Interaction of Boron Trichloride with Hydroxy-esters, and the Fission of Carboxylic Esters.

By M. J. FRAZER and W. GERRARD.

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INTERACTION of boron trichloride with hydroxy-esters has been studied to reveal the influence of the electron-attracting ethoxycarbonyl group. In common with alcohols of ordinary reactivity (such as *n*-butanol) (Gerrard and Lappert, *J.*, 1951, 1020, 2545) the hydroxy-esters (3 mols.) and boron trichloride (1 mol.) readily afforded the borates (1) in

$$3ROH + BCl_3 \longrightarrow B(OR)_3 + 3HCl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

good yield. Although they absorb hydrogen chloride (rather more than 1 mol.) they are not permanently altered by it. They do not form a complex with pyridine, thus showing that the ethoxycarbonyl group is insufficiently powerful to compensate for the " back co-ordination " of the oxygen atoms which appears to account for the non-formation of a complex between a trialkyl borate and pyridine (see Colclough, Gerrard, and Lappert, *J.*, 1955, 907).

Because of the intervention of the ethoxycarbonyl group, which gave ethyl alcohol, the borates could not be isolated by azeotropic removal of water after interaction of a hydroxy-ester and boric acid (see Gerrard and Lappert, *Chem. and Ind.*, 1952, 53). The ethoxycarbonyl group also intervened and gave rise to ethyl chloride when attempts were made to obtain the dichloroboronite, $RO{\cdot}BCl_2$, by the interaction of boron trichloride with the borate or with the hydroxy-ester. Fission of the ethoxycarbonyl group was confirmed by the interaction of boron trichloride with ethyl acetate, which appeared to follow the course shown in (2), and with phenyl acetate (reaction 3) (see Colclough *et al.*, *loc. cit.*).

$$EtOAc + BCl_3 \longrightarrow EtOAc,BCl_3 \longrightarrow AcCl + [EtO{\cdot}BCl_2 \longrightarrow EtCl + BCl_3 + B_2O_3] \quad (2)$$

$$PhOAc + BCl_3 \longrightarrow PhOAc,BCl_3 \longrightarrow AcCl + [PhO{\cdot}BCl_2 \longrightarrow BCl_3 + B(OPh)_3] \; . \quad (3)$$

The first step in the interaction of ethyl acetate and boron trichloride is the formation of a solid complex, stable at 20°. At this stage no permanent selection of mode of fission has been made; for when *n*-octanol (3 mols.) was added, hydrogen chloride (3 mols.), tri-*n*-octyl borate, and ethyl acetate were steadily formed at 20° (reaction 4).

$$EtOAc,BCl_3 + 3ROH \longrightarrow EtOAc + (RO)_3B + 3HCl \quad . \; . \; . \; . \; . \quad (4)$$

Experimental.—Reagents were mixed dropwise and well shaken.

Preparation of borates. The hydroxy-ester (3 mols.) was added to the trichloride (1 mol.) at −80°. (Similar results were obtained when the order of mixing was reversed.) A white solid was formed, which at room temperature gave hydrogen chloride, quantitatively absorbed in potassium hydroxide. Results are recorded in the Table.

Preparation of borates of ethyl esters of hydroxy-acids.

Hydroxy ester	HCl evolved (mols.)	Yield (%)	B. p./0·01 mm.	n_D^{20}	d_4^{20}	Found (%)			Calculated (%)		
						C	H	B	C	H	B
Glycollate	3·0	85 *	124°	1·4290	1·160	45·4	6·8	3·28	45·0	7·5	3·38
β-Hydroxypropionate	2·7	88 *	134	1·4331	1·108	49·8	7·5	3·00	49·7	8·3	2·99
Malate	2·6	80 *	180	1·4408	1·167	49·8	6·9	2·07	49·8	7·3	1·87
Lactate	—	86 †	110	1·4215	1·070	49·9	7·6	3·03	49·7	8·3	2·99

* New compounds. † Reagents mixed in chloroform at −10°, or trichloride added to lactate at − 80° [also from trichloride–pyridine complex (Gerrard and Lappert, *Chem. and Ind.*, 1952, 53)].

Ethyl glycollate (62 g., 6 mols.) and boric acid (6·2 g., 1 mol.) when heated (150°) under a column, afforded ethyl alcohol (14·4 g., 3 mols.), b. p. 79°, n_D^{18} 1·3649, ethyl glycollate (33 g., 3 mols.), a brown viscous liquid (3·4 g.), b. p. 100°/0·005 mm. (Found : B, 5·5%), and a black solid (6·7 g.). Likewise at 135° ethyl lactate (47 g., 4 mols.) gave ethyl alcohol (3 mols.) and a brown gum (35·3 g.) (Found : B, 4·7%).

Attempts to prepare dichloroboronites. Ethyl glycollate (1 mol.) was added to boron trichloride (1 mol.) at −80°. At room temperature the white solid evolved gases and became voluminous. During 2 hr. at 20° and 1 hr. at 60° the solid melted, hydrogen chloride and boron trichloride being continuously evolved, as also when distillation at 10 mm. was unsuccessfully attempted. No further progress was made with ethyl lactate or with ethyl malate, although these were examined in some detail.

Triethoxycarbonylmethyl borate (11·88 g., 1 mol.) was added to boron trichloride (13·05 g., 3 mols.) at −80°. The glass-like solid became voluminous at 0° and during 3 hr., at 20°, a condensate (5·4 g.) collected in the attached trap (−80°). A further condensate (5·4 g.) was obtained when the residue (18·85 g.) was kept at 70° for 3 hr. The final residue (12·25 g.) was a brown solid. To the total condensate, pyridine (7·08 g.) was added, whereupon pyridine–boron trichloride (8·9 g., equiv. to BCl_3, 5·3 g.), m. p. 114° (Found : Cl, 53·9. Calc. for $C_5H_5NCl_3B$: Cl, 54·1%) (Gerrard and Lappert, *J.*, 1951, 1020), was formed, and ethyl chloride (5·2 g.), b. p. approx. 12°, distilled into another trap at −80°. Nothing further was learnt from the other borates.

Fission of carboxylic esters by boron trichloride. Ethyl acetate (9·92 g., 1·0 ml.) was added (0·5 hr.) to boron trichloride (13·20 g., 1·0 mol.) at −80°, and the resulting white solid (23·10 g.) did not lose weight at 20° for 18 hr. During the rest of the experiment the reaction flask was connected to a trap at −80°. The solid melted to a brown liquid at 50°, but there was no loss in weight even at this temperature for 2 hr. The mixture was then heated at 100° for 1 hr., whereupon a liquid refluxed, a white solid formed in the flask, and there was a condensate in the trap. Distillation gave a brown fuming solid (6·0 g.) (Found : B, 12·44; easily hydrolysed Cl 31·95%) and acetyl chloride (7·35 g., 83·1%), b. p. 46—48°, which after two redistillations (boron trichloride and acetyl chloride tend to distil together and are only separated with difficulty) gave acetyl chloride (6·75 g.), b. p. 51°, n_D^{20} 1·3890 (Found : Cl, 45·8. Calc. for C_2H_3OCl : Cl, 45·1%). To the trap condensate (9·4 g.) at −80° pyridine (2·9 g., 0·33 mol.) was added. A violent reaction occurred and pyridine–boron trichloride (7·0 g.) was formed. Ethyl chloride (3·3 g., 45·4%), b. p. 12° approx., was distilled into another trap at −80°. The pyridine–boron trichloride, when washed with water and dried, had m. p. 115° (Found : Cl, 54·1. Calc. for $C_5H_5NCl_3B$: Cl, 54·1%).

The ethyl acetate–boron trichloride complex (7·7 g., 1 mol.) was prepared by the addition of the ester (3·3 g., 1 mol.) to boron trichloride (4·4 g., 1 mol.) at −80°. Octan-1-ol (14·7 g., 3 mols.) was slowly added at −80° (0·5 hr.). As the flask was warmed to 20° the solid began to melt and hydrogen chloride was evolved. The mixture was shaken first at 20° for 2 hr. and hydrogen chloride was collected in potassium hydroxide (Found : HCl, 3·9 g. Calc. for 3 mols. : HCl, 4·1 g.), and then at 15°/10 mm. for 1 hr., whereupon ethyl acetate (3·0 g., 91%), b. p. 77°, n_D^{17} 1·3749, collected in a trap at −80°, and the remaining liquid (12·6 g.) gave a forerun (1·1 g.), b. p. 100—162°/0·2 mm., n_D^{20} 1·4301, and tri-*n*-octyl borate (11·25 g., 75%), b. p. 162°/0·2 mm., n_D^{20} 1·4370, d_4^{20} 0·859 (Found : C, 72·2; H, 12·8; B, 2·9. Calc. for $C_{24}H_{51}O_3B$: C, 72·3; H, 12·8; B, 2·7%).

