans and Price, *J.*, 1959, 2982.
[4] Ziegler and Colonius, *Annalen*, 1930, **479**, 135.
[5] Evans and Owen, *J.*, 1961, 1933.
[6] Gilman and Haubein, *J. Amer. Chem. Soc.*, 1944, **66**, 1515.
[7] Glusker, Stiles, and Yoncoski, *J. Polymer Sci.*, 1961, **49**, 297.

the recrystallised fluorene was very thoroughly dried in a vacuum-desiccator for several days before use. A known quantity of fluorene was introduced into the vacuum system, degassed, and dissolved in a known volume of benzene. The spectrum shows peaks at 274, 290, and 301 mμ, with an extinction coefficient of $\varepsilon_{274} = 1{\cdot}2 \times 10^4$.

First-order dependence of reaction on [Fluorene] when [Butyl-lithium] is in excess.

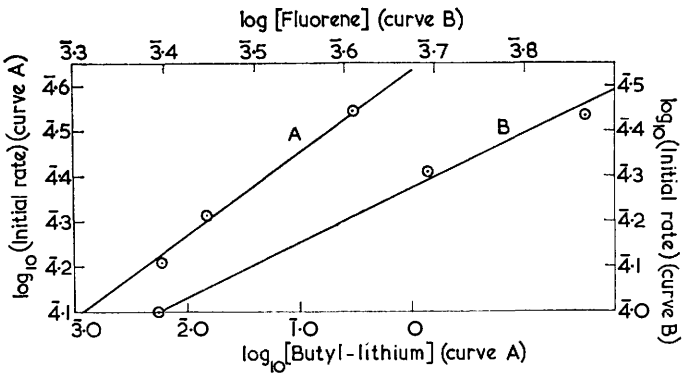
[Fluorene] = $2{\cdot}5 \times 10^{-3}$ mole l.$^{-1}$. [Butyl-lithium] = $1{\cdot}5 \times 10^{-2}$ mole l.$^{-1}$.

Time (hr.)	Reaction (%)	Optical density * (OD) (357 mμ)	$\log\{(OD)_\infty/[(OD)_\infty - (OD)_t]\}$	First-order rate constant (hr.$^{-1}$)
1	0·31	0·45	0·0135	0·031
10	21·4	3·15	0·1047	0·024
40	64·6	9·5	0·4513	0·025
60	80·9	11·9	0·7201	0·028
80	87·8	12·9	0·9120	0·026
100	92·2	13·55	1·1066	0·025
	100·0	14·7		

* Measured in 2 mm. cell, but converted to values which would obtain in a 10 mm. cell.

Benzene solutions of butyl-lithium and of fluorene, of known concentrations, were mixed in the way described earlier [2] and sealed in silica optical cells, and the change in optical density with time was measured on a Unicam S.P. 500 spectrophotometer in a thermostat-controlled cell compartment. The spectrum of fluorenyl-lithium shows peaks at ~274, 357, and 454 mμ. The reaction was followed by measuring (*a*) the rate of increase of the absorption at 357 mμ, and (*b*) the rate of increase of peak 454 mμ. It is not possible to follow the increase in optical density of the main peak (274 mμ) since fluorene and butyl-lithium absorb strongly in this region.

Results.—When benzene solutions of fluorene and butyl-lithium were mixed, a yellow colour appeared which slowly intensified to deep orange, and crystals of fluorenyl-lithium separated from concentrated systems.



Dependence of initial rate of appearance of 357 mμ peak on reagent concentrations at 30°.

(A) [Fluorene] = $4{\cdot}9 \times 10^{-3}$ mole l.$^{-1}$. (B) [Butyl-lithium] = $1{\cdot}5 \times 10^{-2}$ mole l.$^{-1}$.

In experiments where [BuLi] ≫ [Fluorene], the analysis of the optical density–time curve gave a first-order dependence on fluorene concentration for 92% of the reaction (see Table). This shows that in these conditions reaction (2) goes to completion. The extinction coefficients of fluorenyl-lithium found from the optical densities at complete reaction are $\varepsilon_{357} = 5{\cdot}85 \times 10^3$ and $\varepsilon_{454} = 1{\cdot}17 \times 10^3$.

From the initial slopes of the optical density–time curve it was found that the initial rate of reaction depended on [Fluorene]^1 and [Butyl-lithium]$^{0{\cdot}18}$ (see Figure). We interpret these results in terms of the reactions:

$$\tfrac{1}{6}(BuLi)_6 \underset{b}{\overset{a}{\rightleftharpoons}} BuLi \qquad \text{(I)}$$

Assuming that, in benzene solution, butyl-lithium exists almost entirely as the hexamer, we then have the rate of production of fluorenyl-lithium:

$$r = k(BuLi)_6]^{0\cdot18}\,[\text{Fluorene}]$$

and

$$k = k_2k_{1a}/k_{1b}.$$

The value of k at 30° is $1\cdot4 \times 10^{-5}$ $l.^{0\cdot18}$ $mole^{-0\cdot18}$ $sec.^{-1}$, which is similar to that for the addition of butyl-lithium to styrene [8] ($2\cdot3 \times 10^{-5}$ $l.^{0\cdot167}$ $mole^{-0\cdot167}$ $sec.^{-1}$) and to 1,1-diphenylethylene ($4\cdot17 \times 10^{-5}$ $l.^{0\cdot18}$ $mole^{-0\cdot18}$ $sec.^{-1}$).[2]

Thus, for this substitution reaction in benzene, the low order of 1/6 is found for butyl-lithium, as in the case of its addition to a carbon–carbon double bond.

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[*Received, May 20th,* 1963.]

[8] Bywater and Worsfold, *Canad. J. Chem.*, 1960, **38**, 1891.

1147. *Hydrogen Bonding in Complexes of Dimethylglyoxime with Cobalt*(III).

By R. D. GILLARD and G. WILKINSON.

IN several bisdimethylglyoximatocobalt(III) compounds an infrared (i.r.) absorption band occurring around 1750 $cm.^{-1}$ has been attributed to hydrogen bonding, and it has been said that " the presence of the hydrogen bonding is a proof of the *trans*-character of the molecule." [1] Certain discrepancies exist in the literature, however. In some cases, even though the characteristic hydrogen-bonded frequency was observed, *cis*-stereochemistry has been assigned, and in other cases the *cis*-configuration has been deduced for the bisdioximatocobalt(III) moiety on the basis of dubious resolutions into optical isomers. The present work extends the available spectroscopic data, and affords good evidence for the *trans*-configuration in all such bisdioximatocobalt(III) complexes.

The available i.r. data for complexes of cobalt(III), including deuterated species, are given in Table 1. The ν_{O-H} stretching frequency occurs in dimethylglyoxime itself at 3170 $cm.^{-1}$. The symbol DH_2 represents dimethylglyoxime, and DH the anion. Spectra were taken for Nujol mulls, unless otherwise indicated.

The compound usually formulated as " $H[Co(DH)_2Cl_2]$," which has been called [2] " hydrogen dichlorobis(dimethylglyoximato)cobaltate(III)," shows absorptions due to free OH stretching and deformation, as does " $H[Co(DH)_2(NO_2)_2]$." Since these compounds contain no water of crystallisation, and therefore no hydroxonium ions, we prefer the structure shown in (I), in the solid state at least. The *trans*-configuration follows from the hydrogen-bonded OH frequency, in both the parent compounds and salts derived from them by removal of a proton. Since these compounds are strong monobasic acids and the electronic spectra of the sodium salts are identical with those of the parent acids,

[1] Nakahara, Fujita, and Tsuchida, *Bull. Chem. Soc. Japan*, 1956, **29**, 296.
[2] See, *e.g.*, Ablov and Filippov, *Russ. J. Inorg. Chem.*, 1962, **7**, 525; Cotton in " Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience, New York, 1960, p. 390.

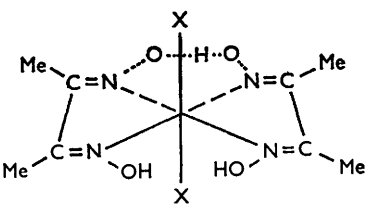
TABLE 1.

Infrared spectra of complexes of cobalt(III) with dimethylglyoxime.

Compound	ν_{O-H} str. ($cm.^{-1}$)	ν_{O-D} str.[a] ($cm.^{-1}$)	O–H · · · O ($cm.^{-1}$)	O–D · · · O ($cm.^{-1}$)	ν_{OH} def. ($cm.^{-1}$)	ν_{NO} [b] ($cm.^{-1}$)	Ref.
$[Co(DH)_2(NO_2)(H_2O)]$	3546 [c]		1770				*, 1
$[Co(DH)_2(NO_2)(D_2O)]$		2530	1783				†
$[Co(DD)_2(NO_2)(D_2O)]$		2530		*ca.* 1200			†
" $H[Co(DH)_2(NO_2)_2]$ " [d] ...	3550		2350		1630		†
			1725				*
$Na[Co(DH)_2(NO_2)_2],H_2O$ ...	3540 [c]		1740		1631 [c]		†
			1740				*, 1
$NH_4[Co(DH)_2(NO_2)_2]$	[e]		1701				†
$[Co(DH)_2(NH_3)Cl]$	3550, 3400		1751				†
	3221, [e] 3107 [e]						
$[Co(DH)_2(py)Cl]$ [f]			1710			1561	†
			1730 [g]			—	†
			1728 [h]			1560	†
$[Co(DH)_2(NH_3)_2]Cl,5H_2O$ [i]			1695				*
$[Co(DH)_2(NH_3)_2](NO_3)$			1703				†
" $H[Co(DH)_2Cl_2]$ "	3200 *j*		1725				*, 1
" $D[Co(DD)_2Cl_2]$ "		2300					†
$[Co(DH)_2(NH_3)(NO_2)]$			1766				1
$[Co(DH)_3]$	3000						†

* Nakahara, *Bull. Chem. Soc. Japan*, 1955, **28**, 473. [1] Nakahara, Fujita, and Tsuchida, *Bull. Chem. Soc. Japan*, 1956, **29**, 296. † This work. [a] In the deuterated compounds, the band assigned to O–H · · · O disappears, but in no case was the O–D · · · O frequency located exactly because of the large number of absorptions in the 1200—1300 $cm.^{-1}$ region. [b] For many of the compounds listed, where vibrations of co-ordinated NH_3 or NO_2 obscure the NO vibration in the DH ligand, no assignment is given in this column. [c] Absorption due to co-ordinated or crystal water. [d] The formulation of compounds in quotation marks is discussed in the text. [e] Absorption due to N–H stretching modes. [f] py = pyridine. [g] In dichloromethane. [h] In chloroform; the compound was recovered unchanged from both these solutions. [i] This compound is discussed in the text. [j] Value read from ref. 2.

the species present in aqueous solution are presumably the symmetrical anions containing two similar hydrogen bonds. The two OH groups in (I) (where X = Cl) can be converted



(I)

into OMe groups by treatment with dimethyl sulphate in the cold; similar compounds of cobalt(III) containing dioxime *O*-monomethyl ethers as ligands were previously described by Brady and Muers.[3] The corresponding reaction with the dinitro-compound does not occur in the cold.

The structure of bisamminebisdimethylglyoximatocobalt(III) nitrate is known [4] from *X*-ray crystallography; the OHO bond length is 2·65 Å, and we have observed the typical hydrogen-bonded frequency at 1703 $cm.^{-1}$. However, the spectrum of the corresponding chloride pentahydrate has an unusual number of absorptions between 1600 and 3000 $cm.^{-1}$, as has the analogous compound of rhodium(III). The band at 3100 $cm.^{-1}$ is probably due to the water of crystallisation, but there is a peak at 2600 $cm.^{-1}$ and there are broad bands at 2150, 1950, 1750, and 1690 $cm.^{-1}$. In view of the large number of possible hydrogen bonds in this compound in the solid state, the assignment [1] of the band at 1690 $cm.^{-1}$ as

[3] Brady and Muers, *J.*, 1930, 1599.
[4] Viswanathan and Kunchur, *Acta Cryst.*, 1961, **14**, 675.

the characteristic hydrogen-bonded frequency is rather arbitrary. The nitrate and the chloride have extremely similar electronic spectra, so that the *trans*-configuration for the chloride is assured. The alleged resolution by means of optically-active quartz [5] is undoubtedly spurious, as is the very odd resolution said to be obtained [6] by making solutions of opposite quarters of the same crystal, when opposite rotations were allegedly observed.

The conclusions based on i.r. spectra are now reinforced by the observation that the intramolecular hydrogen bonds in these complexes give rise to a broad line in the nuclear magnetic resonance (n.m.r.) spectrum at about 1000 c./sec. on the low-field side of tetramethylsilane (TMS). The position of this line is independent of concentration, confirming the assignment as due to hydrogen in an *intra*molecular bond. The compounds showing this absorption are summarised in Table 2, together with the result for potassium hydrogen phthalate, for comparison.

TABLE 2.

Nuclear magnetic resonance evidence for intramolecular hydrogen bonds.

Compound	Solvent	O–H · · · O	τ
$[Co(DH)_2(NH_3)Cl]$	DMSO [a]	1043 [b]	−8·47
$[Co(DH)_2(py)Cl]$	DMSO [a]	1032	−8·28
	CH_2Cl_2 [c]	1017	−8·01
	DMF [d]	1000 [e]	—
$[Co(DH)_2(NO_2)(H_2O)]$	DMF [d]	1042	−8·45
K H phthalate	DMSO [a]	—	−10 [f]

[a] Dimethyl sulphoxide. [b] In c./sec. below TMS. [c] The compound was recovered unchanged. [d] Dimethylformamide. [e] This solution was too dilute for accurate measurement. [f] Forsen (*J. Chem. Phys.*, 1959, **31**, 852) measured this value relative to external water, together with that of the corresponding maleate.

The resolution of chloroamminebisdimethylglyoximatocobalt(III) by differential absorption on optically-active quartz has been claimed [5,7] although its crystals do not show enantiomorphous faces; the compound was said [7] to be the *cis*-isomer, on the basis of the very slight optical activity of the fractions obtained. However, the characteristic O–H · · · O frequency in the i.r. region occurs [1] at 1750 cm.$^{-1}$; we have confirmed this, and we have also observed the n.m.r. absorption due to strong intramolecular hydrogen bonding. The compound is therefore *trans*, and the claimed resolution is spurious. The formula of the compound has been confirmed by analysis, by its diamagnetism, and by its non-conductance in water. The remaining possibility is that the compound exists as the *trans*-isomer in the organic solvents used for our n.m.r. work, but as the *cis*-isomer in the aqueous solution used for the work with active quartz. However, the electronic spectra in water and dimethyl sulphoxide are identical; the compound is therefore *trans*-chloroamminebisdimethylglyoximatocobalt(III).

The preparation of "*cis*-bispyridinebisdimethylglyoximatocobalt(III) iodochloride" has been claimed.[8] However, this has now been shown to exhibit the characteristic OHO frequency at 1711 cm.$^{-1}$, and we reformulate it as the *trans*-compound.

Experimental.—Analyses were by the Microanalytical Laboratory at this College.

Preparation of compounds. The complexes were prepared by the methods given in the literature; references are given in Table 3 together with analytical data; conductivities are given as an additional check on purity.

Trisdimethylglyoximatocobalt(III). The method given in the literature [9] was followed. The complex, which decomposes in boiling ethanolic solution, was obtained as golden-yellow needles (Found: C, 35·7; H, 5·1. Calc. for $C_{12}H_{21}CoN_6O_6$: C, 35·65; H, 5·24%). It was found that if,

[5] Schweitzer and Talbott, *J. Tennessee Acad. Sci.*, 1950, **25**, 143.
[6] Saito, Nakahara, and Kuroya, *J. Inst. Polytechnics, Osaka City Univ.*, 1950, **1**, No. 2, ser. C, p. 15.
[7] Tsuchida, Kobayashi, and Nakamura, *Bull. Chem. Soc. Japan*, 1936, **11**, 38.
[8] Spacu and Popea, *Rev. Chim. (Acad. R.P.R.)*, 1956, **1**, 127.
[9] Nakahara and Tsuchida, *J. Amer. Chem. Soc.*, 1954, **76**, 3103.

TABLE 3.

Bisdioximato-complexes of cobalt(III).

Compound	Ref.	Calc. C	Calc. H	Calc. N	Found C	Found H	Found N	Λ (10^{-3}M) [a] (mhos)
$[Co(DH)_2(NO_2)(H_2O)]$	*	27·20	4·51	19·83	27·1	4·7	19·6	4·2
$[Co(DH)_2(py)Cl]$	†	38·67	4·74	17·35	38·4	4·7	17·1	0 [b] / 6·9
$[Co(DH)_2(NH_3)Cl]$ [c]	‡	28·13	5·02	20·50	28·3	5·0	20·8	4·9
$[Co(DH)(DH_2)(NO_2)_2]$	*	25·14	3·96	21·99	24·9	4·0	22·3	—
$Na[Co(DH)_2(NO_2)_2],H_2O$ [d]	*	22·76	3·82	—	22·9	3·7	—	64·7
$NH_4[Co(DH)_2(NO_2)_2]$	*	24·03	4·54	—	24·3	4·4	—	87·4
$[Co(DH)_2(NH_3)_2]Cl,5H_2O$	‡	21·41	6·74	[f]	21·1	6·4	[f]	134·4 [e]

* Tchugaev, *Ber.*, 1908, **41**, 2226. † *Idem, ibid.*, 1907, **40**, 3498. ‡ *Idem, ibid.*, 1906, **39**, 2692. [a] In water. [b] In nitrobenzene. [c] Unaffected by keeping at 100° for 14 days. [d] Keeping at 100° for 24 hr. did not remove the water. [e] 10^{-4}M-solution. [f] Found: Cl, 7·8%. Calc.: 7·9%.

in the course of recrystallisation from dilute acetic acid, the solution was boiled for more than a few seconds a dark brown material was obtained; this is quite stable in air and is most likely polymeric. It dissolved completely only in glacial acetic and formic acids. The i.r. spectrum showed the presence of acetate groups and dimethylglyoximato-radicals; the material was diamagnetic. Analytical data suggest the presence of only two dimethylglyoximate radicals per cobalt atom. On treatment with concentrated hydrochloric acid, the known green compound, *trans*-dichlorodimethylglyoximatodimethylglyoximecobalt(III), was obtained.

Deuteration procedures. Compounds were simply recrystallised from heavy water, except in one case, that of $[Co(DD)_2(NO_2)(D_2O)]$. Dimethylglyoximedinitrodimethylglyoximato-cobalt(III) (0·3 g., $7·9 \times 10^{-4}$ mole) was warmed with an excess of deuterium oxide (5 ml.) at 80° for 15 min.; the resultant brown precipitate showed only a weak band at 3500 $cm.^{-1}$ but a fairly strong band at 1770 $cm.^{-1}$, and was thus mainly $[Co(DH)_2(NO_2)(D_2O)]$. The product was recrystallised twice from heavy water (2 ml.) containing acetic anhydride (0·1 g.). After the first recrystallisation the band at 3546 $cm.^{-1}$, due to free OH, had disappeared and the band at 1770 $cm.^{-1}$, due to the hydrogen-bonded protons, had become very weak. After the second recrystallisation the band at 1770 $cm.^{-1}$ was not observed; the product was thus $[Co(DD)_2(NO_2)(D_2O)]$, and showed a band due to co-ordinated D_2O at 2530 $cm.^{-1}$ and a band due to O–D • • • O at *ca.* 1200 $cm.^{-1}$.

N.m.r. spectra were obtained in 5-mm. o.d. spinning tubes, on a Varian Associates V-4311 spectrometer. $[Co(DH)_2(py)Cl]$ showed lines due to pyridine in two groups, as observed [10] in other complexes of pyridine; in this case, they were at 506, 518, and 534 c./sec. below TMS (τ 1·04, 0·82, and 0·54, respectively) and at 627 and 637 c./sec. (τ −1·11 and −1·13). The methyl protons in the dimethylglyoximate ligands gave a resonance at 177 c./sec. (τ 6·86). $[Co(DH)_2(H_2O)(NO_2)]$ showed a line due to co-ordinated water at 202 c./sec. (τ 6·42), and the methyl protons gave a signal at 137 c./sec. (τ 7·57).

I.r. spectra were obtained by using a Perkin-Elmer Model 21 spectrometer, with sodium chloride or calcium fluoride optics. Conductivities were measured with a Mullard type E 7576 bridge, with a dipping cell.

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[10] Westland and Westland, *Canad. J. Chem.*, 1961, **39**, 324.

