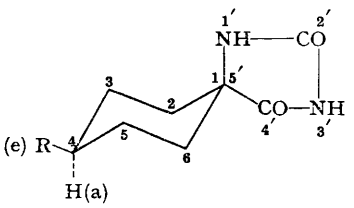
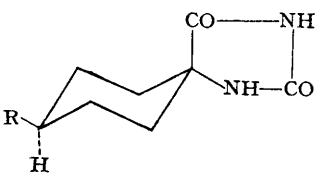
1190. N-*Trichloromethanesulphenylhydantoins.*

By R. J. W. Cremlyn.

Many trichloromethanesulphenyl derivatives are fungicidal,[1] especially those containing the $>N-S\cdot CCl_3$ group.[2] It therefore appeared of interest to examine a range of *N*-trichloromethanesulphenylhydantoins, including those derived from certain alicyclic spiro-5′-hydantoins. The hydantoins were generally obtained by application of the Bucherer synthesis.[3] In the case of substituted alicyclic ketones, Brimelow *et al.*[4] showed that different stereoisomeric hydantoins are formed according to the method of preparation. Thus, Munday[5] concluded that the Bucherer synthesis gives predominantly the *trans*-form (I),* whereas the cyanate route leads to the *cis*-form (II):



(I)



(II)

The various hydantoins were converted into the *N*-trichloromethanesulphenyl derivatives by condensation with the sulphenyl chloride as indicated in the Experimental section. The products may be divided into those derived from: alkyl hydantoins (Table 1); aryl hydantoins (Table 2); and alicyclic spiro-5′-hydantoins (Table 3).

* The terms *cis* and *trans* refer to the relation of the alkyl group (R) to the 4′-carbonyl group of the hydantoin.

[1] T. P. Johnston, W. H. C. Rueggeberg, and S. S. Block, *J. Sci. Food Agric.*, 1957, **5**, 672; R. Pfleger, *Angew. Chem.*, 1953, **65**, 415; C. H. Fawcett, D. M. Spencer, and R. L. Wain, *Ann. Appl. Biol.*, 1958, **46**, 651; H. J. Backer and E. Westerhuis, *Rec. Trav. chim.*, 1952, **71**, 1082; G. Sosnovsky, *J.*, 1956, 3139.

[2] A. R. Kittleson, *Science*, 1952, **115**, 84; R. Gasser, A. Margot, H. Gysin, and R. Waeffler, *Experientia*, 1955, **11**, 265; A. R. Kittleson *et al.*, B.P. 716,553/1954, B.P. 769,711/1957.

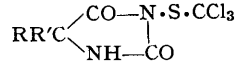
[3] H. Bucherer and W. T. Lieb, *J. prakt. Chem.*, 1934, **141**, 5.

[4] H. C. Brimelow, H. C. Carrington, C. H. Vasey, and W. S. Waring, *J.*, 1962, 2789.

[5] L. Munday, *J.*, 1961, 4372.

TABLE 1.

Alkyl *N*-trichloromethanesulphenylhydantoins.



No.	R	R′	M. p.	Formula	Found (%)*					Required (%)				
					C	H	Cl	N	S	C	H	Cl	N	S
1	H	H	184—186°	$C_4H_3Cl_3N_2O_2S$	19·7	1·1	42·5	11·4	12·7	19·2	1·2	42·7	11·2	12·8
2	Me	Me	164—166	$C_6H_7Cl_3N_2O_2S$	25·3	3·0	39·0	9·7	12·1	24·8	2·5	38·4	10·1	11·5
3	Et	Et	122—124	$C_8H_{11}Cl_3N_2O_2S$	31·4	3·6	35·5	8·9	10·8	31·4	3·6	34·9	9·2	10·5
4	Pr^i	Pr^i	212—214	$C_{10}H_{15}Cl_3N_2O_2S$	35·9	4·4	31·9	7·9	9·5	36·0	4·5	31·9	8·4	9·6
5	Bu^n	Bu^n	119—121	$C_{12}H_{19}Cl_3N_2O_2S$	40·3	6·0	29·1	7·7	8·2	39·8	5·3	29·5	7·7	8·8
6	Me	Bu^i	139—141	$C_9H_{13}Cl_3N_2O_2S$	34·3	4·3	33·9	9·2	10·1	33·8	4·7	33·3	8·8	10·0
7	H	n-C_6H_{13}	122—125	$C_{11}H_{17}Cl_3N_2O_2S$	38·4	5·2	30·1	8·3	9·4	38·0	4·9	30·7	8·0	9·2

TABLE 2.