Phenyl acetate (b. p. 82°/12 mm., n_D^{15} 1·5039) (9·60 g., 1·0 mol.) was added (0·33 hr.) to boron trichloride (8·30 g., 1 mol.) at −80°. A white solid (17·9 g.) was formed which after 0·33 hr. at 20°, started to melt, and after 1·33 hr. was completely liquid (16·4 g.). On distillation this gave a mixture of acetyl chloride and boron trichloride (5·70 g.), b. p. 46—51°. After two redistillations acetyl chloride (4·1 g., 74%), b. p. 51°, n_D^{16} 1·3909 (Found : Cl, 46·8. Calc. for C_2H_3OCl : Cl, 45·1%), was obtained. The residue was kept at 180°/50 mm. for 1 hr. and then weighed 7·3 g. It gave triphenyl borate (5·35 g., 79·5%), m. p. 55—57°, b. p. 150°/0·02 mm. (Found : C_6H_5O, 96·7; B, 3·8. Calc. for $C_{18}H_{15}O_3B$: C_6H_5O, 96·3; B, 3·7%), and a black solid (0·6 g.). Ethyl chloride obtained in these experiments was characterised by approximate b. p. and by analysis (Found : Cl, 54·5. Calc. for C_2H_5Cl : Cl, 55·0%).

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The Structure and Ultraviolet Spectrum of Dianthracene

By C. A. Coulson, L. E. Orgel, W. Taylor, and J. Weiss.

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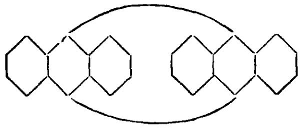
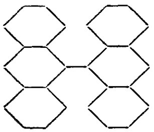
When anthracene is irradiated in solution, a dimer, dianthracene, is formed. It is probable that this dimer plays some part in the self-quenching of fluorescence of anthracene solutions (cf. Weil-Malherbe and Weiss, *J.*, **1944**, 541; *Trans. Faraday Soc.*, 1946, **42**, 133). As Weil-Malherbe and Weiss have suggested, an excited anthracene molecule A* can either (*a*) return by direct fluorescence to its ground state according to the equation $A^* \longrightarrow A + h\nu$; or (*b*) form a dimer in a two-stage process $A^* + A \longrightarrow A^+A^- \longrightarrow A_2$, of which the first stage is essentially an electron-transfer. Reaction (*b*) would lead to self-quenching of the fluorescence, and can be detected by this means. For this reason the structure of the dimer molecule is of some interest. Hengstenberg and Palacios (*Anales Soc. espan. fis. quim.*, 1932, **30**, 5), from *X*-ray diffraction experiments, were led to the view that the two anthracene units were joined by new bonds connecting their *meso* atoms (I). In order for this to be possible each anthracene molecule would need to fold itself out of a plane around the line joining the *meso* carbon atoms rather like the folding of a book. The other likely possibilities (II and III) were excluded on the grounds that if these molecules were assigned reasonable geometrical shapes and sizes, they would not pack together in the unit cell which was determined by *X*-ray analysis. This somewhat negative evidence has recently been supplemented by Medvedev, Mikhailov, Prikhot'ko, and Kharitonova (*Izvest. Akad. Nauk U.S.S.R.*, Ser. Fiz., 1953, **17**, 715), who irradiated pure 9-methylanthracene in acetone solution and crystallised the resulting dimer. These writers found that its ultraviolet spectrum was entirely different from that of the monomer, and appeared to correspond to a loss of much of the aromatic character of the original monomer. No details of the shape of the spectrum were given, although it should be possible from a study of this spectrum to settle the matter unambiguously.


(I)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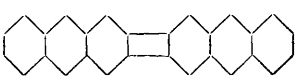
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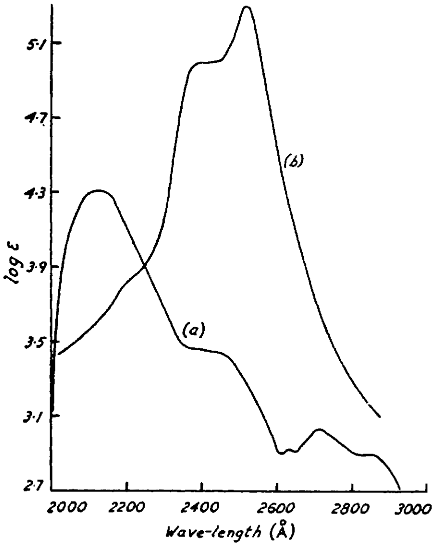

The ultraviolet spectra of (*a*) *dianthracene and* (*b*) *anthracene.*

We have therefore prepared the dimer of anthracene itself, by irradiation of anthracene in ethanol. The precipitate was filtered off and recrystallised from ethanol. Subsequently a solution in light petroleum (b. p. 60—80°) (in which it is sparingly soluble) was chromatographed on alumina, and the material eluted with benzene (5-ml. fractions). The solvent was evaporated off under slightly reduced pressure and the residues were dried and then dissolved in alcohol. The ultraviolet spectrum of each fraction was measured on a " Unicam " S.P.500 spectrophotometer. The first fractions showed the familiar peak at 2520 Å, which is due to the anthracene monomer, together with a new peak at 2175 Å and a band showing some vibrational fine structure at 2600—2800 Å. In the later fractions the peak at 2520 Å grew weaker, and eventually almost disappeared, while the peak at 2175 Å and the band around 2700 Å remained. Collection of fractions was continued until two consecutive fractions gave the same spectrum. The alcohol used as solvent in the measurement of this spectrum was purified by distillation over potassium hydroxide and then refluxing and distillation from magnesium ethoxide. The Figure shows the final curve.

Now if the structure of dianthracene is as in (I) we should expect that the spectral properties of the molecule would resemble those of a superposition of four benzene rings each disubstituted by alkyl groups in *ortho*-positions. The ultraviolet spectra of *o*-dialkylbenzenes, however (see, *e.g.*, the spectrum of *o*-xylene in the Amer. Petrol. Inst. Research Project 44, serial numbers 55, 173), (1) exhibit a peak at about 2120 Å; (2) for this peak have log $\varepsilon_{max.}$ about 3·9; (3) exhibit a band in the region 2600—2800 Å, with vibrational structure showing peaks at 2630 and 2710 Å, no trace of which can be found in the spectrum of anthracene itself; and (4) for this band have log $\varepsilon_{max.}$ about 2·4. Since our model for dianthracene requires that the absorption should be similar to four times that of a dialkylbenzene, the expected values of log $\varepsilon_{max.}$ would be $3{\cdot}9 + 0{\cdot}60 = 4{\cdot}5$, and $2{\cdot}4 + 0{\cdot}60 = 3{\cdot}0$, respectively. The corresponding values in the figure are 4·3 and 3·0. The agreement in all four respects between the experimental results shown in the figure and the values to be expected from our model leaves no reasonable doubt but that the dimer really has the geometrical structure (I).

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The Structure of Tazettine Methine.

By W. I. Taylor, S. Uyeo, and H. Yajima.