1148. *The Acid Hydrolysis of* N-*Acetylimidazole.*

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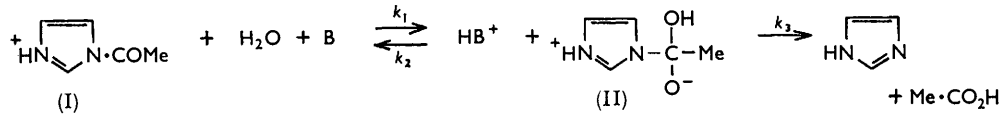
Bunnett has suggested that acid-catalysed reactions should be classified in terms of parameters, w or w^*, which relate reaction rate (at a given acidity) to the activity of water. The values of w or w^* are considered to be diagnostic of mechanism, and for reactions in which $w > 3{\cdot}3$ water is believed to be involved in a kinetically important proton-transfer.[1] For several hydrolyses acid first increases and then decreases rate, and sometimes, as in amide hydrolysis, the rate maximum can be ascribed to complete protonation of the substrate,[2] but this explanation is not always applicable.[3] *N*-Acetylimidazole is sufficiently basic for the hydrolysis of its conjugate acid (I) to be studied in moderately concentrated acid.[4] Hydrolysis of this conjugate acid is retarded by acids, and by most uni-univalent salts; values of w are large and depend on the electrolyte, and reaction rate cannot be correlated with water activity.

In a general discussion of A-2 hydrolyses of esters and amides,[5] Martin has suggested that these reactions are multistage processes, in which nucleophilic addition of a water molecule to the conjugate acid of the substrate may be followed by slow decomposition of an intermediate, and the acid hydrolysis of *N*-acetylimidazole was written as:



(I) (II)

(The base B may be a water molecule.[5])

On the assumption that reaction is a multistage process, and (II) an intermediate, Martin applied the stationary-state approximation to the experimental rate constants, concluded that in moderately concentrated acid $k_2 \simeq k_3$, and predicted that hydrolysis should be accompanied by extensive oxygen-exchange between water and *N*-acetylimidazole.[5] This prediction has been tested for hydrolysis in solutions containing perchloric acid, or mixtures of it and sodium perchlorate. There was very little oxygen-exchange (see Table), although in the experiments in solutions rich in electrolyte k_2/k_3, on Martin's kinetic interpretation,[5] should exceed 1.

Therefore, (i) the intermediate (II) does not exist long enough for its oxygen atoms to become equivalent by proton transfer, which would then have to be slower than changes in a carbon–nitrogen covalency, or (ii) $k_3 \gg k_2$, *i.e.*, the reaction is synchronous or the intermediate (II) always goes forward to products and never reverts to reactants. Explanation (ii) seems the more probable, suggesting that the retarding effects of acids and salts, and the high w values, cannot be explained by a theory which requires the intermediate (II) to revert to reactants. The effects may arise simply because the transition state is stabilised by several water molecules, and electrolytes could destabilise it by competing with it for water molecules.

It seems optimistic to assume that the kinetic forms of all acid-catalysed hydrolyses can be explained fully in terms of Hammett's acidity function and the activity of water,[1] if only because (*a*) protonation of all substrates may not be proportional to h_0, Hammett's acidity function,[6] and (*b*) the activity coefficients of substrate and transition state, and

[1] Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, and accompanying papers.
[2] Edward and Meacock, *J.*, 1957, 2000; Rosenthal and Taylor, *J. Amer. Chem. Soc.*, 1957, **79**, 2684.
[3] Vernon, *Chem. Soc. Special Publ.*, No. 8, 1957, p. 17; Bunton and Hadwick, *J.*, 1958, 3248; 1961, 943; Tillett, *J.*, 1960, 5138.
[4] Marburg and Jencks, *J. Amer. Chem. Soc.*, 1962, **84**, 232.
[5] Martin, *J. Amer. Chem. Soc.*, 1962, **84**, 4130.
[6] Taft, *J. Amer. Chem. Soc.*, 1960, **82**, 2965.

therefore the reaction rate, will depend upon both the nature and the concentration of the electrolyte.[7] The discussions by Bunnett [1] and Martin [5] are valuable because they focus attention on the relation between water activity and reaction rate. However, it seems unnecessary to assume that all acid-catalysed hydrolyses which are retarded by electrolytes are therefore multistage reactions, because reaction rate depends only upon the relative free energies of initial and transition states, and not upon hypothetical pre-equilibria.

Experimental.—Materials. *N*-Acetylimidazole was prepared by acetylating imidazole with isopropenyl acetate.[8] After recrystallisation from isopropenyl acetate it had m. p. (Koffler block) 104° (lit.,[8] 101·5—102·5° in a preheated tube).

Hydrolysis. In preliminary experiments the amide was completely hydrolysed in acidic $H_2{}^{18}O$, and acetic acid was isolated as silver acetate. If the hydrolysis were faster than oxygen exchange the silver acetate should contain more than half the isotopic abundance of the water, but it contained less than half this abundance (see Table). This test is insensitive, and it is

Hydrolysis of *N*-acetylimidazole in aqueous acid at 25°.

Reagent *	Reaction (%) †	Isotopic abundance		
		H_2O	AgOAc	Ac·NHPh
0·15M-$HClO_4$	100	1·31	0·59	—
0·25M-$HClO_4$	,,	1·30	0·60	—
0·1M-$HClO_4$ + 2·8M-$NaClO_4$	,,	1·30	0·57	—
2·9M-$HClO_4$	40	1·13	—	$0·01_5$
3·0M-$HClO_4$	65	0·95	—	$0·00$
0·1M-$HClO_4$ + 2·8M-$NaClO_4$	55	1·33	—	$0·00_3$

* Molarity of acid calc. after neutralisation with amide. † Calc. from results in ref. 4.

suspect because *N*-acetylimidazole is so reactive to water that it may react partially with atmospheric moisture during handling, giving some isotopically normal acetic acid. A more sensitive test involves isolation of the substrate, or a derivative of it, after partial hydrolysis.[9] It is not possible to isolate *N*-acetylimidazole from water, but it will acetylate aniline in water. A large excess of aniline was added to the reaction mixture in acidic $H_2{}^{18}O$, after times sufficient for partial reaction. In most experiments 0·1 g. of amide was added to 20 c.c. of $H_2{}^{18}O$ which contained the acid and salt. The yield of acetanilide was lower than expected from the reaction times and rates,[4] and only 5—10 mg. were isolated after recrystallisation from hot water. Two factors may be responsible for this low yield: (i) some *N*-acetylimidazole reacted during handling; or (ii) aniline did not react sufficiently rapidly with *N*-acetylimidazole to stop hydrolysis, which could even speed up when the acid was partially neutralised by base.[4] If (ii) is important, estimated values of k_3/k_2 will be too small.

The acetanilide (m. p. 112—113°) was heated *in vacuo* with phenylenediamine hydrochloride and guanidine hydrochloride, and the evolved carbon dioxide was analysed mass spectrometrically. The results of both methods are in the Table (isotopic abundances are in atoms % excess above normal). Provided that the oxygen atoms in the intermediate (II) become equivalent, the observed isotopic abundances of the acetanilide give $k_3/k_2 > 50$. This value is approximate because hydrolysis is so rapid that the reaction times are uncertain.

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1149. *Reactions of Fluorosulphur Peroxides.*

By G. PASS.

PEROXYDISULPHURYL DIFLUORIDE reacts with sulphur dioxide and sulphur tetrafluoride to give bisdioxofluorosulphur sulphate, $FSO_2{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}SO_2F$, and tetrafluorosulphur bisfluorosulphate, $FSO_2{\cdot}O{\cdot}SF_4{\cdot}O{\cdot}SO_2F$, respectively.[1,2] In view of the formal similarity between $-SO_2-$ and $-SF_4-$ groups as structural units, an attempt has been made to prepare the corresponding compounds from the peroxides $SF_5{\cdot}O{\cdot}O{\cdot}SF_5$ (analogous to $FSO_2{\cdot}O{\cdot}O{\cdot}SO_2F$) ,$SF_5{\cdot}O{\cdot}SF_4{\cdot}O{\cdot}O{\cdot}SF_5$, and $SF_5{\cdot}O{\cdot}SF_4{\cdot}O{\cdot}O{\cdot}SF_4{\cdot}O{\cdot}SF$. The last two substances can be considered as pentafluorosulphuroxy-derivatives of $SF_5{\cdot}O{\cdot}O{\cdot}SF_5$.

Reaction of bispentafluorosulphur peroxide with sulphur dioxide in the gas phase at 225° gives some bispentafluorosulphur sulphate

$$SF_5{\cdot}O{\cdot}O{\cdot}SF_5 + SO_2 \longrightarrow SF_5{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}SF_5$$

but principally the sulphur dioxide is oxidised to sulphur trioxide, with the reduction of the peroxide to the oxide:

$$SF_5{\cdot}O{\cdot}O{\cdot}SF_5 + SO_2 \longrightarrow SO_3 + SF_5{\cdot}O{\cdot}SF_5$$

The preparation of bispentafluorosulphur sulphate by a similar method has been reported by Merrill and Cady [3] since this work was completed.

Sulphur dioxide reacts with the peroxide, $SF_5{\cdot}O{\cdot}SF_4{\cdot}O{\cdot}OSF_5$ in the liquid phase at 125°, to give the new compound $SF_5{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}SF_4{\cdot}O{\cdot}SF_5$. Less sulphur trioxide was produced than in the corresponding reaction of bispentafluorosulphur peroxide, possibly owing to the lower reaction temperature.

No compound corresponding to $(SF_5{\cdot}O{\cdot}SF_4)_2SO_4$ was formed between sulphur dioxide and the peroxide $(SF_5{\cdot}O{\cdot}SF_4)_2O_2$ at temperatures up to 125°, at which temperature the latter began to decompose appreciably.

Bispentafluorosulphur peroxide oxidised sulphur tetrafluoride to thionyl tetrafluoride under a variety of conditions, but the compound $SF_5{\cdot}O{\cdot}SF_4{\cdot}O{\cdot}SF_5$ was not formed, although an alternative preparation had shown that this does exist.[4] It has also been prepared more recently by a liquid-phase, photochemical reaction between bispentafluorosulphur peroxide and sulphur tetrafluoride.[3]

Since the ease of formation of the compounds $RO{\cdot}SO_2{\cdot}OR$ decreases with increasing molecular weight, the reactions of the other two peroxides with sulphur tetrafluoride were not studied.

Formulation of the products follows from the methods of preparation, elementary analyses, and molecular weights. The infrared spectra confirm the nature of the groups present, with bands at ~1500 and ~1250 cm.$^{-1}$ characteristic of $-SO_2-$.

The methods of preparing bis(pentafluorosulphur) sulphate and the product $SF_5{\cdot}O{\cdot}SF_4{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}SF_5$ indicate that compounds containing $-SO_2-$ groups are more stable than the corresponding compounds containing only $-SF_4-$ groups.

Experimental.—Bispentafluorosulphur peroxide and sulphur tetrafluoride were prepared by known methods.[5,6] Other peroxides were obtained by the reaction of pentafluorosulphur hypofluorite with sulphur tetrafluoride in the presence of oxygen.[4] Sulphur dioxide was purchased (British Drug Houses Ltd.) and used as received.

[1] J. E. Roberts and Cady, *J. Amer. Chem. Soc.*, 1959, **81**, 4166.
[2] Shreeve and Cady, *J. Amer. Chem. Soc.*, 1961, **83**, 4521.
[3] Merrill and Cady, 2nd Internat. Symposium on Fluorine Chemistry, Colorado, July 1962, preprints, p. 428.
[4] Pass and H. L. Roberts, ref. 3, p. 401.
[5] H. L. Roberts, *J.*, 1960, 2774.
[6] Nyman and H. L. Roberts, *J.*, 1962, 3180.

Apparatus and procedure. Three methods were used. (i) The peroxide was carried by a nitrogen stream through a nickel tube (length, ~30″; outside diameter, 1″) kept between 25° and 400° by means of an electrically heated tube furnace. Sulphur dioxide or tetrafluoride was added to the gas stream from weighed cylinders, and the emerging gases were collected in two traps cooled in liquid air. At the end of a run, the volatile products in the traps were collected at room temperature in a 10-l. evacuated globe and analysed by gas chromatography and infrared spectroscopy. Liquid products were refluxed with water and fractionated after drying.

(ii) The peroxide was added to a 55-c.c. " Hastelloy C " autoclave, and sulphur dioxide or sulphur tetrafluoride was condensed in from a weighed cylinder. The autoclave was heated by a copper-block electric furnace. At the end of the reaction the pressure was released at room temperature through two traps cooled in liquid air. This product and the liquid product, decanted from the autoclave in a fume chamber, were treated as in (i).

(iii) A Pyrex bulb (6-l.), fitted with an inner tube of fused quartz containing a Hanovia 509/12 mercury discharge tube, was immersed in a water-bath at 60°. Bispentafluorosulphur peroxide and sulphur dioxide or tetrafluoride were added to measured pressures and the discharge tube was switched on. Pressure changes were recorded by an external mercury manometer, with an isoteniscope between the heated vessel and the manometer. After reaction the gas mixture was condensed in traps cooled in liquid air and examined as described above.

The column used for gas chromatography was packed with " Chromosorb " (Johns Manville Ltd.) on which dibutyl phthalate had been adsorbed.

Infrared spectra were recorded on a Grubb-Parsons G.S. 2A double-beam grating spectrometer.

Reaction of bispentafluorosulphur peroxide with sulphur dioxide. Bispentafluorosulphur peroxide (50 g.) and sulphur dioxide (0·84 l./hr.) were allowed to react at 225° as in method (i). The gaseous products (20 g.) were sulphur hexafluoride, thionyl tetrafluoride, and sulphur dioxide. The liquid products (18 g.) were washed with water to remove sulphur trioxide and then fractionated, giving (1), b. p. 29°, bispentafluorosulphur oxide, (2) b. p. 48°, bispentafluorosulphur peroxide, and (3), b. p. 94°, *bis(pentafluorosulphur) sulphate* (Found: F, 52·8; S, 28·1%; *M*, 346. $F_{10}O_4S_2$ requires F, 54·3; S, 27·4%; *M*, 350), $\nu_{max.}$ 1479s, 1469s, 1238s, 942vs, 896m, 872m, 823vs, 726s, 676m, and 633m cm.$^{-1}$.

Reaction of bispentafluorosulphur peroxide with sulphur tetrafluoride. The three methods were used but the major product of the reaction was thionyl tetrafluoride with no liquid product.

Reaction between bispentafluorosulphur tetrafluoromonoperoxysulphate, $SF_5{\cdot}O{\cdot}SF_4{\cdot}O{\cdot}O{\cdot}SF_5$ *and sulphur dioxide.* Sulphur dioxide (9 g.) and the peroxysulphate (10 g.) were heated at 150° for 12 hr. as in method (ii). The gaseous products (10·4 g.) contained thionyl tetrafluoride and sulphur dioxide. The liquid products (8 g.) were washed with water and fractionated, giving (1) b. p. 25°/20 mm., starting peroxysulphate, (2) b. p. 58°/20 mm., *pentafluorosulphur tetrafluoro(pentafluorosulphuroxy)sulphur sulphate* $SF_5{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}SF_4{\cdot}O{\cdot}SF_5$ (Found: F, 55·1; S, 26·8%; *M*, 480. $F_{14}O_5S_4$ requires F, 56·1; S, 27·0%; *M*, 474).

The saturated vapour pressure of the liquid fraction (2) is given by log p (mm.) = $9{\cdot}55 - 2735/T$, which gives b. p. 137°/760 mm. and ΔH_{vap} = 12,500 cal. mole^{-1}. The infrared spectrum had principal bands at 1500m, 1230m, 1021m, 940vs, 848vs, 798vs, 735m, and 708m cm.$^{-1}$.

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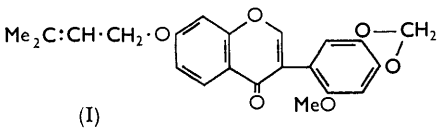
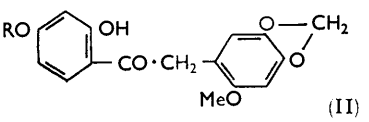
1150. *The Synthesis of "Maxima Substance C."*

By C. A. ANIRUDHAN and W. B. WHALLEY.

FROM the roots of *Tephrosia maxima*, Rangaswami and Sastry [1] isolated several isoflavones which were designated as Maxima substances A, B, and C. Maxima substances A (7,8-methylenedioxy-3',4'-methylenedioxyisoflavone) and B [7-(3-methylbut-2-enyloxy)-3',4'-methylenedioxyisoflavone] have been synthesised.[2] Maxima substance C was allocated structure (I).



(I)



(II)

With the availability from other researches of 2-methoxy-4,5-methylenedioxybenzyl cyanide we have synthesised substance (I). Interaction of the cyanide with resorcinol gave 2,4-dihydroxy-2'-methoxy-4',5'-methylenedioxydeoxybenzoin (II; R = H) which yielded the ether (II; R = CH_2·CH:CMe_2). Cyclisation with ethyl formate then furnished the isoflavone (I). Although direct comparison was not possible, the properties of our isoflavone correspond with those recorded [1,2] for "Maxima substance C."

Experimental.—*2'-Methoxy-7-(3-methylbut-2-enyloxy)-4',5'-methylenedioxyisoflavone.* A solution of the azlactone [3,4] (40 g.) of 2-methoxypiperonaldehyde in 10% aqueous hydroxide (400 ml.) was refluxed for 8 hr. After isolation in the usual way, *2-methoxy-4,5-methylenedioxyphenylpyruvic acid* furnished pale yellow prisms (15 g.), m. p. 211°, from acetic acid (Found: C, 56·0; H, 3·9. $C_{11}H_{10}O_6$ requires C, 55·5; H, 4·2%). The derived *oxime* separated from ethyl acetate in pale yellow needles, m. p. 160° (decomp.) (Found: N, 5·3. $C_{11}H_{11}NO_6$ requires N, 5·5%). Dehydration of this oxime (15 g.) in warm acetic anhydride (30 ml.) gave *2-methoxy-4,5-methylenedioxybenzyl cyanide* (10 g.) which separated from ethyl acetate–light petroleum (b. p. 40—60°) in needles, m. p. 120° (Found: N, 7·3. $C_{10}H_9NO_3$ requires N, 7·3%). The preparation of this cyanide has been recorded [4] without experimental details.

Condensation of this cyanide (4 g.) with resorcinol (20 g.) in ether (150 ml.) containing zinc chloride (3 g.) and aluminium chloride (0·5 g.) at 0° in the presence of hydrogen chloride during 4 hr. yielded *2,4-dihydroxy-2'-methoxy-4',5'-methylenedioxydeoxybenzoin* which formed prisms (2 g.) (from methanol), m. p. 167° (Found: C, 63·7; H, 4·6. Calc. for $C_{16}H_{14}O_6$: C, 63·6; H, 4·7%). Suginome [4] records m. p. 164—165° without experimental details.

Reaction of this deoxybenzoin (1 g.) in boiling acetone (50 ml.) containing potassium carbonate (3 g.) and 3-methylbut-2-enyl bromide (0·5 ml.) occurred during 2 hr., yielding 2-hydroxy-2'-methoxy-4-(3-methylbut-2-enyloxy)-4',5'-methylenedioxydeoxybenzoin which formed prisms (0·9 g.), m. p. 80°, from alcohol (Found: C, 68·1; H, 6·0. Calc. for $C_{21}H_{22}O_6$: C, 68·1; H, 6·0%). Rangaswami and Sastry [2] record m. p. 79—81° for the deoxybenzoin obtained by degradation of "maxima substance C." Cyclisation of this deoxybenzoin (0·8 g.) with sodium (0·5 g.) and ethyl formate gave the 2-hydroxyisoflavanone (cf. Whalley [5]) which was dehydrated in boiling acetic acid during ½ hr. Purification of the product from alcohol gave 2'-methoxy-7-(3-methylbut-2-enyloxy)-4',5'-methylenedioxyisoflavone (0·4 g.), needles, m. p. 146° (Found: C, 69·5; H, 5·5. Calc. for $C_{22}H_{20}O_6$: C, 69·5; H, 5·3%) (lit.,[1,2] m. p. 146° for "Maxima substance C").

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[2] Kukla and Seshadri, *Tetrahedron*, 1962, **18**, 1443.
[3] Rajagopalan and Kosak, *Tetrahedron Letters*, 1959, No. 21, 5.
[4] Suginome, *Tetrahedron Letters*, 1960, No. 19, 16.
[5] Whalley, *J. Amer. Chem. Soc.*, 1953, **75**, 1059.

1151. *Diterpenes from* Podocarpus milanjianus.

By C. W. L. Bevan and D. A. H. Taylor.

Extraction of two different specimens of the timber of *Podocarpus milanjianus* by light petroleum has given totarol and the corresponding 16-alcohol and aldehyde, the same substances as were obtained recently from *Podocarpus manii*.[1] The yields from the two trees were quite different; in particular, *P. milanjianus* contains much more of the aldehyde. This result is interesting, as botanically the two species are very distinct.

A specimen of *Podocarpus gracilior* gave an extract (0·28%) which showed no ultraviolet or infrared aromatic absorption and appeared from the spectra to contain aliphatic esters. This has not been further investigated.