Aryl *N*-trichloromethanesulphenylhydantoins.

8	H	*o*-Cl·C_6H_4	174—176°	$C_{10}H_6Cl_4N_2O_2S$	32·8	1·5	40·0	7·4	9·2	33·3	1·7	39·4	7·8	8·8
9	Me	*p*-MeO·C_6H_4	125—127	$C_{12}H_{11}Cl_3N_2O_3S$	38·6	2·7	29·5	7·2	9·1	39·0	3·0	28·1	7·6	8·7
10	Me	Ph	Liquid	$C_{11}H_9Cl_3N_2O_2S$	39·3	3·0	30·9	7·8	9·2	38·9	2·6	31·4	8·2	9·4

TABLE 3.

Alicyclic *N*-trichloromethanesulphenylhydantoins.

No.	Alicyclic radical	M. p.	Formula	Found (%)*					Required (%)				
				C	H	Cl	N	S	C	H	Cl	N	S
11	$-[CH_2]_4-$	162—164°	$C_8H_9Cl_3N_2O_2S$	31·9	3·0	35·5	9·2	10·6	31·6	3·0	35·1	9·2	10·5
12	$-[CH_2]_5-$	184—185	$C_9H_{11}Cl_3N_2O_2S$	34·3	3·6	34·3	8·4	10·3	34·0	3·5	33·6	8·8	10·1
13	$-CHMe-[CH_2]_4-$	*trans:* 204—206	$C_{10}H_{13}Cl_3N_2O_2S$	36·7	4·25	31·9	7·9	9·9	36·2	3·9	32·1	8·45	9·7
		cis: 191—194	$C_{10}H_{13}Cl_3N_2O_2S$	36·5	3·9	31·8	8·4	9·5	36·2	3·9	32·1	8·45	9·7
14	$-CH_2\cdot CHMe-[CH_2]_3-$	*trans:* 238—239	$C_{10}H_{13}Cl_3N_2O_2S$	35·8	4·0	31·7	7·9	9·8	36·2	3·9	32·1	8·45	9·7
		cis: 230—232	$C_{10}H_{13}Cl_3N_2O_2S$	36·6	3·8	32·6	8·3	9·4	36·2	3·9	32·1	8·45	9·7
15	$-[CH_2]\cdot_2CHMe\cdot[CH_2]_2-$	*trans:* 246—248°	$C_{10}H_{13}Cl_3N_2O_2S$	36·8	3·9	32·1	7·9	9·7	36·2	3·9	32·1	8·45	9·7
16	$-CH_2\cdot[CHMe]_2\cdot[CH_2]_2-$	*trans:* 190—194	$C_{11}H_{15}Cl_3N_2O_2S$	38·5	4·7	30·4	7·8	9·2	38·2	4·3	30·8	8·1	9·3
17	$-CH_2\cdot CHMe\cdot CH_2\cdot CMe_2\cdot CH_2-$	*trans:* 206—209	$C_{12}H_{17}Cl_3N_2O_2S$	40·3	4·7	29·2	7·4	8·9	40·0	4·7	29·6	7·8	8·9
		cis: 202—203	$C_{12}H_{17}Cl_3N_2O_2S$	40·1	4·5	—	7·6	—	40·0	4·7	29·6	7·8	8·9
18	$-CH_2\cdot CHMe[CH_2]_2\cdot CHPr.-$	*trans:* 130—134	$C_{13}H_{19}Cl_3N_2O_2S$	42·2	5·5	28·1	7·4	8·3	41·8	5·1	28·5	7·5	8·6
19	$-[CH_2]_3\cdot CH\cdot CO_2Et-$	*trans:* 158—160	$C_{11}H_{13}Cl_3N_2O_4S$	34·8	3·1	28·8	8·0	8·9	35·2	3·5	28·4	7·5	8·5
20	$-[CH_2]_6-$	209—211	$C_{10}H_{13}Cl_3N_2O_2S$	36·3	3·9	32·5	8·1	9·5	36·2	3·9	32·1	8·45	9·7
21	$-[CH_2]_2\cdot CHMe\cdot[CH_2]_3-$	*trans:* 193—194	$C_{11}H_{15}Cl_3N_2O_2S$	38·3	4·3	31·2	7·9	9·1	38·2	4·3	30·8	8·1	9·3
22	Decalin-2-	226—230	$C_{13}H_{17}Cl_3N_2O_2S$	42·4	5·0	27·9	7·8	8·3	42·0	4·6	28·7	7·5	8·6
23	Tetralin-1-	157—159	$C_{13}H_{11}Cl_3N_2O_2S$	43·2	3·0	28·7	7·2	8·7	42·7	3·0	29·1	7·7	8·8