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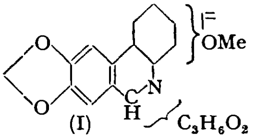
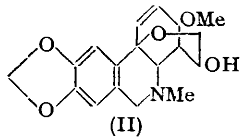
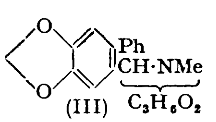
Tazettine was first extensively investigated by Späth and Kahovec (*Ber.*, 1934, **67**, 1501) who arrived at the partial structure (I) for the alkaloid. Kondo and his co-workers (Kondo, Ikeda, and Okuda, *Ann. Report, ITSUU Lab.*, 1950, **1**, 61; Kondo and Ikeda, *ibid.*, 1951, **2**, 55; Kondo, Ikeda, and Takeda, *ibid.*, p. 60; Kondo, Ikeda, and Taga, *ibid.*, 1952, **3**, 65; 1953, **4** 73; 1954, **5**, 72) accumulated much valuable data concerning the base which has been interpreted by Wenkert (*Experientia*, 1954, **10**, 476) leading to the formula (II). Except for (III) (Späth and Kahovec, *loc. cit.*), no structure was specifically assigned to tazettine methine which has been examined more closely by Clemo and Hoggarth (*Chem. and Ind.*, 1954, 1046). It seemed to us however that their results implied the structure (IV) and that, *e.g.*, the action of halogen acids on the methine was S_N2 replacement at the benzylic carbon atom yielding the corresponding 6-phenylpiperonyl halide and salt of dimethylaminoacetic acid (this observation has been confirmed, see Experimental section). The action of methyl iodide on the methine under vigorous conditions in acetone or ethyl methyl ketone could also be readily explained on this basis; the ketone condenses



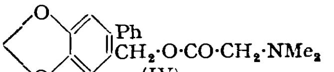
(I)



(II)



(III)



(IV)

$$\begin{array}{l} HO_2C{\cdot}C{\cdot}NMe_3^+\,I^- \\ \qquad\;\;\, \| \\ \qquad\;\, CRR' \end{array}$$

(V)

with the reactive methylene group of the first-formed methine methiodide which is then converted into 6-phenylpiperonyl iodide and the salt (V) (with acetone R = R′ = Me; with ethyl methyl ketone R = Me, R′ = Et) with which Clemo and Hoggarth's analyses are in good agreement. This sequence of reactions is probably correct since betaine iodide itself does not react with acetone under reflux. The most powerful argument against structure (IV) for tazettine methine was the observation by Späth and Kahovec (*loc. cit.*) that it was optically active. We now find that the methine regenerated from its picrate is optically inactive and that reduction with lithium aluminium hydride affords 6-phenylpiperonyl alcohol and 2-dimethylaminoethanol. The synthesis of the ester (IV) was accomplished by treating 6-phenylpiperonyl alcohol successively with chloroacetyl chloride and dimethylamine in dry benzene to yield (IV) whose infrared and ultraviolet spectra and picrate were identical with those of the natural derivative.

Experimental.—Ultraviolet absorption spectra were taken in 95% EtOH.

Tazettine methine. The methine was prepared according to the directions of Späth and Kahovec (*loc. cit.*) and its picrate purified by many crystallisations from acetone to m. p. 178° (Found: C, 53·3; H, 4·1; N, 10·3. Calc. for $C_{18}H_{19}O_4N,C_6H_3O_7N_3$: C, 53·1; H, 4·1; N, 10·3%). The methine regenerated from its picrate had $[\alpha]_D$ ±0° (*c*, 0·8 in $CHCl_3$); ν_{CO} 1754 cm.$^{-1}$ and in the ultraviolet region $\lambda_{max.}$ 257 and 293 mμ (log ε 3·89 and 3·72) practically identical with data for 6-phenylpiperonyl alcohol.

Reduction of the methine. Tazettine methine (150 mg.) and lithium aluminium hydride (100 mg.) in ether (20 ml.) were refluxed for 3 hr. A little water was added and the precipitated inorganic salts were filtered off. The ethereal filtrate after concentration yielded cubic crystals (82 mg.), m. p. 100—102°, unaltered on further crystallisation, which gave no depression in m. p. on admixture with 6-phenylpiperonyl alcohol. The ethereal mother-liquors were combined and treated with a saturated ethereal solution of picric acid. The resulting picrate (48 mg.) had m. p. 92—94° after three crystallisations from ethyl acetate–ether and was identical with 2-dimethylaminoethanol picrate (Found: C, 37·8; H, 4·6; N, 17·5. Calc. for $C_4H_{11}ON,C_6H_3O_7N_3$: C, 37·7; H, 4·4; N, 17·6%).

Action of hydrochloric acid on the methine. The methine (150 mg.) in 18% hydrochloric acid (2 ml.) was heated on a water-bath; after a few minutes an oil separated. After 1 hr. the cooled mixture was extracted with ether, dried ($CaCl_2$), then evaporated to dryness. Trituration of the residue with light petroleum (b. p. 60—80°) furnished 6-phenylpiperonyl chloride (62 mg.), m. p. 58—59° after further crystallisation from the same solvent. The aqueous acidic solution was evaporated to dryness under reduced pressure and the residue after crystallisation from ethanol yielded dimethylaminoacetic acid hydrochloride (26 mg.), m. p. and mixed m. p. 186—189° (Found: C, 34·6; H, 7·4; N, 10·0. Calc. for $C_4H_{10}O_2NCl$: C, 34·4; H, 7·2; N, 10·0%).

Synthesis of tazettine methine. The reaction product from 6-phenylpiperonyl alcohol (560 mg.) and chloroacetyl chloride (0·2 ml.) was heated for a short time *in vacuo* to remove traces of hydrogen chloride, then covered with benzene (5 ml.) containing dry dimethylamine (200 mg.). After 24 hr. the crystalline hydrochloride was filtered off and converted into the free oily base (450 mg.) which was purified by distillation *in vacuo* at 150°. It formed a picrate, yellow hexagonal plates (from methanol), m. p. 178° (Found: C, 53·1; H, 4·1. Calc. for $C_{18}H_{19}O_4,C_6H_3O_7N_3$: C, 53·1; H, 4·1%), on admixture with the methine picrate.

We are indebted to the National Research Council of Canada for a grant and to Mr. W. Fulmor and staff, American Cyanamid Company, Lederle Laboratories Division, for determination of the infrared spectra. We also thank Dr. H. Kondo for his interest and encouragement.

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Vapour Pressures and Densities of Some Lower Alkylphosphonates.

By Gennady M. Kosolapoff.

[Reprint Order No. 6221.]

It was shown earlier (Kosolapoff, *J.*, 1954, 3222) that the dipole moments of dialkyl alkylphosphonates, $R'{\cdot}PO(OR)_2$, do not, in themselves, provide an adequate basis for the postulation of hindered rotation of the various groups in these esters. However, this subject is of relatively great importance in practive since it bears directly upon the chemical reactivities of such esters (cf. Kosolapoff, *loc. cit.*). In the hope that some of the other physical properties of the esters might afford an insight into this matter, observations were made of the vapour pressures and the densities of six lower members of this family over a range of temperature : esters in which the chain-length is inadequate for screening of the central oxygen (by suitable rotation) would be expected to display greater interaction with the neighbouring molecules than members in which the " onion-shaped " molecule could be attained as one of the configurational states.

The results appear to justify these concepts. When the vapour-pressure data were plotted in the form of $\log p$ *versus* $1/T$ (T being in °K), the plots were curvilinear. However, from approximately 140° C to 70—90° C the deviation from the rectilinear form was generally not great, so that a fitting of a straight-line plot could be justified. This fitting, done by the method of least squares, made it possible to calculate the heats of vaporization by conventional methods from the slope of the rectilinear plot $\log p = a + b/T$; this reproduced the experimental values generally within 2%, although it is realized that such a rectilinear representatiom is an oversimplification. The values of the heats of vaporization, thus obtained, are shown in Table 1. The most striking fact about these values is the considerable difference between the isomers diethyl propylphosphonate and di*iso*propyl methylphosphonate, the former being a substance in which a complete screening of the PO group by the three chains is possible, and the latter being one in which such screening is impossible on the side of the methyl group. This difference in the heats of vaporization, amounting to some 3300 cal. per mole, obviously cannot be wholly attributable to the possibility of intramolecular screening. It is nevertheless noteworthy that the remaining esters in this group show a very close grouping of the calculated heats of vaporization and one which clusters about the value calculated for di*iso*propyl methylphosphonate. It may be significant that all these esters are structurally incapable of effecting a complete screening of the central PO group by all three chains attached to the phosphorus atom.

Table 1. *Vapour pressures of esters.*

(*Vapour pressures in mm.* Hg; *temperatures in* ° c.)