The phenolic acetate, m. p. 245°, isolated in small yield from *P. mannii*[1] has now been identified as 13-acetoxy-14-isopropylpodocarpa-8,11,13-trien-16-oic acid by esterification with diazomethane to give the previously known methyl ester.

Experimental.—Extraction of P. milanjianus. The finely ground timber (30·5 kg.) (herbarium specimens are preserved as Forest Herbarium Ibadan No. 47,322) was extracted with light petroleum, the extract (90 g.) was divided into acid and neutral fractions, and the neutral fraction was distilled. The distillate (30 g.), collected up to 250°/1 mm., was partly crystalline. It was chromatographed in benzene on alumina (900 g.). Benzene and then ether eluted totarol (6·1 g.) and its 16-oxo- (2·0 g.) and 16-hydroxy-derivative (0·9 g.), each identical with authentic specimens.[1] The acidic fraction was methylated with dimethyl sulphate and alkali and then acetylated; chromatography gave only amorphous material; the acid obtained from *P. mannii* was not isolated. The second sample of timber gave similar results.

We are grateful to the Forestry Department of Cameroun for the supply of *P. milanjianus*, and the Forestry Research Institute, University College of Addis Ababa, for *P. gracilior*.

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[1] Taylor, *J.*, 1963, 1553.

1152. *The Activation Energy of the Isomerisation of Cyclopropane.*

By G. L. Pratt.

Theories of unimolecular reactions which allow that the specific rate of reaction of activated molecules varies with the degree of activation predict that the measured activation energy should vary with total pressure. Slater's classical harmonic-oscillator theory[1] predicts that the position of the fall-off curve (a plot of $\log_{10} k_p/k_\infty$ versus $\log_{10} p$, where k_p is the first-order rate constant at pressure p) should vary with the absolute temperature T according to:

$$\Delta \log_{10} p = \tfrac{1}{2} n \, \Delta \log_{10} T, \qquad (1)$$

where n is the number of effective normal modes. Correspondingly, and equivalently, the experimental activation energy, E, should vary with pressure, thus:

$$E = E_\infty + \boldsymbol{R} \left(\frac{\partial \ln p}{\partial (1/T)} \right)_{k/k_\infty} \left(\frac{\partial \log_{10} k/k_\infty}{\partial \log_{10} p} \right)_T$$

i.e.,

$$E = E_\infty - \tfrac{1}{2} n \boldsymbol{R} T A(\theta), \qquad (2)$$

[1] Slater, "Theory of Unimolecular Reactions," Methuen, London, 1959.

where $A(\theta)$ is the slope of the fall-off curve for temperature T and θ is a function of T and p.[1]

For the isomerisation of cyclopropane, $n = 13$ or 14, and so the effect is small and requires unusually accurate measurements for its observation. Langrish and Pritchard [2] were unable to detect any such variation. Schlag and Rabinovitch,[3] on the other hand, compared their measurements at 718°K with those of Pritchard, Sowden, and Trotman-Dickenson [4] corrected to 773°K [5] and concluded that equation (1) is not borne out.

Falconer, Hunter, and Trotman-Dickenson [6] have described an attempt to measure curvature in the Arrhenius plot which is predicted by a quantum version of Slater's theory. The accuracy claimed was extremely high and would be more than sufficient to detect the predicted variation of activation energy both with temperature and with pressure. No information on the effect of pressure was obtained since a single, high pressure was used. No significant curvature in the Arrhenius plot was observed, and consequently Slater [7] proposed an empirical modification to his theory.

The random error in the results of Falconer *et al.*[6] was at most a fifth of the predicted effect of temperature. However, these authors considered that the accuracy was limited by the measurement of length of runs, estimation of reaction zone and dead space, timing of short runs, and analysis of products, which together gave rise to systematic errors fully equal to the random error. Two additional possible systematic errors exist. First, no attempt to study the variation of rate constant with extent of reaction was made by these authors, who employed percentage reactions between 25 and 75. Previous workers, *e.g.*, Chambers and Kistiakowsky,[8] have found no change in rate constants during a run, but the accuracy of their experiments lies far below that claimed by Falconer *et al.*[6]. On the other hand, Corner and Pease [9] observed quite marked variations in rate constant during the reaction. Secondly, many investigators have observed polymerisation of the initial product, propene. The products of this polymerisation are exceedingly complex, *e.g.*, in this present work, analysis by gas–liquid chromatography of the products obtained by leaving 760 mm. of cyclopropane at 745°K for 65 hours showed small amounts of more than thirty different hydrocarbons. In view of this complexity it is not easy to estimate the extent of polymerisation from observations on a few of the products. Nor is it easy to say what effect this concurrent radical reaction will have on the isomerisation of cyclopropane.

In the present work the variation of the activation energy of the isomerisation of cyclopropane to propene with pressure was measured. Curvature in the Arrhenius plot was investigated by a technique designed to eliminate as many as possible of the above systematic errors.

Experimental.—The apparatus was essentially as described previously.[10] The cylindrical Pyrex reaction vessel (160 ml.) was contained in an annular metal block, one inch thick. The temperature of the block varied over the length by $\pm 0{\cdot}1°$, and was controlled to better than 0·2° during each run. The mean temperature for a run was measured by a chromel–alumel thermocouple (reading accuracy $\pm 0{\cdot}03°$) calibrated at the m. p. of pure metals. Different metal specimens gave the same calibration within $\pm 0{\cdot}3°$. Small samples were taken from the reaction vessel by means of the rotary sampling valve.[11] Samples were taken in pairs, the first of each pair being rejected to eliminate the effect of dead space. The samples were injected directly into a gas–liquid chromatographic analysis unit, without intermediate operations such as trapping or distillation which are likely to lead to variations of composition. Nor did the samples come into contact with grease, for similar reasons. The column used for the analysis

[2] Langrish and Pritchard, *J. Phys. Chem.*, 1958, **62**, 761.
[3] Schlag and Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996.
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[9] Corner and Pease, *J. Amer. Chem. Soc.*, 1945, **67**, 2067.
[10] Pratt and Purnell, *Proc. Roy. Soc.*, 1961, *A*, **260**, 317.
[11] Pratt and Purnell, *Analyt. Chem.*, 1960, **32**, 1213.

was 8 ft. long, containing 20% w/w of squalane on 140—170 mesh (ASTM) Sil-O-Cel and was operated at 26°, with a carrier inlet pressure of 40 lb./sq. in. gauge, giving a flow of hydrogen of about 200 ml./min. To allow time for the analysis, the minimum inter-sample time used was one minute. Both thermal conductivity (katharometer) and flame-ionisation detectors were used.

The reactant (I.C.I. Medical) was thoroughly de-gassed before use. Gas–liquid chromatographic analysis of this material showed the following impurity content: ethylene 0·01%; ethane 0·008%; propene 0·02%; propane 0·02%. The pressure of reactant admitted at the start of a run was measured on a Pyrex spiral gauge. Between 6 and 12 samples were analysed during each run. This eliminates errors in timing the start of a run and constant errors in timing the removal of samples, and also allows the detection of any trend in the rate constant with increasing extent of reaction. Errors due to dead space are also greatly reduced.

TABLE 1.

Deviations from the Arrhenius expression.

		Mean deviation 10^4 ($\log_{10} k_{exp.} - \log_{10} k_{calc.}$)		
$10^3/T$ (°K^{-1})	No. of values	This work	Ref. 6	Theoretical
1·20671—1·28932	6	+16 ± 24	+20 ± 28	+110
1·31631—1·36677	6	−26 ± 49	−10 ± 19	−210
1·39121—1·43918	5	+12 ± 35	+10 ± 31	+110

Results.—The isomerisation was first studied at a pressure of 50 mm. At very large extents of reaction a significant downward trend in the first-order rate constant was detected. The percentage reaction at which this trend became significant decreased with lowering of the reaction temperature. For the purposes of the activation-energy measurements the extent of reaction was restricted to values such that the rate constant remained constant within the experimental error. Under these conditions, analysis suggested that errors due to polymerisation of propene or other concurrent or subsequent reactions were negligible. To check this point, two methods of measuring the first-order rate constant were used. First, a rate constant k' was evaluated from the analyses taken in pairs as $-\Delta \ln C/\Delta t$, where C is the pressure of cyclopropane in the reaction vessel at time t. This method is independent of subsequent reactions of the propene. Secondly, the rate constants, k, were calculated from $k = \{\Delta \ln (1 + [P/C])\}/\Delta t$, where P is the pressure of propene formed. This equation relies on the reaction's stoicheiometry being exactly correct. Both k' and k were measured for 15 runs over the temperature range 730—830°K. The mean value of k/k' was 1·02 ± 0·01. In subsequent experiments, only k was measured since this measurement is intrinsically more accurate over wider ranges of conditions.

Results for k at 50 mm. pressure and for temperatures between 695° and 830°K were fitted to the Arrhenius expression by the method of least squares, and gave:

$$\log_{10} k \text{ (sec.}^{-1}) = 14{\cdot}84 \pm 0{\cdot}04 - [(64{,}170 \pm 150)/2{\cdot}303\boldsymbol{R}T].$$

The errors quoted throughout this work are standard deviations. In Table 1 the results are evaluated according to the method of Falconer *et al.*[6] The temperature range is divided into three parts and the mean deviations of the experimental points from the least squares line ($\log_{10} k_{exp.} - \log_{10} k_{calc.}$) is given for each range, in column 3. For comparison, column 4 gives the values for this same quantity found by Falconer *et al.*,[6] using a higher pressure (300 mm.) and a somewhat shorter temperature range (693—808°K). The last column gives the deviations predicted by Slater's quantum harmonic-oscillator theory for the latter temperature range.

TABLE 2.

Variation of activation energy with pressure.

Pressure (mm.)	∞	50	10	1·5
Activation energy (kcal./mole)	65·60 ± 0·03 [6]	64·17 ± 0·15	60·79 ± 0·35	60·79 ± 0·37
$A(\theta)$	0·00	0·13	0·23	0·39

The rate was then measured at pressures of 10 mm. and 1·5 mm. at temperatures in the range 745—830°K. The least-squares fits to the Arrhenius plots of this data are:

$$\log_{10}k\ (\text{sec.}^{-1}) = 14{\cdot}04 \pm 0{\cdot}09 - [(61{,}800 \pm 350)/2{\cdot}303\boldsymbol{R}T] \text{ for 10 mm.,}$$

$$\log_{10}k\ (\text{sec.}^{-1}) = 13{\cdot}50 \pm 0{\cdot}10 - [(60{,}785 \pm 370)/2{\cdot}303\boldsymbol{R}T] \text{ for 1·5 mm.}$$

In Table 2 the activation energies measured in this work are given, together with the value for infinite pressure obtained by Falconer *et al.*[6] The second row of Table 2 gives the corresponding mean values of $A(\theta)$ deduced from the results of Pritchard *et al.*[4] The least-squares best-straight-line fit to the results in Table 2 is:

$$E = 65{\cdot}60 \pm 0{\cdot}09 - A(\theta) \times (12{\cdot}4 \pm 2{\cdot}0) \text{ (kcal/mole).}$$

Comparison with equation (2), with $T = 790°$K, yields $n = 15{\cdot}7 \pm 2{\cdot}5$.

Discussion.—The close agreement between k and k' gives some confidence in the absence of systematic errors due to varying stoicheiometry. The results of the search for curvature in the Arrhenius plot for 50 mm. pressure are in excellent agreement with those of Falconer *et al.*[6] for 300 mm. pressure. The absence of the curvature predicted by the unmodified quantum-harmonic oscillator theory of Slater is confirmed. The measured variation of activation energy with pressure is, within the experimental error, in good agreement with the predictions of equations (1) and (2) of Slater's classical theory when the number of normal modes is taken as about 14. This result is in disagreement with the conclusion of Schlag and Rabinovitch.[3]

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1153. *Heterocyclic Compounds with Bridgehead Nitrogen Atoms. Part I. Synthesis of 2-Ethynylpyridine and Some Derived Quinolizinones.*

By D. Leaver, and (in part) W. K. Gibson and J. D. R. Vass.

2-Ethynylpyridine had been prepared[1] in very low yield from 2-acetylpyridine but its reactions had not been studied. We have prepared it in better yield from 2-vinylpyridine and investigated its use in the synthesis of quinolizine derivatives.

2-Vinylpyridine reacted rapidly with bromine to give an unstable dibromide which, on treatment with triethylamine, gave an amorphous black solid together with a trace of a bromo-compound believed to be 2-1′-bromovinylpyridine because of the presence of a strong absorption band (:CH_2 out-of-plane deformation) at 905 cm.$^{-1}$ in its infrared spectrum. Although this band does not lie within the range (885—895 cm.$^{-1}$) normally accepted[2] for 1,1-disubstituted ethylenes, it is related to the corresponding band (890 cm.$^{-1}$) of α-bromostyrene in the same way as the CH_2 absorption of 2-vinylpyridine (930 cm.$^{-1}$) is related to that of styrene (912 cm.$^{-1}$).

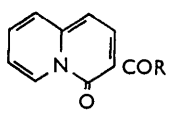
Dehydrobromination of the dibromide by boiling with ethanolic potassium hydroxide for 3 hours gave a good yield of an ethoxyvinylpyridine which was separated into two isomers, A and B in order of elution, by chromatography on alumina. Compounds A and B were shown to be the *trans*- and the *cis*-isomer, respectively, of 2-2′-ethoxyvinylpyridine

[1] Haug and Fürst, *Chem. Ber.*, 1960, **93**, 593.
[2] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd Edn., 1958, p. 34.

on the basis of the following evidence: (*a*) both isomers, in acid solution, gave the same 2,4-dinitrophenylhydrazone (of 2-pyridylacetaldehyde), which was different from that of 2-acetylpyridine; (*b*) isomer B was also obtained by base-catalysed addition (*trans*-addition giving the *cis*-isomer) of ethanol to 2-ethynylpyridine; (*c*) infrared absorptions at 1178 and 1650 (doublet) cm.$^{-1}$ in the spectrum of isomer A and at 1100 and 1650 (singlet) cm.$^{-1}$ in that of isomer B were comparable to the corresponding bands in the respective spectra of *trans*- and *cis*-but-1-enyl butyl ethers; [3] (*d*) the infrared spectrum of isomer A showed an absorption band (absent for B) at 940 cm.$^{-1}$ attributable to the C–H out-of-plane deformation mode of the *trans*-vinylene group.

Treatment of the mixture of the *cis*- and the *trans*-ethoxyvinyl compound with sodium ethoxide in boiling ethanol caused further addition, giving 2-2′,2′-diethoxyethylpyridine.

Although a small amount of 2-ethynylpyridine was isolated after boiling the dibromide with ethanolic potassium hydroxide for a shorter time, the best yield (30%) of the compound was obtained by dehydrobromination with powdered potassium hydroxide in boiling t-butyl alcohol, under nitrogen and in presence of quinol. Under these conditions the only significant by-product was an amorphous black solid; presumably hydroxide ion is not a sufficiently strong base to catalyse the addition of t-butyl alcohol to the ethynyl group. The identity of the product was shown by infrared absorptions at 3300 (:C–H stretch) and 2120 cm.$^{-2}$ (C:C stretch), by the formation of an insoluble silver derivative, and by hydration, in presence of mercuric ion, to 2-acetylpyridine.



(I)

Treatment of 2-ethynylpyridine with diethyl sodiomalonate resulted in Michael addition followed by cyclisation, yielding the known [4] 3-ethoxycarbonylquinolizin-4-one (I; R = OEt). Base-catalysed reactions with ethyl acetoacetate and ethyl benzoylacetate proceeded similarly to give 3-acetyl- (I; R = Me) and 3-benzoyl-quinolizin-4-one (I; R = Ph), respectively. All attempts to prepare the same compounds by Michael addition to the more easily preparable 2-2′-ethoxyvinylpyridine failed.

Experimental.—Solvent extracts were dried over sodium sulphate and evaporated under reduced pressure. The light petroleum had b. p. 60—80°.

2-1′,2′-Dibromoethylpyridine. 2-Vinylpyridine (21 g.) in carbon tetrachloride (40 ml.) was added dropwise to a vigorously stirred, ice-cooled solution of bromine (11 ml.) in carbon tetrachloride (50 ml.). The solution was then decanted from a gummy by-product and evaporated under reduced pressure at 40° to yield the crude dibromide (46 g.) which slowly polymerised at room temperature. Distillation (b. p. 89°/0·3 mm.) led to extensive polymerisation but the distillate yielded a *picrate*, m. p. 118—119° (from ethanol) (Found: C, 31·8; H, 2·2; Br, 32·4; N, 11·3. $C_{13}H_{10}Br_2N_4O_7$ requires C, 31·6; H, 2·0; Br, 32·3; N, 11·3%).

Dehydrobromination of the dibromide. (*a*) Triethylamine (40 ml.) was added dropwise to the stirred, ice-cooled, crude dibromide (23 g.), and the mixture was set aside at room temperature for 1 hr., before dilution with an equal volume of ether. The ether solution was filtered from an amorphous black solid, washed with 2N-sodium hydroxide, dried, and evaporated. The residue was distilled to yield 2-1′-bromovinylpyridine (*ca.* 1 g.), b. p. 98°/15 mm., which darkened rapidly in air. The *picrate* formed yellow plates (from ethanol), m. p. 134° (softening from 130°) (Found: C, 37·6; H, 2·3; Br, 20·1; N, 14·1. $C_{13}H_9BrN_4O_7$ requires C, 37·8; H, 2·2; Br, 19·3; N, 13·6%).

(*b*) The crude dibromide (46 g.) was added during 15 min. to potassium hydroxide (40 g.) in boiling ethanol (200 ml.) and the mixture was boiled for a further 3 hr. and then diluted with water. Extraction with ether, evaporation of the washed (with water) and dried extract, and distillation of the residue afforded *2-2′-ethoxyvinylpyridine* (20 g.; *cis–trans*-mixture), b. p. 64—65°/0·1 mm. (Found: C, 72·2; H, 7·6; N, 9·4. $C_9H_{10}NO$ requires C, 72·4; H, 7·4; N, 9·4%).

(*c*) The crude dibromide (23 g.) in t-butyl alcohol (30 ml.) was added, in a stream of nitrogen, during 30 min., to powdered potassium hydroxide (20 g.) in vigorously stirred, boiling t-butyl

[3] Hall, Philpotts, Stern, and Thain, *J.*, 1951, 3341.
[4] Bohlmann, Englisch, Politt, Sander, and Weise, *Chem. Ber.*, 1955, **88**, 1831.

alcohol (100 ml.) containing quinol (1 g.). After addition was complete, the solution was stirred and boiled for a further 1·5 hr., diluted with ether (100 ml.), and filtered from an amorphous black solid. The filtrate was washed with water and the aqueous phase was extracted twice more with ether. The combined ether solutions were washed with water, dried, and evaporated to give a dark brown liquid which, upon distillation, yielded 2-ethynylpyridine (3·1 g.), b. p. 77—78°/14 mm., n_D^{22} 1·559 (lit.,[1] b. p. 86—88°/14 mm., n_D^{21} 1·5534) (Found: C, 81·5; H, 5·0; N, 13·6. Calc. for C_7H_5N: C, 81·6; H, 4·9; N, 13·6%).

Separation of cis- *and* trans-2-2′-*ethoxyvinylpyridines*. The mixture (2 g.) of ethoxyvinyl compounds in light petroleum–benzene was applied to a column of alumina (P. Spence, Type H; 200 g.). Elution with benzene gave the *trans*-isomer followed by a small mixed fraction, and elution with ether gave the *cis*-isomer. Both isomers were redistilled for measurement of their infrared spectra. The *cis*-isomer had n_D^{19} 1·549, $\lambda_{max.}$ (in ethanol) 260 and 292 mμ (log ε 4·13 and 3·98), and gave a *picrate*, needles, m. p. 155—156° (from ethanol) (Found: C, 47·4; H, 3·9; N, 15·3. $C_{15}H_{14}N_4O_8$ requires C, 47·6; H, 3·7; N, 14·8%). The *trans*-isomer had n_D^{19} 1·562, $\lambda_{max.}$ (in ethanol) 257 and 292 mμ (log ε 4·16 and 3·92), and gave a *picrate*, needles, m. p. 144—145° (from ethanol) (Found: C, 47·9; H, 3·9; N, 14·1%). Both isomers, on treatment with a saturated solution of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid, slowly formed 2-*pyridylacetaldehyde* 2,4-*dinitrophenylhydrazone hydrochloride*, fibrous yellow needles, m. p. 190—191° (from acetic acid) (Found: C, 46·0; H, 3·4; Cl, 10·5; N, 21·2. $C_{13}H_{12}ClN_5O_4$ requires C, 46·2; H, 3·6; Cl, 10·5; N, 20·7%).

cis-2-2′-*Ethoxyvinylpyridine*. 2-Ethynylpyridine (1 g.) was boiled for 2 hr. with potassium hydroxide (2 g.) in ethanol (10 ml.) and the solution was then diluted with water and extracted with ether. Evaporation of the dried extract and distillation of the residue gave *cis*-2-2′-ethoxyvinylpyridine (1 g.) whose infrared spectrum was identical with that of a specimen isolated by chromatography of the mixture of isomers.