* In some cases difficulty was experienced in obtaining reasonable analytical figures; repeated recrystallisation from ethanol appeared to cause partial decomposition of the trichloromethanesulphenyl derivatives.

Experimental.—Preparation of the hydantoins. These were generally prepared by the Bucherer synthesis as described by Brimelow *et al.*,[4] and included the following new spiro-5′-hydantoins: *cyclopentane-*, colourless needles, m. p. 202° (from aqueous ethanol) (Found: C, 55·0; H, 6·8; N, 18·3. $C_7H_{10}N_2O_2$ requires C, 54·5; H, 6·5; N, 18·2%); *3-methylcycloheptane-*, feathery needles, m. p. 208—210° (from ethanol) (Found: C, 61·0; H, 8·3; N, 14·3. $C_{10}H_{16}N_2O_2$ requires C, 61·2; H, 8·2; N, 14·3%); *2-ethoxycarbonylcyclopentane-*, needles, m. p. 202—204° (from methanol) (Found: C, 53·5; H, 6·3; N, 12·6. $C_{10}H_{14}N_2O_4$ requires C, 53·1; H, 6·2; N, 12·4%); *2-ethoxycarbonylcyclohexane-*, lustrous platelets, m. p. 200° (from ethanol) (Found: C, 55·2; H, 6·8; N, 12·2. $C_{11}H_{16}N_2O_4$ requires C, 55·0; H, 6·7; N, 11·7%); *5-methyl-5-nonylhydantoin*, white powder, m. p. 100—102° (from ethanol) (Found: C, 64·7; H, 10·0; N, 11·7. $C_{13}H_{24}N_2O_2$ requires C, 65·0; H, 10·0; N, 11·7%).

In the case of substituted alicyclic spiro-5′-hydantoins, sometimes the *cis*-isomer was also obtained by the cyanate route.[4]

Condensation with trichloromethanesulphenyl chloride. The general preparative procedure is illustrated by the following examples:

(*a*) N-*Trichloromethanesulphenyl-4-methylcyclohexanespiro-5′-hydantoin* (trans-*form*). The hydantoin (3·6 g.) was dissolved in water (60 c.c.) containing sodium hydroxide (0·8 g.), and an ethereal solution of the sulphenyl chloride (3·7 g. ≡ 2·2 c.c.) was dropped into the stirred solution at 0°. After being stirred for 2 hr., the mixture was set aside overnight and the solid product was filtered off and recrystallised twice from ethanol, yielding the trans-N-*trichloromethanesulphenylhydantoin* as feathery clusters (3 g.), m. p. 246—248°.

