NOTES.

844. *A Convenient Solid for Calibration of the Gouy Magnetic Susceptibility Apparatus.*

By B. N. Figgis and R. S. Nyholm.

The measurement of magnetic susceptibilities by the Gouy method is a relative one, the apparatus being calibrated in terms of a substance of known susceptibility, for which water, nickel chloride solution, and powdered cupric sulphate pentahydrate or ferrous ammonium sulphate hexahydrate have been used. The low suceptibility of water is often inconvenient if small tubes are being calibrated. Nickel chloride solution requires accurate analysis before use and ferrous ammonium sulphate is often of questionable purity. This substance and copper sulphate do not pack well and several different values for the susceptibilities of both solids have been reported.

The required properties for a calibrant are: (1) Readily available pure; (2) an accurately known and moderate susceptibility ($\chi_g \approx 10^{-5}$); (3) stability in moist air; (4) χ_g must vary in a known and simple way, at least at room temperature; (5) easily and reproducibly packable into the Gouy tube. The complex mercury tetrathiocyanatocobaltate $HgCo(CNS)_4$ offers some advantages and its susceptibility has therefore been accurately determined.

Pure water [absolute susceptibility taken as 0·7199 ($\pm$0·01%) × 10^{-6} at 20°] [2] being used as reference, the gram susceptibility of the complex is 16·44 ($\pm$0·08) × 10^{-6} at 20°. As reported elsewhere,[1] it obeys the Curie–Weiss law, $\chi_g \propto (T + 10)^{-1}$ where T is expressed in degrees absolute. Three different samples were prepared and measurements made on specimen lengths of 8, 10, and 12 cm. The following mean measurements of $10^6\chi_g$ were made: preparation no. 1, 16·45 ($\pm$0·2%); no. 2, 16·40 ($\pm$0·2%); no. 3, 16·48 ($\pm$0·3%); measurements at 8 cm., 16·38 ($\pm$0·2%); at 10 cm., 16·44 ($\pm$0·4%); at 12 cm., 16·49 ($\pm$0·4%).

It is concluded that within the experimental error of 0·4% there is no difference between

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[1] Figgis and Nyholm, to be published.

[2] Piccard and Devaud, *Arch. Sci. Phys. Nat.*, 1920, **2**, 455.

the preparations or the uniformity of packing at the three lengths. Allowing for possible systematic error of 0·1% arising from uncertainty in the correction for air dissolved in, or displaced by, the water calibrant, we conclude that the susceptibility of $CoHg(CNS)_4$ is 16·44 (±0·08) × 10^{-6} and that it is a very convenient substance for standardising Gouy tubes.

EXPERIMENTAL

The Gouy tube consisted of a 30 cm. piece of " Pyrex " glass tube of 1·2 cm. (±0·01 mm.) bore, cut into halves and cemented together with a flat glass plate between the halves. The tube hung from the pan of an aperiodic semimicro-balance so that the separating plate was in the centre of the pole gap of an electromagnet (10-cm. pole diameter, 4-cm. inter-pole gap). The force on the Gouy tube alone was then −0·14 mg. The Gouy tube was surrounded by a water jacket; the temperature was constant for long periods but varied from day to day between 19·5° and 20·5°. The temperature near to the specimen was measured frequently by means of a thermocouple; a correction was made according to $d\chi_g/dT = 0{\cdot}012\%$ for water[4] and 0·33% for $HgCo(SCN)_4$ at 20°.

An electromagnet of the Bates–Lloyd Evans[5] type was used, the current (10·0 A) being reproducible to within 0·1%. The magnetic field was approximately 10,000 gauss and since the magnet was approaching saturation field reproducibility was better than 0·1%; heating of the coils and core was kept to a minimum. By using a rider with the semimicro-balance, the beam deflection was kept within 0·5 mg. of the centre and this corresponded with a change in specimen position of approx. 0·5 mm. No deviation from linearity was noticed even when considerably larger beam deflections were allowed. The force developed on the water specimen varied from 23 to 24·5 mg. and that on the complex from 0·75 to 0·8 g.

The Gouy tube was calibrated at 8, 10, and 12 cm. marks with conductivity water which had come to equilibrium with the atmosphere. An allowance for dissolved air was made, based on its solubility in water, its partial pressure, and the value $\chi_g = 108 \times 10^{-6}$ at 20° for oxygen.[3] The calibration was also performed in nitrogen; the two calibrations agreed within experimental error, but the fluctuations introduced into the measurement of the force on the specimen by the provision of the nitrogen atmosphere were greater (0·2%) than the uncertainty introduced by the corrections for dissolved oxygen (0·1%). The volume of the meniscus was determined and allowed for. The mercury tetrathiocyanatocobaltate was introduced into the tube in lots of 1—2 g., *i.e.*, 5—10% of the total weight, and the bottom of the tube tapped firmly on wood 100 times after each addition. Three separate preparations of the substance were made and the tube was packed with each to each mark three times, a total of 27 measurements. The measurement of the force developed on each specimen was the mean of 9 observations.

The following preparation gives the complex in uniform and suitable crystal size with excellent packing properties. A solution " AnalaR " cobalt sulphate heptahydrate (28 g.) and " AnalaR " ammonium thiocyanate (30 g.) in distilled water (50 ml.) was added, at the boiling point and in one lot, to a boiling filtered solution of " AnalaR " mercuric chloride (27 g.) in distilled water (300 ml.), with vigorous stirring. The precipitated crystals are of about 0·5 mm. size. Boiling is continued for 1—2 min. with vigorous stirring. The product is washed several times by decantation and then dried at 120° (yield, 15 g.) (Found: C, 9·9; N, 11·35; S, 26·1. Calc. for $HgCo(SCN)_4$: C, 9·8; N, 11·4; S, 26·0%). The infrared spectrum of a sample stored under atmospheric conditions for a long time showed no significant water content.

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[*Received, April 29th,* 1958.]

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[3] Bauer and Piccard, *J. Physique*, 1920, **1**, 97.

[4] Auer, *Ann. Physik*, 1933, **8**, 593.

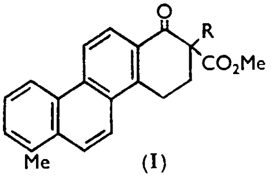
[5] Bates and Lloyd-Evans, *Proc. Phys. Soc.*, 1933, **45**, *A*, 425.

845. *Polycyclic Systems. Part III.*[1] *A Synthesis of 1 : 2 : 9-Trimethylpicene.*

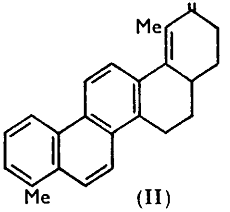
By D. NASIPURI.

SYNTHESIS of picene[1] by the Robinson ring-extension of 2-alkoxycarbonyl-1 : 2 : 3 : 4-tetrahydro-1-oxochrysene (*e.g.*, I; R = H) can be extended[2] to 1-substituted picenes by using β-chloro-ketones in place of the methiodide of Mannich bases. This method has now been used for the synthesis of 1 : 2 : 9-trimethylpicene (III), an expected dehydrogenation product of α-amyrin, on the basis of the structure proposed by Meisels, Jeger, and Ruzicka.[3]

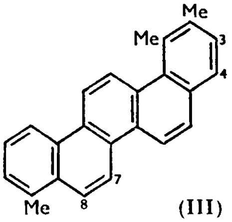
The sodio-derivative of the β-oxo-ester[2] (I; R = H) was condensed with 1-chloropentan-3-one;[4] the resultant dioxo-ester (I; $R = CH_2{\cdot}CH_2{\cdot}COEt$) on acidic hydrolysis afforded the unsaturated ketone (II) in good yield. Condensation with methylmagnesium iodide followed by dehydration and dehydrogenation with 30% palladium–charcoal then gave 1 : 2 : 9-trimethylpicene (III), characterised as 2 : 4 : 7-trinitrofluorenone complex and by its ultraviolet absorption.



(I)



(II)



(III)

This synthetic hydrocarbon, m. p. 266—268°, is found to be different from that, m. p. 306°, obtained in the dehydrogenation of α-amyrin,[5] the latter being apparently 2 : 9-dimethylpicene. Phillips and Tuites[6] also synthesised a trimethylpicene, m. p. 252—254°, which they represented by the same formulation (III), but their compound differs significantly from the present one particularly in the trinitrofluorenone complex. However, some of the steps in Phillips and Tuites's synthesis were not entirely free from ambiguity, the products of the last few steps not homogeneous, and the purity of the final compound was, therefore, questionable. The ultraviolet absorption spectra are very similar and it is probable that the trinitrofluorenone complex exists in polymorphs. We failed, however, to obtain a sample for comparison.

Experimental.—1 : 2 : 3 : 4-*Tetrahydro-2-methoxycarbonyl-7-methyl-1-oxo-2-3′-oxopentylchrysene* (I; $R = CH_2{\cdot}CH_2{\cdot}COEt$). To a cooled suspension of the sodio-derivative of the β-oxo-ester (I; R = H), prepared from methyl γ-(2-methoxycarbonyl-8-methyl-1-phenanthryl)-butyrate (4 g.), sodium methoxide (0·7 g.), and dry benzene (25 ml.), was added a solution of 1-chloropentan-3-one (4 g.) in benzene (15 ml.). The mixture was shaken for 1 hr., then left overnight, refluxed in the steam-bath for 30 min., and then decomposed with cold dilute sulphuric acid. The product, isolated in the usual way and crystallised from ethyl acetate (charcoal), gave the *ester* (I; $R = CH_2{\cdot}CH_2{\cdot}COEt$) (3 g.), m. p. 165—167° (Found: C, 77·2; H, 6·7. $C_{26}H_{26}O_4$ requires C, 77·6; H, 6·5%).

2 : 3 : 4 : 4a : 5 : 6-*Hexahydro-*1 : 9-*dimethyl-*2-*oxopicene* (II). The above dioxo-ester (2 g.), acetic acid (50 ml.), concentrated hydrochloric acid (25 ml.), and water (5 ml.) were refluxed under carbon dioxide for 20 hr., then cooled, and diluted with water. The *product* was filtered off, dried, passed in benzene through activated alumina, recovered, and crystallised from

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[1] Parts I and II, *J.*, 1958, 2618, 2734.
[2] Roy and Nasipuri, *Science and Culture*, 1958, **24**, 34.
[3] Meisels, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1949, **32**, 1075; 1950, **33**, 700.
[4] McMahon, Roper, Utermohlen, Hasek, Harris, and Brant, *J. Amer. Chem. Soc.*, 1948, **70**, 2971.
[5] Ruzicka and Morgeli, *Helv. Chim. Acta*, 1936, **19**, 377; Spring and Vickerstaff, *J.*, 1937, 249.
[6] Phillips and Tuites, *J. Amer. Chem. Soc.*, 1956, **78**, 5438.

benzene, forming plates (0·9 g.), m. p. 209—210° (Found: C, 88·1; H, 6·8. $C_{24}H_{22}O$ requires C, 88·3; H, 6·7%).

1 : 2 : 9-*Trimethylpicene* (III). The foregoing ketone (0·5 g.) in benzene was treated with excess of methylmagnesium iodide, and the crude product (0·55 g.) was heated with 30% palladium–charcoal [7] (100 mg.) at 340° for 1 hr. The melt was extracted with benzene, then filtered, and the solvent evaporated. The residue was passed in benzene–light petroleum through alumina and crystallised from ethanol–benzene, to give 1 : 2 : 9-trimethylpicene, plates, m. p. 266—268° (Found: C, 93·8; H, 6·3. Calc. for $C_{25}H_{20}$: C, 93·7; H, 6·3%), $\lambda_{max.}$ (in $CHCl_3$) 262, 281, 292, 326, 340, 365, 380, and 385 mμ (log ε 4·74, 4·83, 4·96, 4·36, 4·38, 3·70, 3·61, and 3·55 respectively). The 2 : 4 : 7-trinitrofluorenone complex crystallised from acetic acid as a red powder, m. p. 245—246° (Found: C, 71·9; H, 4·1; N, 6·85. Calc. for $C_{25}H_{20},C_{13}H_5O_7N_3$: C, 71·8; H, 3·9; N, 6·6%). Phillips and Tuites [6] give 252—254° and 203—205°.

The author is grateful to Mrs. Chhabi Dutta for microanalyses.

UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA. [*Received, May 6th,* 1958.]

[7] Linstead and Thomas, *J.*, 1940, 1127.

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846. *Chalcones and Related Compounds. Part VII.* Catalysed Exchange of Hydrogen Cyanide between Acetone Cyanohydrin and Chalcones.*

By B. E. BETTS and W. DAVEY.

NAZAROV and his co-workers [1] have described the addition of hydrogen cyanide to saturated and unsaturated carbonyl compounds by an exchange with acetone cyanohydrin. We have now used this reaction to add hydrogen cyanide to substituted chalcones (I) and other unsaturated ketones.

The optimum conditions for this exchange with chalcone itself were treatment of a solution in methanol with 3 mols. of acetone cyanohydrin and 0·1 mol. of 5—10% aqueous sodium carbonate. A 95% yield of the adduct (II; X = Y = H) was thus obtained. Use of triethylamine or saturated methanolic potassium hydroxide as catalyst resulted in lower yields. Reaction in dilute ethanolic solution with a tenfold excess of chalcone and saturated methanolic potassium hydroxide catalyst gave a 66% yield of 3-cyano-1 : 3 : 4 : 6-tetraphenylhexane-1 : 6-dione (III).[2]

$X{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}Y$ (I)

$X{\cdot}C_6H_4{\cdot}CH(CN){\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}Y$ (II)

$Ph{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CPh(CN){\cdot}CH_2{\cdot}CO{\cdot}Ph$ (III)

(IV) $Ph{\cdot}CH{:}CH{\cdot}CO{\cdot}Me$

$CO(CH{:}CH{\cdot}Ph)_2$ (VII)

(V) $p\text{-}(Ph{\cdot}CO{\cdot}CH{:}CH)_2C_6H_4$

$m\text{-}(Ph{\cdot}CO{\cdot}CH{:}CH)_2C_6H_4$ (VI)

By suitable modification of the optimum conditions a series of adducts (II) of alkyl-, alkoxy-, halogeno-, and dimethylamino-substituted chalcones (I) were prepared (see Table 1). Lower yields were again obtained when triethylamine was used as catalyst.