$Me{\cdot}PO(OMe)_2$		$Et{\cdot}PO(OMe)_2$		$Me{\cdot}PO(OEt)_2$		$Me{\cdot}PO(OPr^i)_2$		$Et{\cdot}PO(OEt)_2$		$Pr{\cdot}PO(OEt)_2$	
t	*p*	*t*	*p*	*t*	*p*	*t*	*p*	*t*	*p*	*t*	*p*
135·0°	190·5	137·0°	168·6	129·0°	112·6	133·0°	114·5	133·5°	97·3	134·0°	59·4
128·0	154·5	128·0	123·6	119·0	80·6	125·0	84·5	125·0	71·8	124·0	37·4
117·0	100·5	118·5	85·1	110·0	56·1	116·0	60·5	116·0	50·3	115·0	24·9
106·0	64·5	108·0	55·6	101·0	35·6	107·0	41·0	105·5	31·3	105·0	14·9
98·0	44·5	98·0	35·6	89·0	22·1	98·0	28·5	95·5	19·3	95·5	7·9
90·0	30·5	88·5	21·1	81·3	14·1	89·0	18·5	85·5	9·3	87·3	3·9
80·5	18·5	78·2	11·1	74·5	9·1	77·0	7·0	76·5	4·3		
70·3	9·7	69·4	5·6	70·0	5·2	70·0	2·0				
63·0	4·9	60·2	1·6								

Calculated constants for the equation $\log p = a + b/T$.

a	9·0123	9·2569	8·7973	8·5459	8·8670	10·07271
b	−2736·3	−2872·7	−2706·8	−2634·4	−2792·7	−3374·1

Calculated heats of vaporization (*cal. per mole*).

12,500	13,100	12,400	12,050	12,800	15,400

The densities of these esters over a range of temperature are shown in Table 2. Plots of density against temperature (°c) were sensibly linear and afforded a computation of the thermal expansion coefficients, $a = (v_t - v_0)/v_0t$, and the rates of the change of molar volume with temperature, $(\partial V/\partial t)_p$. The values of a are very nearly identical among the entire group of esters, while the values of $(\partial V/\partial t)_p$ show a progressive increase with the molecular size.

TABLE 2. *Densities.*

d_4	t	V	d_4^t	t	V	d_4	t	V
Me·PO(OMe)$_2$			Me·PO(OEt)$_2$			Me·PO(OPr^i)$_2$		
1·1507	30·0°	107·8	1·0406	30·0°	146·2	0·9734	30·0°	185·1
1·1366	42·0	109·2	1·0234	47·0	148·6	0·9619	41·0	187·3
1·1242	53·5	110·4	1·0125	57·0	150·2	0·9547	49·0	188·7
1·1164	60·0	111·1	1·0024	67·0	151·8	0·9428	61·5	191·1
1·1047	71·0	112·3	0·9937	76·0	153·1	0·9313	72·0	193·5
1·0958	79·0	113·2	0·9881	81·0	153·9	0·9238	81·0	195·1
1·0846	89·0	114·4	0·9784	90·0	155·5	0·9144	91·0	197·1
1·0717	100·5	115·8	0·9683	100·2	157·1	0·9050	100·0	199·1
a = 0·00108			a = 0·00110			a = 0·00112		
$(\partial V/\partial t)_p$ = 0·1126			$(\partial V/\partial t)_p$ = 0·1554			$(\partial V/\partial t)_p$ = 0·1998		
Et·PO(OMe)$_2$			Et·PO(OEt)$_2$			Pr·PO(OEt)$_2$		
1·1029	30·0	125·2	1·0158	32·0	163·6	0·9937	30·0	181·3
1·0850	45·0	127·3	1·0008	46·0	166·0	0·9839	40·0	183·1
1·0731	56·0	128·7	0·9888	58·0	168·1	0·9755	48·0	184·7
1·0623	67·0	130·0	0·9826	65·0	169·1	0·9660	57·0	186·5
1·0561	72·5	130·8	0·9746	73·0	170·5	0·9576	68·5	188·2
1·0462	82·0	132·0	0·9642	83·0	172·3	0·9495	77·0	189·8
1·0394	89·0	132·9	0·9580	89·5	173·5	0·9390	88·0	191·9
1·0279	100·0	134·4	0·9473	100·3	175·4	0·9275	99·5	194·3
a = 0·00108			a = 0·00110			a = 0·00106		
$(\partial V/\partial t)_p$ = 0·1306			$(\partial V/\partial t)_p$ = 0·1683			$(\partial V/\partial t)_p$ = 0·1864		

The results obtained, particularly among the measurements of the vapour pressures, may signify some reality of the ideas of partly hindered rotation in the phosphonates (Arbuzov and Vinogradova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1952, 882, 865, 505; 1951, 733; 1947, 459).

Experimental.—The compounds were prepared as described previously (Kosolapoff, *loc. cit.*). Vapour pressures were determined with the original design of the isoteniscope (Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1413) of small volume. This device was agitated during the runs by a flexible tip attached to the mechanical stirrer in the thermostat. The electrically controlled thermostat was kept within 0·1° of the selected temperatures. The pressure readings, made with a mercury manometer, were corrected for temperature, altitude, and latitude. It is realized that the isoteniscope is not reliable at the lower pressures and the last values in Table 1 are not trustworthy; these, of course, were not included in the calculations.

The densities were determined conventionally by means of a pyknometer which had been calibrated with water; the determinations were made with the aid of an electrically regulated thermostat and were probably correct within 0·0002 unit. The molar volumes, V, and the thermal coefficients of expansion were calculated from conventional formulæ.

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The Preparation and Rate of Alkaline Hydrolysis of 2-Acetamidoethyl Thiolacetate.

By F. J. McQuillin and J. Stewart.

[Reprint Order No. 6242.]

Hawkins and Tarbell (*J. Amer. Chem. Soc.*, 1953, **75**, 2982) reported the rate of hydrolysis of 2-acetamidoethyl thiolacetate by alkali at 0°. It was of interest to extend the temperature range so as to derive the Arrhenius parameters for this reaction.

Hydrolysis was followed by the change in the characteristic thiolacyl absorption at 233 mμ (cf. Cunneen, *J.*, 1947, 134; Hawkins and Tarbell, *loc. cit.*; Schwyzer, *Experientia*, 1954, **10**, 61). 2-Acetamidoethanethiol was found by electrometric titration to have a pK_a value of 9·2. Calculation of rate constants has therefore been based on the equation: $Me\cdot CO\cdot SR + 2HO^- \longrightarrow RS^- + Me\cdot CO_2^- + H_2O$. The results are given in the Table. The activation energy and probability terms have values very similar to those reported for the alkaline hydrolysis (in more or less aqueous acetone) of simple alkyl thiolacetates which do not contain the acylamino-group (Schaefgen, *J. Amer. Chem. Soc.*, 1948, **70**, 1308; Rylander and Tarbell, *ibid.*, 1950, **72**, 3021). By use of these values of E and $\log_{10} A$, the rate constant at 0° is calculated as 0·021 in comparison with Hawkins and Tarbell's observed values of 0·0178—0·0192 (*loc. cit.*). It is possible that our value of E may be slightly low, but there may also have been some small difference in the samples of 2-acetamidoethyl thiolacetate used; our material gave $\varepsilon = 4{\cdot}63 \times 10^3$ at 233 mμ, Hawkins and Tarbell give $\varepsilon = 4{\cdot}51 \times 10^3$.

Temp.	Ester (10⁻³ mol. l.⁻¹)	[HO⁻] (10⁻³ mol. l.⁻¹)	$k_{obs.}$ (mol. l.⁻¹ sec.⁻¹)	$k_{calc.}$ * (mol. l.⁻¹ sec.⁻¹)
22·6°	1·159	6·68	0·128	0·125
27·4	1·183	3·579	0·174	0·177
28·2	1·152	3·88	0·180	0·188
32·5	1·183	3·52	0·258	0·252

* Calc. by using E 12·7 kcal./mole and $\log_{10} A$ 8·5.