(*b*) N-*Trichloromethanesulphenyl-3,4-dimethylcyclohexanespiro-5′-hydantoin* (trans-*form*). The hydantoin (2 g.) in water (40 c.c.) and sodium hydroxide (0·5 g.) was cooled to 0°, and the sulphenyl chloride (2 g.) in ether (15 c.c.) gradually introduced with mechanical stirring. Stirring was continued for 2 hr. and then the mixture was heated at 35° for 1½ hr. After cooling, the solid product was collected and recrystallised from ethanol, giving the N-*trichloromethanesulphenyl derivative* as needles (2·1 g.), m. p. 190—194°.

A similar condensation was also carried out with 5-ethyl-3-methyl-5-phenylbarbituric acid, giving the corresponding N-*trichloromethanesulphenyl derivative* as needles, m. p. 150—152° (from ethanol) (Found: C, 42·8; H, 3·5; Cl, 27·0; N. 6·9; S, 7·9. $C_{14}H_{13}Cl_3N_2O_3S$ requires C, 42·5; N, 3·3; Cl, 26·9; N, 7·1; S, 8·1%).

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1191. *The Infrared Spectra of Some Sulphonyl Hydrazides and Sulphonylhydrazones.*

By R. J. W. Cremlyn and D. N. Waters.

The preparation of some hydrazone derivatives of 4-acetamidonaphthalene-1-sulphonylhydrazide has been described by Cremlyn.[1] As part of a study of their physical and biological properties, we have investigated the infrared spectra of these and of some related compounds, containing either of the groupings $-SO_2NH{\cdot}NH_2$ or $-SO_2NH{\cdot}N{:}C<$. These compounds and the frequencies observed for the N–H and S–O stretching vibrations are listed in Tables 1 and 2.

N–H Stretching Vibrations.—All the sulphonylhydrazones show a single N–H stretching frequency in the range 3205—3310 cm.$^{-1}$. Since some of these compounds contain the secondary amide grouping as well as the $-SO_2NH-$ grouping, it appears that both these groupings show nearly the same N–H frequency. The sulphonyl hydrazides contain an additional NH_2 group, and in consequence show more bands in the N–H stretching region. The asymmetric mode of the NH_2 group is in all cases readily identified as the highest-

[1] R. J. W. Cremlyn, *J.*, 1963, 1329.

TABLE 1.

N–H and S–O stretching frequencies of sulphonyl hydrazides, $Ar{\cdot}SO_2NHN{\cdot}H_2$.

Compound	Ar	ν_{N-H} (cm.$^{-1}$)	ν_{S-O} (cm.$^{-1}$)
(I)	*p*-Me·C_6H_4	3390m, 3311w, 3257s	1309s, 1157s
(II)	*p*-Me·CONH·C_6H_4	3367m, 3311m, 3226m, 3175m	1311s, 1164s
(III)	1,4-Me·CONH·$C_{10}H_6$	3378m, 3311m, 3155m, 3067w	1314s, 1147s
(IV)	1,4-Pr^n·CONH·$C_{10}H_6$	3356m, 3300m, 3268m, 3226m	1321s, 1151s
(V)	1,4-Ph·CONH·$C_{10}H_6$	3367m, 3322m, 3289m	1333s, 1157s
(VI)	1,4-(*p*-Me·$C_6H_4{\cdot}SO_2NH$)$C_{10}H_6$	3390m, 3257m, 3049w	1304s, 1156s

TABLE 2.

N–H and S–O stretching frequencies of sulphonylhydrazones, $Ar{\cdot}SO_2NH{\cdot}N{:}CR'R''$.