No crystalline products could be obtained from the exchange with 2′-, 3-, 3′-, 4-, and 4′-nitrochalcones, sodium carbonate catalyst being used. When triethylamine was used 3′-nitrochalcone gave a crystalline adduct, while the 2′-, 3-, 4-, and 4′-nitro-compounds were recovered unchanged.

The ketones (IV), (V), and (VI) gave good yields of the corresponding adducts. From

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* Part VI, *J.*, 1958, 2606.

[1] Nazarov and Zavyalov, *J. Gen. Chem.* (*U.S.S.R.*), 1954, **24**, 475 (U.S. translation); Nazarov, Akhrem, and Kamernitsky, *ibid.*, 1955, **25**, 1291; see also Ames and Davey, *J.*, 1957, 3480; De Ruggieri, *Gazzetta*, 1957, **87**, 795; Spanish P. 229,413 (*Chem. Abs.*, 1957, **51**, 9723).

[2] Michael and Weiner, *J. Amer. Chem. Soc.*, 1937, **59**, 744.

TABLE 1. *Hydrogen cyanide adducts.*

From substituted chalcones (I)

			Yield			Found (%)				Required (%)			
X	Y	Form *	(%) ‡	M. p.	Formula	C	H	N	Hal	C	H	N	Hal
H	H	Plates [a]	92	127° [1]	$C_{16}H_{13}ON$	—	—	—	—	—	—	—	—
p-Me	H	Plates [b]	99	137	$C_{17}H_{15}ON$	82·1	6·1	5·5	—	81·9	6·1	5·6	—
o-MeO	H	Prisms [b]	82	89	$C_{17}H_{15}O_2N$	76·7	5·6	5·3	—	77·0	5·7	5·3	—
m-MeO	H	Prisms [b]	83	112	$C_{17}H_{15}O_2N$	77·5	6·0	5·1	—	77·0	5·7	5·3	—
p-MeO	H	Plates [b]	81	119 [2]	$C_{17}H_{15}O_2N$	77·0	5·8	5·2	—	77·0	5·7	5·3	—
m-I	H	Needles	65	95	$C_{16}H_{12}ONI$	53·5	3·6	3·5	34·9	53·2	3·3	3·9	35·1
p-I	H	Needles	83	126	$C_{16}H_{12}ONI$	53·5	3·2	3·9	34·8	53·2	3·3	3·9	35·1
p-NMe$_2$	H	Yellow needles [a]	70	103	$C_{18}H_{18}ON_2$	77·5	6·3	9·7	—	77·7	6·5	10·1	—
H	*o*-Me	Needles [b]	94	95	$C_{17}H_{15}ON$	81·6	6·6	5·5	—	81·9	6·1	5·6	—
H	*p*-Cl	Needles	86	121 [3]	$C_{16}H_{12}ONCl$	71·0	4·8	5·4	12·9	71·2	4·5	5·2	13·1
H	*p*-Br	Prisms	89	125 [4]	$C_{16}H_{12}ONBr$	61·3	4·1	4·7	—	61·2	3·9	4·5	—
H	*p*-I	Needles	90	151	$C_{16}H_{12}ONI$	52·7	3·3	4·2	35·6	53·2	3·3	3·9	35·1
H	*m*-Cl	Needles	22	80	$C_{16}H_{12}ONCl$	70·5	4·5	5·3	13·1	71·2	4·5	5·2	13·1
H	*m*-Br	Needles	64	89	$C_{16}H_{12}ONBr$	60·9	3·9	4·4	25·8	61·2	3·9	4·5	25·4
H	*m*-I	Needles	87	104	$C_{16}H_{12}ONI$	53·2	3·8	3·9	34·5	53·2	3·3	3·9	35·1
H	*m*-NO$_2$	Needles [a]	62	128	$C_{16}H_{12}O_3N_2$	68·4	4·1	10·3	—	68·6	4·3	10·0	—

From other compounds

(III)		Prisms [c]	66 [e]	237 [5]	$C_{31}H_{25}O_2N$	83·4	5·3	3·0	—	83·9	5·7	3·2	—
(IV)		Needles	54	46	$C_{11}H_{11}ON$	76·0	6·2	8·2	—	76·3	6·4	8·1	—
(V)		Prisms [c]	72	228	$C_{26}H_{20}O_2N_2,\frac{1}{2}H_2O$	78·2	5·1	7·1	—	77·8	5·3	7·0	—
(VI)		Prisms [a]	70	152	$C_{26}H_{20}O_2N_2,\frac{1}{2}H_2O$	78·3	5·2	7·1	—	77·8	5·3	7·0	—
(VII)	monoadduct	Plates	23 [d]	126	$C_{18}H_{15}ON$	82·3	5·7	5·7	—	82·7	5·8	5·4	—
(VII)	diadduct	Prisms	43	121	$C_{19}H_{16}ON_2$	78·9	5·1	9·9	—	79·1	5·6	9·7	—

[*] From light petroleum (b. p. 60—80°) unless otherwise stated: [a] From EtOH. [b] From MeOH. [c] From 2-ethoxyethanol.

[†] 10% Aqueous sodium carbonate was used as catalyst unless otherwise stated. [d] NEt_3. [e] Saturated KOH–MeOH.

[1] Mixed m. p. undepressed with authentic specimen. [2] Robertson and Stephen (*J.*, 1931, 863) give m. p. 118°. [3] Kohler and Shohan (*J. Amer. Chem. Soc.*, 1926, **48**, 2430) give m. p. 121°. [4] Allen and Frame (*Canad. J. Res.*, 1932, *6*, 605) give m. p. 124°. [5] Michael and Weiner (*J. Amer. Chem. Soc.*, 1937, **59**, 744) give m. p. 237°.

TABLE 2. *Ultraviolet absorption spectra (in ethanol) of hydrogen cyanide adducts (italic numerals denote an inflexion).*

Adducts from chalcones (I)

X	Y	$\lambda_{max.}$ (mμ)	ε	X	Y	$\lambda_{max.}$ (mμ)	ε	X	Y	$\lambda_{max.}$ (mμ)	ε	X	Y	$\lambda_{max.}$ (mμ)	ε
H	H	244	14,300	*m*-MeO	H	227	10,700	*p*-NMe$_2$	H	256	25,700	H	*m*-Cl	243	11,900
		268	1,300			244	14,200			*303*	3,000			290	1,900
		281	1,100			273	3,700			422	2,500	H	*m*-Br	245	11,700
p-Me	H	*221*	9,100			*281*	3,500	H	*o*-Me	255	16,200			290	1,700
		244·5	14,400	*p*-MeO	H	230	16,000	H	*p*-Cl	254	18,500	H	*m*-I	226	26,800
		273	1,700			244	14,700	H	*p*-Br	258	20,200			*250*	9,400
o-MeO	H	222	10,100			*248*	13,800			*263*	18,500			299	1,500
		244	14,400			275	2,900	H	*p*-I	*224*	8,600	H	*m*-NO$_2$	*208*	6,800
		273	4,200			282	2,700			269	18,100			229	9,900
		278	4,000	*m*-I	H	235·5	19,800			*276*	16,700			*260*	2,800
						244	17,000			307	1,300				
						279	2,000								
				p-I	H	237	25,800								
						244	17,000								
						278	1,400								

Adducts from other compounds

Compd.	$\lambda_{max.}$ (mμ)	ε	Compd.	$\lambda_{max.}$ (mμ)	ε	Compd.	$\lambda_{max.}$ (mμ)	ε	Compd.	$\lambda_{max.}$ (mμ)	ε
(III)	*218*	13,300	(IV)	*230*	30	(VII) monoadduct	222	10,600	(VII) diadduct	*242*	178
	244	14,200		*242*	77		*226*	10,200		*247*	236
	283	3,300		*247*	108		293	22,800		252	318
(V)	244	30,000		251·5	150					257·5	393
	273—82	3,400		257·5	186					264	313
(VI)	244	28,700		263·5	151					*267*	185
	274—82	2,400		*267*	86					*283*	57
				278	34						
				282	29						

TABLE 3. *Methyl esters derived from hydrogen cyanide adducts.*

Esters X·C_6H_4·CH(CO_2Me)·CH_2·CO·C_6H_4·Y

						Found (%)				Required (%)			
X	Y	Form *	Yield (%)	M. p.	Formula	C	H	N	Hal	C	H	N	Hal
p-Me	H	Plates	97	107°	$C_{18}H_{18}O_3$	76·1	6·6	—	—	76·6	6·4	—	—
m-MeO	H	Prisms	95	101	$C_{18}H_{18}O_4$	72·7	6·1	—	—	72·5	6·1	—	—
p-I	H	Plates	86	137	$C_{17}H_{15}O_3I$	51·6	3·9	—	31·6	51·8	3·8	—	32·2
p-NMe$_2$	H	Plates	81	105	$C_{19}H_{21}O_3N$	73·5	7·0	4·7	—	73·3	6·8	4·5	—
H	*o*-Me	Plates	98	88	$C_{18}H_{18}O_3$	76·9	6·6	—	—	76·6	6·4	—	—
H	*m*-I	Needles	70	73	$C_{17}H_{15}O_3I$	52·3	3·9	—	32·2	51·8	3·8	—	32·2
H	*p*-I	Needles	73	131	$C_{17}H_{15}O_3I$	51·8	3·6	—	32·7	51·8	3·8	—	32·2
H	*m*-NO$_2$	Needles	65	90	$C_{17}H_{15}O_5N$	64·9	4·9	4·5	—	65·2	4·8	4·5	—
					Methyl esters from other adducts								
(VII) diadduct		Needles [a]	40	121	$C_{21}H_{22}O_5$	70·9	6·1	—	—	71·2	6·3	—	—
(V)		Prisms [b]	80	171	$C_{28}H_{26}O_6,\frac{1}{2}H_2O$	72·4	5·8	—	—	71·9	5·8	—	—
(VI)		Prisms [b]	82	155	$C_{28}H_{26}O_6$	72·8	5·7	—	—	73·3	5·7	—	—

* From methanol unless otherwise stated. [a] From light petroleum (b. p. 60—80°). [b] From 2-ethoxyethanol.

1 : 5-diphenylpenta-1 : 4-dien-3-one (VII), with aqueous sodium carbonate as catalyst there was obtained the diadduct, 1 : 5-dicyano-1 : 5-diphenylpentan-3-one, while the use of triethylamine gave the monoadduct, 1-cyano-1 : 5-diphenylpent-4-en-3-one. These structures were confirmed by the ultraviolet absorption spectra.

Starting material was recovered from attempted exchanges with 1-phenylhexa-1 : 3-dien-5-one and 1 : 9-diphenylnona-1 : 3 : 6 : 8-tetraen-5-one.

The ultraviolet absorption spectra are recorded in Table 2.

A number of the adducts were converted[3] into the corresponding methyl esters (Table 3).

Experimental.—Preparation of adducts. (i) To the compound (4 mol.) in acetone cyanohydrin (10 mol.) and methanol (sufficient to dissolve the compound) was added 10% aqueous sodium carbonate (1 mol.) or triethylamine (0·5 mol.); the mixture was refluxed for 1·5—4·0 hr. In most cases the product crystallised when the concentrated mixture cooled; otherwise the solution was poured into water, the product separating immediately.

(ii) Saturated methanolic potassium hydroxide (0·025 c.c. per g. of acetone cyanohydrin) was added to the compound dissolved in acetone cyanohydrin, and the mixture set aside overnight. The solution was then poured into water and the product collected.

THE POLYTECHNIC, 309 REGENT STREET, LONDON, W.1. [*Received, May 7th,* 1958.]

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[3] Davey and Tivey, *J.*, 1958, 1230.

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847. *Some Properties of Solid Carbon Monosulphide.*

By M. A. P. HOGG and J. E. SPICE.

IT is well established that CS, obtained by the action of an electric discharge on carbon disulphide vapour, behaves as a normal, though unstable molecule in the gaseous state, rather than as a short-lived radical.[1] A brown substance described as polymeric CS condenses[2] when the gases from the discharge are cooled to liquid-nitrogen temperature. During investigations into the production of free radicals we repeated this experiment.

Experimental.—Carbon disulphide vapour, at a pressure of about 1 mm. flowing at about 0·5 mmole/min., was passed through a high-voltage A.C. glow discharge, and then through a trap cooled in liquid nitrogen. A narrow brown ring always formed about 1 cm. above the level of the liquid nitrogen, and in this region the temperature, as determined with a thermocouple, was about 135° K. Any unchanged carbon disulphide condensed above the brown ring. Below the ring was a whitish layer extending to about the level of the nitrogen, and lower still a colourless condensate.

Provided the layer of colourless condensate was sufficiently thin, it was quite stable at the temperature of liquid nitrogen, no change being observed (after the flow of gas had stopped) for up to 2 hr. With very thin layers, the colourless condensate gradually turned brown on warming, the rate of change depending on the rate of warming. With thicker layers, however, the change on warming was much more violent, being accompanied by a flash and a sharp report; a black deposit (presumably of carbon) was then observed as well as the brown substance. Whenever such an explosion occurred, the inside surface of the Pyrex trap became covered with numerous small cracks, sometimes extending right through the glass. The violence of the explosion was surprising: on one occasion when the total weight of product could not have exceeded 1 mg., and the total heat evolved could not therefore have exceeded a few calories, the thick trap was badly cracked. Presumably the layer of condensate was so thin, and the energy release so nearly adiabatic, that a very high temperature was attained instantaneously. Explosion normally occurred if the condensation was continued for more than a few minutes,

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[1] For references, see Dyne and Ramsay, *J. Chem. Phys.*, 1952, **20**, 1055.

[2] *Idem, ibid.*; Dewar and Jones, *Proc. Roy. Soc.*, 1911, *A*, **85**, 574; Klemenc, *Z. Elektrochem.*, 1930, **36**, 722.

probably because the condensate was a poor conductor of heat, and its surface therefore became steadily warmer. If, however, the Dewar vessel was slowly raised, so as to spread the condensate over a larger area, it could be collected for as long as 20 min. before exploding. The amount of condensate probably never exceeded a few mmoles of CS. Attempts were made to collect the brown product directly, without explosion, by keeping the surface of the trap at 135° K. A heavy brown layer was formed, but explosion still occurred after about 12 min. The nature of the condensing surface was unimportant; normal condensation with explosion on warming occurred both in a trap packed with glass-wool, and on a nickel mirror. In the latter case there was no apparent reaction with the mirror.