2-2′,2′-*Diethoxyethylpyridine*. 2-2′-Ethoxyvinylpyridine (mixed isomers; 6·5 g.) was boiled for 3·5 hr. in ethanol (100 ml.) containing sodium ethoxide (from 5 g. of sodium). Part of the ethanol was removed by distillation and the remaining solution was diluted with water and extracted with ether. Evaporation of the dried extract yielded an oil which, on repeated fractional distillation, gave 2-2′,2′-*diethoxyethylpyridine*, b. p. 67—68°/0·1 mm., n_D^{23} 1·483 (Found: C, 68·1; H, 8·3; N, 7·2. $C_{11}H_{17}NO_2$ requires C, 67·6; H, 8·8; N, 7·2%); *picrate*, m. p. 119—120° (from ethanol) (Found: C, 48·3; H, 4·7; N, 13·2. $C_{17}H_{20}N_4O_9$ requires C, 48·1; H, 4·8; N, 13·2%).

2-*Acetylpyridine*. 2-Ethynylpyridine (1·8 g.) was boiled for 1 hr. in 50% aqueous acetic acid (20 ml.) containing sulphuric acid (2·3 g.) and mercuric sulphate (0·8 g.). The solution was then neutralised with sodium carbonate and extracted with ether. Evaporation of the dried extract and distillation of the residue gave a pale yellow liquid (1 g.) which formed a 2,4-dinitrophenylhydrazone (m. p. 198—199°) identical (mixed m. p.) with that from 2-acetylpyridine.

3-*Ethoxycarbonylquinolizin*-4-*one*. 2-Ethynylpyridine (3 g.), diethyl malonate (9·6 g.), and ethanol (5 ml.) containing sodium ethoxide (from 0·2 g. of sodium) were heated at 100° for 2 hr. and poured into water. Extraction with ether and evaporation of the dried extract gave the quinolizinone (1·8 g.), yellow needles, m. p. 115—116° (from light petroleum–acetone) (lit.,[4] m. p. 115°). The compound (1·2 g.) was boiled for 2 hr. in concentrated hydrochloric acid (50 ml.) and the solution, after being evaporated to a small volume, was neutralised with potassium carbonate. Extraction with benzene then afforded quinolizin-4-one (0·5 g.), yellow deliquescent crystals, m. p. 71° (after sublimation at 0·1 mm.) (lit.,[5] m. p. 71—72°).

3-*Acetylquinolizin*-4-*one*. Sodium (1 g.) was dissolved in ethyl acetoacetate (15 g.) and the solution was heated with 2-ethynylpyridine (2·5 g.) at 100° for 12 hr. Water and light petroleum were added and the yellow solid so produced was recrystallised from acetone to yield the *quinolizinone* (1 g.), yellow needles, m. p. 184—185° (Found: C, 70·6; H, 4·4; N, 7·6. $C_{11}H_9NO_2$ requires C, 70·6; H, 4·8; N, 7·5%). Use of ethanol as reaction solvent gave a lower yield.

3-*Benzoylquinolizin*-4-*one*. 2-Ethynylpyridine (3·5 g.), ethyl benzoylacetate (14 g.), and ethanol (4 ml.) containing sodium ethoxide (from 0·4 g. of sodium) were heated at 100° for 10 hr. Dilution with 2N-sulphuric acid and shaking with light petroleum gave a precipitate of

[5] Boekelheide and Lodge, *J. Amer. Chem. Soc.*, 1951, **73**, 3681.

the *quinolizinone* (6 g.), orange prisms, m. p. 241—242° (from acetic acid) (Found: C, 76·7; H, 4·6; N, 5·8. $C_{16}H_{11}NO_2$ requires C, 77·0; H, 4·4; N, 5·6%).

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DEPARTMENT OF CHEMISTRY, UNIVERSITY OF EDINBURGH. [*Received, May 23rd,* 1963.]

1154. *The Basicities of the Isomeric Aminophenanthrenes and Aminotriphenylenes.*

By P. H. GORE and A. M. LUBIENSKY.

THE ionization constants of four of the five aminophenanthrenes have recently been determined,[1] together with other arylamines. It was found that unhindered amines (*e.g.*, β-naphthylamine) had pK_a values which were all higher than those for *peri*-substituted amines (*e.g.*, 9-aminophenanthrene), whilst the *meso*-substituted 9-anthrylamine had the lowest value of all (pK_a 2·7). The basicity of the missing 4-aminophen-

pK_a values of arylamines.

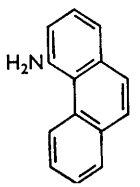
	Present work			Recorded values			
Aryl *	pK_a at 20°	Solvent (% EtOH)	pK_a in 4% EtOH at 20°	pK_a	Temp.	Solvent	Ref.
Ph	4·74	4	4·74	4·19	20	50% EtOH	1
				4·33	20	50% EtOH	6
				4·62			
				−4·72	25	H_2O	7—9
				4·58	21	H_2O	10
				4·51	15	H_2O	11
p-Tolyl ...	5·27	4	5·27	5·05			
				−5·30	25	H_2O	7, 9, 10
1-$C_{10}H_7$ ...	4·16	4	4·16	3·40	20	50% EtOH	1
				3·89			
				−4·00	25	H_2O	7
				3·92	22	H_2O	10
				4·45	15	H_2O	11
2-$C_{10}H_7$ ...	4·39	1	4·31	3·77	20	50% EtOH	1
	4·38	2		4·20			
	4·31	4		−4·30	25	H_2O	7
	4·10	14		4·11	23	H_2O	10
	3·97	20		4·59	15	H_2O	11
1-P	3·29	10	3·43 †	3·23	20	50% EtOH	1
2-P	4·04	4	4·04	3·60	20	50% EtOH	1
3-P	4·11	4	4·11	3·59	20	50% EtOH	1
4-P	3·30	4	3·30				
9-P	3·54	10	3·68 †	3·19	20	50% EtOH	1
				3·57	20	50% EtOH	12
1-T	2·35	20	2·75 †				
2-T	3·30	20	3·70 †				

* P = phenanthryl, T = triphenylenyl. † Extrapolated.

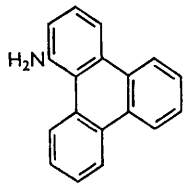
anthrene is, however, of special interest, since it was predicted [2] that it would have unusually high basicity (low pK_a). In a related study [3] of the reaction rates of arylamines with 1-chloro-2,4-dinitrobenzene, all the amines (including 9-anthrylamine) accurately fitted the plot of log rate against localization energy of the aryl position, except

[1] Elliott and Mason, *J.*, 1959, 2352.
[2] Gore, *J.*, 1954, 3166.
[3] Sixma, *Rec. Trav. chim.*, 1955, **74**, 168.

for 4-aminophenanthrene (I). This anomaly was stated to be due to steric repulsions, giving rise to an out-of-plane twisting of the amino-group. Related cases have alternatively been explained in terms of an increase in steric strain in forming the conjugate acid [4] and of steric hindrance to solvation of the charged ion.[5]



(I)



(II)

It was considered of interest, therefore, to examine the basic strengths of 4-aminophenanthrene, the sterically related 1-aminotriphenylene (II), and their isomers, as well as reference compounds (see Table). The sequence of increasing pK_a values was 1-triphenylenyl < 4-phenanthryl < 1-phenanthryl < 9-phenanthryl < 2-triphenylenyl < 2-phenanthryl < 3-phenanthryl < 1-naphthyl < 2-naphthyl < phenyl < *p*-tolyl. The prediction of low pK_a values [2] for highly hindered amines of this type has thus been verified.

Experimental.—Materials. Standard procedures were used for the preparation and purification of 1-amino- [13,14] and 2- and 3-aminophenanthrenes.[14] Samples of 4- and 9-aminophenanthrene, and 1- and 2-aminotriphenylene, kindly presented by Professor M. J. S. Dewar,[15] were purified before use.

Measurements. Spectrophotometric analysis, by a Unicam S.P. 500 spectrophotometer, was applied to the base and its conjugate acid, in aqueous buffers of ionic strength 0·05—0·10. A region of the spectrum was selected in which the light absorption of the base B was much higher than that of its conjugate acid BH^+. A plot of pH (measured by a Marconi pH-meter) against ε gave a titration curve which was satisfactorily linear near half-neutralization. The pK_a ($K_a = [B][H_3O^+]/[BH^+]$) was taken as the pH where $[B] = [BH^+]$, no correction being applied for ionic strengths. Not less than three wavelengths were taken in each case, the maximum deviation from the mean value (given in the Table) being ±0·06 pH unit (overall average 0·02 pH unit). In most cases a 4% v/v ethanol solution was employed, but the less soluble 1- and 9-aminophenanthrene required 10% ethanol, and both aminotriphenylenes 20% ethanol. These values were extrapolated to " 4% ethanol " by the use of a calibration curve determined on β-naphthylamine at 1, 2, 4, 14, and 20% ethanol, which was precisely linear.

Department of Chemistry, Brunel College, London W.3. [*Received, May 29th,* 1963.]

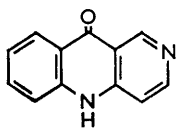
[4] Brown and Cahn, *J. Amer. Chem. Soc.*, 1950, **72**, 2939.
[5] Wepster, *Rec. Trav. chim.*, 1957, **76**, 357.
[6] Carswell, Cymerman, and Lyons, *J.*, 1952, 430.
[7] Farmer and Worth, *J.*, 1904, **85**, 1726; Flürscheim, *J.*, 1909, **95**, 718; Goldschmidt and Mathieson, *Z. phys. Chem.*, 1926, **119**, 439.
[8] Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1953, **75**, 2421.
[9] Gutbezahl and Grunwald, *J. Amer. Chem. Soc.*, 1953, **75**, 559.
[10] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.
[11] Veley, *J.*, 1908, **93**, 2137.
[12] Allen, Cymerman-Craig, and Diamantis, *J.*, 1954, 234.
[13] Gore, *J. Org. Chem.*, 1957, **22**, 135.
[14] Bachman and Boatner, *J. Amer. Chem. Soc.*, 1936, **58**, 2097.
[15] Bavin and Dewar, *J.*, 1955, 4477.

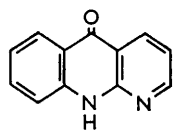
1155. *Synthesis of Pyrido*[3,4-b]*quinolin*-5(10*H*)-*one and Pyrido*[3,2-b]-*quinolin*-10(5*H*)-*one.*

By R. E. CORBETT and B. J. SWEETMAN.

DURING certain degradative studies it became desirable to examine the ultraviolet spectra of pyridoquinolones as model substances. Pyrido[4,3-*b*]quinolin-10(5*H*)-one [1] (I) and pyrido(2,3-*b*]quinolin-5(10*H*)-one [2] (II) have been prepared by others. This Note describes the synthesis of the remaining two members of the series (III and IV).

N-3′- and *N*-4′-Pyridylanthranilic acid are not cyclised by the usual reagents (phosphorus oxychloride or concentrated sulphuric acid),[3,4] but the use of an aluminium chloride–sodium chloride melt has been used successfully to obtain compound (I).[1a] We have found that by this method *N*-3′-pyridylanthranilic acid hydrochloride undergoes ring closure exclusively at position 2′, to give the [3,2-*b*]-compound (III). The alternative route, cyclisation of 2-phenylaminonicotinic acid by polyphosphoric acid has been used to obtain the isomer (II); [2] we have shown that this method is also applicable to 3-phenylaminoisonicotinic acid and have thereby obtained the remaining member of the series, (IV).


(I)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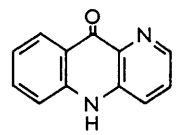
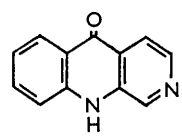

(III)


(IV)

Earlier workers [3] have not given complete experimental details or yields for the preparation of *N*-3′-pyridylanthranilic acid. In our work, the yield in the Ullmann condensation of 3-aminopyridine with potassium *o*-chlorobenzoate was the same (*ca.* 10%) whether pentanol or nitrobenzene was used as solvent. In the former case the major product was pentyl salicylate. The yield of anthranilic acid was not affected by addition of potassium carbonate to the reaction, nor was the formation of pentyl salicylate.

The ultraviolet absorption spectra of the two new pyridoquinolones (see below) show bathochromic shifts of the principal ultraviolet and long-wavelength bands in both acid and alkaline media. These shifts are of value for characterising the individuals.

Experimental.—M. p.s were taken on a Kofler block and are corrected. Ultraviolet spectra were measured on a Shimadzu recording spectrophotometer, model RS 27.

N-3′-*Pyridylanthranilic acid.* Potassium *o*-chlorobenzoate (4·15 g.), copper powder (0·1 g.), 3-aminopyridine (2·14 g.), and pentanol (20 ml.) were rapidly stirred for 6 hr. at 125°. The brown solid which was filtered (filtrate A) from the cooled mixture was washed with water and pentanol. After two crystallisations from ethanol it gave *N*-3′-pyridylanthranilic acid (0·52 g.) as prisms, m. p. 237° (lit.,[3] 237°, 237—238°).

Removal of the solvent from the filtrate A under reduced pressure gave a red gum which was dissolved in ethanol and filtered from a small amount of insoluble matter. After removal of the ethanol the residual oil was distilled, to give pentyl salicylate (1·5 g.), b. p. 187—192°/16 mm. (Found: C, 69·4; H, 7·8; O, 22·8. Calc. for $C_{12}H_{16}O_3$: C, 69·2; H, 7·7; O, 23·0%). Identification was by infrared spectrum. The yield of anthranilic acid was not appreciably changed if nitrobenzene was used as solvent or if potassium carbonate was added to the reaction.

Pyrido[3,2-*b*]*quinolin*-10(5*H*)-*one.* *N*-3′-Pyridylanthranilic acid (1·0 g.) was added to a stirred, homogeneous melt of anhydrous aluminium chloride (10·0 g.) and sodium chloride

[1] (*a*) Ferrier and Campbell, *Chem. and Ind.*, 1958, 1089; (*b*) Coscia and Dickermann, *J. Amer. Chem. Soc.*, 1959, **81**, 3098.
[2] Carboni, *Gazetta*, 1955, **85**, 1194.
[3] Kermac and Weatherhead, *J.*, 1942, 726; Petrow, *J.*, 1945, 927.
[4] Bachman and Barker, *J. Org. Chem.*, 1949, **14**, 97.

(1·5 g.) at 230—240°. After 1 hr. the solution was cooled, basified to pH 10 by addition of 30% aqueous sodium hydroxide, and continuously extracted for 30 hr. with ethyl acetate. The extract, after concentration, deposited an orange solid (0·4 g.), m. p. 350—360°. Purification by ammonia diffusion from solution in 0·1N-hydrochloric acid, or by sublimation at 250—260°/0·03 mm., gave *pyrido*[3,2-*b*]*quinolin*-10(5*H*)-*one* as pale yellow prisms, m. p. 369—371° (decomp.) (Found: C, 73·4; H, 3·9. $C_{12}H_8ON_2$ requires C, 73·5; H, 4·1%); $\lambda_{max.}$ (in 95% ethanol) 257, 296, 386, 401·8 mμ (log ε 4·76, 3·65, 3·89, 3·90), $\lambda_{min.}$ 225, 320, 395 mμ (log ε 4·08, 3·33, 3·85); $\lambda_{max.}$ (in 0·01N-HCl) 235, 267, 322 (infl.), 422 mμ (log ε 4·05, 4·55, 3·41, 3·67), $\lambda_{min.}$ 232, 240, 348 mμ (log ε 3·99, 3·90, 2·75); $\lambda_{max.}$ (in 0·01N-NaOH) 231, 266·5, 328, 400 (infl.), 415, 435 (infl.) mμ (log ε 2·98, 4·63, 2·17, 2·73, 2·82, 2·66), $\lambda_{min.}$ 227, 233·5, 320, 340 mμ (log ε 2·95, 2·96, 2·15, 2·00).

3-*Phenylaminoisonicotinic acid.* 3-Iodoisonicotinic acid (2·0 g.), redistilled aniline (5·0 ml.), anhydrous potassium carbonate (1·2 g.), and copper powder (0·02 g.) were heated at 160—165° for 2·5 hr., until evolution of carbon dioxide had ceased. The solution, diluted with water (30 ml.), was steam-distilled, and the still hot residue was filtered. Acidification of the cooled filtrate with glacial acetic acid gave a green solid (0·66 g.) which crystallised as pale green prisms (from pyridine–ethanol), m. p. 305—306° (lit.,[4] 304—305°).

Pyrido[3,4-*b*]*quinolin*-5(10*H*)-*one.* 3-Phenylaminoisonicotinic acid (0·8 g.), polyphosphoric acid (8 g.; 80% P_2O_5) and phosphorus oxychloride (0·8 ml.) were heated at 100° for 1 hr. Ice (10 g.) was added to the cooled solution, which was filtered and neutralised with sodium carbonate. This gave brown crystals (0·6 g.) that were dissolved in the minimum quantity of N-hydrochloric acid. The solution was treated with ammonia by diffusion, until precipitation of a yellow product (0·4 g.) was complete. Sublimation at 160—170°/0·02 mm. gave orange-yellow prisms of *pyrido*[3,4-*b*]*quinolin*-5(10*H*)-*one*, m. p. 328—330° (decomp.) (Found: C, 73·1; H, 4·45. $C_{12}H_8ON_2$ requires C, 73·5; H, 4·1%; $\lambda_{max.}$ (in 95% ethanol) 242, 254, 261—262 (infl.), 267, 395, 414 mμ (log ε 4·33, 4·15, 4·27, 4·35, 3·89, 3·87), $\lambda_{min.}$ 222, 250, 255, 324, 405 mμ (log ε 4·12, 4·17, 4·10, 2·9, 3·75); $\lambda_{max.}$ (in 0·01N-HCl) 223, 242, 247—250 (infl.), 273—275 (infl.), 280, 423 mμ (log ε 4·36, 4·33, 4·27, 4·23, 4·25, 3·76), $\lambda_{min.}$ 235, 259, 340 mμ (log ε 4·27, 4·04, 2·57); $\lambda_{max.}$ (in 0·01N-NaOH) 248, 271, 328, 345, 404, 423, 448 mμ (log ε 4·50, 4·62, 3·59, 3·70, 3·82, 3·90, 3·73), $\lambda_{min.}$ 256, 310, 335, 354, 410, 437 mμ (log ε 4·19, 3·46, 3·56, 3·26, 3·69, 3·71).

Both products (III) and (IV) were soluble in dilute acids and dilute sodium hydroxide, and were recovered from acid solution by ammonia diffusion. The solutions in ethanol had an intense blue fluorescence.

This work has been assisted by grants from the Research Fund of the University of New Zealand and from the Mellor Research Fund. Analyses were by the microanalytical laboratory of this Department, under the direction of Dr. A. D. Campbell.

CHEMISTRY DEPARTMENT, UNIVERSITY OF OTAGO,
DUNEDIN, NEW ZEALAND.

[*Received, May 31st,* 1963.]

1156. *Simple Syntheses of Cyclic Phosphate Esters.*

By A. M. MESTON.

PHENYL trimethylene phosphate has been prepared by a method that is simpler than the two previously used;[1,2] the new method, involves the reaction of trimethylene glycol with phenyl phosphorodichloridate: a cyclic phosphate is formed, even when an excess of glycol is present. The method has been applied also to three other examples.

The reaction of certain 1,3-glycols with polyphosphoric acid has been found to be another simple route to cyclic phosphate esters. An earlier example of this was given by Mosher and his co-workers.[3]

[1] Khorana, Tener, Wright, and Moffat, *J. Amer. Chem. Soc.*, 1957, **79**, 430.
[2] Keay and Crook, *J.*, 1961, 710.
[3] Mosher, Reinhart, and Prosser, *J. Amer. Chem. Soc.*, 1953, **75**, 4899.

Experimental.—Phenyl trimethylene phosphate. Phenyl phosphorodichloridate (21·1 g., 0·1 mole) was added dropwise to a cooled, stirred solution of trimethylene glycol (36 g., 0·4 mole) and pyridine (16 g., 0·2 mole) in dry acetone. The mixture was then refluxed for 2 hr., cooled, filtered, added to benzene, washed with water, and dried. The solvent was removed, to give an oil, which gradually afforded needles of phenyl trimethylene phosphate, m. p. 75° (lit., 76°,[1] 74—75° [2]) (from ether–light petroleum or water) (Found: C, 50·6; H, 5·2; P, 14·6. Calc. for $C_9H_{11}O_4P$: C, 50·6; H, 5·15; P, 15·0%).