Compound	Ar	R′	R″	ν_{N-H}(cm.$^{-1}$)	ν_{S-O}(cm.$^{-1}$)
(VII)	*p*-Me·C_6H_4	Me	Me	3226s	1333s, 1160s
(VIII)	*p*-Me·C_6H_4	Me	Et	3205s	1335s, 1161s
(IX)	1,4-Me·CONH·$C_{10}H_6$	Me	Me	3268m	1333s, 1155s
(X)	1,4-Me·CONH·$C_{10}H_6$	Me	Et	3310m	1328s, 1153s
(XI)	1,4-Me·CONH·$C_{10}H_6$	Me	n-C_6H_{13}	3257m	1333s, 1157s
(XII)	1,4-Me·CONH·$C_{10}H_6$	H	Pr^i	3300m	1330s, 1157s
(XIII)	1,4-Me·CONH·$C_{10}H_6$	H	*o*-$C_6H_4{\cdot}NO_2$	3311m	1340s, 1152s
(XIV)	1,4-Pr^n·CONH·$C_{10}H_6$	Me	Me	3247m	1335s, 1156s

frequency band observed in the spectra (always above 3350 cm.$^{-1}$), but the symmetric mode of this group occurs in the same region as the vibrations of the other N–H groups in the molecules, and hence is less certainly assigned.

S–O Stretching Vibrations.—The asymmetric and symmetric vibrations of the $>SO_2$ groups appear near 1325 and 1160 cm.$^{-1}$, respectively, and are in all cases strong. In the sulphonylhydrazones these bands are always of slightly higher frequency than in the corresponding (*i.e.*, "parent") sulphonyl hydrazide. This frequency displacement appears to be somewhat greater (*ca.* 20 cm.$^{-1}$) for the asymmetric mode than for the symmetric mode (*ca.* 10 cm.$^{-1}$).

Other Bands.—Although the sulphonyl hydrazide and sulphonylhydrazone groupings might be expected to show other characteristic frequencies, such as those associated with N–H deformation and N=C stretching modes, these are not well marked in the spectra of these compounds, probably because they are partially masked by more intense bands, particularly aromatic-ring vibrations, in the same spectral regions. However, a medium or fairly strong band is found in the range 923—937 cm.$^{-1}$ in the spectra of all the sulphonylhydrazones but none of the sulphonyl hydrazides examined: this band seems to be of some diagnostic value but its assignment is uncertain.

Experimental.—Preparations. Toluene-*p*-sulphonyl hydrazide (I), m. p. 110—112°, was prepared by shaking a benzene solution of toluene-*p*-sulphonyl chloride with 50% aqueous hydrazine hydrate as described by Albert and Royer[2] (cf. ref. 3). The corresponding acetone hydrazone (VII), m. p. 153°, was obtained by boiling the hydrazide with excess of acetone.[4] The ethyl methyl ketone hydrazone (VIII), m. p. 124—125°, was similarly prepared (cf. ref. 5). *N*-Acetylsulphanilohydrazide (II), m. p. 188—190°, was obtained by the method of Curtius and Stoll[6] (cf. ref. 7). The preparation of the remaining compounds has been described previously.[1]

Infrared spectra. These were obtained on a Grubb-Parsons GS3 instrument, with samples in pressed discs in potassium bromide.

BRUNEL COLLEGE, ACTON, LONDON, W.3. [*Received, June 12th,* 1964.]

[2] A. Albert and R. Royer, *J.*, 1949, 1148.
[3] L. Friedman, R. L. Little, and W. R. Reichle, *Org. Synth.*, 1960, **40**, 93.
[4] W. R. Bamford and T. S. Stevens, *J.*, 1952, 4735.
[5] C. H. DePuy and D. H. Froemsdorf, *J. Amer. Chem. Soc.*, 1960, **82**, 634.
[6] T. Curtius and W. Stoll, *J. prakt. Chem.*, 1926, **112**, 117.
[7] R. J. W. Cremlyn, *J.*, 1962, 2133.

1192. *Triethylammonium Hydrogen Selenide.*

By N. N. Greenwood and M. J. Sprague.

Although tertiary amine hydrogen sulphides, R_3NHSH, have been known for many years[1] the analogous hydrogen selenides have not previously been reported. During an attempted hydroboronation of the selenocyanate ion we observed that reaction of potassium selenocyanate and triethylamine–borane at 140° yields triethylamine, hydrogen, and a small quantity of the new compound triethylammonium hydrogen selenide, Et_3NHSeH, together with a charred brown residue of unknown composition. The amine hydrogen selenide is probably formed by the production of the adduct KBH_3SeCN and its subsequent pyrolysis in the presence of triethylamine.