We believe that the colourless deposit consisted of the compound CS, possibly as a glass, whereas the whitish layer was crystalline CS. By analogy with the b.p.s of CO, CO_2, and CS_2, molecular CS ought to condense at about 135° K. On warming a little above liquid-nitrogen temperature, it might polymerise to $(CS)_x$.

It was not possible to purify the polymeric deposit, but micro-analysis of the crude product gave $C : S = 2{\cdot}8 : 1$, indicating that polymerisation was accompanied by considerable decomposition, with volatilisation of some sulphur.

Although gaseous CS is quite stable, for we have condensed it in a trap as far from the discharge as 1 m., or even in a trap attached to a side tube at some 30 cm. from the main gas stream, yet it completely decomposed on passage through 15 cm. of tubing packed with glass-wool at about 300° C. When boron trichloride vapour was introduced into the gas stream a brown film was condensed direct. CS condensed on solid ammonia without reaction, but when ethylene had been previously condensed in the collecting trap, the CS appeared to dissolve in the liquid ethylene, and no polymerisation occurred until all the liquid had evaporated.

In order to calculate the heat content changes of some processes involving CS, we use Cottrell's values[3] for bond-energy terms, corrected where necessary to the now generally-accepted value of 170 kcal./g.-atom for the heat of sublimation of carbon, and we ignore the difference between ΔH and ΔU. Thus, the heat of formation of gaseous CS from solid carbon and sulphur is: $\Delta H_f = -D(\text{CS}) + 236$ kcal./mole. Gaydon[4] gives the heat of dissociation of CS as 166 ± 23 kcal./mole, so that ΔH_f for CS is $+70 \pm 23$ kcal./mole. The corresponding figure for CO is -27 kcal./mole. The heat of formation of solid CS would not, of course, differ from the above figure by more than a few kcal. A solid $(CS)_x$ polymer might consist of carbon chains cross-linked by sulphur atoms. On this basis, its heat of formation from gaseous CS would be $\Delta H_{\text{polym.}} \sim -47 \pm 23$ kcal./mole of CS. Further, the heat of formation of the solid polymer from the elements would be $\Delta H_f \sim +20$ kcal./mole of CS, a value which may be compared with that of $+13$ kcal. derived by Dewar and Jones[2] from the heat of combustion of their brown product which, no doubt, had already partly decomposed into carbon and sulphur.

On the basis of these figures, there is no difficulty in accounting for the instability of CS or for its ease of polymerisation. The heat of polymerisation of CO to a solid with a structure analogous to that postulated for $(CS)_x$ would, on the other hand, be $\Delta H_{\text{polym.}} = +7$ kcal./mole. This difference is due to the greater stability of multiple links between carbon and oxygen than of those between carbon and sulphur. The relative stability of gaseous CS is to be contrasted with its extreme reactivity as a solid, except at those very low temperatures at which it appears to be stabilised. The high reactivity of solid CS is probably due to the juxtaposition of the CS molecules in the condensate.

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[3] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 1954.

[4] Gaydon " Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, London, 1953.

848. *The Oxidation of Aromatic Amines. Part VII.* The Action of Persulphate on Some Aromatic Amines.*

By E. BOYLAND and PETER SIMS.

THE conversion, by alkaline persulphate, of a number of primary or tertiary aromatic amines into *o*-aminophenyl sulphates was described previously.[1] The oxidation has been extended to include the secondary amines, *N*-methylaniline and diphenylamine, and the heterocyclic amines 2- and 4-aminopyridine, all of which yield the corresponding *ortho*-substituted sulphuric esters. 4-Aminopyridine also yielded 4 : 4′-azoxypyridine.

4-Amino-2′ : 3-dimethyldiphenyl, which Walpole, Williams, and Roberts[2] showed to cause intestinal tumours in rats, yielded 4 : 4′-azo- and 4 : 4′-hydrazo-2′ : 3-dimethyldiphenyl as well as the expected sulphuric ester. 3 : 6 : 1- and 2 : 6 : 1-Xylidine also yielded sulphuric esters: with the latter amine, where both positions *ortho* to the amino-group are blocked by methyl groups, substitution by the entering sulphuric group in the *para*-position. All the above esters yielded the corresponding aminophenols on acid-hydrolysis.

Experimental.—The persulphate oxidations and the working up were carried out as previously described.[1]

Oxidation of N-*methylaniline.* This yielded *potassium* o-*methylaminophenyl sulphate* in plates (from methanol–ether) (1·2 g. from 5 g. of base) (Found: N, 5·7; S, 12·8. $C_7H_8O_4NSK$ requires N, 5·7; S, 13·3%). The ester with 2N-hydrochloric acid at 100°, in 15 min., yielded *o*-methylaminophenol, separating from light petroleum (b. p. 60—80°) in plates, m. p. 95—97° (lit.,[3] m. p. 96—97°) (Found: N, 11·4. Calc. for C_7H_9ON: N, 11·4%).

Oxidation of diphenylamine. The sulphuric ester from this oxidation formed a greenish gum, from which hydrolysis with 2N-hydrochloric acid yielded 2-hydroxydiphenylamine, prismatic needles (from water) (0·95 g. from 5 g. of base), m. p. 66—67° (lit.,[3] m. p. 69—70°) (Found: N, 7·7. Calc. for $C_{12}H_{11}ON$: N, 7·6%).

Oxidation of the aminopyridines. (*a*) Oxidation of 2-aminopyridine (5 g.) yielded a crude potassium salt, a strong aqueous solution of which was acidified with concentrated hydrochloric acid. The solid (1·2 g.) which separated was recrystallised four times from propan-1-ol–water, to yield 2-*amino*-3-*pyridyl hydrogen sulphate* in prisms, m. p. 222—224° (softening at 210°) (Found: C, 31·55; H, 3·2; N, 14·7; S, 17·15. $C_5H_6O_4N_2S$ requires C, 31·6; H, 3·2; N, 14·7; S, 16·85%). The ester (1 g.) in water (5 ml.) was heated to 100° for 15 min. with concentrated hydrochloric acid (1 ml.). A small excess of sodium hydrogen carbonate was added and the solution was extracted with ether for 4 hr. Removal of the ether afforded solid 2-amino-3-hydroxypyridine (0·48 g.), which crystallised from ethanol–light petroleum (b. p. 80—100°) in plates, m. p. 166—167° (lit.,[4] m. p. 163—167·5°) (Found: C, 54·2; H, 5·25; N, 25·4. Calc. for $C_5H_6ON_2$: C, 54·5; H, 5·5; N, 25·5%). The picrate separated from aqueous ethanol in yellow prisms, m. p. 256° (decomp.) (lit.,[4] m. p. 257°) (Found: N, 20·4. Calc. for $C_{11}H_9O_8N_5$: N, 20·65%). When 2-amino-3-hydroxypyridine in pyridine was treated with an excess of benzoyl chloride a *tribenzoyl derivative* was obtained; this separated from aqueous ethanol in needles, m. p. 169—170° (Found: C, 73·8; H, 4·4; N, 6·6. $C_{26}H_{18}O_4N_2$ requires C, 73·9; N, 6·6%).

(*b*) During oxidation of 4-aminopyridine (5 g.) orange plates (1·1 g.) separated: four recrystallisations from light petroleum (b. p. 80—100°) yielded 4 : 4′-azoxypyridine in yellow plates, m. p. 126—127° (lit.,[5] m. p. 125—126°) (Found: N, 27·9. Calc. for $C_{10}H_8ON_4$: N, 28·0%). When the product was heated with iron filings, 4 : 4′-azopyridine was formed, which separated from

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* Part VI, Sims, *J.*, 1958, 44.

[1] Boyland, Manson, and Sims, *J.*, 1953, 3623; Boyland and Sims, *J.*, 1954, 980; Sims, *J.*, 1958, 44.

[2] Walpole, Williams, and Roberts, *Brit. J. Indust. Med.*, 1952, **9**, 255.

[3] Heilbron and Bunbury, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1943.

[4] Bojarka-Dahlig and Urbanski, *Prace Placowck Nank-Badawez Munsterstwa Przemyslu Chem.*, 1952, **1**, 1.

[5] Hertog, Henkens, and van Roon, *Rec. Trav. chim.*, 1952, **71**, 1145.

water in red needles, m. p. 105° (lit.,[5] m. p. 107—108°) (Found: N, 30·3. Calc. for $C_{10}H_8N_4$: N, 30·4%).

The oxidation mixture was worked up in the usual manner, the sulphuric ester being obtained as in (*a*). 4-*Amino*-3-*pyridyl hydrogen sulphate* (1·55 g.) crystallised from water in red-brown plates, m. p. 245—256° (decomp.) (Found: C, 31·9; H, 3·4; N, 14·6; S, 17·0%). The ester (500 mg.) in water (5 ml.) and concentrated hydrochloric acid (3 ml.) was heated to 100° for 15 min. and the solution was treated with a small excess of sodium hydrogen carbonate and extracted with butan-1-ol (3 × 50 ml.). The butanol extract was evaporated to dryness and the residue was extracted twice with hot ethanol–light petroleum (b. p. 80—100°) (1 : 10) (20 ml.). The combined extracts were evaporated almost to dryness; red crystals (95 mg.) of 4-*amino*-3-*hydroxypyridine* separated; from ethanol–light petroleum (b. p. 80—100°) they formed pink crystals, m. p. 240—242° (Found: C, 54·6; H, 5·6; N, 25·35. $C_5H_6ON_2$ requires C, 54·5; H, 5·5; N, 25·4%). Benzoylation with an excess of benzoyl chloride in pyridine yielded a *tribenzoyl derivative*, which formed needles (from aqueous ethanol), m. p. 144—145° (Found: C, 73·7; H, 4·54; N, 6·7).

Oxidation of 4-*amino*-2′ : 3-*dimethyldiphenyl.* The amine (2·26 g.) was oxidised with persulphate as before. The reddish-brown solid (1·85 g.) which separated overnight was collected and dissolved in a minimum of boiling ethanol. The plates which separated on cooling were recrystallised from ethanol, to yield 4 : 4′-*azo*-2′ : 3-*dimethyldiphenyl* (590 mg.) in red plates with a golden lustre, m. p. 164° (Found: C, 86·6; H, 7·05; N, 7·1. $C_{28}H_{26}N_2$ requires C, 86·1; H, 6·7; N, 7·2%). The crystallisation mother-liquors were evaporated to small volume and allowed to crystallise. The product was recrystallised from ethanol to yield 4 : 4′-*hydrazo*-2′ : 3-*dimethyldiphenyl* (140 mg.) in plates, m. p. 211° (Found: C, 85·7, 85·4; H, 7·6, 7·1; N, 7·1. $C_{28}H_{28}N_2$ requires C, 85·7; H, 7·2; N, 7·1%). Evaporation of the mother-liquors afforded a brown amorphous solid which was not further investigated.

The mother-liquors from the oxidation were evaporated to about 150 ml. under reduced pressure and washed with ether. The evaporation was continued until crystals separated. These were collected and recrystallised from aqueous ethanol to yield *potassium* 4-*amino*-2′ : 3-*dimethyl*-5-*diphenylyl sulphate* (850 mg.) in plates (Found: C, 50·3; H, 4·6; N, 4·2; S, 9·6; K, 11·9. $C_{14}H_{14}O_4NSK$ requires C, 50·7; H, 4·3; N, 4·2; S, 9·7; K, 11·8%). The ester, hydrolysed with hydrochloric acid, yielded 4-*amino*-5-*hydroxy*-2′ : 3-*dimethyldiphenyl*, needles [from light petroleum (b. p. 80—100°)], m. p. 184—185° (Found: C, 78·8; 4, 7·1; N, 6·55. $C_{14}H_{15}ON$ requires C, 78·8; H, 7·1; N, 6·6%).

Oxidation of the xylidines. (*a*) 3 : 6 : 1-Xylidine (5 g.) yielded *potassium* 2-*amino*-3 : 6-*dimethylphenyl sulphate* (2·2 g.), separating from 90% aqueous ethanol in plates (Found: C, 37·5; H, 3·9; N, 5·3. $C_8H_{10}O_4NSK$ requires C, 37·6; H, 3·95; N, 5·5%). Acid-hydrolysis yielded 2-amino-3 : 6-dimethylphenol, separating from benzene in pinkish plates, m. p. 147—149° (lit.,[3] m. p. 149—150°) (Found: N, 10·2. Calc. for $C_8H_{11}ON$: N, 10·2%), which formed a dibenzoyl derivative as needles (from aqueous ethanol), m. p. 177—178° (lit.,[3] m. p. 178—179°) (Found: N, 4·3. Calc. for $C_{22}H_{19}O_3N$: N, 4·1%).

(*b*) 2 : 6 : 1-Xylidine (5 g.) yielded *potassium* 4-*amino*-3 : 5-*dimethylphenyl sulphate* (1·9 g.), separating from aqueous ethanol in flat needles (Found: C, 37·8; H, 4·1; N, 5·45; S, 12·3%). When a strong aqueous solution of the potassium salt (prepared either as above or from the free acid) was acidified with concentrated hydrochloric acid, feathery needles separated, which rapidly changed to short rods. 4-*Amino*-3 : 5-*dimethylphenyl hydrogen sulphate* recrystallised from aqueous ethanol in rods, m. p. 258—259° (decomp.) (darkening at 246°) (Found: N, 6·2; S, 14·4. $C_8H_{11}O_4NS$ requires N, 6·45; S, 14·8%).

Acid-hydrolysis of the ester yielded 4-amino-3 : 5-dimethylphenol, plates (from chloroform), m. p. 180—181° (lit.,[3] m. p. 181°) (Found: N, 10·35%).

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849. *Acid-stable Organic Azides, and the Schmidt Reaction with Heterocyclic Ketones.*

By M. M. COOMBS.

THE behaviour [1] of 9-azido-9-methylfluorene indicates that in sulphuric acid an equilibrium exists between the proton-adduct of the azide, the 9-methyfluorenyl cation, and hydrazoic acid. An azide which gives rise to a stable carbonium ion should tend to be stable to acids, since the $>C\overset{\curvearrowright}{—}N_3H^+$ bond will break rather than the $-N\overset{\curvearrowright}{—}N^+{\equiv}N$ bond. The inertness of triphenylmethyl azide [2] and the stability of the triphenylmethyl cation support this conclusion. Delocalisation of the positive charge over the heterocyclic ring gives a high degree of stability to the 9-phenyl-xanthenyl and -thiaxanthenyl cations [3] and it was of interest to study the azides derived from these. When this work was nearing completion Loudon *et al.*[4] described the preparation and thermal decomposition of these azides. Our results are essentially similar, and are summarised in the Experimental section; various other observations concerning the stability of these azides are now reported.