Under similar conditions, phenyl phosphorodichloridate (21·1 g., 0·1 mole) and tetramethylene glycol (18 g., 0·2 mole) form *phenyl tetramethylene phosphate*, m. p. 61—63° (from ether) (Found: C, 52·85; H, 5·55. $C_{10}H_{13}O_4P$ requires C, 53·0; H, 5·7%). OO-*Methylenepentaerythritol phenyl phosphate* (5,5-*bishydroxymethyl*-1,3-*dioxan phenyl phosphate*) was prepared from phenyl phosphorodichloridate (21·1 g., 0·1 mole) and *OO*-methylenepentaerythritol (29·6 g., 0·2 mole). It formed thick needles, m. p. 173—175°, from water, or ethanol (Found: C, 50·6; H, 5·2. $C_{12}H_{15}O_6P$ requires C, 50·4; H, 5·2%).

p-*t-Octylphenyl trimethylene phosphate.* *p*-t-Octylphenyl phosphorodichloridate (64·6 g., 0·2 mole) was added dropwise to trimethylene glycol (76 g., 1·0 mole), and the mixture was set aside for 16 hr., then dissolved in ether. The ether solution was washed with water, dried, and evaporated. The residual *ester* recrystallised from benzene–light petroleum, yielding plates, m. p. 89° (Found: C, 62·4; H, 8·2; P, 9·5. $C_{17}H_{27}O_4P$ requires C, 62·6; H, 8·3; P, 9·5%).

2,2-*Dimethyltrimethylene hydrogen phosphate.* 2,2-Dimethyltrimethylene glycol (10 g.) was dissolved in polyphosphoric acid [from phosphorus pentoxide (31 g.) and 90% phosphoric acid (20 ml.)],and the solution heated for 16 hr. on the steam-bath, then poured into water. Crystals (5·5 g.) slowly separated. They were collected and recrystallised from xylene or water (charcoal), to give needles, m. p. 172—174° (Found: C, 36·45; H, 6·3; P, 18·7%; *M*, 168; Equiv., 165. Calc. for $C_5H_{11}O_4P$: C, 36·15; H, 6·6; P, 18·7%; *M*, 166; Equiv., 166). McConnell and Coover [4] isolated a similar compound, m. p. 174°, which they formulated as a monohydrate, $C_5H_{11}O_4P,H_2O$. The compound prepared by the method described above is, however, anhydrous: a sample recrystallised from water and dried over sulphuric acid at 18°/760 mm. gave only one active hydrogen on Zerewitinoff estimation (Found: Active H, 0·7. Calc. for $C_5H_{11}O_4P$: Active H, 0·6. Calc. for $C_5H_{11}O_4P,H_2O$: Active H, 1·1%).

2,2-*Di(chloromethyl)trimethylene hydrogen phosphate.* 2,2-Di(chloromethyl)trimethylene glycol (22 g.) was dissolved in polyphosphoric acid [from phosphorus pentoxide (93 g.) and 90% phosphoric acid (60 ml.)], and the solution heated at 100° for 16 hr., then poured into water. No precipitate appeared. The aqueous solution was extracted with ether. From the ether extract, there was obtained an oil which slowly crystallised. This *product*, recrystallised from benzene (charcoal), had m. p. 145—148° (Found: C, 25·6; H, 3·6; P, 13·0%; Equiv., 235. $C_5H_9Cl_2O_4P$ requires C, 25·5; H, 3·8; P, 13·2%; Equiv., 235).

I thank the Microanalytical Section of this Department for carrying out the analyses.

RESEARCH AND DEVELOPMENT DEPARTMENT,
IMPERIAL CHEMICAL INDUSTRIES LIMITED, NOBEL DIVISION,
STEVENSTON, AYRSHIRE. [*Received, May 31st*, 1963.]

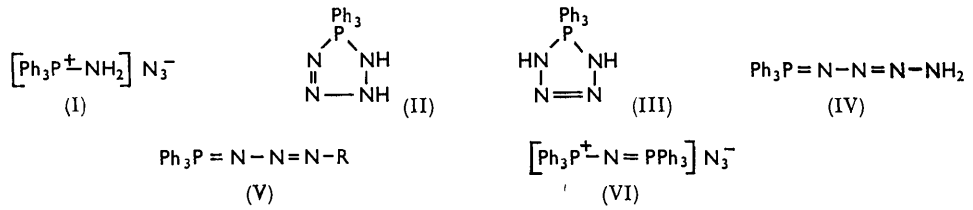
[4] McConnell and Coover, *J. Org. Chem.*, 1959, **24**, 630.

1157. *Pyrolysis of Triphenylphosphiniminium Azide.*

By R. C. Cookson and A. N. Hughes.

Triphenylphosphine reacts [1] with hydrazoic acid to give a compound of formula $Ph_3P{:}NH,HN_3$. Staudinger and Hauser [1] state that this compound is not a salt since it does not give azide reactions, although Horner and Oediger [2] list it as triphenylphosphiniminium azide. Accepting Staudinger and Hauser's report, Leffler *et al.*[3] put forward a cyclic structure such as (II) or (III) and suggested that similar intermediates occur in the reaction of hydrazoic acid with triphenylmethyl azide–triphenylphosphine complexes. Another possible structure is (IV).

However, we found that a cold aqueous solution of the compound gives an immediate white precipitate with aqueous silver nitrate or lead acetate and, more conclusively, gives an immediate blood-red colour with ferric chloride, thus showing that azide ion is in fact present. Moreover, the infrared spectrum (Nujol mull) shows a very strong absorption at 2020 cm.$^{-1}$ which is inconsistent with structures (II), (III), and (IV).



(I) (II) (III) (IV)

(V) (VI)

There is no longer any reason to doubt that Staudinger and Hauser's compound is the simple azide salt (I). So hydrogen azide seems to react with triphenylphosphine like aryl azides: in each case the imine is formed, perhaps by loss of nitrogen from an initial adduct (V; R = H or aryl), but in the case of hydrazoic acid a second molecule is then bound in the form of the salt (I).

Pyrolysis of the azide (I) at 200—210° under nitrogen yields ammonium azide as a sublimate and a residue of a compound $(Ph_3P)_2N_4$ which can be crystallised from water and polar organic solvents, gives azide reactions, is hydrolysed in alkaline, but not acid, conditions to give triphenylphosphine oxide, and has strong infrared absorption at 2020 cm.$^{-1}$. This evidence strongly suggests that it has structure (VI). The " bistriphenylphosphinenitride " cation, $PPh_3{:}N{\cdot}PPh_3^+$, has previously been prepared by Appel and Hauss [4] as the bromide by the action of triphenylphosphine dibromide on triphenylphosphinimine. The product of pyrolysis was converted into the bromide, which was identical with Appel and Hauss's salt.[4] The purity of the pyrolysis residue, estimated by conversion into the perchlorate, which is readily purified with little loss, was at least 90%.

The reaction probably proceeds by initial loss of hydrazoic acid to give triphenylphosphinimine which then attacks unchanged salt to give the azide (VI) and ammonia.

Experimental.—" *Bistriphenylphosphinenitride azide* " [*triphenyl(triphenylphosphoranylideneamino)phosphonium azide*]. Triphenylphosphiniminium azide [1] (1 g.) was heated rapidly to 200° in a current of nitrogen and kept at 200—210° for 20 min. Ammonium azide (*ca.* 45 mg., 50%) collected as a sublimate and was identified by tests for ammonium and azide ion and by comparison of its infrared spectrum with that of sodium azide. The crude residue (m. p. 206—209°) recrystallised from acetone (or water), to give " *bistriphenylphosphinenitride azide* "

[1] Staudinger and Hauser, *Helv. Chim. Acta*, 1921, **4**, 861.
[2] Horner and Oediger, *Annalen*, 1959, **627**, 142.
[3] Leffler, Honsberg, Tsuno, and Forsblad, *J. Org. Chem.*, 1961, **26**, 4810.
[4] Appel and Hauss, *Z. anorg. Chem.*, 1961, **311**, 290.

(VI) (0·62 g.), m. p. 214—216°, as colourless plates (Found: C, 74·1; H, 5·4; N, 9·6; P, 11·0. $C_{36}H_{30}N_4P_2$ requires C, 74·5; H, 5·2; N, 9·7; P, 10·7%), $\nu_{max.}$ 698, 722, 750, 802, 998, 1120, 1268, 1441, and 2020 cm.$^{-1}$.

The azide (1 g.) was dissolved in hot water (60 ml.), and 48% hydrobromic acid (5 ml.) was added. On cooling, the solution deposited crystals (0·7 g.) of the bromide, m. p. and mixed m. p. 253—255° (lit.,[4] 256°) (Found: C, 69·7; H, 4·8; N, 2·4; P, 10·3; Br, 12·7. Calc. for $C_{36}H_{30}BrNP_2$: C, 69·9; H, 4·9; N, 2·3; P, 10·0; Br, 12·9%). The infrared spectra of this and an authentic sample were identical.

The crude azide (0·5 g.) was dissolved in hot methanol (10 ml.), and a few drops of 70% perchloric acid were added. On cooling, the solution deposited colourless needles (0·47 g.), of the *perchlorate*, m. p. 264—266° (Found: C, 67·7; H, 5·0; N, 2·1; P, 10·0; Cl, 5·8. $C_{36}H_{30}ClNO_4P_2$ requires C, 67·8; H, 4·7; N, 2·2; P, 9·7; Cl, 5·6%).

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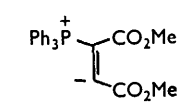
THE UNIVERSITY, SOUTHAMPTON. [*Received, June 4th,* 1963.]

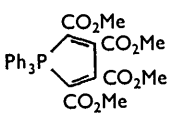
1158. *Synthesis of a Pyrazole by Removal of Oxygen from an Ester-carbonyl Group with Triphenylphosphine.*

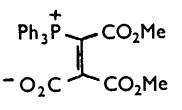
By R. C. COOKSON and J. M. LOCKE.

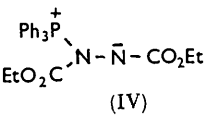
TRIPHENYLPHOSPHINE reacts rapidly with dimethyl acetylenedicarboxylate to give a bis-adduct (II), that soon rearranges with migration of a phenyl group.[1] Johnson and Tebby's success in diverting the reaction to the compound (III) in the presence of carbon dioxide justifies the guess that the dipole (I) is an intermediate.

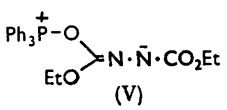
Triphenylphosphine, diethyl azodicarboxylate, and water rapidly give triphenylphosphine oxide and diethyl hydrazodicarboxylate:[2] the analogous dipole (IV) seemed a possible intermediate here, which could add water before undergoing elimination of triphenylphosphine oxide (see VII).

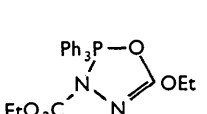

(I)

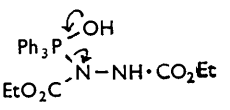

(II)

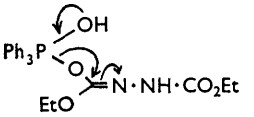

(III)


(IV)


(V)


(VI)

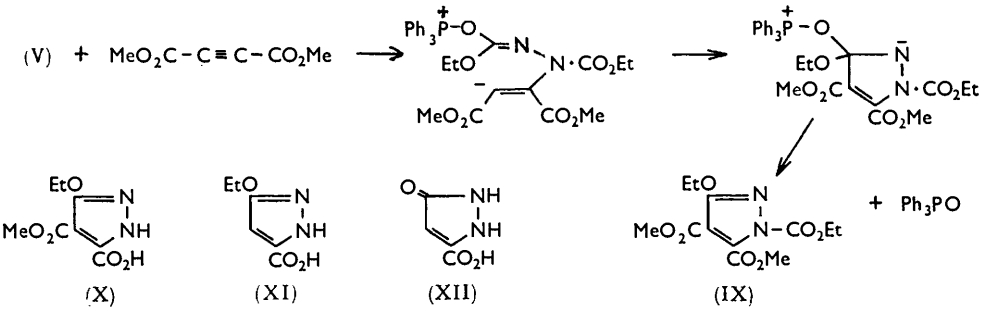

(VII)


(VIII)

We made some experiments to find whether the hypothetical 1 : 1 adducts (I and IV) would add other dipolarophiles[3] to form five-membered heterocyclic compounds (cf. II) or products of their subsequent rearrangement. In fact, triphenylphosphine, dimethyl acetylenedicarboxylate, and diethyl azodicarboxylate reacted in dioxan to give triphenylphosphine oxide and a product whose analyses corresponded to (azo-ester + acetylene-ester − O). Since triphenylphosphine was unchanged in dioxan solution in the absence

[1] Johnson and Tebby, *J.*, 1961, 2126.
[2] Morrison, *J. Org. Chem.*, 1958, **23**, 1072.
[3] Cf. Huisgen, *Proc. Chem. Soc.*, 1961, 357.

of the two esters, and in any case the course of the reaction was not affected by exclusion of oxygen and water, the oxygen atom appearing in the oxide must have come from one of the esters: $Ph_3P + C_6H_6O_4 + C_6H_{10}O_4N_2 \longrightarrow Ph_3PO + C_{12}H_{16}O_7N_2$.



The product (A) had peaks in its infrared spectrum expected for ether, ester, and C=N groups, but no NH absorption. The probable presence of a pyrazole nucleus was indicated by acid hydrolysis to pyrazolone-5-carboxylic acid (XII). Dilute sodium hydroxide gave an acid still containing an ethoxy-group, but no ester. Further hydrolysis with acid again produced the pyrazolone acid (XII), so the ethoxy-acid from alkaline treatment must be (XI). The initial product (A) contains two more ester groups, and can therefore only be the fully substituted pyrazole (IX). Methanolic alkali hydrolysed it to an ethoxy-ester-acid, either (X) or the isomer with ester and carboxyl groups interchanged.

The first step in this unusual reaction may be formation of the acetylene-adduct (I) or, more probably, one of the azo-adducts (IV—VI). The attached scheme, involving (V), seems simplest, and the same adduct (V) may equally be the intermediate in oxidation of triphenylphosphine with the azo-ester and water (VIII rather than VII as first assumed).

Experimental.—Infrared spectra of Nujol mulls were measured on a Unicam S.P. 100 spectrometer.

4,5-Dimethyl 1-ethyl 3-ethoxypyrazole-1,4,5-tricarboxylate (IX). Triphenylphosphine (1·31 g., 0·005 mole) in dry dioxan (10 ml.) was added during 15 min. to dimethyl acetylenedicarboxylate (0·72 g., 0·005 mole) and diethyl azodicarboxylate (0·87 g., 0·005 mole) in dry dioxan (20 ml.). After 24 hours' boiling, the dioxan was evaporated and the red oil that remained was triturated with ether (10 ml.). The triphenylphosphine oxide that separated was filtered off and washed with ether. Chromatography of the ether solution on silica gel gave the *pyrazole* (IX) (0·74 g., 49%), m. p. 92·5—93·5° [from light petroleum (b. p. 60—80°)], $\nu_{max.}$ 1060, 1580, and 1755 cm.$^{-1}$ (Found: C, 48·2; H, 5·6; N, 9·4. $C_{12}H_{16}N_2O_7$ requires C, 48·0; H, 5·4; N, 9·3%).

Chloroform eluted triphenylphosphine oxide, which, with the previous sample (total 0·82 g., 59%), had m. p. 151—155°.

Alkaline hydrolysis. The triester (IX) (0·5 g.) in N-methanolic potassium hydroxide (25 ml.) was boiled for 2 hr., then neutralised with dilute hydrochloric acid, and the product (0·28 g., 80%) was removed by filtration. After crystallisation from ethanol the *acid-ester* melted at 208—210° and had $\nu_{max.}$ 1063, 1610, 1715, and 3255 cm.$^{-1}$ (Found: C, 45·0; H, 4·7; N, 12·7. $C_8H_{10}N_2O_5$ requires C, 44·9; H, 4·7; N, 13·1%).

After 4 hours' boiling, a solution of the triester (IX) (1·0 g.) in 10% aqueous sodium hydroxide (30 ml.) was neutralised. Carbon dioxide was given off. Evaporation of an ether extract left *3-ethoxy-1H-pyrazole-5-carboxylic acid* (XI) (0·22 g., 42%), m. p. 162—164° (from toluene or water), $\nu_{max.}$ 1045, 1570, 1695, 1710, and 3280 cm.$^{-1}$ (Found: C, 46·3; H, 5·25, N, 16·85. $C_6H_8N_2O_3$ requires C, 46·15; H, 5·2; N, 17·9%).

Acid hydrolysis. The triester (IX) (0·48 g.) was boiled for 5 days in concentrated hydrochloric acid (20 ml.). Evaporation then left 5-oxo-3-pyrazoline-3-carboxylic acid (XII) (0·16 g., 100%), m. p. 270° (decomp.), mixed with authentic acid (XII) from hydrolysis of its ester,[4] m. p. 272°. The infrared spectra of the two samples were identical.

[4] v. Rothenburg, *Ber.*, 1893, **26**, 2055.

Hydrolysis of the ethoxy-acid (XI) in the same way for 2·5 days also gave the pyrazolone-acid (XII) in high yield.

J. M. L. gratefully acknowledges a NATO Fellowship administered by D.S.I.R.

CHEMISTRY DEPARTMENT,
THE UNIVERSITY, SOUTHAMPTON. [*Received, June 26th,* 1963.]

1159. *Orientation in the Nitration of 2,5-Dimethylacetophenone.*

By C. A. HOWE and (MRS.) A. HOWE.

SEVERAL 1,2,5-trisubstituted benzenes with a *meta*-directing substituent at position 1 and *ortho–para*-directing substituents at positions 2 and 5 have been reported to undergo nitration extensively (in most cases, predominantly) in the 6-position. It has been suggested that such substitution, which is not predicted by the classical rules, results from stabilization of the transition state, either by conjugation between the ring substituents[1] at positions 1 and 2, or by dipole–dipole interaction[2] between the entering electrophilic reagent and the substituent at position 1. The following compounds have been reported to exhibit this orientation: 2,5-dimethoxybenzaldehyde, 2,5-dialkoxyacetophenones, and 1,4-dimethyl-, 1,4-diethoxy-, and 1,4-dihalogeno-2-nitrobenzenes.[3] In contrast, the nitration of 2,5-dimethylacetophenone in mixed acid has been reported to yield a mixture of the 3- and 4-nitro-derivatives, with no 6-nitration.[4] The apparent discrepancy in orientation prompted us to undertake a quantitative study of this nitration.

We have found that in mixed acid nitration occurs in the 3- and the 6-position, the two mononitro-derivatives being formed in the ratio 1·3 : 1. No evidence of the 4-nitro-derivative was found, by fractional crystallization or by gas chromatography on a variety of columns under various conditions. When 2,5-dimethylacetophenone was treated with concentrated nitric acid alone, no ring-substitution occurred. Prolonged treatment led to the formation of bis-(2,5-dimethylbenzoyl)furoxan. In contrast, 2,5-dialkoxyacetophenones undergo ring-substitution readily under these conditions.[3b]

Experimental.—Quantitative gas chromatography was carried out by using a 12 ft. column (internal diameter 4 mm.) packed with 20% D–C silicone grease on Chromosorb P, at 200°; benzil was used as the internal standard; response factors were determined with artificial mixtures; peak areas were measured with a planimeter.

Nitrations in mixed acid. A mixture of concentrated sulphuric acid (3·0 ml.) and concentrated nitric acid (*d* 1·42; 2·0 ml.) was added to a solution of 2,5-dimethylacetophenone[5] (3·58 g.), b. p. 85—87°/2 mm., n_D^{20} 1·5297, in concentrated sulphuric acid (7·5 ml.) at −20° during 40 min. The mixture was then poured on ice and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution and water. The pale yellow, viscous residue (3·54 g.) obtained on removal of the solvent, yielded, on fractional crystallization from ethanol, two mononitro-derivatives, shown by their infrared spectra and by gas chromatography to be free from each other. One of these was obtained as white plates, m. p. 53° (Found: C, 61·8; H, 5·8; N, 7·5. $C_{10}H_{11}NO_3$ requires C, 62·2; H, 5·7; N, 7·3%). This was shown to be 3,6-*dimethyl-2-nitroacetophenone* by bromination in chloroform in the presence of ultraviolet light, followed by treatment with yellow ammonium sulphide solution to give a dark blue product with typical indigoid properties.[3b] The other mononitro-isomer was

[1] Dewar, *J.*, 1949, 463.
[2] Hammond, Modic, and Hedges, *J. Amer. Chem. Soc.*, 1953, **75**, 1388.
[3] (*a*) Rubenstein, *J.*, 1925, **127**, 1998; (*b*) Howe, Pecore, and Clinton, *J. Org. Chem.*, 1962, **27**, 1923; (*c*) Kobe and Levin, *Ind. Eng. Chem.*, 1950, **42**, 356; (*d*) Nietzki and Rechberg, *Ber.*, 1890, **23**, 1211; (*e*) Hammond, Modic, and Hedges, ref. 2.
[4] Buu-Hoï, Eckert, and Royer, *J. Org. Chem.*, 1952, **17**, 1000.
[5] Freund and Fleischer, *Annalen*, 1918, **414**, 5.

obtained as white needles, m. p. 83° (Found: C, 62·3; H, 5·8; N, 7·2%). This failed to yield an indigotin and was shown to be 2,5-*dimethyl*-3-*nitroacetophenone* by conversion with hypochlorite into 2,5-*dimethyl*-3-*nitrobenzoic acid*, white needles (from ethanol), m. p. 168—170° (Found: C, 55·2; H, 4·5; N, 7·3. $C_9H_9NO_4$ requires C, 55·4; H, 4·7; N, 7·2%). The latter compound was demonstrated to differ from 2,5-dimethyl-4-nitrobenzoic acid,[6] white needles (from ethanol), m. p. 164—166° (lit.,[6] m. p. 165·5—166·5°) (Found: C, 55·4; H, 4·5; N, 7·2%), by a mixed m. p. determination and comparison of infrared spectra. Gas chromatography showed that the 3·54 g. of nitration product contained 1·83 g. (52%) of 2,5-dimethyl-3- and 1·40 g. (40%) of 3,6-dimethyl-2-nitroacetophenone, with 0·20 g. (6%) of unchanged 2,5-dimethylacetophenone. A second nitration, carried out in identical conditions, gave essentially the same results. Higher temperatures caused tar formation and lower yields of the two mononitro-derivatives.