Triethylammonium hydrogen selenide is more conveniently prepared by the direct reaction of triethylamine with a slight excess of hydrogen selenide, followed by removal of the excess under reduced pressure. No evidence for formation of the selenide itself, $(Et_3NH)_2Se$, was observed in this system at room temperature. Triethylammonium hydrogen selenide forms volatile, white needles which melt with decomposition at 140°; it is photosensitive, soluble in methylene chloride, slightly soluble in diethyl ether and in tetrahydrofuran, and decomposes instantly on exposure to air. Formulation of the compound as triethylammonium hydrogen selenide was confirmed by analysis and infrared spectroscopy. The infrared spectra of mulls in Nujol and hexachlorobutadiene and as a solid on a potassium bromide plate at −140° were identical with that of triethylammonium chloride, except for an additional broad band at approximately 2400 cm.$^{-1}$, assigned to the H–Se$^-$ stretching vibration (cf. 2558 cm.$^{-1}$ for the isoelectronic molecule HBr).[2]

The compound dissociates reversibly according to the equation

$$Et_3NHSeH\ (s) \rightleftharpoons Et_3N\ (g) + H_2Se\ (g)$$

Infrared spectra of the compound in a heated gas cell (60°) indicate that there is effectively complete dissociation in the vapour phase. The dissociation pressure over a range of temperature was determined using a Bourdon gauge to avoid contact with mercury, and the least-squares line of best fit to the results can be expressed by the equation

$$\log_{10} p\ (\text{mm.}) = 11{\cdot}6353 - 3269{\cdot}7/T.$$

Since for this system the equilibrium constant K_p is $P^2/4$, where P is the dissociation pressure in atmospheres, this leads to values of $\Delta H = 29{\cdot}92$ kcal. mole^{-1} and $\Delta S = 77{\cdot}35$ cal. deg.$^{-1}$ mole^{-1} for the average heat and entropy of dissociation of triethylammonium hydrogen selenide. These results may be compared with the figures of $\Delta H = 27{\cdot}6$ kcal. mole^{-1} and $\Delta S = 73{\cdot}9$ cal. deg.$^{-1}$ mole^{-1} for ammonium hydrogen selenide[3] between 15° and 30°.

Dissociation pressure of Et_3NHSeH.

Temp.	$25{\cdot}5_5°$	$30{\cdot}4_5$	$36{\cdot}4$	$41{\cdot}6$	$47{\cdot}3$	$52{\cdot}0$	$58{\cdot}2_5$	$63{\cdot}7$	$70{\cdot}4_5$	$74{\cdot}3$
p(mm.)	4·9	6·9	11·9	18·6	27·7	38·3	58·7	85·7	130·0	164·1

Experimental.—Triethylamine (Hopkin and Williams) was distilled from lithium hydride. Hydrogen selenide was prepared by hydrolysis of aluminium selenide, and distilled from phosphorus pentoxide immediately before use. Potassium selenocyanate (B.D.H.) was purified as before,[4] and triethylamine–borane was prepared from triethylammonium chloride and lithium borohydride in ether.[5]

[1] M. Achterhof, R. F. Conaway, and C. E. Boord, *J. Amer. Chem. Soc.*, 1931, **53**, 2682.
[2] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963, p. 72.
[3] F. F. Mikus and F. J. Poss, *J. Amer. Chem. Soc.*, 1949, **71**, 429.
[4] E. E. Aynsley, N. N. Greenwood, and M. J. Sprague, *J.*, 1964, 702.
[5] N. N. Greenwood and J. H. Morris, *J.*, 1960, 2922.

Triethylammonium hydrogen selenide. This *compound* was prepared by allowing triethylamine to react with a 5% excess of hydrogen selenide in an evacuated all-glass system. The yield was quantitative. Analysis of the resublimed product, m. p. 140° (sealed tube), was performed by sealing a sample into a fragile glass bulb which was then broken under dilute hydrochloric acid. Selenium was determined as the element and nitrogen by the Kjeldahl method (Found: Se, 43·0; N, 7·5. $C_6H_{17}NSe$ requires Se, 43·3; N, 7·7%).