9-Azido-9-phenylxanthen dissolved in sulphuric acid with the yellow colour and green fluorescence characteristic of the 9-phenylxanthenyl cation. The presence of freely available hydrazoic acid was demonstrated by the formation of phenanthridone when fluorenone was added to the solution, and on dilution of this mixture with water 9-hydroxyphenylxanthen was isolated in good yield. The azide was largely recovered when its solution in sulphuric acid was poured into water, and, even after 24 hours' treatment, no rearrangement products were detected. The deep red colour of the 9-phenylthiaxanthenyl cation was shown by a solution of 9-azido-9-phenylxanthen in sulphuric acid and, similarly, the azide was recovered almost quantitatively. Inhibition of delocalisation of the positive charge on $C_{(9)}$ was expected to decrease this stability and, indeed, this was found with 9-hydroxy-9-phenylthiaxanthen dioxide which reacted readily with hydrazoic and sulphuric acid with evolution of nitrogen and formation of thiaxanthone dioxide anil in high yield. The same product was formed when the sulphone was added to a sulphuric acid solution of 9-azido-9-phenylthiaxanthen, thus proving the availability of hydrazoic acid in this solution. The anil, rather than the isomeric ring-enlarged thiazepine dioxide, is to be expected [5] since the electron-density is greater in the $C_{(9)}$–Ph bond than in the bonds joining the condensed benzene rings to $C_{(9)}$, owing to the strong electron-withdrawal by the *ortho*-substituent in these rings.

Jones and Mann [6] have pointed out that charge separation in heterocyclic ketones lowers the frequency of the infrared carbonyl band. Xanthone and thiaxanthone absorb at 1660 and 1645 cm.$^{-1}$ respectively, and therefore considerable delocalisation of the positive charge from the carbonyl group is to be expected in sulphuric acid solution. The failure of these ketones to undergo the Schmidt reaction while thiaxanthone dioxide, which shows a normal carbonyl adsorption at 1684 cm.$^{-1}$, reacts quantitatively to give the lactam of 2-amino-2′-carboxydiphenyl sulphone, confirms this expectation. Also Caronna and Palazzo's observation [7] that anthrone (1656 cm.$^{-1}$) does not react with hydrazoic and sulphuric acid whereas anthraquinone (1684 cm.$^{-1}$) gives the lactam of 2-aminobenzophenone-2′-carboxylic acid has been confirmed. Thus an abnormally low carbonyl frequency indicates that a ketone will not undergo the Schmidt reaction. However, the opposite is not true. Thus fluorenone (1715 cm.$^{-1}$) reacts readily to give phenanthridone, but the

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[1] Coombs, *J.*, 1958, 3454.

[2] Senior, *J. Amer. Chem. Soc.*, 1916, **38**, 2718.

[3] Elderfield, "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, 1951, Vol. II, pp. 469, 477, 546—547.

[4] Galt, Loudon, and Sloan, *J.*, 1958, 1588.

[5] Arcus and Coombs, *J.*, 1954, 4319.

[6] Jones and Mann, *J.*, 1958, 294.

[7] Caronna and Palazzo, *Gazzetta*, 1953, **83**, 533.

reaction fails with 4 : 5-diazafluorenone which has almost the same carbonyl frequency (1718 cm.$^{-1}$). Presumably with this compound protonation occurs at one of the ring-nitrogen atoms rather than at the carbonyl group. Similar behaviour is exhibited by the pyridinecarboxylic acids, anthranilic acid, and the aliphatic amino-acids, with which the reaction fails.[8]

Experimental.—98% Sulphuric acid was used thoughout.

9-*Azido-9-phenylxanthen.* This compound was obtained quantitatively when 9-hydroxy-9-phenylxanthen (5 g.) was stirred with sodium azide (5 g.), trichloroacetic acid (50 g.), and chloroform (50 ml.). It formed needles (from light petroleum), m. p. 114—115° (Found: C, 76·3; H, 4·1; N, 14·3. Calc. for $C_{19}H_{13}ON_3$: C, 76·25; H, 4·4; N, 14·05%). Loudon[4] reports m. p. 110°.

The bright yellow solution of this azide (2·00 g.) in sulphuric acid (3 ml.) and chloroform (15 ml.) was stirred for 8 hr. at room temperature and left for a further 16 hr. The mixture was poured into water and shaken, and the chloroform layer was washed with sodium hydrogen carbonate solution and dried (Na_2SO_4). Evaporation left a crystalline solid (1·94 g.) which on fractional crystallisation from light petroleum gave the azide (1·32 g.), m. p. 102—107° and mixed m. p. 102—108°, and 9-hydroxy-9-phenylxanthen (0·11 g.), m. p. and mixed m. p. 158°. When this experiment was repeated, but with stirring for 2½ hr., the azide (1·46 g.), m. p. 105—111° and mixed m. p. 106—112°, was recovered.

The azide (300 mg.) in sulphuric acid (3 ml.) was stirred at 25° while fluorenone (170 mg.) was added during ½ hr., and stirring was continued for a further 2½ hr. The dark mixture was then diluted with ice (10 g.), and the cream solid was collected and crystallised from ethanol, yielding phenanthridone (110 mg.), m. p. and mixed m. p. 294—295°. The yellow filtrate was further diluted with water (100 ml.) and the white precipitate of 9-hydroxy-9-phenylxanthen was collected and dried; it amounted to 180 mg. and had m. p. and mixed m. p. 156—157°.

9-*Azido-9-phenylthiaxanthen.*—9-Hydroxy-phenylthiaxanthen, stirred with sodium azide, trichloroacetic acid, and chloroform, yielded 9-*azido*-9-*phenylthiaxanthen*, tablets (from light petroleum), m. p. 57° (Found: C, 72·55; H, 4·5; N, 13·1. $C_{19}H_{13}N_3S$ requires C, 72·35; H, 4·15; N, 13·3%). This azide (2·00 g.) was stirred with sulphuric acid and chloroform as described above, and the red solution was diluted with water after 24 hr. The chloroform solution, on evaporation, gave a crystalline mass (1·93 g.), m. p. 49—52°, and 51—55° when mixed with the pure azide.

Reactions with 9-*hydroxy*-9-*phenylthiaxanthen dioxide.* This sulphone (2·00 g.; m. p. 214—216° [9]) was added portionwise to a vigorously stirred mixture of sodium azide (1 g.), sulphuric acid (3 ml.), and chloroform (20 ml.) at 25° during 1 hr. Nitrogen was evolved and the sulphuric acid became deep yellow. After a further 2 hr. the mixture was diluted with ice and water, and the chloroform layer was washed with water and dried ($MgSO_4$). Removal of the solvent gave a solid (1·85 g.) which was recrystallised from ethanol. *Thiaxanthone dioxide anil* formed yellow prisms (1·65 g.), m. p. 236—237° (Found: C, 71·4; H, 4·3; N, 4·5. $C_{19}H_{13}O_2NS$ requires C, 71·45; H, 4·1; N, 4·4%).

The anil (0·5 g.) was heated on the steam-bath with 5N-hydrochloric acid (30 ml.) until all the colour was discharged, and the solid was collected and dried. It (0·32 g.) had m. p. 188° alone and when mixed with thiaxanthone dioxide.

9-Hydroxy-9-phenylthiaxanthen dioxide (0·5 g.) was added to the red solution of 9-azido-9-phenylthiaxanthen (0·5 g.) in sulphuric acid (5 ml.) at 25° with stirring during ½ hr.: nitrogen was evolved after each addition. After an additional 2 hr. the mixture was added to an excess of ice-cold 2N-sodium carbonate, and the suspension was extracted with chloroform. Evaporation of the dried ($MgSO_4$) extract gave a resinous yellow solid from which thiaxanthone dioxide anil (0·33 g.), m. p. 133° alone and 136—137° when mixed with the pure specimen, was obtained by recrystallisation from ethanol.

Thermal decomposition. 9-Azido-9-phenylxanthen (1·00 g.) was heated at 170° for 2 hr. in decalin (10 ml.). Evaporation of the orange solution and fractional crystallisation of the residue gave 11-phenyldibenz[*b*,*f*]-1 : 4-oxazepine (0·56 g.), m. p. 109—110° after recrystallisation from methanol (Found: C, 84·4; H, 5·1; N, 5·15. Calc. for $C_{19}H_{13}ON$: C, 84·1; H, 4·85;

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[8] Smith, " Organic Reactions," John Wiley and Sons, Inc., New York, 1946, Vol. III, p. 312.

[9] Gomberg and Britton, *J. Amer. Chem. Soc.*, 1921, **43**, 1946.

N, 5·15%), and xanthone anil (0·22 g.), m. p. 136—138°. Loudon[4] reports m. p.s 108° and 135° for these two compounds. The anil (100 mg.), on hydrolysis with 5N-hydrochloric acid, gave xanthone (60 mg.), m. p. 174—176° and mixed m. p. 176—178°.

Similarly 9-azido-9-phenylthiaxanthen (3·6 g.) gave thiaxanthone anil (2·1 g.), m. p. 150°, which on hydrolysis yielded thiaxanthone, m. p. and mixed m. p. 212° (210 mg. from 300 of anil). The dark mother-liquors were concentrated and chromatographed on alumina with light petroleum (b. p. 40—60°), from which was isolated pale yellow needles of 11-phenyldibenzo[*b*,*f*]-1 : 4-thiazepine (0·3 g.), m. p. 116—117°. Loudon[4] reports m. p. 117° for this compound, and 153° for the anil.

Schmidt reactions with the ketones. The ketone (1·00 g.) in sulphuric acid (10 ml.) was stirred at 30° while sodium azide (1 g.) was added during 2 hr. Next day, the mixture was poured into water, and the product was collected and dried.

Anthraquinone gave the lactam of 2-aminobenzophenone-2′-carboxylic acid (1·00 g.), m. p. 243—245°. Recrystallisation from acetic acid yielded needles, m. p. 250—251° (Found: N, 6·35. Calc. for $C_{14}H_9O_2N$: N, 6·25%). Caronna *et al.*[7] report m. p. 245°.

Thiaxanthone dioxide gave 2-amino-2′-carboxydiphenyl sulphone lactam (1·05 g.), m. p. 290—292° (Found: N, 5·25. Calc. for $C_{13}H_9O_3NS$: N, 5·4%). McClelland and Peters[10] record m. p. 290° for this compound prepared by the cyclisation of the amino-acid.

The following ketones were recovered (weight, m. p. of the recovered material, and mixed m. p.): Anthrone (0·95 g., 155°, 155—157°); xanthrone (0·95 g., 177—179°, 176—178°); thiaxanthone (0·95 g.; 214—216°, 215—216°); 4 : 5-diazafluorenone (m. p. 211°[11]) (0·81 g., 205—207°; 207—209°).

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[10] McClelland and Peters, *J.*, 1947, 1229.

[11] Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 842.

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850. *Thiophen Derivatives. Part XIII.* Some Reactions of 3-Methylthiophen.*

By J. Lamy, Denise Lavit, and Ng. Ph. Buu-Hoï.

3-Methylthiophen, now available commercially, has become the most accessible source for many 3-substituted thiophens, 3-bromomethylthiophen, for instance, the product of its side-chain bromination with *N*-bromosuccinimide,[1] being an important intermediate. It has now been found that chlorination with *N*-chlorosuccinimide, even in the presence of benzoyl peroxide, gives mainly 2-chloro-3-methylthiophen (II), along with negligible amounts of the expected 3-chloromethylthiophen (I), probably because of allylic rearrangement of the latter under the influence of the succinimide formed in the reaction. This is in line with an earlier record of the rearrangement of 2-bromomethyl-5-methylthiophen to 3-bromo-2 : 5-dimethylthiophen catalysed by another weak alkali, cuprous cyanide.[2]

It is known that 3-methylthiophen undergoes acetylation with acetic anhydride in the presence of phosphoric acid, to give a mixture of mainly 2-acetyl-3-methylthiophen and some of the 4-methyl isomer;[3] however, its formylation with dimethylformamide in

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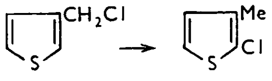
* Part XII, Buu-Hoï, *J.*, 1958, 2418.

[1] Cf. Buu-Hoï, *Annalen*, 1944, **556**, 1; Buu-Hoï and Lecocq, *Compt. rend.*, 1946, **222**, 1441; Campaigne and Le Suer, *J. Amer. Chem. Soc.*, 1948, **70**, 1556; Dittmer, Martin, Hertz, and Cristol, *ibid.*, 1949, **71**, 1201.

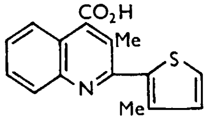
[2] Lecocq and Buu-Hoï, *Compt. rend.*, 1947, **224**, 658.

[3] Hartough and Kosak, *J. Amer. Chem. Soc.*, 1947, **69**, 3093; Hartough and Conley, *ibid.*, p. 3096.

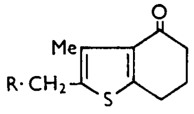
the presence of phosphorus oxychloride now yielded only 3-methyl-2-thenaldehyde. This aldehyde failed to react with thiosemicarbazide, although 5-ethyl-4-methyl-2-thenaldehyde readily gave a thiosemicarbazone; this abnormality recalls the inability, ascribed to steric hindrance, of 2-acetyl-3-ethylthionaphthen to give a semicarbazone or to undergo Pfitzinger reactions.[4] It is to be noted, however, that 2-acyl-3-methylthiophens gave normal Pfitzinger reactions, 3-methyl-2-propionylthiophen, for instance, affording 3-methyl-2-(3-methyl-2-thienyl)cinchoninic acid (III) which, on thermal decarboxylation, yielded the corresponding quinoline; similar cinchoninic acids and quinolines were obtained from 2-acetyl-4-methylthiophen.



(I) (II)



(III)



(IV)

2 : 3-Dimethyl-, 2-ethyl-3-methyl-, 2-ethyl-4-methyl-, and 2-ethyl-4 : 5-dimethyl-thiophen (the two last-named being new) were readily prepared by Wolff–Kishner reduction of the corresponding oxo-compounds. Succinoylation of 2 : 3-dimethyl-thiophen and 2-ethyl-3-methylthiophen, and reduction of the resulting keto-acids, yielded the substituted butyric acids, whose cyclisation afforded 4 : 5 : 6 : 7-tetrahydro-2 : 3-dimethyl-4-oxo- (IV; R = H) and 2-ethyl-4 : 5 : 6 : 7-tetrahydro-3-methyl-4-oxo-thianaphthen (IV; R = Me).