Nitrations in nitric acid. 2,5-Dimethylacetophenone (3·55 g.) was added with stirring to concentrated nitric acid (*d* 1·42) (20 ml.) at 0° during 15 min. The mixture was stirred for 24 hr. at 0°, then quenched and extracted by the procedure described in the preceding section. Gas chromatography of the crude product showed neither mononitro-derivative to be present. Recrystallization from methanol gave *bis*-(2,5-*dimethylbenzoyl*)*furoxan* (0·75 g.), white needles, m. p. 145—146° (Found: C, 68·2; H, 5·1; N, 8·2. $C_{20}H_{18}N_2O_4$ requires C, 68·6; H, 5·2; N, 8·0%), with an infrared spectrum characteristic of the furoxan structure.[7] In a second nitration the reaction time was shortened to 2·5 hr.; gas chromatography showed the product to consist almost entirely of starting material; neither mononitro-derivative was present.

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[6] Fisher and Walling, *J. Amer. Chem. Soc.*, 1935, **57**, 1700.
[7] Boyer, Czerniak, Gutowsky, and Snyder, *J. Amer. Chem. Soc.*, 1955, **77**, 4238.

1160. *The Mechanism of Epoxide Reactions. Part VI.*[1] *The Reactions of Benzylamine with a Series of* meta- *and* para-*Substituted* 1,2-*Epoxyethylbenzenes in Methanol.*

By R. M. Laird and R. E. Parker.

The reactions of benzylamine with a series of *meta*- and *para*-substituted 1,2-epoxyethylbenzenes, previously studied at three temperatures in 99·8% ethanol,[2] have now been studied in 99·8% methanol at 40°, and the results for both solvents are collected in Table 1. The techniques used were as before and, for the 3,4-dimethyl and the *m*-trifluoromethyl compounds, the reactions have been shown to be of the first order each in oxide and in amine. The rate constants are higher in methanol than in ethanol for all the abnormal reactions and for all the normal reactions except those of the *p*-bromo- and the *m*-chloro-compound. These greater rates in methanol are the expected result of a change to a solvent of higher dielectric constant, since the reactions all involve creation of charge in the formation of the transition state.[3] It is noticeable that the rate changes are greatest for reactions producing a minor isomer, *e.g.*, the normal reaction of the 3,4-dimethyl compound or the abnormal reaction of the *m*-trifluoromethyl compound. Consequently, there is a levelling effect and the Hammett ρ values for the normal and the abnormal reactions are both nearer to zero in methanol than in ethanol (Table 2).

[1] Part V, Addy and Parker, *J.*, 1963, 915.
[2] Laird and Parker, *J. Amer. Chem. Soc.*, 1961, **83**, 4277.
[3] Hughes and Ingold, *J.*, 1935, 252.

TABLE 1.

Rate constants, proportions of normal isomers, and rate constants for normal and abnormal attack for the reactions of benzylamine with substituted 1,2-epoxyethylbenzenes (k's in l. mole^{-1} sec.$^{-1}$).

	In methanol				In ethanol			
		Normal isomer				Normal isomer		
Subst.	10^5k_2	(%)	10^5k_N	10^5k_A	10^5k_2	(%)	10^5k_N	10^5k_A
3,4-Me_2 ...	11·80	30	3·54	8·26	6·91	20	1·41	5·50
p-Me	8·34	47	3·92	4·42	6·11	45	2·74	3·37
m-Me	7·29	61	4·45	2·84	4·91	51	2·51	2·40
H §	9·15	62	5·67	3·48 *	6·28	78	4·90	1·38 *
m-MeO ...	9·68	57	5·52	4·16	7·95	66	5·26	2·69
p-Br	7·49	63	4·72	2·77 *	8·66	81	7·00	1·66 *
m-Cl	9·03	72·5	6·55	2·48	7·94	92	7·28	0·66 *
m-CF_3	7·43	78	5·80	1·63 †	6·19	89	5·50	0·69 ‡

* Estimated ±20%. † Estimated ±25%. ‡ Estimated ±40%. Others, estimated ±10% or less. § Reaction in methanol, unpublished work by Parker and Rockett.

This levelling effect may also be considered to be the expected result of a change to a solvent of higher dielectric constant, since the energy necessary to produce the charged transition state from the uncharged reactants will be smaller in the solvent of higher dielectric constant, and changes in this energy brought about by variation of the substituent are also likely to be smaller (*i.e.*, the reactions in methanol are faster and less affected by substituents).

The presence of a partial positive charge on the attacked carbon atom (conjugated with the benzene ring) in the transition state for the abnormal reactions [2] is again clearly shown by the better correlation with σ^* than with σ. The most striking result, however, is the large change in selectivity between normal and abnormal attack (ρ_N/ρ_A) with change of solvent, from 0·76 in ethanol to 0·43 in methanol. This may be contrasted with the very much smaller change, from 0·78 to 0·72, that results from a 40° change in temperature for the reactions in ethanol [2] (where the levelling effect, bringing ρ_N and ρ_A nearer to zero, is comparable).

Selectivity between normal and abnormal attack is determined by the interplay of steric and electronic factors. As the abnormal position is the more hindered, steric factors will inhibit abnormal attack, but, because the benzylamine molecules will be hydrogen-bonded to solvent molecules [4] and will therefore be effectively smaller in methanol, a greater

TABLE 2.

Values of ρ for the normal and the abnormal reactions of benzylamine with a series of substituted 1,2-epoxyethylbenzenes at 40° (ρ is the slope of the line of regression of log k on σ or σ^*, as appropriate †).

Reaction	Solvent	Substituent constant	ρ	Correlation coefficient	Standard deviation
Normal	Methanol	σ	+0·30	0·847	0·048
Abnormal	,,	σ	−0·70	0·864	0·118
Abnormal	,,	σ^*	−0·61	0·889	0·085
Normal	Ethanol	σ	+0·87	0·903	0·114
Abnormal	,,	σ	−1·15	0·912	0·143
Abnormal	,,	σ^*	−1·11	0·943	0·113

† For σ, see Jaffé, *Chem. Rev.*, 1953, **53**, 191; for σ^*, see Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913; 1958, **80**, 497.

proportion of abnormal attack would be expected in this solvent than in ethanol. This is, in fact, the case for most of the oxides and it can be clearly seen in the reaction of 1,2-epoxyethylbenzene itself (22% abnormal isomer in ethanol, 38% in methanol).

[4] Trotman-Dickenson, *J.*, 1949, 1293; Hall, *J. Amer. Chem. Soc.*, 1957, **79**, 5441.

That the reduction in the steric effect is not the only result of the change of solvent can be seen from the reaction of, for example, the 3,4-dimethyl compound, where there is less abnormal product in methanol (70%) than in ethanol (80%). This must indicate that electronic factors are also operating and two such factors seem likely. The first of these is the stronger hydrogen-bonding to the epoxide oxygen atom by the more acidic methanol,[5] which would accelerate the abnormal more than the normal reaction, since the abnormal transition state is more S_N1-like and therefore more susceptible to such acceleration (cf. the increased proportion of abnormal isomer in the acid-catalysed reactions of epoxides [1]). However, this effect is in the same direction as the steric effect and could not therefore explain the results for the reaction of the 3,4-dimethyl compound.

A second electronic effect arises because of the greater distance between the substituent and the reaction centre in the normal reaction than in the abnormal reaction, and the consequently greater charge separation between the substituent and the reaction centre in the transition state for the normal reaction. This greater charge separation will be relatively more stabilised in the solvent of higher dielectric constant and hence a bigger proportion of normal product will be expected in methanol than in ethanol.

If it is assumed that the second electronic effect outweighs the first, it is then reasonable to suppose that the resultant electronic effect and the steric effect together determine the change of selectivity between normal and abnormal attack on change of solvent.

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THE UNIVERSITY, SOUTHAMPTON. [*Received, June 4th*, 1963.]

[5] Hine and Hine, *J. Amer. Chem. Soc.*, 1952, **74**, 5266.

1161. *A Xylan from Giant Star Grass* (Cynodon plectostachyus).

By R. J. MCILROY.

HEMICELLULOSES of a limited number of grasses and cereal straws have been studied, *e.g.*, cocksfoot grass,[1] esparto grass,[2] wheat straw,[3] wheat leaf,[4] and oat straw.[5] In general, these hemicelluloses contain a backbone of D-xylose residues to which L-arabinofuranose residues are linked as side-chains, usually to position 3 of D-xylose, while in many cases D-glucuronic acid or its 4-*O*-methyl ether also occurs linked to position 2 or 3 of the xylose.[6]

No study of the hemicelluloses of tropical pasture grasses has been recorded. An exploratory examination of the hemicellulose of giant star grass (*Cynodon plectostachyus*), a pasture grass of importance to the cattle industry in West and East Africa, is herein reported.

First-growth giant star grass, about 2 ft. in height, cut in September (late rains) after one year's growth, was extracted successively with boiling benzene–ethanol (2 : 1) to remove pigments, lipids, and soluble sugars, with water to remove soluble polysaccharides, and with 0·5% aqueous ammonium oxalate to remove pectic substances. Total hemicellulose extracted from the residual grass by N-sodium hydroxide and precipitated by acidified alcohol was delignified by acidified sodium chlorite solution. The polysaccharide,

[1] Aspinall and Cairncross, *J.*, 1960, 3877.
[2] Haworth, Hirst, and Oliver, *J.*, 1934, 1917; Bywater, Haworth, Hirst, and Peat, *J.*, 1937, 1983; Aspinall, Hirst, Moody, and Percival, *J.*, 1953, 1631.
[3] Adams, *Canad. J. Chem.*, 1952, **30**, 698; Ehrenthal, Montgomery, and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 5509; Aspinall and Meek, *J.*, 1956, 3830.
[4] Adams, *Canad. J. Chem.*, 1954, **32**, 186.
[5] Aspinall and Wilkie, *J.*, 1956, 1072.
[6] Aspinall, *Adv. Carbohydrate Chem.*, 1959, **14**, 437; *Ann. Rev. Biochem.*, 1962, **31**, 79.

purified by precipitation from aqueous solution with acetone, was apparently homogeneous. Decarboxylation gave 3—4% of uronic anhydride. Hydrolysis yielded xylose and arabinose (characterised as crystalline di-*O*-benzylidenexylose dimethyl acetal and arabinose diphenylhydrazone respectively), traces of glucose, and an acid oligosaccharide fraction (separated as barium salt). Upward mutarotation on hydrolysis indicated a predominance of β-glycosidic linkages. The sugar fraction contained 49% of xylose, estimated by the modified method of Breddy and Jones,[7,8] that indicated an ~1 : 1 ratio xylose : arabinose.

Mild acid-hydrolysis of the polysaccharide removed most of the arabinose, suggesting that the arabinose residues were present mainly in the furanose form.

Conversion of the barium salt into its methyl ester, reduction by potassium borohydride, and hydrolysis of the reduction product gave glucose, xylose, and arabinose, indicating that the resistant oligosaccharide fragment consisted of glucuronic acid linked to arabinose and xylose.

Cynodon hemicellulose appears to be a xylan consisting of a main chain of β-linked xylose residues to which are attached arabinofuranose residues as side-chains and an aldobiouronic acid containing residues of glucuronic acid, xylose, and arabinose. While the linkages in the polysaccharide remain to be determined these preliminary results indicate similarity to the xylans of other grasses and cereal straws.

Experimental.—Paper partition chromatography was carried out on Whatman No. 1 filter paper at *ca.* 25° with the following solvent systems (v/v): (A) ethyl acetate–acetic acid–water (3 : 1 : 3, upper layer); (B) butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3, upper layer); (C) ethyl acetate–pyridine–water (10 : 4 : 3); (D) butan-1-ol–ethanol–water (4 : 1 : 5, upper layer). Chromatograms were run for 24 hr. *p*-Anisidine hydrochloride was used as spray reagent. Evaporations were done *in vacuo* at below 50°.

Isolation of Cynodon *xylan.* First-growth giant star grass (400 g.), oven-dried and pulverised, was extracted with boiling benzene–ethanol (2 : 1; 4 l.) to remove pigments and lipids. The air-dried residual grass was extracted with (1) water (4 l.) at room temperature (4 hr.) and at 80° (4 hr.) to remove soluble polysaccharides and (2) 0·5% ammonium oxalate solution (4 l.) at 85° (2 × 4 hr.) to remove pectic substances, and was finally washed with hot water, ethanol, and ether successively and air-dried. The residual grass was then extracted twice with N-sodium hydroxide (4 l.; 2 × 48 hr.) at room temperature under nitrogen with occasional shaking. The combined extracts, acidified to pH 4—5 with glacial acetic acid, were poured into 90% ethanol (3 vol.) to precipitate crude total hemicellulose (110 g.). The product was delignified by acidified sodium chlorite solution.[9] Purification was effected by repeated dissolution in N-sodium hydroxide and reprecipitation of the acidified solution by ethanol. The impure polysaccharide (Found: ash, 8%) was dissolved in water at 60°, filtered, and reprecipitated by pouring the solution into acetone (5 vol.). This gave *Cynodon* xylan as a white powder (Found: ash, 2·0%; uronic anhydride by decarboxylation,[10] 3—4%), $[\alpha]_D^{25}$ −97·3° (*c* 0·51 in 4% sodium hydroxide). Attempts to separate the polysaccharide into significantly different fractions were unsuccessful.

Partial hydrolysis. Xylan (50·1 mg.) was heated in 0·02N-oxalic acid (25 ml.) for 3 hr. at 100°. Chromatography of the hydrolysate (solvents A and B) showed only arabinose, identical with a reference spot of L-arabinose on the same paper. Addition of ethanol (5 vol.) to the hydrolysate precipitated unhydrolysed xylan (31·0 mg.) which was heated with N-sulphuric acid (25 ml.) at 100° for 4 hr. Chromatography of the final hydrolysate (solvents A and B) showed the presence of xylose and a trace of arabinose. A yellow spot, R_{xylose} 0·07, near the origin indicated the presence of an aldobiouronic acid.

Hydrolysis by N-*sulphuric acid.* Xylan (5·0 g.) was heated with N-sulphuric acid (250 ml.) at 100° for 4 hr. {$[\alpha]_D^{24}$ +35° const. (*c* 2·0)}. The hydrolysate, filtered from a small amount of insoluble material, was neutralised with barium carbonate to Congo Red and filtered, and the

[7] Breddy and Jones, *J.*, 1945, 738.
[8] Wise and Ratliff, *Ind. Eng. Chem., Analyt. Edn.*, 1947, **19**, 694.
[9] Wise, Murphy, and D'Addieco, *Paper Trade J.*, 1946, **122**, No. 2, 35.
[10] Barker, Foster, Sidiqui, and Stacey, *Talanta*, 1958, **1**, 216.

insoluble matter was washed with water. The combined filtrate and washings were concentrated to *ca.* 50 ml. and poured into methanol (5 vol.). The precipitated barium salt (12·1 mg.) was washed with methanol. Evaporation of the filtrate and washings from the barium salt yielded a syrup, A (4·7 g.).

Examination of syrup A. Chromatography of syrup A in solvents B, C, and D showed the presence of xylose and arabinose as major components and traces of glucose. Xylose was characterised as di-*O*-benzylidenexylose dimethyl acetal, m. p. and mixed m. p. 212° (corr.), and arabinose as diphenylhydrazone, m. p. and mixed m. p. 204° (corr.). Quantitative estimation of the former sugar as di-*O*-benzylidenexylose dimethyl acetal by the method of Breddy and Jones [7] modified by Wise and Ratliff [8] gave 49% of xylose.

Examination of the barium salt. The salt (12 mg.) was refluxed with boiling 4% methanolic hydrogen chloride for 4 hr., to form the methyl ester. The product, after neutralisation with silver carbonate, was reduced with potassium borohydride (35 mg.) in water (5 ml.) for 20 hr. at 5°. The excess of hydride was destroyed by the addition of glacial acetic acid (3 drops), and the acid solution was shaken with Amberlite IR-120 and IR-4B for 30 min. The solution was filtered and the filtrate evaporated to dryness with frequent additions of methanol to remove borate by distillation. The residue was heated with N-sulphuric acid (3 ml.) at 100° for 5 hr. Chromatography of the hydrolysate in solvent B showed the presence of glucose and xylose, corresponding to reference spots of these sugars on the same paper, and a yellow spot, R_{xylose} 0·09, which was presumed to be unhydrolysed oligosaccharide. Hydrolysis of the reduction product by N-sulphuric acid at 100° was continued for a further 15 hr. and the hydrolysate again examined by chromatography. Three spots were observed, in solvents B, C, and D, corresponding to glucose, xylose, and arabinose applied as reference sugars.

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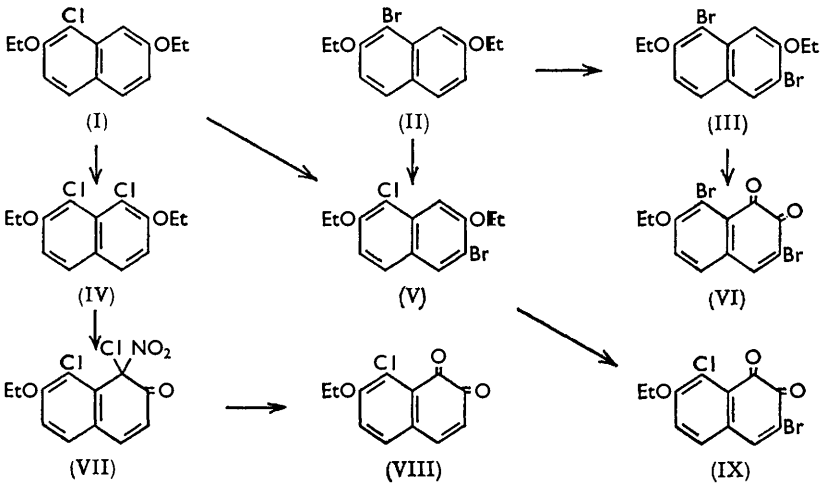
1162. *The Halogenation of 2,7-Diethoxynaphthalene.*

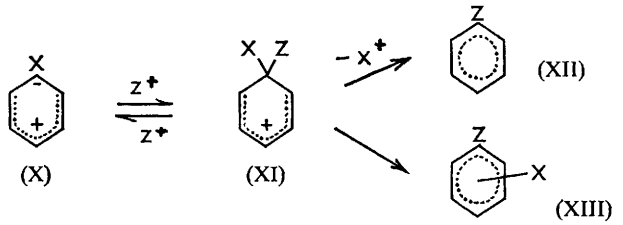
By F. BELL and K. R. BUCK.

THE series of reactions (I)—(IX) appears to establish that migration of bromine occurs in the change (II) ⟶ (V), for the following reasons. Compound (V) was shown to be uniform by gas chromatography. Compounds (I) and (II), (III) and (V), and (VI) and (IX) had infrared spectra which had the very closest resemblance to each other; on the other hand, the infrared spectrum of the 1,8-dichloro-compound (IV) differed sharply from that

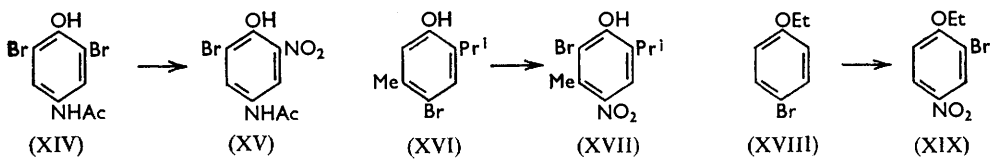


of the 1,6-dihalide (V), as also did that of the mono- (VIII) from that of the di-halogeno-quinone (IX). There was complete agreement of all the infrared bands of compound (V) prepared from the 1-chloro- (I) and from the 1-bromo-compound (II) (cf. Table).