Reaction between potassium selenocyanate and triethylamine–borane. In a typical experiment potassium selenocyanate (5·25 g., 36·4 mmoles) was pumped to high vacuum for several hours, and triethylamine–borane (1·18 g., 10·2 mmoles) added in an atmosphere of dry nitrogen. After the mixture had been frozen in liquid nitrogen the system was re-evacuated and the mixture heated to 140°. Droplets of triethylamine and white crystals of triethylammonium hydrogen selenide were evolved from the mixture, which turned dark brown. Hydrogen (29·8 ml. at s.t.p., 1·33 mmoles) was evolved slowly and was removed periodically by means of a Töpler pump; the other volatile materials were then distilled back on to the reactants and the mixture reheated. The process was repeated until no further hydrogen was evolved. In order to isolate triethylammonium hydrogen selenide from this reaction mixture the volatile products were sublimed slowly under a vacuum to yield large crystals. These were then freed from most of the adhering triethylamine by drying on paper in an atmosphere of dry nitrogen followed by evacuation to constant pressure. The resublimed crystals (m. p. 141° decomp.) were analysed as described above (Found: Se, 42·4; N, 8·4. Calc. for Et_3NHSeH: Se, 43·3; N, 7·7%). In a series of experiments, variable quantities of hydrogen were evolved and the yield of triethylammonium hydrogen selenide was approximately 15% (based on Et_3NBH_3).

We thank the D.S.I.R. for a research studentship (to M. J. S.).

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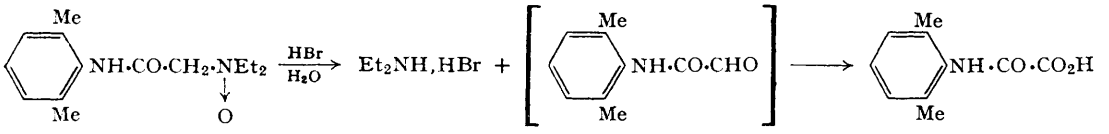
1193. N-*Diethylaminoacetyl*-2,6-*xylidine* (*Lignocaine*) N′-*Oxide and its Decomposition in Acid Solution.*

By R. G. JOHNSTON and DAVID KIDD.

THE *N*-oxide (I) of the local anaesthetic lignocaine (*N*-diethylaminoacetyl-2,6-xylidine), prepared here for pharmacology was isolated as a stable monohydrate. An attempted preparation of the *N*′-oxide hydrobromide from the monohydrate in chloroform gave

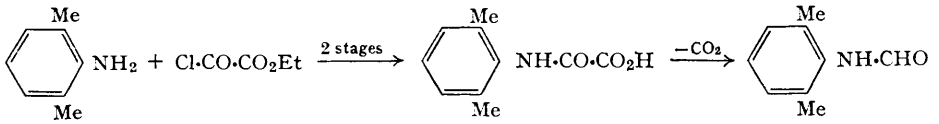


(I) (II) (III) (IV)

diethylamine hydrobromide (II), and when hydrobromic acid was added to a warm aqueous solution of the monohydrate, 2,6-dimethyloxanilic acid (IV) was isolated. This acid was also isolated on passage of sulphur dioxide through a warm aqueous solution of the monohydrate.

The identity of the decomposition product as 2,6-dimethyloxanilic acid (IV) was confirmed by synthesis of this acid from 2,6-xylidine and ethoxalyl chloride.[1] A mixed m. p. showed no depression and the infrared absorptions were identical. On heating above 110°, decarboxylation gave the known *N*-formyl-2,6-xylidine[2] (V).

[1] Bergmann and Kalmus, *J.*, 1952, 4521.
[2] Heilbron and Bunbury, "Dictionary of Organic Compounds," 2nd edn., Vol. IV, p. 682.