Experimental.—Acetylation and formylation of 3-*methylthiophen.* (*a*) Reaction of 3-methylthiophen (98 g.) with acetic anhydride (122 g.) in the presence of phosphoric acid (5 g.), performed according to Hartough *et al.*,[3] afforded a 90% total yield of 2-acetyl-3-methylthiophen (93·5 g.), b. p. 98—99°/14 mm., and the 4-methyl isomer (33 g.), b. p. 108—109°/14 mm.

(*b*) Reaction of 3-methylthiophen (98 g.) with dimethylformamide (84 g.) in the presence of phosphoric oxychloride (200 g.), performed in the usual way,[5] gave as sole product 3-methyl-2-thenaldehyde (88·5 g.), b. p. 112—113°/24 mm., $n_{\rm D}^{20\cdot5}$ 1·6013; no thiosemicarbazone was obtained, even on prolonged heating in ethanol.

Preparation of 2-*ethyl*-3- *and* -4-*methylthiophen.* The appropriate ketone (10 g.) and 98% hydrazine hydrate (10 g.) in diethylene glycol (30 c.c.) were heated for a few minutes at 80° to allow the hydrazone to be formed, potassium hydroxide (10 g.) was then added, and the mixture was boiled until the product had ceased to distil off (3 hr.). The distillate was extracted in ether, washed with dilute hydrochloric acid, then with water, dried ($CaCl_2$), recovered, and fractionated. An 83% yield was obtained of 2-ethyl-3-methylthiophen, b. p. 158—161°, $n_{\rm D}^{22\cdot5}$ 1·5225, and of 2-*ethyl*-4-*methylthiophen*, b. p. 160—161°, $n_{\rm D}^{22\cdot5}$ 1·5218 (Found: C, 66·7; H, 8·0. $C_7H_{10}S$ requires C, 66·7; H, 8·0%). 2 : 3-Dimethylthiophen, b. p. 142—143°, $n_{\rm D}^{22\cdot5}$ 1·5250, was prepared in the same way, in 66% yield, from 3-methyl-2-thenaldehyde.

5-*Ethyl*-4-*methyl*-2-*thenaldehyde.* To an ice-cooled mixture of 2-ethyl-3-methylthiophen (25 g.) and dimethylformamide (15 g.), phosphorus oxychloride (50 g.) was added dropwise with stirring; after the reaction had subsided, the mixture was refluxed on a water-bath for 1 hr. and, after cooling, was shaken with 25% aqueous sodium acetate (200 c.c.). The product was taken up in chloroform, washed successively with dilute hydrochloric acid, 5% aqueous sodium carbonate, and water, dried (Na_2SO_4), recovered, and fractionated *in vacuo*. The *aldehyde* (18 g.) had b. p. 126—127°/14 mm., $n_{\rm D}^{22}$ 1·5809 (Found: C, 62·3; H, 6·5. $C_8H_{10}OS$ requires C, 62·3; H, 6·5%). The *thiosemicarbazone*, prepared by briefly heating an ethanolic solution of the aldehyde with thiosemicarbazide, formed pale yellow prisms, m. p. 203°, from ethanol (Found: N, 18·4. $C_9H_{13}N_3S_2$ requires N, 18·5%).

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[4] Buu-Hoï and Cagniant, *Ber.*, 1943, **76**, 1269; for similar observations in the benzofuran group, see Bisagni, Buu-Hoï, and Royer, *J.*, 1955, 3688.

[5] Cf. Steinkopf, " Die Chemie des Thiophens," Steinkopff, Dresden and Leipzig, 1941, p. 53.

2-*Ethyl*-3 : 5-*dimethylthiophen*. This *compound* (8 g.), prepared by reduction of the foregoing aldehyde (15 g.) with hydrazine hydrate (15 g.) and potassium hydroxide (10 g.) in diethylene glycol (50 c.c.), had b. p. 179—180°, $n_D^{22.5}$ 1·5158 (Found: C, 68·4; H, 8·6. $C_8H_{12}S$ requires C, 68·5; H, 8·6%).

Chlorination of 3-*methylthiophen with* N-*chlorosuccinimide*. A stirred mixture of 3-methylthiophen (55 g.), *N*-chlorosuccinimide (67 g.), and dry carbon tetrachloride (160 c.c.) was refluxed with benzoyl peroxide (0·5 g.) for 12 hr.; after cooling, the succinimide formed was filtered off and washed with carbon tetrachloride, the filtrate evaporated off, and the residue fractionated *in vacuo*. The lower-boiling portion consisted of 2-chloro-3-methylthiophen [5] (II) (20 g.), b. p. 53—54°/15 mm., $n_D^{24.5}$ 1·5529; the higher-boiling portion consisted of 3-*chloromethylthiophen* (I), a lachrymatory oil with a pungent odour (1·5 g.), b. p. 74—75°/14 mm. (Found: C, 45·0; H, 3·5. C_5H_5SCl requires C, 45·3; H, 3·8%).

3-*Methyl*-2-(3-*methyl*-2-*thienyl*)*cinchoninic acid* (III). A solution of 3-methyl-2-propionylthiophen [6] (3 g.), isatin (3 g.), and potassium hydroxide (3·3 g.) in ethanol (25 c.c.) was gently refluxed for 24 hr.; the solvent was then distilled off, the residue taken up in water, the neutral impurities were extracted in ether, and the aqueous layer was acidified with acetic acid. The *acid* formed yellowish prisms, m. p. 241—242°, from ethanol (Found: C, 67 5; H, 4·5. $C_{16}H_{13}O_2NS$ requires C, 67·8; H, 4·6%). 3-*Methyl*-2-(3-*methyl*-2-*thienyl*)*quinoline*, obtained by heating this acid above its m. p. and distilling the residue *in vacuo*, formed yellowish prisms, m. p. 67—68°, from ethanol (Found: N, 6·1. $C_{15}H_{13}NS$ requires N, 5·9%).

2-(4-*Methyl*-2-*thienyl*)*cinchoninic acid*. Prepared from 2-acetyl-4-methylthiophen (4·6 g.), isatin (5·5 g.), and potassium hydroxide (5·6 g.) in ethanol (60 c.c.; 4 hours' refluxing), this *acid* (5·2 g.) formed yellow prisms, m. p. 233° (Found: C, 66·9; H, 4·0. $C_{15}H_{11}O_2NS$ requires C, 66·9; H, 4·1%). 2-(4-*Methyl*-2-*thienyl*)*quinoline* crystallised as colourless prisms, m. p. 159° (Found: N, 6·4. $C_{14}H_{11}NS$ requires N, 6·2%), giving a picrate, yellow leaflets, m. p. 224—225°, from ethanol.

6-*Methyl*-2-(4-*methyl*-2-*thienyl*)*cinchoninic acid*. Prepared from 2-acetyl-4-methylthiophen (1·5 g.), 5-methylisatin (2 g.), and potassium hydroxide (2 g.), this *acid* (2 g.) formed yellowish needles, m. p. 220°, from ethanol (Found: C, 67·5; H, 4·6. $C_{16}H_{13}O_2NS$ requires C, 67·8; H, 4·6%). 6-*Methyl*-2-(4-*methyl*-2-*thienyl*)*quinoline* formed colourless needles, m. p. 115°, from ethanol (Found: N, 5·7. $C_{15}H_{13}NS$ requires N, 5·9%), giving a *picrate*, yellow leaflets, m. p. 198—199°, from ethanol (Found: N, 11·8. $C_{21}H_{16}O_7N_4S$ requires N, 12·0%).

β-(4 : 5-*Dimethyl*-2-*thenoyl*)*propionic acid*. To an ice-cooled solution of 2 : 3-dimethylthiophen (48 g.) and succinic anhydride (48 g.) in nitrobenzene (350 c.c.), aluminium chloride (150 g.) was added in small portions with stirring, and the brown-red mixture left for 16 hr. at room temperature; after decomposition with ice and steam-distillation the solid product was purified by dissolution in aqueous sodium carbonate and reprecipitation with hydrochloric acid. The *keto-acid* (69 g.) formed colourless prisms, m. p. 161°, from *cyclo*hexane–benzene (Found: C, 56·7; H, 5·6. $C_{10}H_{12}O_3S$ requires C, 56·6; H, 5·7%).

γ-(4 : 5-*Dimethyl*-2-*thienyl*)*butyric acid*. The foregoing acid (70 g.), potassium hydroxide (60 g.), and hydrazine hydrate (70 g.) in warm diethylene glycol (300 c.c.) were refluxed for 6 hr. with removal of water. After cooling and dilution with water, acidification with hydrochloric acid furnished a product which was taken up in chloroform and purified by distillation *in vacuo*. The *acid* (32 g.) formed colourless prisms, b. p. 213—214°/40 mm., m. p. 44° (from *cyclo*hexane) (Found: C, 60·5; H, 7·1. $C_{10}H_{14}O_2S$ requires C, 60·6; H, 7·1%).

4 : 5 : 6 : 7-*Tetrahydro*-2 : 3-*dimethyl*-4-*oxothionaphthen* (IV; R = H). γ-(4 : 5-Dimethyl-2-thienyl)butyryl chloride, prepared from the above acid (30 g.), thionyl chloride (13 c.c.), and pyridine (6 drops) in dry ether (100 c.c.), formed a pale yellow oil (15 g.), b. p. 150—151°/18 mm. To a solution of this acid chloride (15 g.) in dry carbon disulphide (150 c.c.), stannic chloride (11 c.c.) was added in small portions with stirring, and the mixture refluxed for 3 hr. After cooling and decomposition with ice and hydrochloric acid, the product was taken up in chloroform, the organic layer washed with aqueous sodium carbonate, then with water, dried (Na_2SO_4), and evaporated, and the residue fractionated *in vacuo*. The *ketone* (6·5 g.) formed colourless prisms, b. p. 153—154°, m. p. 48—49°, from *cyclo*hexane (Found: C, 61·2; H, 6·2. $C_{10}H_{12}OS$ requires C, 61·2; H, 6·2%). The *semicarbazone* crystallised as needles, m. p. 199°, from ethanol (Found: N, 17·5. $C_{11}H_{15}ON_3S$ requires N, 17·7%).

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[6] Cf. Buu-Hoï and Hoán, *Rec. Trav. chim.*, 1949, **68**, 5.

β-(5-*Ethyl*-4-*methyl*-2-*thenoyl*)*propionic acid*. Prepared as for the lower homologue, from 2-ethyl-3-methylthiophen (23 g.), succinic anhydride (25 g.), and aluminium chloride (70 g.) in nitrobenzene (120 c.c.), this *acid* crystallised as colourless prisms (23 g.), m. p. 128°, from toluene (Found: C, 58 7; H, 6 1. $C_{11}H_{14}O_3S$ requires C, 58·4; H, 6·2%).

γ-(5-*Ethyl*-4-*methyl*-2-*thienyl*)*butyric acid*. Prepared from the foregoing acid (22 g.) with hydrazine hydrate (22 g.) and potassium hydroxide (22 g.) in diethylene glycol (120 c.c.), this *acid* (13 g.) formed a pale yellow oil, b. p. 193—195°/14 mm. (Found: C, 62·2; H, 7·6. $C_{11}H_{16}O_2S$ requires C, 62·3; H, 7·6%). The corresponding chloride (8·5 g.), prepared from the acid (13 g.) with thionyl chloride (6 c.c.) and pyridine (3 drops) in ether (50 c.c.), had b. p. 159—161°/12 mm. Cyclisation of this chloride (8 g.) with stannic chloride (6 c.c.) in carbon disulphide furnished 2-*ethyl*-4 : 5 : 6 : 7-*tetrahydro*-3-*methyl*-4-*oxothionaphthen* (IV; R = Me) (5 g.), b. p. 164—165°/16 mm. (Found: C, 67·9; H, 7·3. $C_{11}H_{14}OS$ requires C, 68·0; H, 7·3%).

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851. *Kinetics of the Reaction of Methyl Radicals with Toluene.*

By S. J. W. PRICE and A. F. TROTMAN-DICKENSON.

WHEN a metal alkyl is pyrolysed in the presence of a large excess of toluene, methane is formed by reaction (1) and ethane by reaction (2):

$$CH_3\cdot + C_6H_5\cdot CH_3 = CH_4 + C_6H_5\cdot CH_2\cdot \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$2CH_3\cdot = C_2H_6 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The decompositions of dimethyl-mercury, -cadmium,[1a] and -zinc,[1b] trimethyl-bismuth and -antimony, and dimethyltin dichloride,[1c] all of which yield methyl radicals, have recently been studied. From the complete analytical results [2] we have calculated the rate constant of reaction (1) using the equation

$$k_1 = k_2^{\frac{1}{2}}.R_{\text{methane}}/R_{\text{ethane}}^{\frac{1}{2}}\,[C_6H_5\cdot CH_3]$$

where R_{methane} is the rate of formation of methane. A least-squares treatment of the results derived from the 131 runs performed with the six alkyls at about 16 mm. pressure of toluene yields the relation

$$\log k_1 = (12{\cdot}92 \pm 0{\cdot}08) - (13{,}030 \pm 270/2{\cdot}303\boldsymbol{R}T)$$

if $\log k_2 = 13{\cdot}36$,[3] where the units of the bimolecular rate constants are, as throughout, mole^{-1} cm.^{3} sec.$^{-1}$, and the error limits correspond to the most probable error: systematic errors and possible errors in k_2 were disregarded. The Table lists the Arrhenius parameters for reaction (1) obtainable by a least-squares treatment of the results with each alkyl. The Arrhenius parameters obtained by use of the individual sources differ considerably from those from the complete results. The largest discrepancies are attributable to the difficulty of estimating accurately the very small quantities of ethane formed in the lower-temperature runs with the zinc and tin compounds. No rate constant falls very far from the mean line (columns 6 and 7), so it is unlikely that large systematic

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[1] Price and Trotman-Dickenson, *Trans. Faraday Soc.*, 1957, **53**, (*a*) 939, (*b*) 1208; (*c*) 1958, **54**, in the press.

[2] Price, Ph.D. thesis, Edinburgh, 1958.

[3] Shepp, *J. Chem. Phys.*, 1956, **24**, 939.