The 2-acetamidoethyl thiolacetate (III) required for these experiments was obtained by acetylation of 2-acetamidoethanethiol (II) which was prepared in good yield from 2-bromoethylammonium bromide and potassium thioacetate. The corresponding thiolbenzoate (IV) was similarly prepared. This route to 2-acetamidoethanethiol avoids the use of ethyleneimine (cf. Kuhn and Quadbeck, *Chem. Ber.*, 1951, **84**, 844; Wieland and Bokelmann, *Annalen*, 1951, **576**, 20; Bestian, *ibid.*, 1950, **566**, 210; Mills and Bogert, *J. Amer. Chem. Soc.*, 1940, **62**, 1173), and the less convenient route *via* 2-thiothiazoline (Mills and Bogert, *loc. cit.*; Gabriel and Leupold, *Ber.*, 1898, **31**, 2837). The method was based on the S→N acetyl migration to be expected, under alkaline conditions, of the 2-aminoethyl thiolacetate (I) which is presumably first formed. The reverse migration under acid conditions was not realised; with alcoholic hydrochloric acid, 2-acetamidoethanethiol was hydrolysed to 2-aminoethanethiol.

$$\begin{array}{c}{}^{+}NH_3CH_2\cdot CH_2Br\}Br^- \\ + \\ Me\cdot CO\cdot SK\end{array} \longrightarrow \underset{(I)}{[Me\cdot CO\cdot S\cdot CH_2\cdot CH_2\cdot NH_2]} \longrightarrow \underset{(II)}{NHAc\cdot CH_2\cdot CH_2\cdot SH} \longrightarrow \underset{(III)}{NHAc\cdot CH_2\cdot CH_2\cdot S\cdot Ac}$$

$$\underset{(IV)}{NHAc\cdot CH_2\cdot CH_2\cdot SBz} \qquad \underset{(V)}{NHAc\cdot CH_2\cdot CH_2\cdot O\cdot SO_2\cdot C_6H_4Me} \qquad \underset{(VI)}{C_6H_4Me\cdot SO_2\cdot NH\cdot CH_2\cdot CH_2\cdot OAc}$$

2-Acetamidoethanol is readily available from 2-aminoethanol and ethyl acetate. The *O*-toluene-*p*-sulphonyl derivative (V) by reaction with potassium thioacetate should also lead to 2-acetamidoethyl thiolacetate. On attempting the toluene-*p*-sulphonylation of 2-acetamidoethanol, however, rearrangement was encountered. The product proved to be toluene-*p*-sulphonamidoethyl acetate (VI). The rearrangement must be ascribed to N→O acetyl migration, catalysed by pyridinium ion, which is rapid in comparison with

O-toluenesulphonylation. The yield was low through loss of material, no doubt as the oxazoline.

Experimental.—Hydrolysis of 2-*acetamidoethyl thiolacetate.* Aqueous sodium hydroxide and a solution of 2-acetamidoethyl thiolacetate, both in oxygen- and carbon dioxide-free water, were brought to equilibrium in the thermostat under oxygen- and carbon dioxide-free nitrogen in a Warburg-type flask with a side limb. After mixing, samples (2 c.c.) were withdrawn and run into 0·01N-hydrochloric acid and the absorptions of the solutions at 233 mμ measured. The residual thiolacetate concentration was calculated, using $\varepsilon = 4{\cdot}63 \times 10^3$.

(i) 22·6°. Ester, $1{\cdot}159 \times 10^{-3}$M; alkali, $6{\cdot}680 \times 10^{-3}$M.

Time (sec.)	287	403	588	648	705	765	846	903	1010	1061
10^4 [Ester]	9·64	8·40	7·46	7·18	6·71	6·63	6·28	5·96	5·56	5·46
10^3k	122	139	131	128	135	127	127	128	126	124

(ii) 27·4°. Ester, $1{\cdot}183 \times 10^{-3}$M; alkali $3{\cdot}579 \times 10^{-3}$M.

Time (sec.)	184	304	374	453	540	631
10^4 [Ester]	10·55	10·07	9·59	9·21	8·74	8·34
10^3k	183	157	170	169	174	175

(iii) 28·2°. Ester, $1{\cdot}152 \times 10^{-3}$M; alkali, $3{\cdot}88 \times 10^{-3}$M.

Time (sec.)	66	127	245	334	418	511	603	701
10^4 [Ester]	11·0	10·6	9·86	9·27	8·77	8·32	7·94	7·83
10^3k	182	176	179	179	184	182	178	176

(iv) 32·5°. Ester, $1{\cdot}183 \times 10^{-3}$M; alkali, $3{\cdot}527 \times 10^{-3}$M.

Time (sec.)	74	142	211	279	343	416	480	583
10^4 [Ester]	11·1	10·5	9·83	9·37	8·88	8·40	8·09	7·73
10^3k	254	255	264	258	260	260	254	238

2-*Acetamidoethanethiol.* Anhydrous potassium carbonate (14·5 g.) under ethyl alcohol (60 c.c.) was cooled (ice) and treated with thioacetic acid (10 g.) in an atmosphere of nitrogen. After the reaction 2-bromoethylammonium bromide (20 g.) in alcohol (100 c.c.) was added with stirring. The mixture was kept under nitrogen for 12 hr., refluxed for 8 hr., cooled, and filtered. The filtrate, evaporated *in vacuo* under nitrogen and extracted with chloroform, gave 2-acetamidoethanethiol (6·9 g.), b. p. 105°/0·1 mm. (Found: C, 40·7; H, 7·6. Calc. for C_4H_9ONS: C, 40·4; H, 7·5%), characterised by aerial oxidation to di-(2-acetamidoethyl) disulphide, m. p. 87—88° (Kuhn and Quadbeck, *loc. cit.*), and as the *S*-*p*-nitrobenzyl derivative prepared with *p*-nitrobenzyl chloride and dry potassium carbonate in boiling acetone. 2-*Acetamidoethyl* p-*nitrobenzyl sulphide* formed prisms, m. p. 112°, from benzene (Found: C, 52·4; H, 5·8. $C_{11}H_{14}O_3N_2S$ requires C, 52·0; H, 5·5%).

2-*Acetamidoethyl thiolacetate.* 2-Acetamidoethanethiol (5 g.) with acetic anhydride (10 c.c.) in dry pyridine (40 c.c.) afforded 2-acetamidoethyl thiolacetate (4·2 g.), b. p. 123—125°/0·1 mm., m. p. 26° (Found: C, 45·2; H, 6·9. Calc. for $C_6H_{11}O_2NS$: C, 44·7; H, 6·8%).

2-*Acetamidoethyl thiolbenzoate*, prepared by benzoylation of the thiol in pyridine–benzene, formed prisms, m. p. 87—88°, from benzene–light petroleum (Found: C, 59·2; H, 5·9. $C_{11}H_{13}O_2NS$ requires C, 59·2; H, 5·8%).

Hydrolysis of 2-*acetamidoethanethiol.* The thiol (1 g.) in methanolic hydrogen chloride (8%; 5 c.c.) was gently refluxed (3 hr.), then evaporated *in vacuo*, giving 2-aminoethanethiol hydrochloride, m. p. 67° (from alcohol–ethyl acetate) (Found: C, 21·2; H, 7·2. Calc. for C_2H_8NSCl: C, 21·1; H, 7·1%).

Reaction of 2-*acetamidoethanol with toluene*-p-*sulphonyl chloride.* (*a*) 2-Aminoethanol (12·2 g.) was heated under reflux for 4 hr. with ethyl acetate (50 c.c.) and distilled, to give 2-acetamidoethanol (15 g.), b. p. 120—122°/0·1 mm., n_D^{17} 1·4722 (Found: C, 46·8; H, 8·9. Calc. for $C_4H_9O_2N$: C, 46·6; H, 8·75%).

(*b*) 2-Acetamidoethanol (7 g.) in dry pyridine (25 c.c.), cooled in ice, was treated gradually with toluene-*p*-sulphonyl chloride (16 g.). After 24 hr. the product was isolated (3·5 g.) and identified as 2-toluene-*p*-sulphonamidoethyl acetate, m. p. and mixed m. p. 58—59° (Slotta and Behnisch, *J. prakt. Chem.*, 1932, **135**, 225, give m. p. 56°) (Found: C, 51·6; H, 6·1. Calc. for $C_{11}H_{15}O_4NS$: C, 51·4; H, 5·8%).

One of us (J. S.) is indebted to the Northumberland County Council for an award.

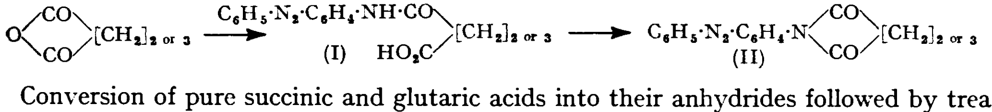
KING'S COLLEGE, NEWCASTLE-UPON-TYNE, 1. [*Received, March 17th*, 1955.]

Isolation and Characterisation of Succinic and Glutaric Acids as p-*Phenylazoanils.*

By H. B. Henbest and T. C. Owen.

[Reprint Order No. 6244.]