We suggest that in this and similar changes the first step is localisation of electrons on the carbon atom to which the halogen is attached (X). Subsequent attack by an electrophilic species Z^+ can result in an intermediate (XI), possibly in equilibrium with the initial compound and an alternative (XII). The production of (XII) would set free the halogen but in certain compounds the halogen might be retained as a π-complex (XIII),



and from this it may be able to re-enter the nucleus in some alternative, appropriate position. The initial localisation of electrons in proximity to the halogen atom will be favoured by the presence of electron-donating groups, such as hydroxyl and ethoxyl, in either the *ortho*- or the *para*-position. Examples of these types of reaction are provided by the ready displacement of bromine from bromobenzene by chlorine [1] and by the conversion of the dibromo- (XIV) into the nitro-compound (XV).[2] Of the many examples of halogen displacement with migration may be instanced the conversions (XVI) ⟶ (XVII) [3] and (XVIII) ⟶ (XIX).[4] If the complex is produced in a polynuclear system, there is no necessity for the halogen to re-enter the nucleus in which it was originally situated and the present Note appears to provide an example of this type of migration.



It has usually been assumed [5] that tetrahalogenated 2,7-dihydroxy(and 2,7-dimethoxy)-naphthalenes carry the substituents in positions 1, 3, 6, 8 but it is now found that tetrabromo-2,7-dimethoxynaphthalene yields with nitric acid a tetrabromo-1,2-naphthaquinone. This could arise by migration of a bromine atom in the course of the oxidation, or it might indicate that a bromine atom is not present in position 8 in the starting material.

Experimental.—*2,7-Diethoxynaphthalene.* A mixture of 2,7-dihydroxynaphthalene (20 g.), diethyl sulphate (50 c.c.), acetone (200 c.c.), and freshly heated potassium carbonate (30 g.) was boiled for ½ hr. and the acetone removed in steam. Sodium hydroxide solution was added to the residue, and the insoluble part was crystallised from acetic acid. The coloured crop was dissolved in cold chloroform and filtered from coloured impurities, and the filtrate

[1] Eibner, *Ber.*, 1903, **36**, 1229.
[2] Robertson and Briscoe, *J.*, 1912, **101**, 1964; Gibbs and Robertson, *J.*, 1914, **105**, 1885.
[3] Robertson, *J.*, 1902, **81**, 1475.
[4] Reverdin, *Ber.*, 1899, **32**, 160.
[5] Ioffe and Fedorova, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 1079; Bell, Gibson, and Wilson, *J.*, 1956, 2335.

was evaporated. The residue, on recrystallisation from acetic acid, gave 2,7-diethoxynaphthalene as colourless plates, m. p. 104°.

Chlorination of 2,7-diethoxynaphthalene. (*a*) Sulphuryl chloride (1·9 g.) in chloroform (5 c.c.) was added dropwise to the compound (3 g.) in chloroform (15 c.c.). The chloroform was removed and the residue recrystallised from acetic acid, to yield the 1-*chloro-derivative* (I) as needles, m. p. 96—98° (Found: C, 66·9; H, 5·8. $C_{14}H_{15}ClO_2$ requires C, 67·0; H, 6·0%). (*b*) Procedure as in (*a*) but with more sulphuryl chloride (3·8 g.) gave the 1,8-*dichloro-derivative* (IV), m. p. 80° (Found: C, 58·9; H, 4·9. $C_{14}H_{14}Cl_2O_2$ requires C, 59·0; H, 4·9).

Bromination of 2,7-diethoxynaphthalene. (*a*) Bromine (2·2 g.) in chloroform (5 c.c.) was added dropwise to a solution of the compound (3 g.) in chloroform (15 c.c.). The chloroform was removed and the residue recrystallised from acetic acid, to give an impure 1-bromo-derivative (II) as needles, m. p. 95—97° (Found: C, 55·8; H, 4·9. Calc. for $C_{14}H_{15}BrO_2$:

Infrared bands (cm.$^{-1}$) for potassium bromide discs.

I	II	IV	V	III	VIII	IX	VI
			522				
			615				
670			675w			677s	
		720w			722w		
			735	738	740w	745w	742w
759	756	767					
793	790	780w	786s			788w	785w
			799	796s			
828vs	825vs	820s	824s	824	825w	818	818
838sh	838sh	840w	845	848		828	828
857	855		875		856s	845	845
894	892	900	883w	888s			906
			890w		908	908	918
930s	926s	933s	930	926s	943	918	942
992s	980s					968	
1014w	1010w		1010	1000			
			1020	1020	1020s	1020	1020
1050s	1050s	1052vs	1048s	1048s			
1065vs	1063s		1066s	1065s	1075w	1080	1075
1112s	1112s	1110s	1112s	1110s	1110	1110	1108
1130	1130					1136	1125
1160	1155	1160	1152w	1155w	1160		
1220vs	1220vs		1200	1200	1200	1205	1200
			1228vs	1230vs		1233	1230
1250s	1245s	1240s	1245s		1240vs		
1270s	1265s	1270vs	1260s	1260	1280vs	1282vs	1285vs
1318s	1310	1320vs	1300s	1295s	1305sh	1312	1310
1350s	1350s		1340s	1340s		1340w	1340w
			1360			1360w	1360w
1385s	1380s	1385	1385s	1380s	1388	1395	1395
1425	1420		1415	1410w	1408		
1455	1450	1445	1450	1445			
1475	1472	1470	1470	1470	1465s	1460	1455
1510vs	1510vs	1510vs	1500s	1495s			
			1590	1590	1550s	1550	1540
						1565	
						1595	1590
1630vs	1630vs	1620vs	1615s	1610s	1610		
					1660vs	1670vs	1670vs
					1700sh		

C, 56·9; H, 5·1%). Gas chromatography showed that the impurity was the dibromo-derivative, which was not eliminated by use of a wide variety of solvents, by sublimation, or by zone refining (which resulted in some decomposition). (*b*) Procedure as in (*a*) but with more bromine (4·4 g.) gave the 1,6-*dibromo-derivative* (III) as needles, m. p. 89—90° (Found: C, 45·1; H, 3·6. $C_{14}H_{14}Br_2O_2$ requires C, 44·9; H, 3·7%). Wilson [6] has given m. p. 154·5—155·5° for this compound but we believe he isolated 1,3-dibromo-2,7-diethoxynaphthalene.

[6] Wilson, *Tetrahedron*, 1960, **11**, 262.

6-*Bromo*-1-*chloro*-2,7-*diethoxynaphthalene*. (*a*) Bromine (1 g.) in chloroform (2 c.c.) was added dropwise to a solution of 1-chloro-2,7-diethoxynaphthalene (1·5 g.) in chloroform (10 c.c.). The chloroform was evaporated and the residue crystallised from acetic acid, to give 6-*bromo*-1-*chloro*-2,7-*diethoxynaphthalene* (V) as needles, m. p. 92—94° (Found: C, 51·4; H, 4·2. $C_{14}H_{14}BrClO_2$ requires C, 51·0; H, 4·2%). (*b*) Sulphuryl chloride (1 g.) in chloroform (2 c.c.) was added dropwise to 1-bromo-2,7-diethoxynaphthalene (2·2 g.) in chloroform (10 c.c.). The chloroform was evaporated and the residue crystallised from acetic acid. The crop gave an infrared spectrum identical with that of the compound from (*a*).

1,2-Naphthaquinones were prepared by addition of fuming nitric acid (1 c.c.) in acetic acid (4 c.c.) to the compound (1 g.) in warm acetic acid (5 c.c.). After ½ hr. the crop was removed and purified by recrystallisation from acetic acid. 1,6-Dibromo-2,7-diethoxynaphthalene gave 3,8-*dibromo*-7-*ethoxy*-1,2-*naphthaquinone* (VI) as maroon plates, m. p. 236° (Found: C, 40·2; H, 2·6. $C_{12}H_8Br_2O_3$ requires C, 40·0; H, 2·2%), which gave an emerald-green colour with sulphuric acid.

6-Bromo-1-chloro-2,7-diethoxynaphthalene gave 3-*bromo*-8-*chloro*-7-*ethoxy*-1,2-*naphthaquinone* (IX) as maroon plates, m. p. 247° (Found: C, 45·2; H, 2·6. $C_{12}H_8BrClO_4$ requires C, 45·6; H, 2·5%), which gave an emerald-green colour with sulphuric acid.

1,8-Dichloro-2,7-diethoxynaphthalene gave canary-yellow 1,8-*dichloro*-7-*ethoxy*-1,2-*dihydro*-1-*nitro*-2-*oxonaphthalene* (VII) as needles (from methanol) (Found: C, 47·9; H, 2·8. $C_{12}H_9Cl_2NO_4$ requires C, 47·7; H, 3·0%), $\nu_{max.}$ 680w, 722, 732, 796, 812, 842, 918, 1018, 1072, 1103, 1155, 1200, 1218, 1280vs, 1300, 1320, 1385, 1480, 1550, 1590vs, and 1690vs cm.$^{-1}$. Above 120° it evolved nitrosyl chloride and gave 8-*chloro*-7-*ethoxy*-1,2-*naphthaquinone* (VIII) as maroon plates, m. p. 220° (from *o*-dichlorobenzene) (Found: C, 60·2; H, 3·8. $C_{12}H_9ClO_3$ requires C, 60·9; H, 3·8%), which gave an emerald-green colour with sulphuric acid. The original mother-liquor contained 3-*nitro*-8-*chloro*-7-*ethoxy*-1,2-*naphthaquinone*, which crystallised from *o*-dichlorobenzene in copper-coloured plates, m. p. 265° (Found: C, 51·7; H, 2·8. $C_{12}H_8ClNO_5$ requires C, 51·2; H, 2·8%), which gave a violet colour with sulphuric acid and had $\nu_{max.}$ 762, 800, 822, 855, 908, 928, 978, 1020s, 1110, 1118, 1170, 1240s, 1283s, 1312, 1390, 1460, 1550s, 1610, and 1685s cm.$^{-1}$. This compound was obtained in almost quantitative yield by adding the dichloro-compound (1 g.) to a mixture of fuming nitric acid (5 c.c.) and acetic acid (5 c.c.) and then pouring the whole into water.

Tribromo-7-*methoxy*-1,2-*naphthaquinone*, from tribromo-2,7-dimethoxynaphthalene, formed red needles, m. p. 224° (Found: C, 30·9; H, 1·6. $C_{11}H_5Br_3O_3$ requires C, 31·1; H, 1·2%), $\nu_{max.}$ 694, 767, 839vs, 936, 953, 974, 1062, 1142, 1190, 1220w, 1260vs, 1328, 1370, 1460, 1520, 1555, and 1675vs cm.$^{-1}$. It gave an immediate yellow precipitate with *o*-phenylenediamine.

Tetrabromo-7-*methoxy*-1,2-*naphthaquinone*. Tetrabromo-2,7-dimethoxynaphthalene was added to cold fuming nitric acid and the dark red solution poured into water. The very sparingly soluble product was best recrystallised from *o*-dichlorobenzene, to give the 1,2-*naphthaquinone* as red needles, m. p. 236° (decomp.) (Found: C, 26·6; H, 1·5; Br, 64·4. $C_{11}H_4Br_4O_3$ requires C, 26·2; H, 0·8; Br, 63·5%), $\nu_{max.}$ 714, 742w, 799, 868, 899, 954, 983, 1074, 1155, 1192, 1242, 1268vs, 1332, 1356, 1380, 1445, 1495, 1520, 1600, and 1690vs cm.$^{-1}$. With *o*-phenylenediamine in acetic acid it gave an immediate precipitate of yellow needles, m. p. 228°

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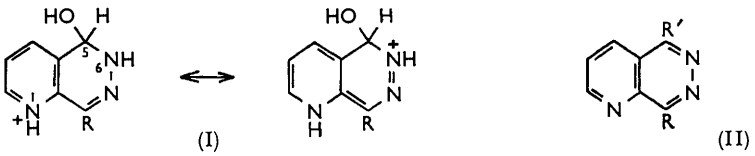
1163. *Triazanaphthalenes. Part V.*[1] *A Search for Covalent Hydration in 8-Methyl-1,6,7-triazanaphthalene.*

By W. L. F. Armarego.

The anhydrous nature of phthalazine, 1-methylphthalazine, and their cations in water has been deduced from ultraviolet spectroscopy.[2] This was confirmed in the present work by the constancy of the optical density, at several wavelengths, when acid solutions were rapidly neutralised by buffers of pH ~ 8·5. The high basicity of phthalazine (pK_a 3·50) was attributed to the high single-bond character of the N–N link.[2] No resonance would be possible in the cations of phthalazines, unlike that of quinazoline, if they were hydrated across position 1,2 or 3,4.

Electron-deficiency and resonance-stabilisation are two common properties found in heterocyclic nitrogen compounds which undergo covalent hydration.[3] It was therefore argued that if the benzene ring in phthalazine was replaced by a pyridine ring then, in addition to increasing the electron-deficiency in the pyridazine ring, a resonance-stabilised hydrated cation would be possible (*i.e.*, I; R = H). All attempts to prepare 1,6,7-triazanaphthalene from 5,8-dichloro-1,6,7-triazanaphthalene were unsuccessful. 8-Methyl-1,6,7-triazanaphthalene, however, was prepared, but, as with phthalazine and its 1-methyl derivative, ultraviolet spectra and rapid neutralisations showed no hydration in the neutral species or the cation in aqueous solution. It was, therefore, concluded that the parent substance (II; R = R′ = H) is also predominantly anhydrous because it was previously shown that a methyl group could effect very little dehydration (by its $-I$ effect) when it was not attached to the carbon atom involved in covalent hydration.[4] If the compound (I; R = H) were to be hydrated, water could add only across positions 5,6 in order to give a resonance-stabilised cation.



8-Methyl-1,6,7-triazanaphthalene was synthesised by the following sequence: 2-acetylnicotinic acid 1-oxide ⟶ 8-methyl-1,6,7-triazanaphthalene 1-oxide ⟶ (II; R = Me, R′ = OH) ⟶ (II; R = Me, R′ = Cl) ⟶ 8-methyl-5-(*N*′-toluene-*p*-sulphonylhydrazino)-1,6,7-triazanaphthalene hydrochloride ⟶ (II; R = Me, R′ = H). Attempts to dechlorinate substance (II; R = Me, R′ = Cl) by catalytic reduction with 5% palladium–charcoal, boiling with red phosphorus and hydriodic acid, or decomposing the 5-hydrazino-derivative with copper sulphate were unsuccessful. Decomposition of 5-(*N*′-toluene-*p*-sulphonylhydrazino)-derivative was satisfactory only with boiling 10% aqueous sodium carbonate solution. The structure (II; R = Me, R′ = Cl) was deduced from the similarity of the ultraviolet spectrum with that of the analogue (II; R = R′ = Cl) obtained from the diol (II; R = R′ = OH) of known structure, which was in turn prepared from quinolinic anhydride and hydrazine.[5] "2-Acetylnicotinic acid 1-oxide *p*-nitrophenylhydrazone anhydride" prepared by Bain and Saxton[6] is undoubtedly 8-methyl-6-*p*-nitrophenyl-5-oxo-1,6,7-triazanaphthalene 1-oxide.

[1] Part IV, Albert and Barlin, *J.*, 1963, 5737.
[2] Albert, Armarego, and Spinner, *J.*, 1961, 2689.
[3] Albert and Armarego, *J.*, 1963, 4237.
[4] Armarego, *J.*, 1962, 561; Albert, Howell, and Spinner, *J.*, 1962, 2595.
[5] Gheorghiu, *Bull. Soc. chim. France*, 1930, **47**, 630.
[6] Bain and Saxton, *J.*, 1961, 5216.

Experimental.—Microanalyses were by Dr. J. E. Fildes and her staff. The purity of materials was examined as before,[7] and evaporations were carried out in a rotary evaporator at 30°/15 mm. Physical measurements were made as before.[8]

Preparation of 1-methylphthalazine, as described recently,[9] resulted in poor yields due to losses incurred in the purification of the hydrochloride. It was more convenient to convert the product, isolated by sublimation or distillation (b. p. 124—125°/0·5—0·6 mm.), into its picrate with saturated ethanolic picric acid. The picrate (m. p. 204—205°; lit.,[10] m. p. 205°) was decomposed in the usual manner [11] with 5N-aqueous sodium hydroxide. The sublimed material (80% yield) gave one spot on paper chromatography (Whatman No. 1) in 3% ammonium chloride and in butan-1-ol–5N-acetic acid (3 : 1), and was deliquescent. It had m. p. 72—73° (lit.,[9] 70·5—71·5°) in a Pyrex capillary sealed in a dry-box (Found, for material handled in a dry-box: C, 75·2; H, 5·6; N, 19·2. Calc. for $C_9H_8N_2$: C, 75·0; H, 5·6; N, 19·4%).

5,8-*Dichloro*-1,6,7-*triazanaphthalene*. 5,8-Dihydroxy-1,6,7-triazanaphthalene [5] (3·26 g., 1 mol.), phosphorus pentachloride (9·16 g., 2·2 mol.), and phosphorus oxychloride (50 ml.) were refluxed until a clear solution was obtained (6—8 hr.). The solvent was removed *in vacuo*, and the residue treated with ice, neutralised with saturated sodium hydrogen carbonate, and extracted with chloroform. The residue obtained on evaporation of the dried (Na_2SO_4) extract, was passed in benzene through an alumina column (6 × 1 in.; B.D.H.), and eluted with benzene. Evaporation of the eluates, and recrystallisation of the residue from large volumes of light petroleum (b. p. 80—100°), gave 5,8-*dichloro*-1,6,7-*triazanaphthalene* (2·6 g., 65%) as needles, m. p. 163—164° (Found: C, 41·9; H, 1·5; Cl, 35·35. $C_7H_3Cl_2N_3$ requires C, 42·0; H, 1·5; Cl, 35·4%), $\lambda_{max.}$ 228 (log ε 4·27), 269 (log ε 3·77), and $\lambda_{infl.}$ 236 mμ (log ε 4·22) in aqueous buffer (pH 7·0). When the above preparation was repeated on ten times the scale, the yield decreased to 40%.

5-*Hydroxy*-8-*methyl*-1,6,7-*triazanaphthalene* 1-*oxide*. A suspension of 2-acetylnicotinic acid 1-oxide [6] (17 g., 1 mol.) in ethanol (50 ml.) and hydrazine hydrate (5·3 ml., 1·1 mol.) became clear after 5 min. at 100°. After 15 min., a white solid separated and heating was continued for 1 hr. The solid was collected, and recrystallisation from ethanol gave 5-*hydroxy*-8-*methyl*-1,6,7-*triazanaphthalene* 1-*oxide* (14·7 g., 88%) as colourless prisms, m. p. 274—275° (decomp.) (Found: C, 54·7; H, 4·0; N, 23·7. $C_8H_7N_3O_2$ requires C, 54·2; H, 4·0; N, 23·7%).

5-*Hydroxy*-8-*methyl*-1,6,7-*triazanaphthalene*. A suspension of the preceding *N*-oxide (3·0 g.) and phosphorus trichloride (25 ml.) was refluxed for 45 min. and the solvent removed *in vacuo*. The residue was treated with water, filtered off, and dried. Recrystallisation from ethanol gave 5-*hydroxy*-8-*methyl*-1,6,7-*triazanaphthalene* (2·5 g., 91%) as needles, m. p. 249—250° (Found: C, 59·8; H, 4·5. $C_8H_7N_3O$ requires C, 59·6; H, 4·4%. Dumas nitrogen analyses were low.)

5-*Chloro*-8-*methyl*-1,6,7-*triazanaphthalene*. 5-Hydroxy-8-methyl-1,6,7-triazanaphthalene 1-oxide (9·0 g.) and phosphorus trichloride (50 ml.) were refluxed for 35 min., phosphorus oxychloride (100 ml.) was added, and boiling continued for 45 min. Evaporation of the solvent at 60°/15 mm., followed by treatment of the residue as above for 5,8-dichloro-1,6,7-triazanaphthalene, gave, after recrystallisation from light petroleum (b. p. 60—80°), pale pink plates of 5-*chloro*-8-*methyl*-1,6,7-*triazanaphthalene* (6·0 g., 66%), m. p. 162—163° (Found: C, 53·3; H, 3·4; Cl, 19·6. $C_8H_6ClN_3$ requires C, 53·5; H, 3·4; Cl, 19·7%), $\lambda_{max.}$ 223 (log ε 4·33), 262 (log ε 3·71), and $\lambda_{infl.}$ 231 mμ (log ε 4·25) in aqueous buffer of pH 7·0. The chloro-compound was obtained in similar yield when 5-hydroxy-8-methyl-1,6,7-triazanaphthalene was used instead of the *N*-oxide.