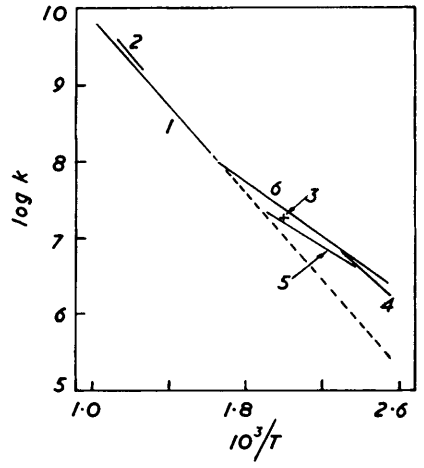
errors occur, though they are probably greater than the random errors. Unless a full mathematical analysis is made of the results, large errors can arise in the determination in a plug-flow reaction vessel of the ratios of rate constants of reactions that are of first and second order with respect to the concentration of a radical produced in a pyrolysis. In particular, the effective volume of the vessel varies with temperature, giving a low apparent activation energy for the first-order reaction. The difficulty was largely overcome by using sources with different rates of decomposition to cover the temperature range.

Radical source	Runs	log A_1	E_1	Temp.	log k_1 *	log k_1 †	Temp.
Dimethylzinc	20	13·7	16·2	573—701°	9·6	9·65	600°
Dimethylcadmium	17	11·8	12·4	469—571	9·4	9·23	500
Dimethylmercury	16	13·2	14·1	465—608	9·4	9·45	550
Trimethylantimony	30	13·3	14·3	475—582	9·4	9·41	540
Trimethylbismuth	27	13·4	12·2	346—409	8·7	8·74	390
Dimethyltin dichloride ...	21	14·6	20·2	554—637	9·6	9·69	610
Dimethylmercury[4]	15	13·0	13	518—610	9·5	9·45	550

* Rate constants for the temperature listed in last column calculated from the Arrhenius parameters for individual alkyls.

† Rate constants calculated from the least-squares line for the complete data.

Two sets of results obtained under comparable conditions have been reported. Gowenlock, Polanyi, and Warhurst[4] pyrolysed dimethylmercury in a flow system with 7 mm. of nitrogen and 3·2 mm. of toluene. Arrhenius parameters and rate constant deduced therefrom are shown in the Table. A correction of —0·2 logarithmic unit has been added to A to allow for the slightly lower value of k_2 under their conditions than in 16 mm. of toluene.[1a, 5] The agreement is all that could be expected.



Arrhenius plots for the abstraction of a hydrogen atom from toluene by a methyl radical.

1, This work.
2, Gowenlock, Polanyi, and Warhurst.[4]
3, Murawski, Roberts, and Szwarc.[6]
4, Szwarc and Roberts.[7]
5, Rebbert and Steacie.[8]
6, Trotman-Dickenson and Steacie.[11]

Only one rate constant at 230° can be deduced from the study of the pyrolysis of di-*tert.*-butyl peroxide by the toluene-carrier technique because the analyses of the products were inadequate.[6] The value of log k_1 = 7·52 is in reasonable agreement with ours (7·29).

Before these results can be compared with those obtained in static systems, a correction must be applied to allow for the change from a pressure of about 16 mm. to one of about 100 mm. Its exact magnitude is uncertain but must be about —0·2 logarithmic unit.[1a, 5]

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[4] Gowenlock, Polanyi, and Warhurst, *Proc. Roy. Soc.*, 1953, *A*, **218**, 269.

[5] Dodd and Steacie, *ibid.*, 1954, *A*, **223**, 283.

[6] Murawski, Roberts, and Szwarc, *J. Chem. Phys.*, 1951, **19**, 698.

Hence at 100 mm. log $k_1 = 12{\cdot}7 - (13{,}000/2{\cdot}303\boldsymbol{R}T)$. Szwarc and Roberts [7] obtained a similar activation energy, using the pyrolysis of di-*tert.*-butyl peroxide as a source of methyl in a static system, but their rate constants and *A* factors are discordant.

The apparently more reliable work of Rebbert and Steacie [8] yields log $k_1 = 10{\cdot}6 - (7300/2{\cdot}303\boldsymbol{R}T)$, which differs from our value by many times the combined experimental errors. The disagreement with the later interpretation [9] of Taylor and Smith's work,[10] log $k_1 = 9{\cdot}8 - (7000/2{\cdot}303\boldsymbol{R}T)$, is less significant as the experimental results were not very complete. The relations between all these results are shown in the Figure.

The interpretation of Trotman-Dickenson and Steacie's work on the reaction of $CD_3\cdot$ with toluene [11] is uncertain because it is based on a value for the rate constant of reaction (3) given [12] by log $k_3 = 11{\cdot}4 - (10{,}300/2{\cdot}303\boldsymbol{R}T)$. The experiments were done with

$$CD_3 + CD_3{\cdot}CO{\cdot}CD_3 = CD_4 + {\cdot}CD_2{\cdot}CO{\cdot}CD_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

insufficiently deuterated acetone. More recent work indicates that [13] log $k_3 = 11{\cdot}6 - (11{,}600/2{\cdot}303\boldsymbol{R}T)$. However it is doubtful whether the results with toluene can be corrected by applying this value for k_3 which would give log $k_1 = 11{\cdot}2 - (9600/2{\cdot}303\boldsymbol{R}T)$. The true value probably lies somewhere between this expression and that originally proposed: log $k_1 = 11{\cdot}0 - (8300/2{\cdot}303\boldsymbol{R}T)$. It can be maintained that results from both low-temperature photolyses and high-temperature flow experiments are correct within the limits of the experimental errors and that the Arrhenius plot is really curved owing to a change in mechanism with temperature. Perhaps the strongest argument against this conclusion is the very high *A* factor which the high-temperature reaction would require. Some fifty metatheses of methyl radicals have been studied; [14] as predicted by transition-state theory, none has a well-established *A* factor greater than $10^{12{\cdot}0}$. Further investigation of this reaction, particularly in the range 250—450°, is needed.

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[7] Szwarc and Roberts, *Trans. Faraday Soc.*, 1950, **46**, 625.
[8] Rebbert and Steacie, *J. Chem. Phys.*, 1953, **21**, 1723.
[9] Trotman-Dickenson and Steacie, *J. Phys. Chem.*, 1951, **55**, 908.
[10] Taylor and Smith, *J. Chem. Phys.*, 1940, **8**, 543.
[11] Trotman-Dickenson and Steacie, *ibid.*, 1951, **19**, 329.
[12] *Idem, ibid.*, 1950, **18**, 1097.
[13] Whittle and Steacie, *ibid.*, 1953, **21**, 993; McNesby, Davis, and Gordon, *J. Amer. Chem. Soc.*, 1954, **76**, 823.
[14] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955.

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852. *Complex Formation involving Silver and the 2-Hydroxyethylamines.*

By D. J. ALNER and A. G. SMEETH.

STABILITIES of complexes between silver salts and 2-hydroxyethylamines were previously determined by pH methods.[1] We have measured the solubility of silver oxide in solutions of mono-, bis-, and tris-2-hydroxyethylamines (" ethanolamines "); together with data obtained electrometrically it again demonstrates formation of complexes, whose compositions and stability constants are correlated with the basic strengths of the amines.

Experimental.—Dissociation constants of the 2-hydroxyethylamines at 20°. Distilled under reduced pressure, the purified amines (99·7% w/w in each case, by titration with hydrochloric

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[1] Bjerrum, " Metal Ammine Formation in Aqueous Solution," Haase, Copenhagen, 1941.

acid) were characterised through refractive indices (Hilger–Chance refractometer): 2-Hydroxyethylamine, n_D^{20} 1·4545 (lit.,[2,3] 1·4539; lit.,[4] for sample containing 97%, n_D^{20} 1·4544); bis-2-hydroxyethylamine, n_D^{20} 1·4780 (lit.,[2] 1·4776); tris-2-hydroxyethylamine, n_D^{20} 1·4851 (lit.,[2] 1·4851). Dissociation constants of the amines were determined by measuring the hydrogen-ion activities set up during the neutralisation in the cell:

$$H_2(1\text{ atm.}) \mid \text{Base} + HCl \mid KCl\text{ bridge} \mid \text{Sat. calomel}$$

Dilute solutions of the bases were titrated with hydrochloric acid at 20°, and the pH values, as defined by $-\log\{H^+\}$, where braces {} represent activities, were calculated from the measured e.m.f.'s. These titrations are represented in Table 1; K refers to the equilibrium $B + H_2O \rightleftharpoons BH^+ + OH^-$; $K = \{BH^+\}\{OH^-\}/\{B\}$; I is the ionic strength.

TABLE 1. *Dissociation constants at* 20°

HCl (ml.)	pH (obs.)	10^2I	pK		HCl (ml.)	pH (obs.)	10^3I	pK	
2-Hydroxyethylamine									
50 *ml.* of 0·0494M-*base titrated with* 0·50M-HCl					50 *ml.* of 0·00988M-*base titrated with* 0·100M-HCl				
1·00	10·22	0·98	4·59		1·00	10·15	1·96	4·61	
1·50	10·00	1·46	4·58		1·50	9·94	2·91	4·59	
2·00	9·82	1·92	4·58		2·00	9·77	3·85	4·59	
2·50	9·64	2·38	4·59		2·50	9·59	4·76	4·59	
3·00	9·47	2·83	4·58		3·00	9·41	5·66	4·58	
3·50	9·27	3·27	4·59		3·50	9·19	6·54	4·60	Mean 4·59
4·00	9·02	3·70	4·60	Mean 4·59					
Bis-2-hydroxyethylamine									
50 *ml. of* 0·0505M-*base titrated with* 0·50M-HCl					50 *ml. of* 0·10M-*base titrated with* 0·100M-HCl				
1·00	9·64	0·98	5·22		1·00	9·59	1·96	5·20	
1·50	9·41	1·46	5·19		1·50	9·37	2·91	5·20	
2·00	9·22	1·92	5·19		2·00	9·19	3·85	5·19	
2·50	9·06	2·38	5·19		2·50	9·01	4·76	5·20	
3·00	8·88	2·83	5·20		3·00	8·84	5·66	5·20	
3·50	8·70	3·27	5·19		3·50	8·64	6·54	5·21	Mean 5·20
4·00	8·47	3·70	5·20	Mean 5·20					
Tris-2-hydroxyethylamine									
50 *ml.* of 0·050M-*base titrated with* 0·50M-HCl					50 ml. *of* 0·01M-*base titrated with* 0·100M-HCl				
1·00	8·84	0·98	6·34		1·00	8·46	1·96	6·33	
1·50	8·25	1·46	6·34		1·50	8·22	2·91	6·34	
2·00	8·06	1·92	6·35		2·00	8·04	3·85	6·33	
2·50	7·89	2·38	6·35		2·50	7·86	4·76	6·34	
3·00	7·71	2·83	6·36		3·00	7·68	5·66	6·35	
3·50	7·52	3·27	6·36		3·50	7·49	6·54	6·35	
4·00	7·29	3·70	6·36	Mean 6·35	4·00	7·25	7·41	6·36	Mean 6·35

Corrections were applied for the extent of ionisation of the uncombined base, and for the hydrolysis of the amine hydrochloride formed. The activity coefficients of the univalent ions were calculated from $-\log f = 0{\cdot}505\sqrt{I}/(1 + \sqrt{I})$,[5] the activity coefficient of the un-ionised, uncombined base being assumed to be unity.

Dissociation constants of the 2-hydroxyethylamines at 20° are new. Our values represent true activity constants, and although close to those found [6] for solutions of greater ionic strength at 25°, differ from them by an activity factor.

Solubility product K_S *of silver oxide at* 20°. Variations in pH were measured with a glass

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[2] Knorr, *Ber.*, 1897, **30**, 909.

[3] Reitmeier, Sivertz, and Tartar, *J. Amer. Chem. Soc.*, 1940, **62**, 1943.

[4] Leibush and Shorina, *J. Appl. Chem., U.S.S.R.*, 1947, **20**, 691.

[5] Guggenheim and Schindler, *J. Phys. Chem.*, 1934, **38**, 539.

[6] *E.g.*, Bruehlman and Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401; Bjerrum, *Chem. Rev.*, 1950, **46**, 381; Bjerrum and Refn, *Suomen Kem.*, 1956, *B*, **29**, 68.

electrode (with exclusion of carbon dioxide) during titrations of dilute solutions of silver nitrate with carbonate-free sodium hydroxide (Table 2).

It was assumed that silver hydroxide was precipitated stoicheiometrically, since no basic salt appeared to be formed; the inflexion in the pH curve appeared at the stoicheiometric end-point. From the concentrations and ionic strengths used, the activities of the silver ions remaining in solution were calculated, the negligible solubility of the precipitate being ignored.

We used our value, a true constant for $K_s = \{Ag^+\}\{OH^-\} = 1{\cdot}413 \times 10^{-8}$ at 20°, which agrees well with concentration solubility products $[Ag^+][OH^-]$ [$1{\cdot}44 \times 10^{-8}$ (ref. 7); $3{\cdot}42 \times 10^{-8}$ (ref. 8)], in deriving the stability constants for the complexes.

TABLE 2. *Titration of* 0·01M-*silver nitrate* (100 *ml.*) *with* 0·10M-*sodium hydroxide at* 20°.

NaOH (ml.)	1·00	2·00	3·00	4·00	5·00	6·00	7·00	8·00
pH (obs.)	8·36	8·46	8·53	8·61	8·69	8·79	8·92	9·10
$10^2 I$	0·990	0·980	0·979	0·962	0·952	0·943	0·933	0·926
pK_s	7·90	7·86	7·85	7·86	7·85	7·85	7·85	7·85

Solubility of silver oxide in aqueous solutions of the 2-*hydroxyethylamines at* 20°. Tamisier[9] determined the solubility of silver chloride (but not the oxide) in solutions of 2-hydroxyethylamine and demonstrated complex formation.

Silver hydroxide was precipitated from dilute silver nitrate solution with the stoicheiometric amount of sodium hydroxide, washed with hot water until free from electrolytes, and filtered. Excess of the moist silver oxide was added to solutions of the amines of known concentration, and shaken mechanically in black bottles at 20° until equilibrium was reached.

TABLE 3. *Solubility of silver oxide at* 20°.