Acids of the succinic and glutaric acid type are often formed during the oxidative degradation of organic compounds, but isolation in a pure form is frequently hampered by their water-solubility and by the presence of other acidic products which inhibit crystallisation. It is now reported that these acids may be converted in high yields into coloured, highly crystalline *p*-phenylazoanils (II), which can be readily purified by chromatography on alumina. These derivatives are also readily isolated from less pure samples of the acids (see below).



$$O\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}[CH_2]_{2\text{ or }3} \longrightarrow \begin{matrix} C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO \\ HO_2C \end{matrix}[CH_2]_{2\text{ or }3} \longrightarrow C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}[CH_2]_{2\text{ or }3}$$

(I) (II)

Conversion of pure succinic and glutaric acids into their anhydrides followed by treatment with *p*-aminoazobenzene in chloroform solution led to the separation of the relatively insoluble anilic acids (I) in 90% yields. Cyclisation of the anilic acids to the anils (II) could be effected in 90% yields by acetyl chloride in chloroform. As an example of a more heavily substituted acid, αα-dimethylsuccinic acid was converted into its *p*-phenylazoanil in 80% overall yield, intermediates not being isolated.

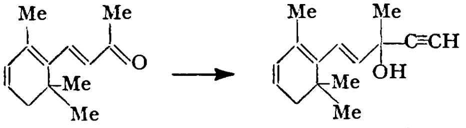
The new derivatives are stable to alumina and give deep yellow bands on a chromatogram and are readily separated; with the compounds studied the order of elution was αα-dimethylsuccino-*p*-phenylazoanil (first), *p*-acetamidoazobenzene, glutaro-*p*-phenylazoanil, succino-*p*-phenylazoanil, and *p*-aminoazobenzene. The use of acetic acid derivatives in the preparation of the cyclic anils led to the possibility that *p*-acetamidoazobenzene might be encountered; it was included therefore in the chromatographic experiments.

Light absorption in chloroform solutions.

	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$		$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$
p-*N*-Dimethylaminoazobenzene *	4100	27,100	Succino-*p*-phenylazoanil	3230	22,000
p-Aminoazobenzene *	3700	25,000	Glutaro-*p*-phenylazoanil	3210	19,100
p-Acetamidoazobenzene	3470	23,400	Azobenzene	3190	11,400
αα-Dimethylsuccino-*p*-phenylazoanil	3250	19,900			

* Data given by Brode, Gould, and Wyman (*J. Amer. Chem. Soc.*, 1953, **75**, 1856).

A further advantage of these derivatives is that small quantities may be estimated by spectrographic methods. Their light-absorption properties are summarized in the Table together with data on related compounds. As expected, progressive acylation of the *p*-amino-group causes shifts of $\lambda_{max.}$ to shorter wavelengths as well as a reduction of intensity.



(III) (IV)

The *p*-phenylazoanil derivatives were first devised in order to identify oxidation products in the vitamin A_2 field. Thus ozonolysis of 3-dehydro-β-ionone (III) (Henbest, *J.*, 1951, 1074) or of the derived (crystalline) ethynyl alcohol (IV) afforded an acidic fraction from which only very small amounts of the expected αα-dimethylsuccinic acid could be isolated by crystallisation. Formation of the *p*-phenylazoanil without isolation of intermediate compounds followed by chromatographic purification gave the αα-dimethylsuccinic acid derivative in reproducible 20—25% yields.

Experimental.—*Succino*-p-*phenylazoanil.* A mixture of succinic acid (6 g.) and acetic anhydride (20 c.c.) was heated at 100° for 30 min. Acetic acid and anhydride were removed under reduced pressure, and the residue in chloroform (20 c.c.) was refluxed with a solution of chromatographically purified *p*-aminoazobenzene (10 g.) in chloroform (20 c.c.) for 30 min. and then cooled to give the virtually pure *anilic acid* (13·5 g.). Crystallisation from ethanol afforded golden needles, m. p. 217° (decomp.) (Found : C, 64·4; H, 4·9; N, 14·3. $C_{16}H_{15}O_3N_3$ requires C, 64·65; H, 5·1; N, 14·15%). A mixture of the anilic acid (1·1 g.) and acetyl chloride (30 c.c.) was heated under reflux until the acid dissolved. Removal of the solvent under reduced pressure gave a product that was chromatographed on alumina (P. Spence, grade H, 100 g.). The single yellow band was eluted with benzene–ether (3 : 1) to give the *anil* (0·9 g.); crystallisation from ethanol yielded pure material, m. p. 214° (Found : C, 69·0; H, 4·8; N, 15·3. $C_{16}H_{13}O_2N_3$ requires C, 68·8; H, 4·7; N, 15·05%). Dehydration of the anilic acid by heating it at 260° under reduced pressure (20 mm.) for 30 min. gave a dark brown product, which afforded a 50% yield of pure anil on chromatography.

Glutaro-p-*phenylazoanil.* The anilic acid was obtained in over 90% yield from glutaric anhydride (1·4 g.) and *p*-aminoazobenzene (2·61 g.) by the procedure given above. Crystallisation from aqueous acetone afforded an *acid*, m. p. 190—192° (Found : C, 66·0; H, 5·8; N, 13·75. $C_{17}H_{17}O_3N_3$ requires C, 65·6; H, 5·5; N, 13·5%). Cyclisation of the anilic acid by acetyl chloride gave a 90% yield of the *anil*, m. p. 219° (Found : C, 69·7; H, 5·6; N, 14·3. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·2; N, 14·35%).

αα-Dimethylsuccino-p-*phenylazoanil.* αα-Dimethylsuccinic acid (1 g.) and acetic anhydride (10 c.c.) were heated at 100° for 30 min. Removal of solvent at 80°/20 mm. gave the cyclic anhydride as a yellow oil, which was heated under reflux with a solution of pure *p*-aminazobenzene (1·34 g.) in chloroform for 30 min. The solvent was removed under reduced pressure and the mixture of anilic acids treated with acetyl chloride as above. Chromatography of the product gave the crystalline *anil* (1·6 g., 80%), m. p. 136° (from aqueous ethanol or aqueous acetic acid) (Found : C, 70·4; H, 5·45; N, 14·0. $C_{18}H_{17}O_2N_3$ requires C, 70·35; H, 5·6; N, 13·7%).

Oxidation of 3-*dehydro*-β-*ionone* (III). The ketone (0·44 g.) in carbon tetrachloride (5 c.c.) at 0° was treated with ozonised oxygen (*ca.* 5%; 100 c.c./min.) for 1 hr., during which a gummy ozonide separated. Acetic acid (10 c.c.) was added to dissolve the gum and ozonisation was continued for a further hour. After addition of 5N-sulphuric acid (1 c.c.) the solution was evaporated to about 6 c.c. under reduced pressure. A hot solution of sodium permanganate (1 g.) in 5N-sulphuric acid (25 c.c.) was then added, and the mixture allowed to cool to room temperature during 2 hr. After treatment with sulphur dioxide, the solution was extracted 10 times with ether to yield a semicrystalline acid (0·3 g.), which was treated as above to give αα-dimethylsuccino-*p*-phenylazoanil (0·17 g., 25%), m. p. and mixed m. p. 136°. This procedure gave reproducible yields of anil; if the permanganate treatment was omitted the yield of anil was less than 10%.

Preparation and oxidation of the ethynyl alcohol (IV). Lithium acetylide was prepared by addition of finely cut lithium (1 g.) to a solution of acetylene in liquid ammonia (200 c.c.) in a Dewar vessel. A stream of purified acetylene was passed through the stirred liquid for 20 min. and was continued while a solution of 3-dehydro-β-ionone (15 g.) in dry ether (50 c.c.) was added slowly. Stirring and passage of acetylene were continued for 3 hr., then ammonium chloride (15 g.) was added, and the product was isolated with ether after evaporation of ammonia. Distillation under reduced pressure gave a mixture of alcohol and unchanged ketone which were separated by chromatography on alumina. Distillation gave the pure *alcohol* (5·5 g.), m. p. 31° (Found : C, 83·1; H, 9·25. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%). Ultraviolet light absorption in EtOH; $\lambda_{max.}$ 2860 Å (ε 8400).

Oxidation of this alcohol (1 g.) as described for 3-dehydro-β-ionone gave αα-dimethylsuccino-*p*-phenylazoanil (0·35 g., 23%), m. p. and mixed m. p. 136°.

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p-*Phenylazomaleinanil : A Reagent for Conjugated Dienes.*

By P. Nayler and M. C. Whiting.