5-*Hydrazino*-8-*methyl*-1,6,7-*triazanaphthalene*. 5-Chloro-8-methyl-1,6,7-triazanaphthalene (1·79 g., 1 mol.) in ethanol (30 ml.) and hydrazine hydrate (1·1 ml., 2·2 mol.) were allowed to react at 20° for 5 hr. The yellow crystals were filtered off and recrystallised from ethanol or concentrated aqueous solution, to give 5-*hydrazino*-8-*methyl*-1,6,7-*triazanaphthalene* (1·4 g., 80%), decomp. >180° (Found: C, 51·9; H, 5·5. $C_8H_9N_5\frac{1}{2}H_2O$ requires C, 52·2; H, 5·5%), $\nu_{max.}$ 782, 925, 1164, 1455, 1635, 1652, 3050, 3200, and 3300 cm.$^{-1}$ (KBr disc).

8-*Methyl*-1,6,7-*triazanaphthalene*. 5-Chloro-8-methyl-1,6,7-triazanaphthalene (2·8 g., 1 mol.)

[7] Armarego, *J.*, 1961, 2697.
[8] Armarego, *J.*, 1962, 4094.
[9] Stephenson, *J.*, 1963, 1913.
[10] Gabriel and Eschenbach, *Ber.*, 1897, **30**, 3022.
[11] Albert, Armarego, and Spinner, *J.*, 1961, 5267.

in chloroform (15 ml., B.P.) and toluene-*p*-sulphonylhydrazine (2·91 g., 1 mol.) in hot chloroform (20 ml.), were allowed to react at 20° for 6 days. The pale brown crystalline 8-methyl-5-(*N'*-toluene-*p*-sulphonylhydrazino)-1,6,7-triazanaphthalene hydrochloride separated quantitatively and was filtered off. This crude compound (2·5 g.) was heated in 10% aqueous solution of sodium carbonate (200 ml.) on a steam-bath for 30 min., then refluxed for 30 min. The cooled solution was extracted with chloroform, and the extract dried (Na_2SO_4) and evaporated. The red crystalline residue was passed, in benzene, through an alumina column (6 × 1 in. Merck, Standard). The column was eluted with benzene (1 l.) but evaporation of the eluates gave no residue and a second elution with chloroform–benzene (1 : 1) removed an orange band. Evaporation of this gave an orange solid which was dissolved in ethanol (3 ml.), diluted with light petroleum (b. p. 40—60°), and set aside at 0° for 48 hr. The orange crystals (m. p. 111—113°) were sublimed at 90—95°/0·02 mm. The colourless sublimate showed one spot on paper chromatography (as above) and, after recrystallisation from light petroleum (b. p. 60—80°), it gave 8-*methyl*-1,6,7-*triazanaphthalene* (0·40 g., 40%), m. p. 114—115° (Found, after 24 hr. in air: C, 66·3; H, 5·0; N, 29·0. $C_8H_7N_3$ requires C, 66·2; H, 4·9; N, 28·95%). It had pK_a 2·96 ± 0·04 (analytical wavelength 294 mμ, 1·25 × 10^{-4}M, ionic strength 0·01), $\lambda_{max.}$ 222 + *225* + *239*, 258 + *286* + *296* mμ (log ε 4·35 + *4·31* + *3·59*, 3·60 + *3·11* + *2·90*) in cyclohexane, $\lambda_{max.}$ *217* + *244*, 250 + *284* mμ (log ε *4·45* + *4·30*, 3·62 + *3·15*) in aqueous buffer of pH 6·0, and $\lambda_{max.}$ 216, 253 + *283* + *294* mμ (log ε 4·58, 3·62 + *3·30* + *3·14*) in aqueous hydrochloric acid of pH 0·80 (inflexions are in italics).

The *picrate*, prepared in benzene and recrystallised from methanol, had m. p. 173—174° (decomp.) (Found: C, 45·0; H, 2·9; N, 22·6. $C_{14}H_{10}N_6O_7$ requires C, 44·9; H, 2·7; N, 22·5%).

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1164. *Preparation of an Eighteen-membered Heterocycle.*

By R. P. Houghton.

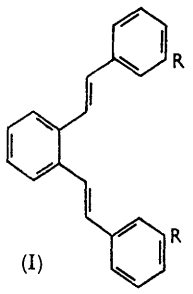
The preparation of the *trans-trans*-diacid (I; R = CO_2H) has recently been described [1] in connection with the synthesis of a macrocyclic bis-(1,3-diketone). The present Note concerns the conversion of this diacid into the eighteen-membered heterocycle (II) and the preparation of other compounds of type (I).

The method previously described for the preparation of the diacid (I; R = CO_2H) from *o*-phthalaldehyde and the diylide derived from methyl *m*-bromomethylbenzoate was modified to give a higher yield (93%; cf. 76%). The diacid was converted through its chloride into the dimethyl ester [1] (I; R = CO_2Me) which was reduced with lithium aluminium hydride to the diol (I; R = CH_2·OH). Oxidation with chromium trioxide in pyridine then gave the dialdehyde (I; R = CHO) which condensed with *o*-phenylenediamine in refluxing butan-1-ol to give the macrocyclic compound (II) as yellow needles, m. p. >360°. As the product was not sufficiently soluble in the common organic solvents to allow a molecular-weight determination by the usual methods, the derivative (III) was prepared by treatment with methyl-lithium and it gave the correct molecular weight (Rast).

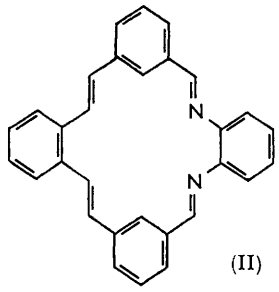
Although the eighteen-membered ring in compound (II) is completely conjugated, the system cannot be stabilised by resonance (cf. cyclo-octadecanonaene [2]) as it involves linkages in the *meta*-positions of two benzene rings.

[1] Coombs and Houghton, *J.*, 1961, 5015.
[2] Jackman, Sondheimer, Amiel, Ben-Efraim, Gaoni, Wolovsky, and Bothner-By, *J. Amer. Chem. Soc.*, 1962, **84** 4307.

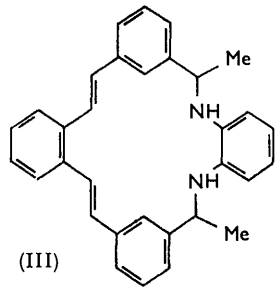
Treatment of the diol (I; R = CH_2·OH) with phosphorus tribromide afforded the dibromide which was converted into the hydrocarbon (I; R = Me) by reduction with lithium aluminium hydride in refluxing tetrahydrofuran, and also by treatment of the



(I)



(II)



(III)

bistriphenylphosphonium salt (I; R = CH_2·PPh_3^+ Br^-) with ethanolic lithium ethoxide, followed by water.

The ultraviolet absorption spectrum of compound (II) in chloroform has a very broad band with a maximum at 284 mμ (ε 51,500) and an inflexion at 322 mμ (ε 27,900). It is similar to spectra of the acyclic compounds (I) which show two bands at about 283 and 310 mμ (ε 37,000—40,000 and 27,000—29,000, respectively) and a band at shorter wavelengths if the substituents (R) are unsaturated and conjugated with the benzene rings.[1] The spectrum of the derivative (III) also shows these two absorption bands, but at slightly longer wavelengths ($\lambda_{max.}$ 288 and 326 mμ; ε 41,000 and 24,000), possibly owing to strain in the molecule.

Experimental.—ωω-o-*Phenylenedi*-(m-trans-*vinylbenzoic acid*). Lithium ethoxide (from lithium, 0·50 g.) in dry ethanol (100 ml.) was added in one portion to the triphenylphosphonium salt of methyl *m*-bromomethylbenzoate (29 g.) in dry ethanol (300 ml.) under nitrogen, and the mixture was stirred for 2 min. Phthalaldehyde (3·20 g.) was then added in small portions (~0·1 g.) with rapid stirring during 4 min. and the mixture was kept at room temperature for 18 hr. Ethanol (250 ml.) was distilled off and the acidic material was isolated as a viscous gum as described previously.[1] This was dissolved in benzene (75 ml.) containing iodine (20 mg.), and the solution was irradiated at reflux by a 1000-w bulb for 1½ hr. The mixture was cooled and filtered periodically, to give the diacid (8·21 g., 93%), m. p. 273—275° (lit.,[1] 277—278°).

ωω-o-*Phenylenedi*-(m-trans-*vinylbenzyl alcohol*) (I; R = CH_2·OH). A suspension of the dimethyl ester (I; R = CO_2Me) (6·07 g.) in tetrahydrofuran (100 ml.) was added with stirring to a refluxing suspension of lithium aluminium hydride (0·60 g.) in tetrahydrofuran (50 ml.). The mixture was refluxed for 30 min., then cooled and decomposed by water (400 ml.). Extraction with chloroform gave the *diol* (4·90 g., 94%), m. p. 106—107°, raised to 108—109° by recrystallisation from benzene (Found: C, 84·1; H, 6·3. $C_{24}H_{22}O_2$ requires C, 84·2; H, 6·5%), $\lambda_{max.}$ 282 and 321 mμ (ε 40,300 and 28,400, respectively) in ethanol.

ωω-o-*Phenylenedi*-(m-trans-*vinylbenzaldehyde*) (I; R = CHO). The foregoing diol (1·00 g.) in pyridine (10 ml.) was added to the complex prepared from chromium trioxide (1·90 g.) and pyridine (30 ml.), and the mixture was kept for 18 hr. The solid was filtered off and the filtrate was diluted with chloroform (100 ml.), kept at 0° for 30 min., and then filtered. The filtrate was passed through a column of alumina (Spence's type H, 40 g.) and the organic material was eluted with chloroform (200 ml.). The eluate was concentrated under reduced pressure to leave an oil which was dissolved in chloroform (25 ml.), washed with N-hydrochloric acid, and evaporated under reduced pressure, leaving the crude *dialdehyde* as a gum, b. p. 270—280° (bath)/0·1 mm., $\nu_{max.}$ (in $CHCl_3$) 2837, 2740, 1702, and 964 cm.$^{-1}$, $\lambda_{max.}$ 255, 285, and 315 mμ (Found: C, 85·0; H, 5·5. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·4%). The *mono*-2,4-*dinitrophenylhydrazone*, which was obtained by treatment with an excess of Brady's reagent at room temperature, crystallised from dioxan, and had m. p. 164—166° (decomp.) (Found:

C, 69·45; H, 4·45; N, 10·7. $C_{30}H_{22}N_4O_5$ requires C, 69·5; H, 4·3; N, 10·8%) and $\nu_{max.}$ 1701 cm.$^{-1}$.

Tetrabenzo[b,fg,k,op][1,4]*diazacyclo-octadecine* (II). The crude dialdehyde obtained from the diol (I; R = CH_2·OH) (1·00 g.) was refluxed with *o*-phenylenediamine (320 mg.) in butan-1-ol (100 ml.) for 3 hr., cooled, and filtered to give the *product* (630 mg., 53% based on diol) as yellow needles, m. p. >360°. A sample was recrystallised from chlorobenzene (Found: C, 87·9; H, 5·6; N, 7·0. $C_{30}H_{22}N_2$ requires C, 87·8; H, 5·4; N, 6·8%) which gave an infrared absorption spectrum almost indistinguishable from that of the crude material.

1,4,5,18-*Tetrahydro*-5,18-*dimethyltetrabenzo*[b,fg,k,op][1,4-*diazacyclo-octadecine* (III). Compound (II) (410 mg.) was extracted (Soxhlet) during 2 hr. into refluxing benzene (70 ml.) containing methyl-lithium prepared from methyl iodide (0·86 g.) and lithium (84 mg.) in ether (5 ml.). The mixture was cooled, water (100 ml.) was added, and the benzene layer was separated, washed with water, and evaporated under reduced pressure. The residue recrystallised from benzene to give the *diamine* (247 mg., 56%), m. p. 228—231° raised to 234—235° by two further recrystallisations from benzene (Found: C, 86·6; H, 6·7; N, 6·0%; *M*, 438. $C_{32}H_{30}N_2$ requires C, 86·9; H, 6·8; N, 6·3%; *M*, 443).

ωω-o-*Phenylenedi*-(m-trans-*vinylbenzyl bromide*) (I; R = CH_2Br). Phosphorus tribromide (2·0 ml.) was added to the diol (2·00 g.) in dry chloroform (50 ml.). After 4 hr. chloroform (50 ml.) was added and the mixture was washed with water (50 ml.) and saturated sodium hydrogen carbonate (100 ml.) and evaporated under reduced pressure to give the dibromide (2·07 g., 76%), m. p. 135—137° raised to 138—139° by recrystallisation from light petroleum (b. p. 80—100°) (Found: C, 61·6; H, 4·6; Br, 33·7. $C_{24}H_{20}Br_2$ requires C, 61·5; H, 4·3; Br, 34·1%).

ωω-o-*Phenylenedi*-[*triphenyl*-(m-trans-*vinylbenzyl*)*phosphonium bromide*] (I; R = CH_2·PPh_3^+ Br^-). The preceding dibromide (100 mg.) and triphenylphosphine (500 mg.) were refluxed in xylene (15 ml.) for 24 hr. The mixture was cooled and the solid was filtered off and washed with hot benzene (50 ml.) to leave the solvated *salt* (180 mg., 76%), m. p. >360° (Found: C, 73·9; H, 4·9; Br, 14·9. $C_{60}H_{50}Br_2P_2,C_8H_{10}$ requires C, 74·3; H, 5·5; Br, 14·5%).

o-*Bis*-trans-m-*tolylvinylbenzene* (I; R = Me). (*a*) The dibromide (I; R = CH_2Br) (724 mg.) in tetrahydrofuran (20 ml.) was added dropwise during 30 min. to a stirred refluxing suspension of lithium aluminium hydride (392 mg.) in tetrahydrofuran (100 ml.). The mixture was refluxed for a further 2 hr., then cooled and worked up in the usual manner, to give the *hydrocarbon* (423 mg., 88%), b. p. 220° (bath)/0·1 mm. (Found: C, 92·6; H, 7·3. $C_{24}H_{22}$ requires C, 92·9; H, 7·1%), $\lambda_{max.}$ 282 and 319 mμ (ε 37,600 and 27,000, respectively) in ethanol.

(*b*) Lithium ethoxide (from lithium, 140 mg.) in ethanol (50 ml.) was added to a stirred suspension of the salt (I; R = CH_2·PPh_3^+ Br^-) (992 mg.) in ethanol (50 ml.). The mixture was kept at 40° for 20 min., then added to water (100 ml.). The organic material was extracted with chloroform (50 ml.) and dried ($MgSO_4$). Evaporation under reduced pressure and chromatography of the residual oil in light petroleum (b. p. 40—60°) on alumina (Spence's type H; 15 g.) gave the hydrocarbon (142 mg., 51%) which had an infrared absorption spectrum indistinguishable from that of the sample described above.

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1165. *A New Synthesis of Isobornylamines.*

By I. A. Kaye and J. Linsk.

Recent interest in the synthesis of isobornylamines [1,2] prompts us to describe a procedure which we employed several years ago for the preparation of *N*-benzyl- and *N*-benzyl-*N*-ethyl-isobornylamines.[3] Most of the relatively few secondary isobornylamines described so far have been prepared by alkylation, with an alkyl halide in the presence of base, of isobornylamine, which is usually obtained from camphor oxime by catalytic hydrogenation or by the Leuckart reaction.[1,4] A variant procedure involves reduction of an *N*-isobornylalkanamide with a complex hydride; [2,4] a few *N*-arylisobornylamines have been prepared by reduction of camphor anils.[5,6] Several *N*-alkylisobornylamines have been converted into *N*-alkyl-*N*-methylisobornylamines by alkylation with the alkyl halide.[1] In all but one of these preparations camphor was the starting compound from which the isobornylamines have been prepared. In the one exception, isobornylaniline was prepared by heating α-pinene with aniline at about 200°.[6]

In our procedure, involving Ritter and Minieri's reaction,[7] *N*-isobornylbenzamide was prepared from camphene and benzonitrile in acid solution. Reduction of the amide with lithium aluminium hydride yielded *N*-benzylisobornylamine which, on acetylation followed by reduction with lithium aluminium hydride, afforded *N*-benzyl-*N*-ethylisobornylamine.

Since Ritter and Minieri [7] provided no proof in their publication of the structure of their *N*-isobornylbenzamide, our product was debenzylated by catalytic hydrogenolysis. The infrared spectrum of the hydrochloride of the isobornylamine produced was identical with that of an authentic sample.

Among the advantages of this procedure are its high stereo-selectivity, the convenience of preparation from readily available reactants, the purity of the products, and the possibility of its application to the preparation of a variety of substituted isobornylamines, since several *N*-isobornylalkanamides have been prepared by the Ritter and Minieri reaction.[7,8]

Experimental.—N-*Isobornylbenzamide.* A solution of racemic camphene (136·2 g.) in benzonitrile (113·3 g.) was added to a stirred mixture of isopropyl ether (175 ml.) and 98% sulphuric acid (100 g.) at <50°. The mixture was kept at room temperature for 16 hr., then poured on ice (1 kg.) and neutralised with aqueous ammonia. The product was isolated by extraction with methylene chloride and purified by crystallisation from hexane (m. p. 130—131°; 114·0 g., 44%).[7] Recrystallised twice from the same solvent, it had m. p. 133—134° (needles) and $\nu_{max.}$ 3310 (NH) and 1629 (amide C=O) cm.$^{-1}$.

N-*Benzylisobornylamine.* Reaction of *N*-isobornylbenzamide (35·7 g.) with lithium aluminium hydride (31·2 g.) in ether (600 ml.) gave N-*benzylisobornylamine*, b. p. 130—135°/0·8 mm. (28·4 g., 84%). The *hydrochloride*, prepared by adding ethereal hydrogen chloride to a solution of the base in ether and crystallised twice from isopropyl alcohol, had m. p. 261—262° (Found: C, 72·8; H, 9·4. $C_{17}H_{26}ClN$ requires C, 73·0; H, 9·4%). An analytical sample of the amine, obtained by treating a hot solution of the hydrochloride in ethanol with alcoholic sodium hydroxide, had b. p. 103—104°/0·15 mm., n_D^{20} 1·5293 (Found: C, 83·7; H, 9·9. Calc. for $C_{17}H_{25}N$: C, 83·9; H, 10·3%). Zakharkin and Khorlina [2] reported b. p. 142—143°/2 mm. and n_D^{20} 1·5247.

N-*Benzyl*-N-*isobornylacetamide.* The *amide*, m. p. 89·5—90·5°, was prepared by heating *N*-benzylisobornylamine (12·2 g.) with acetic anhydride (20 ml.) at 100° for 17 hr., and recrystallised

[1] Trojanek, Prospisek, and Cekan, *Coll. Czech. Chem. Comm.*, 1961, **26**, 2602.
[2] Zakharkin and Khorlina, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1959, 2146.
[3] Linsk, M.A. Thesis, Brooklyn College, 1959.
[4] McKenna and Slinger, *J.*, 1958, 2759.
[5] Takeshito and Kitajima, *Nippon Kagaku Zasshi*, 1960, **81**, 1284.
[6] Kawamoto, *J. Chem. Soc. Japan*, 1941, **62**, 1190.
[7] Ritter and Minieri, *J. Amer. Chem. Soc.*, 1948, **70**, 4045.
[8] Roberts and Maskaleris, *J. Org. Chem.*, 1959, **24**, 926.

twice from hexane (10·2 g., 71%) (Found: C, 79·9; H, 9·5. $C_{19}H_{27}NO$ requires C, 80·0; H, 9·5%).

N-*Benzyl*-N-*ethylisobornylamine*. The product, formed on reducing a solution of *N*-benzyl-*N*-isobornylacetamide in ether with lithium aluminium hydride, was converted into the *hydrochloride*. The crude salt, obtained in almost quantitative yield, had m. p. 179·5—181·5° when recrystallised three times from isopropyl alcohol (Found: C, 73·9; H, 9·9. $C_{19}H_{30}ClN$ requires C, 74·1; H, 9·8%). The *amine*, liberated by treating the salt with sodium hydroxide, had b. p. 110—112°/0·07 mm. and n_D^{20} 1·5310 (Found: C, 83·7; H, 10·7. $C_{19}H_{29}N$ requires C, 84·1; H, 10·8%). There was no absorption at *ca.* 3333 $cm.^{-1}$ (NH absent) in the infrared spectrum. The *perchlorate*, prepared by adding the calculated amount of 70—72% perchloric acid to a solution of the amine in acetic acid and recrystallised three times from methanol–ether, melted at 150—151° (Found: C, 60·9; H, 8·1. $C_{19}H_{30}ClNO_4$ requires C, 61·4; H, 8·1%).

Isobornylamine hydrochloride. A solution of *N*-benzylisobornylamine in isopropyl alcohol (50 ml.) was hydrogenated at 60 lb./sq. in. in the presence of 5% palladium–carbon (2·5 g.). The viscous oil (7·65 g.) isolated from this reaction was evaporatively distilled at 80—85°/30 mm. and the distillate (5·27 g., 72%) was converted into the hydrochloride. The salt, recrystallised three times from carbon tetrachloride, had m. p. 325°, and did not depress the m. p., and gave an infrared spectrum identical with that of isobornylamine hydrochloride.

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