2-Hydroxyethylamine				Bis-2-hydroxyethylamine				Tris-2-hydroxyethylamine			
Base (10^{-2}N)	Ag_2O (10^{-2}N)	pH (obs.)	log β_2	Base (10^{-2}N)	Ag_2O (10^{-3}N)	pH (obs.)	log β_2	Base (10^{-2}N)	Ag_2O (10^{-3}N)	pH (obs.)	log β_2
5·1	1·1	11·98	6·91	5·0	4·2	11·72	5·80	10·1	1·6	11·35	4·24
10·2	2·25	12·31	6·91	10·0	8·6	11·98	5·80	15·2	2·4	11·53	4·23
15·3	3·45	12·48	6·92	15·0	13·2	12·12	5·81	20·2	3·2	11·64	4·22
20·4	4·67	12·55	6·92	20·0	17·8	12·23	5·80	25·3	4·0	11·73	4·22
22·5	5·86	12·61	6·91	25·0	22·4	12·31	5·81			Mean	4·23
		Mean	6·91			Mean	5·80				

The pH's of these solutions were determined with a glass electrode, and the silver content of the clear filtrates by Volhard's thiocyanate method. Table 3 gives our results, together with calculated values of the stability constants of the silver complexes, as defined by $\beta_2 = \{AgB_2^+\}/\{Ag^+\}\{B\}^2$.

Discussion.—The high pH values found in the amine solutions saturated with silver oxide (Table 3) demonstrated that strong bases of the type AgB_2OH were formed, since the bases themselves could not cause them. The solubility can be explained in terms of the stability constant of the complex cation formed and of the solubility product of silver hydroxide, or conversely can be used to calculate the stability constant of the complex cation.

The combination of silver hydroxide with the base can be represented by $AgOH + nB \rightleftharpoons AgB_n^+ + OH^-$. The complex cation itself must be in equilibrium with silver ions, $AgB_n^+ \rightleftharpoons Ag^+ + nB$, hence $\beta_n = \{AgB_n^+\}/\{Ag^+\}\{B\}^n$.

If the concentration of base is C equiv./l., the amount of silver hydroxide dissolved

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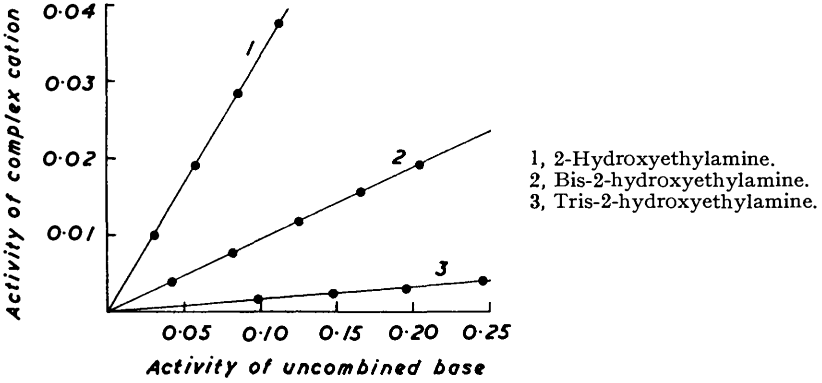
[7] Laue, *Z. anorg. Chem.*, 1927, **165**, 324.

[8] Noyes and Kohr, *J. Amer. Chem. Soc.*, 1902, **24**, 144; Whitby, *Z. anorg. Chem.*, 1910, **67**, 387.

[9] Tamisier, *Bull. Soc. chim. France*, 1933, **53**, 156.

S equiv./l., and f is the activity coefficient (calc.) of the univalent ions, then $Sf = \{AgB_n^+\} = \{OH^-\}$. The excesses of the amines can be considered as being un-ionised because of the ionisation of the complex base; thus, the activity coefficient being assumed to be unity, then $(C - nS)$ equiv./l. is the concentration, and hence the activity of the un-ionised, uncombined amine B. Since the solution was also saturated with silver oxide, $\{Ag^+\}\{OH^-\} = K_s$, whence $\beta_n = (fS)^2/K_s(C - nS)^n$. If n has the most probable value of 2 in the case of silver, then $fS = K'(C - 2S)$, where $K' = \sqrt{(\beta_n K_s)}$, and a plot of the activity of the complex cation against the activity of the excess of uncombined base should be straight (see Figure).



The dissociation constants show the order of basic strengths to be mono- > bis- > tris-2-hydroxyethylamine. The stabilities of the complex cations formed between silver and these bases are in the same order.

We thank Messrs. Oxirane Ltd. for samples of hydroxy-ethylamines.

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853. *Reactions with Asymmetric Diarylethylenes. Part V.*[1] *Conversion of* 2 : 2-*Di*-p-*alkoxyphenylvinyl Chloride or Bromide in Alkaline Medium into the Corresponding Tolane.*

By Wadie Tadros, Alfy Badie Sakla, and Moheb Sadek Ishak.

The mechanism of conversion of 2 : 2-di-*p*-alkoxyphenylvinyl chlorides or bromides into 1 : 1 : 4 : 4-tetra-arylbuta-1 : 3-dienes has been already discussed.[1] On the other hand, they are converted by alcoholic sodium ethoxide at 180—200° in a sealed tube [2,3] (however, neither the quantity nor the concentration of the reagent was specified) or by potassium amide in liquid ammonia [4,5] into the corresponding tolanes. The mechanism of the reaction has been discussed by Coleman, Holst, and Maxwell,[5] but comment on this is postponed. However, Harris and Frankforter's statement [3] that 2 : 2-di-*p*-methoxy(or

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[1] Part IV, Tadros and Sakla, *J.*, 1957, 3210.

[2] Wiechell, *Annalen*, 1894, **279**, 337.

[3] Harris and Frankforter, *J. Amer. Chem. Soc.*, 1926, **48**, 3144.

[4] Coleman and Maxwell, *ibid.*, 1934, **56**, 132.

[5] Coleman, Holst, and Maxwell, *ibid.*, 1936, **58**, 2310.

ethoxy)phenylvinyl bromide gave rise to the tolane when treated with ethanolic sodium ethoxide on the water-bath, could not be substantiated by us.

The present paper reports a preliminary study of this reaction effected with sodium 2-hydroxyethoxide in ethylene glycol. The vinyl bromide reacted more readily than the chloride. As pointed out by Coleman and Maxwell,[4] it is notable that in these arrangements a given substituent in the *para*-position in the phenyl group is found in the *para*-position in the tolane. A mixture of 2 : 2-di-*p*-methoxy- and 2 : 2-di-*p*-ethoxy-phenylvinyl bromide gave both 4 : 4′-dimethoxy- and 4 : 4′-diethoxy-tolane, but no mixed tolane. Pending confirmation we assume that the reaction is intramolecular, but the formation of the 4 : 4′-disubstituted tolanes indicates that, although the migrating aryl group suffers complete severance, it may have remained in the domain of the molecule. 4-Ethoxy-4′-methoxytolane was obtained from both forms of 2-*p*-ethoxyphenyl-2-*p*-methoxyphenylvinyl bromide obtained by bromination of 1-*p*-ethoxyphenyl-1-*p*-methoxyphenylethylene. Partial demethylation usually accompanied formation of the tolanes, in amounts dependent on the time of the reaction. When the alkaline filtrate, after the removal of 4 : 4′-dimethoxytolane, was acidified *p*-hydroxyphenyl 4′-methoxybenzyl ketone was obtained;[6] this is also obtained when the 4 : 4′-dimethoxytolane is similarly treated. With 2-*p*-ethoxyphenyl-2-*p*-methoxyphenylvinyl bromide, acidification of the alkaline filtrate gave 4-ethoxybenzyl *p*-hydroxyphenyl ketone, the structure of which was proved by comparison of the methylation products of the two possible isomers.[7]

Experimental.—*4-Ethoxy-4′-methoxybenzophenone.* Prepared by Friedel–Crafts[8] reaction or by ethylation of 4-hydroxy-4′-methoxybenzophenone[9] (2·28 g. of ketone, 0·37 g. of sodium dissolved in 50 c.c. of alcohol; 2·34 g. of ethyl iodide), this ketone, crystallised from alcohol, had m. p. 112° (Found: C, 74·8; H, 6·0. Calc. for $C_{16}H_{16}O_3$: C, 75·0; H, 6·25%).

1-p-*Ethoxyphenyl*-1-p-*methoxyphenylethylene* was prepared by Grignard reactions. (*a*) 4-Ethoxy-4′-methoxybenzophenone (25·6 g.) was added to the Grignard reagent (magnesium, 3·6 g.; methyl iodide, 21·3 g.; ether, 200 c.c.). Decomposition with aqueous ammonium chloride and extraction with ether gave the ethylene (21 g.) which, separated from alcohol, had m. p. 124° (Found: C, 80·0; H, 7·0. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·3%). (*b*) 4-Ethoxyacetophenone (16·4 g.) was added to the Grignard reagent (magnesium, 3·6 g.; *p*-bromoanisole, 28 g.; ether, 200 c.c.) and afforded 19 g. of the ethylene.

2-p-*Ethoxyphenyl*-2-p-*methoxyphenylvinyl bromides.* The product from bromine (8·0 g.) and the ethylene (12·7 g.) in ether (270 c.c.) was washed with 10% aqueous sodium hydroxide, followed by water, and after recovery was heated on the water-bath with sodium hydroxide (3 g.) in alcohol (60 c.c.) for 30 min., diluted with water, cooled, filtered, and washed with water. Recrystallisation from alcohol or light petroleum (b. p. 50—70°) gave two fractions of bromide: (i) m. p. 70—72°; (ii) m. p. 48—50° (Found: Br, 23·6. Calc. for $C_{17}H_{17}O_2Br$: Br, 24·0%).

*Action of sodium 2-hydroxyethoxide in ethylene glycol on 2 : 2-di-*p*-alkoxyphenylvinyl halide.* (*a*) The procedure and products obtained are exemplified as follows: 2 : 2-Di-*p*-methoxyphenylvinyl bromide (1·595 g.) and a solution from sodium (0·23 g.) in ethylene glycol (15 c.c.) were boiled for 5 hr., then cooled and diluted with water, and the precipitate was filtered off. 4 : 4′-Dimethoxytolane separated from alcohol or acetic acid as colourless crystals (0·8 g.), m. p. 142—143° (Found: C, 80·3; H, 5·9. Calc. for $C_{16}H_{14}O_2$: C, 80·7; H, 5·9%). Acidification of the alkaline filtrate with acetic or hydrochloric acid and recrystallisation of the precipitate from dilute alcohol gave *p*-hydroxyphenyl 4′-methoxybenzyl ketone (0·4 g.; m. p. and mixed m. p. 175°). Ethylation gave *p*-ethoxyphenyl 4′-methoxybenzyl ketone, m. p. and mixed m. p. 101—102°. Other tolanes were similarly obtained (yield *ca.* 90—95%) and recrystallised from alcohol or acetic acid as colourless crystals: 4 : 4′-diethoxy-, m. p. 162—163° (Found: C, 81·1; H, 6·7. Calc. for $C_{18}H_{18}O_2$: C, 81·2; H, 6·8%); 4 : 4′-*di*-n-*propoxy*-, m. p. 133—135° (Found:

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[6] Tadros, Ekladius, and Sakla, *J.*, 1954, 2351.

[7] Carter and Hey, *J.*, 1948, 150.

[8] Schönberg, Schütz, and Nickel, *Ber.*, 1928, **61**, 1375; Migita, *Bull. Chem. Soc. Japan*, 1932, **7**, 341; Jones, *J.*, 1936, 1854.

[9] Auwers, *Ber.*, 1903, **36**, 3893.

C, 81·2; H, 7·4. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%); 4 : *4′-di*iso*propoxy-*, m. p. 162—165° (Found: C, 81·3; H, 7·1. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%); *4 : 4′-di-*n*-butoxy-tolane*, m. p. 127—128° (Found: C, 81·6; H, 8·0. $C_{22}H_{26}O_2$ requires C, 82·0; H, 8·45%).

(ii) The tolane (0·1 g.) was obtained when the above experiment was repeated with the di-*p*-ethoxyvinyl chloride (1·51 g.). Using 0·575 g. of sodium gave 0·5 g. of tolane.

(iii) 2-*p*-Ethoxyphenyl-2-*p*-methoxyphenylvinyl bromide, m. p. 48—50° or 70—72° (1·665 g.), and sodium (0·23 g.) in ethylene glycol (15 c.c.) were treated as above. *4-Ethoxy-4′-methoxytolane* (0·8 g.), crystallised from acetic acid, had m. p. 138—139° (Found: C, 80·6; H, 6·3. $C_{17}H_{16}O_2$ requires C, 81·0; H, 6·3%). Acidification of the alkaline filtrate yielded *4-ethoxybenzyl 4′-hydroxyphenyl ketone* (0·3 g.), m. p. 160—162° (from dilute alcohol) (Found: C, 74·6; H, 6·2. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·25%). With dimethyl sulphate it gave 4-ethoxybenzyl *p*-methoxyphenyl ketone, m. p. and mixed m. p. 100°.

*Reaction with 2 : 2-di-*p*-methoxy- and 2 : 2-di-*p*-ethoxy-phenylvinyl bromides.* Repeating experiment (i) with equimolecular quantities of 2 : 2-di-*p*-methoxy- (1·595 g.) and 2 : 2-di-*p*-ethoxy-phenylvinyl bromide (1·735 g.), sodium (0·46 g.), and ethylene glycol (30 c.c.) gave 4 : 4′-diethoxytolane (1·1 g.), m. p. 162—163°, separating readily at room temperature from acetic acid. Dilution of the acetic acid mother-liquor and recrystallisation from alcohol gave 4 : 4′-dimethoxytolane (0·5 g.), m. p. and mixed m. p. 142—143°. On acidification of the alkaline mother-liquor gave *p*-hydroxyphenyl 4′-methoxybenzyl ketone (0·3 g.), m. p. and mixed m. p. 175°. It is remarkable that dealkylation occurs more readily with the methoxyl group.

Action of sodium 2-hydroxyethoxide in ethylene glycol on 4 : 4′-dimethoxytolane. 4 : 4′-Dimethoxytolane (1·195 g.) and sodium (0·23 g.) in ethylene glycol (15 c.c.) were heated at the b. p. for 5 hr. Dilution with water gave unchanged tolane (0·5 g.). Acidification of the alkaline filtrate gave 4-hydroxyphenyl 4′-methoxybenzyl ketone (0·3 g.).