[Reprint Order No. 6245.]

p-Phenylazoanils of substituted succinic and glutaric acids (Henbest and Owen, preceding note) are convenient derivatives for the characterisation of these acids. By appropriately modifying the acylation conditions, the corresponding derivative of maleic acid has now been obtained; since maleinanil and its analogues have not been conveniently obtainable hitherto, the method described may be of general value. The *p*-phenylazoanil, however, is particularly useful in that it undergoes Diels–Alder reactions with conjugated dienes to give coloured adducts which can be separated from unchanged reagent, and presumably from each other, by chromatography on alumina with particular ease because of their strong colour. The adducts are high-melting and crystallise well, while the large weight factor is an additional advantage.

Ultraviolet absorption spectra of the adducts and reagents in chloroform are tabulated below. Intensities are so consistent—excluding the *cyclo*pentadiene adduct, which is exceptionally strained—that the reagent could be used for estimating the molecular weight of an unknown diene.

	$\lambda_{max.}$ (Å)	ε
p-Phenylazomaleinanilic acid	3600	22,500
Cf. *p*-acetamidoazobenzene...	3470	23,400
p-Phenylazomaleinanil	3280	22,400

p-Phenylazomaleinanil adduct with :	$\lambda_{max.}$ (Å)	ε
Butadiene	3250	22,700
*cyclo*Pentadiene	3240	24,000
*cyclo*Hexadiene	3250	22,900
Cosmene (bis-adduct)	3280	45,100
Cf. *p*-phenylazosuccinanil	3230	22,000

The *p*-phenylazoanils of succinic and maleic acid and the four adducts prepared all showed strong infrared bands at 683 ± 2 and 771 ± 6 cm.$^{-1}$ and one or more in the 830—855-cm.$^{-1}$ region. In addition that from butadiene showed bands at 670, 697, and 898 cm.$^{-1}$, that from *cyclo*pentadiene at 718 cm.$^{-1}$ and that from *cyclo*hexadiene at 708 and 808 cm.$^{-1}$. None absorbed intensely between 900 and 1000 cm.$^{-1}$ where vinyl and *trans*-CH=CH-groupings have characteristic bands. The possibilities of structural diagnosis in this region, and the advantages of observing the spectra of readily isolated solids, are obvious. Numerous other bands consistent with the assigned structures but without diagnostic significance were observed.

Experimental.—p-*Phenylazomaleinanilic acid.* Maleic anhydride (5 g.) in chloroform (50 c.c.) was added to a solution of *p*-aminoazobenzene (10 g.) in chloroform (70 c.c.). After 1 hr. at 20° the precipitate was filtered off, washed with ether until the washings were colourless, dried, and added to sodium carbonate solution (100 c.c., 10%). The mixture was stirred until the pink colour had changed to yellow, then filtered; the residual solid was washed repeatedly with ether to remove *p*-aminoazobenzene, dissolved in hot water, and acidified with hydrochloric acid; the precipitated acid was washed with water until the washings were no longer strongly acid to litmus, then once with ethanol, and dried at room temperature, giving the *anilic acid* (11 g., 73%) as pale orange needles, m. p. 215° (Found : C, 65·2; H, 4·9; N, 14·2. $C_{16}H_{13}O_3N_3$ requires C, 65·1; H, 4·5; N, 14·25%). Less carefully purified material consistently gave unsatisfactory results on dehydration.

p-*Phenylazomaleinanil.* The above anilic acid (9 g.) was stirred at 80° with acetic anhydride (100 c.c.) until it dissolved. On cooling, a solid separated which, crystallised from benzene, gave the *anil* (6·5 g., 77%) as orange needles, m. p. 162° (Found : C, 69·55; H, 3·85; N, 15·5. $C_{16}H_{11}O_2N_3$ requires C, 69·3; H, 4·0; N, 15·15%).

Diels–Alder adducts. These were prepared by treating a solution of the anil (740 mg.) in benzene (80 c.c.) with the diene (160—200 mg.) at 20° for 18 hr., evaporation, and chromatography on neutral alumina (200 g.; Peter Spence, Ltd., Grade " H "). Elution of the main band with benzene containing 10% of ether and crystallisation from benzene–light petroleum gave the adduct. Thus buta-1 : 3-diene gave the p-*phenylazoanil* of *cyclo*hex-4-ene-1 : 2-dicarboxylic acid in 55% yield, as needles m. p. 174°, depressed to *ca.* 140° on admixture with the reagent (Found : C, 72·3; H, 5·05; N, 12·45. $C_{20}H_{17}O_2N_3$ requires C, 72·5; H, 5·15; N, 12·7%) : *cyclo*pentadiene gave the *adduct* of 3 : 6-*endo*methylene*cyclo*hex-4-ene-1 : 2-dicarboxylic acid (65%), m. p. 176—177° (Found : C, 73·3; H, 4·85; N, 11·55. $C_{21}H_{17}O_2N_3$ requires C, 73·45; H, 5·0; N, 12·25%) ; and *cyclo*hexa-1 : 3-diene gave the *adduct* of 3 : 6-*endo*ethylene*cyclo*hex-4-ene-1 : 2-dicarboxylic acid (50%), m. p. 191—192° (Found : C, 73·7; H, 5·3; N, 11·55. $C_{22}H_{19}O_2N_3$ requires C, 73·95, H, 5·35; N,11·75%).

A more complex diene, 2 : 7-dimethylocta-1 : 3 : 5 : 7-tetraene (" cosmene;" Nayler and Whiting, *J.*, 1954, 4006) (160 mg.) and the anil (840 mg.) in dry benzene (80 c.c.) were heated to 50° for 5 hr. in nitrogen. Chromatography on alumina (200 g.; Grade " H ") gave (*a*) the unchanged reagent (300 mg.), m. p. and mixed m. p. 162—163°, and (*b*), by elution with ether, an adduct, m. p. 138—139° after crystallisation, depressed to *ca.* 120° on admixture with the reagent (Found : C, 72·3; H, 4·7; N,11·35. Calc. for $C_{42}H_{36}O_4N_6$: C, 73·25; H, 5·25; N, 12·2%). Essentially this was the bis-*p*-phenylazoanil of 2 : 3'-dimethyldi*cyclo*hex-2-enyl-4 : 5 : 4' : 5'-tetracarboxylic acid, but the tetraene rapidly absorbs oxygen, and impurities containing additional oxygen are evidently retained by the adduct in small amount.

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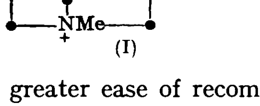
The Production of 1 : 4-*Dialkylpiperazines by the Thermal Decomposition of* 1 : 1 : 4 : 4-*Tetra-alkylpiperazinium Salts.*

By J. I. G. CADOGAN.

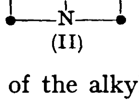
[Reprint Order No. 6310.]

THE thermal decomposition of quaternary ammonium halides to give tertiary amines and the corresponding alkyl halide has received considerable attention (Hurd, " Pyrolysis of Organic Compounds," Chemical Catalogue Co., New York, 1929, p. 317). The reaction has not however been exploited as a means of preparation of 1 : 4-dialkylpiperazines. Hromatka and Kraupp (*Monatsh.*, 1951, **82**, 880) and McElvain and Bannister (*J. Amer. Chem. Soc.*, 1954, **76**, 1126) noted that compounds related to 1 : 4-dialkylpiperazines can be obtained by the pyrolysis of quaternary halides. The former workers obtained 1 : 4-diaza*bicyclo*[2 : 2 : 2]octane (II) from the decomposition of the diquaternary salt (I), while the latter similarly obtained hexahydro-1 : 4-dimethyl-1 : 4-diazepine (1 : 4-dimethylhomopiperazine) from its dimethobromide. These reactions are similar to those described in this Note.

Several 1 : 1 : 4 : 4-tetra-alkylpiperazinium dihalides have been prepared and their pyrolysis products studied. All the dichlorides investigated gave the 1 : 4-dialkylpiperazine and alkyl chloride smoothly in 72—88% yield at atmospheric pressure. A lower yield of the base was obtained from the dibromides under comparable conditions, owing to the greater ease of recombination of the alkyl bromide and base. Further, a steric effect appears to be operative, since 1 : 1 : 4 : 4-tetramethylpiperazinium dibromide gave a very low yield (10%) of 1 : 4-dimethylpiperazine, whereas 1 : 4-diethyl-1 : 4-dimethylpiperazinium dibromide, under comparable conditions, gave a much higher yield of a mixture of 1 : 4-diethyl- and 1 : 4-dimethyl-piperazine. The method, when applied to the chlorides, is one of synthetic value, and its extensions are readily apparent.