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854. o-*Cyanophenylhydrazine and 3-Aminoindazole.*

By F. C. COOPER.

THE reduction of 3 : 4-dihydro-4-hydroxyimino-1 : 2 : 3-benzotriazine by stannous chloride and hydrochloric acid gave a compound to which Pinnow and Sämann [1] assigned the constitution 1 : 2-(or 2 : 3-)dihydro-1 : 2 : 3-benzotriazine. Gabriel [2] thought this compound to be identical with one he obtained by reducing diazotised *o*-cyanoaniline with stannous chloride and which he considered to be *o*-cyanophenylhydrazine. Reissert and Grube record,[3] however, that a similar reduction gave, instead of *o*-cyanophenylhydrazine, the isomeric 3-aminoindazole; Kwartler and Lucas [4] used a similar route to 3-aminoindazole. The close similarity of the recorded properties of Gabriel's compound to those of 3-aminoindazole [5] prompted direct comparison.

3-Aminoindazole can be obtained by coupling *o*-tolyldiazonium chloride with indazole and reducing the resulting azo-compound with ammonium sulphide [5] or sodium dithionite: this, together with its possession of an amino-group capable of being diazotised and hence conversion into the known 3-chloroindazole,[5] is adequate proof of structure. Samples of compounds prepared by the methods of Pinnow and Sämann,[1] of Gabriel,[2] and of

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[1] Pinnow and Sämann, *Ber.*, 1896, **29**, 623.
[2] Gabriel, *Ber.*, 1903, **36**, 800.
[3] Reissert and Grube, *Ber.*, 1909, **42**, 3710.
[4] Kwartler and Lucas, *J. Amer. Chem. Soc.*, 1943, **65**, 1804.
[5] Bamberger and von Goldberger, *Annalen*, 1899, **305**, 339.

Reissert and Grube [3] have been compared with an authentic specimen of 3-aminoindazole (m. p. and mixed m. p. of bases, picrates, diacetyl and dibenzoyl derivatives; ultraviolet absorption spectra); the results show the so-called *o*-cyanophenylhydrazine to be identical with 3-aminoindazole.

Experimental.—3-*Aminoindazole.* (*a*) To a solution of 3-*o*-tolylazoindazole [5] (3·55 g.) in ethanol (50 ml.) were added sodium hydroxide (2·5 g.) and sodium dithionite (6·2 g.) in water (50 ml.). The mixture was refluxed for 30 min., evaporated to about 30 ml. at 60°/15 mm., and then steam-distilled to remove *o*-toluidine (benzoyl derivative, m. p. and mixed m. p. 144—145°). Extraction of the cooled residue with ether gave 3-aminoindazole (2·00 g.; 100%), which crystallised from benzene as plates, m. p. 154·5—155° (Found: C, 63·1; H, 5·15. Calc. for $C_7H_7N_3$: C, 63·15; H, 5·3%). Its *picrate*, needles from glacial acetic acid, had m. p. 236° (decomp.) (Found: C, 43·3; H, 2·75; N, 23·1. $C_{13}H_{10}O_7N_6$ requires C, 43·1; H, 2·8; N, 23·2%). The diacetyl derivative, needles from benzene, had m. p. 181—181·5° (Found: C, 61·2; H, 4·95; N, 19·05. Calc. for $C_{11}H_{11}O_2N_3$: C, 60·8; H, 5·1; N, 19·35%): the dibenzoyl derivative, needles from ethanol, had m. p. 183—184° (Found: C, 73·8; H, 4·35. Calc. for $C_{21}H_{15}O_2N_3$: C, 73·85; H, 4·45%). Bamberger and von Goldberger record m. p. 153·5—154·5°, 177—178°, and 182° for the base, its diacetyl, and its dibenzoyl derivative, respectively.[5]

(*b*) A well-stirred ice-cold solution of diazotised sulphanilic acid (4·5 g.) and indazole (3·0 g.) in dilute hydrochloric acid was slowly made alkaline with sodium hydroxide solution. Next day, after precipitated indazole (2·01 g.) had been removed, reduction of the filtrate with sodium dithionite afforded 3-aminoindazole (0·20 g.), m. p. and mixed m. p. 154·5—155°.

Below are recorded m. p.s of bases and derivatives made by the methods of Pinnow and Sämann [1] (A), Gabriel [2] (B), and Reissert and Grube [3] (C): there was no depression of m. p. on admixture, as appropriate, with 3-aminoindazole or its derivatives.

	M. p.s			
	Base	Picrate	Diacetyl derivative	Dibenzoyl derivative
A	155—155·5°	237—238° (decomp.)	180·5—181·5°	184·5—185·5°
B	154·5—155	236—237 (decomp.)	181—182	184·5—185
C	154—155	236—237 (decomp.)	181—182	183·5—184·5

The ultraviolet absorption spectra of the bases were determined in ethanol ($\lambda_{max.}$ in mμ; ε in parentheses). Figures in italics denote submerged maxima.

	Absorption maxima		
A	217(21,800)	*ca. 260*(1380)	310(4410)
B	217(20,100)	*ca. 260*(1330)	310(4300)
C	217(22,200)	*ca. 260*(1290)	310(4370)
3-Aminoindazole	217(20,500)	*ca. 260*(1300)	310(4500)

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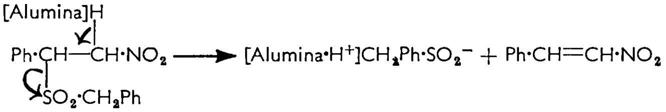
855. *The Decomposition of 2-Nitro-1-phenylethyl Sulphones at an Alumina Surface.*

By C. L. Arcus and P. A. Hallgarten.

During attempts to separate optically active α-methylphenethyl 2-nitro-1-phenylethyl sulphones from other compounds by chromatography on alumina, losses in rotatory power were noticed, and it was further found that acetone solutions of the (+)-sulphone-A (assigned[1] the l_Rd_α configuration, where the suffix R refers to the α-methylphenethyl and α to the 2-nitro-1-phenylethyl group), on treatment with alumina, undergo progressive racemisation. β-Nitrostyrene was isolated from the solutions, so that elimination had occurred, accounting for part of the loss in rotatory power. The recovered sulphone had a lowered m. p., so that racemisation at one or both centres had contributed to the fall in rotation, but it was not practicable to determine the proportion of the four diastereoisomers in the recovered material.

For further investigation, (±)-benzyl 2-nitro-1-phenylethyl sulphone was used; its acetone solution, after being shaken with alumina, yielded β-nitrostyrene, and an alkaline extract of the alumina gave, with benzyl chloride, dibenzyl sulphone, so that it had contained sodium toluene-ω-sulphinate. For sulphone solution–alumina mixtures, there were determined at intervals the total solute and (spectrophotometrically) the β-nitrostyrene present in solution (Table 2). It is seen that the rate of elimination decreases progressively, and that (from 20 min.) the quantity of sulphone adsorbed at any one time is about one-tenth of that present in solution.

Elimination by the *E*2 mechanism is probable, the electron-attracting nitro-group facilitating the removal of a proton at $C_{(2)}$ by the alumina:



The results illustrate the unsuitability, which has been noted in other connections,[2] of chromatography on alumina for the separation of compounds susceptible to proton-removal.

Experimental.—M. p.s are corrected.

Alumina (100 g.) was heated on a steam-bath for 2 hr. with acetic acid (150 ml.) and methanol (15 ml.), kept overnight, and reheated for 5 hr. The acid was decanted and the alumina washed with cold, then hot, methanol, and dried, first at 80°, then at 160°. Acetone was refluxed for 8 hr. with potassium permanganate, then distilled, and redistilled from potassium carbonate. Treatment of solutions with alumina was carried out at 25·5° ± 0·5°.

Table 1.

Time, min.	0	13	61	130	285	1470	2730
α^{25}_{5893}	1·12°	0·92°	0·70°	0·73°	0·60°	0·42°	0·11°

A solution of (+)-α-methylphenethyl 2-nitro-1-phenylethyl sulphone-A (m. p. 140·5°; 0·201 g.) in acetone (8·0 ml.) was shaken intermittently with alumina (1·002 g.). The rotatory power (*l*, 1·0) fell (Table 1). Sublimation (60°/1 mm.) of the product from evaporation of the

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[1] Arcus and Hallgarten, *J.*, 1957, 3407.

[2] E. and M. Lederer, "Chromatography," Elsevier Publ. Co., Amsterdam, 2nd edn., 1957, pp. 61—65.

solution gave β-nitrostyrene (19 mg.), m. p. 56°, mixed m. p. 56·5°. The remaining sulphone (0·11 g.) had m. p. 124—125° and, after recrystallisation, m. p. 137·5° and m. p. 140° when mixed with the original sulphone. (The sulphones-A are the less-soluble diastereoisomers.[1])

Toluene-ω-thiol (22·0 g.) and β-nitrostyrene (26·5 g.) were heated under coal-gas for 9 hr. at 120° with benzoyl peroxide (0·1 g.). The product solidified after a week, and, on being washed with ice-cold methanol, yielded benzyl 2-nitro-1-phenylethyl sulphide, m. p. 39° (Found: N, 5·0; S, 11·3. Calc. for $C_{15}H_{15}O_2NS$: N, 5·1; S, 11·7%). To the sulphide (22·0 g.) in acetic acid (50 ml.) was added acetic acid–34% hydrogen peroxide (25 ml. each), the whole being kept below 40°. Next day the product was collected, washed with acetic acid and with methanol, and recrystallised from acetone–methanol, yielding benzyl 2-nitro-1-phenylethyl sulphone (10·5 g., 43%), m. p. 140—140·5°. Cason and Wanser[3] obtained the sulphide as an oil which on oxidation at 100° gave the sulphone in 18% yield.

(*a*) Benzyl 2-nitro-1-phenylethyl sulphone (1·0 g.) in acetone (27 ml.), intermittently shaken for 8 hr. with alumina (5·0 g.), gave β-nitrostyrene (0·15 g.), m. p. and mixed m. p. 56·5—57°, and unchanged sulphone (0·56 g.), m. p. 139—140°, mixed m. p. 140·5°.

(*b*) The sulphone (10·5 g.) in acetone (125 ml.) was mechanically shaken for several days with alumina (32 g.). The latter was separated and washed with acetone, then shaken with 0·2N-sodium hydroxide (20 ml.); the extract was filtered, then boiled with benzyl chloride (1 g.) for 1 hr. After removal of excess of benzyl chloride by passage of steam, the whole was extracted with chloroform. The product from the extract was washed with methanol and recrystallised from ethanol; it yielded dibenzyl sulphone, m. p. 150° (Found: O, 13·5; S, 13·4. Calc. for $C_{14}H_{14}O_2S$: O, 13·0; S, 13·0%). Fromm and de Seixas Palma[4] record m. p. 151°.

(*c*) In each experiment of Table 2, benzyl 2-nitro-1-phenylethyl sulphone (0·500 g.) in acetone (12·5 ml.) was shaken at constant speed with alumina (2·50 g.). After the stated time the solution was filtered through sintered glass, and the concentration of β-nitrostyrene determined by use, at 420 mμ, of a Unicam S.P. 600 spectrophotometer. By evaporation of the filtrate the total solute was determined, and hence, by difference, the sulphone in solution. β-Nitrostyrene was not detectably adsorbed by alumina during 24 hr. under the conditions used.

TABLE 2. *Decomposition of benzyl 2-nitro-1-phenylethyl sulphone on alumina.*

Time (min.)	11	20	30	45	60	65	95	120	152	180	208	6 days
β-Nitrostyrene, (*a*) *	4	7	8	9	10	13	13	14	14	16	15	20
Sulphone in soln., (*b*) *	68	85	79	84	82	79	76	82	81	75	75	70
100 − (*a* + *b*)	28	8	13	7	8	8	11	4	5	9	10	10

* As moles % of the original sulphone.

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[3] Cason and Wanser, *J. Amer. Chem. Soc.*, 1951, **73**, 142.
[4] Fromm and de Seixas Palma, *Ber.*, 1906, **39**, 3319.

856. *The Isolation of Solasodine from the Berries of* Solanum macranthum.

By D. A. H. TAYLOR.

Solanum macranthum is a large shrub or small tree, commonly planted in the tropics. It has blue flowers, and berries similar in size to tomatoes. Hydrolysis of the juice of the minced green berries gave an insoluble hydrochloride, from which only solasodine was obtained on basification. Extraction of the basified mother liquor gave, after chromatography, solaso-3 : 5-diene. The author is grateful to Dr. R. K. Callow for infrared spectra, and to Mr. G. K. Berrie, of the College Department of Botany, for identification of the specimen, growing on the College site.

Experimental.—*Solanum macranthum* berries (3·94 kg.) were minced and the juice (2·75 l.) expressed through cloth. This was mixed with methanol (2·75 l.) and kept for three days. After centrifugation, concentrated hydrochloric acid (275 c.c.) was added, the solution refluxed for 1 hr., and concentrated to 2 l. under reduced pressure. The precipitated hydrochloride was filtered, shaken with chloroform and concentrated aqueous ammonia, and the chloroform layer evaporated. The crystalline residue was taken up in benzene and chromatographed on alumina (50 g.). Benzene containing chloroform (25%) eluted solasodine, which recrystallised from acetone–chloroform as colourless crystals (3·7 g.), m. p. 201°, $[\alpha]_D^{20}$ (MeOH) $-100°$ (Found: C, 74·7; H, 10·5; O, 11·3; N, 3·3. Calc. for $C_{27}H_{43}O_2N,H_2O$: C, 75·1; H, 10·5; O, 11·1; N, 3·25%). The infrared spectrum was identical with an authentic sample kindly provided by Professor L. H. Briggs. The basified mother liquor was extracted with chloroform and the extract chromatographed on alumina. Light petroleum (b. p. 60—80°) containing chloroform eluted a solid which crystallised from acetone–chloroform as shining plates of solaso-3 : 5-diene (130 mg.), m. p. 170°, $[\alpha]_D^{20}$ ($CHCl_3$) $-180°$, $\lambda_{max.}$ (hexane) 236 mμ (log ε 4·3) (Found: C, 81·4; H, 10·4; O, 4·6. Calc. for $C_{27}H_{41}ON$: C, 82·0; H, 10·45; O, 4·0%). The physical properties agree with those recorded in the literature.[1]

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[1] Prelog and Jeger, "The Alkaloids," vol. iii, ed. Holmes and Manske, Academic Press Inc., New York, 1953, p. 265.