(I)



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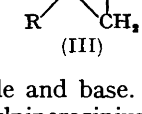

(III)

The tetra-alkylpiperazinium dichlorides were prepared by the dimerisation of the corresponding 2-dialkylaminoethyl chlorides in ethanol. Many workers (Hanby, Hartley, Powell, and Rydon, *J.*, 1947, 519; Bartlett, Ross, and Swain, *J. Amer. Chem. Soc.*, 1947, **69**, 2971; Hay, Thompson, and Winkler, *Canad. J. Res.*, 1948, **26**, *B*, 175) have postulated that this type of reaction proceeds through the ethyleniminium ion (III), although the absolute mechanism still appears to be in doubt. Thus 2-dimethylamino-1-methylethyl chloride might give 1 : 1 : 2 : 4 : 4 : 5- and/or 1 : 1 : 2 : 4 : 4 : 6-hexamethylpiperazinium dichloride. The pyrolysis of this dimerisation product could therefore give 1 : 2 : 4 : 5- and/or 1 : 2 : 4 : 6-tetramethylpiperazine. Abderhalden and Haas (*Z. physiol. Chem.*, 1925, **149**, 94) obtained the former as a syrup (dimethiodide, m. p. 250°), while Pope and Read (*J.*, 1914, **105**, 219) describe the mono- and the di-methiodide (m. p. 227° and 241°) of the latter. Our product gave a monomethiodide, m. p. 251°.

Experimental.—Solids, which were all colourless, were dried at 100°/10 mm. over P_2O_5 before analyses and m. p. determinations.

1 : 1 : 4 : 4-*Tetraethylpiperazinium dichloride.* 2-Diethylaminoethyl chloride hydrochloride (0·5 mole) was added to a vigorously stirred ice-cold mixture of water (500 ml.) and ether (250 ml.), the mixture was basified with solid potassium carbonate, and the layers were quickly separated. The ether layer was dried ($MgSO_4$) and removal of the solvent left the base as a yellow oil. This was boiled under reflux with ethanol (250 ml.) for 3 hr., 1 : 1 : 4 : 4-tetraethylpiperazinium dichloride separating as plates which, recrystallised from methanol–acetone (yield 80%), had m. p. >300°.

2-Ethylmethylaminoethyl bromide hydrobromide, prepared in 85% yield from 2-ethylmethylaminoethanol (cf. *Org. Synth.*, **18**, 13), similarly gave the 1 : 4-diethyl-1 : 4-dimethylpiperazinium dibromide (65%), m. p. 295° (from aqueous ethanol) (Found: C, 35·8; H, 7·5. Calc. for $C_{10}H_{24}N_2Br_2$: C, 36·15; H, 7·3%).

1 : 1 : 4 : 4-Tetramethylpiperazinium dibromide, prepared by the condensation of ethylene dibromide with *NNN'N'*-tetramethylethylenediamine in ethanol in 83% yield, had m. p. >330° (from aqueous ethanol).

1 : 1 : 4 : 4-*Tetra*-n-*propylpiperazinium dichloride.* Ethylene oxide (40 g.) was led into di-*n*-propylamine (101 g.) in a flask fitted with a condenser containing methanol–solid carbon dioxide. There was no reaction, even at 40°, until N-hydrochloric acid (20 ml.) was added (cf. Biel, *J. Amer. Chem. Soc.*, 1949, **71**, 1308). The mixture became dark and was kept at 60° for 2 hr. after the initial reaction had subsided. After being cooled, the organic layer was dried ($MgSO_4$) and fractionated. Di-*n*-propylamine (25%) was recovered, and 2-di-*n*-propylaminoethanol (n_D^{25} 1·4375; 75% based on amine consumed) was collected at 90—92°/20 mm. Burnett *et al.* (*J. Amer. Chem. Soc.*, 1937, **59**, 2248) give n_D^{20} 1·4402.

The alcohol was converted into 2-di-*n*-propylaminoethyl chloride hydrochloride by the action of excess (1·4 mol.) of thionyl chloride in dry benzene at 0°. The free base was isolated and converted as described above into the tetra-alkylpiperazinium salt, which was recrystallised to constant m. p. (295°) from ethanol–ethyl acetate, forming needles (51%).

2-Di-*n*-butylaminoethanol (68%; b. p. 104°/10 mm., n_D^{25} 1·4422; Burnett *et al.*, *loc. cit.*, give n_D^{20} 1·4444), from di-*n*-butylamine and ethylene oxide, similarly (thionyl chloride in chloroform, etc.) gave 1 : 1 : 4 : 4-*tetra*-n-*butylpiperazinium dichloride monohydrate* (47%), m. p. 239° (from aqueous ethanol–ethyl acetate) (Found: C, 60·1; H, 11·8. $C_{20}H_{44}N_2Cl_2,H_2O$ requires C, 59·8; H, 11·5%).

Hexamethylpiperazinium dichloride. 1-Dimethylaminopropan-2-ol was converted into 2-dimethylamino-1-methylethyl chloride hydrochloride (71%; m. p. 183—184°) by the method of Schultz and Sprague (*ibid.*, 1948, **70**, 48), who established that the isomeric 2-dimethylaminopropyl chloride hydrochloride is not formed by this method. The hydrochloride was converted, in the usual way, into the hexamethylpiperazinium dichloride (65%), which crystallised as hygroscopic needles, m. p. 275° from ethanol–benzene (Found: C, 49·9; H, 9·8. Calc. for $C_{10}H_{24}N_2Cl_2$: C, 49·4; H, 9·95%).

Dry distillation of tetra-alkylpiperazinium salts. The salt was gently warmed with a naked flame until decomposition began. Slight suction was maintained in order to draw the volatile alkyl halides into a cold trap (carbon dioxide–acetone), thus reducing the possibility of recombination of the halide and dialkylpiperazine. This tendency is very slight in the case of the alkyl chlorides, but increases if the halogen is bromine. In all cases tabulated below, the decomposition was very smooth, complete volatilisation of the piperazinium dichlorides being achieved. The base was collected in a cold receiver and was usually yellow. It was fractionated from potassium hydroxide and a portion was converted into the dimethiodide.

Piperazinium salt $R_2N(<[CH_2]_2>)_2NR_2\}X_2$		Alkyl in 1 : 4-dialkylpiperazine	B. p./ 10 mm.	n_D^{25}	Yield (%)	Analyses (%) *				
						Base		Dimethiodide		
R	X					C	H	C	H	M. p.
Et	Cl	Et	68°	1·4520	88	67·2	12·6	28·2	5·34	240° [a]
						67·5	12·8	28·2	5·68	
Pr^n	Cl	Pr^n	84	1·4514	80	70·3	12·8	31·1	6·35	228 [b]
						70·5	13·0	31·4	6·21	
Bu^n	Cl	Bu^n	112 [c]	1·4542	72	72·5	13·1	34·8	6·64	215 [d]
						72·7	13·2	35·0	6·69	
Me	Br	Me	130/ 760 mm.	1·4448	10	62·8	12·2	24·0	5·1	310 [e]
						63·1	12·4	24·1	5·1	
Hexamethyl dichloride		Me$_4$	62	1·4522	87	67·4	12·8	37·6	7·2 [f]	251 [f]
						67·6	12·8	38·0	7·3	

* Upper rows = Found; lower rows = Calc.

[a] Smith, Curry, and Eifert (*J. Amer. Chem. Soc.*, 1950, **72**, 2969), m. p. 240°. [b] Smith *et al.* (*loc. cit.*), m. p. 227°. [c] Forsee and Pollard (*ibid.*, 1935, **57**, 1788), b. p. 195°/12 mm. [d] Smith *et al.* (*loc. cit.*), m. p. 213°. [e] Mann and Senior (*J.*, 1954, 4476), m. p. 310°. [f] Monomethiodide.

The base obtained from 1 : 4-diethyl-1 : 4-dimethylpiperazinium dibromide gave fractions boiling over a range. Analysis of the combined fractions indicated that the product was a mixture of 1 : 4-diethyl- and 1 : 4-dimethyl-piperazine. Infrared analysis of the basic fraction and the alkyl halide confirmed this conclusion.

Microanalyses were carried out by Mr. F. E. Charlton and Mrs. B. Coddington, and the infrared determinations were by Mr. L. C. Thomas. This work was carried out during the tenure of a Civil Service Research Fellowship, and is published by permission of the Chief Scientist, Ministry of Supply.

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