(V)

The acid decomposition of *N*-oxides to aldehydes is well known.[3] If lignocaine *N*-oxide decomposes similarly the intermediate glyoxal derivative (III) would result and this in turn might lead to 2,6-dimethyloxanilic acid (IV) by atmospheric oxidation.

Experimental.—N-*Diethylaminoacetyl*-2,6-*xylidine* N′-*oxide* (I). To a solution of *N*-diethylaminoacetyl-2,6-xylidine (100 g.) in alcohol (1·5 l.) was added 30% hydrogen peroxide (57 ml.) in portions, with mixing. After 48 hr. at room temperature most of the alcohol was removed at the water pump and benzene (500 ml.) added to the residue. A white solid hydrate [55 g.; m. p. 105—107° (decomp.); infrared similar to monohydrate, below] separated. This was taken up in benzene–ethanol (1:1; 500 ml.) and the volume reduced to approximately 1/5th; the *monohydrate* (27 g., 24%) then crystallised as large white blades, m. p. 232—234° (Found: C, 62·8; H, 8·9; N, 10·6. $C_{14}H_{22}N_2O_2,H_2O$ requires C, 62·7; H, 9·0; N, 10·5%), $\nu_{max.}$ 3300 (NH), 1660, and 1650 cm.$^{-1}$ (NH·CO).

Diethylamine hydrobromide (II). A solution of hydrogen bromide in ethanol was added to *N*-diethylaminoacetyl-2,6-xylidine *N*-oxide monohydrate (2·5 g.) in chloroform (50 ml.) until the mixture was acid. Addition of ether (100 ml.) gave a white solid (1·0 g., 70%) that crystallised from ethanol as white plates, m. p. 212—213° (lit. 213°) (Found: C, 31·0; H, 7·6; Br, 52·3; N, 8·8. Calc. for $C_4H_{11}N,HBr$: C, 31·2; H, 7·8; Br, 52·0; N, 9·1%).

2,6-*Dimethyloxanilic acid* (IV). (1) 48% Hydrobromic acid (8·0 ml.) was added to a solution of the *N*′-oxide (5·7 g.) in warm water (75 ml.). After being kept at room temperature the *acid* separated as white plates (3·3 g., 82·5%). Recrystallisation gave material of m. p. 178°—180° (decomp.) (Found: C, 62·1; H, 5·7; N, 7·2. $C_{10}H_{11}NO_3$ requires C, 62·2; H, 5·8; N, 7·2%); $\nu_{max.}$ 3350 (NH), 1790 (COOH), and 1700 cm.$^{-1}$ (CO·NH). (2) Sulphur dioxide was passed into a solution of the *N*′-oxide (3·0 g.) in warm water (70 ml.) for 1 hr. The white crystalline acid (1·7 g., 79%) was collected, washed, and dried. Crystallisation from water gave large white plates, m. p. 178—180° (decomp.), identical with the product from (1). (3) Ethoxalyl chloride (13·7 g.) in dry chloroform (100 ml.) was added to 2,6-xylidine (24·2 g.) in dry chloroform (150 ml.) below 20° with stirring during 1 hr. After a further 1 hr. at room temperature the chloroform layer was washed with water (2 × 100 ml.), dried (Na_2SO_4), and concentrated. The residue crystallised from light petroleum (b. p. 60—80°) to give *ethyl* 2,6-*dimethyloxanilate* as large white blades (17·5 g., 80%) m. p. 68—71° (Found: C, 65·2; H, 6·9; N, 6·3. $C_{12}H_{15}NO_3$ requires C, 65·2; H, 6·8; N, 6·3%). This ester (4·4 g.) was added to a solution of sodium (0·46 g.) in 99% ethanol (50 ml.). Almost immediately the sodium salt separated and was filtered off. On adding this salt to dilute hydrochloric acid, 2,6-dimethyloxanilic acid (3·5 g., 91%) separated. Recrystallisation from water gave white plates with m. p. and mixed m. p. with the product from (1) 178—180° (decomp.).

N-*Formyl*-2,6-*xylidine* (V). 2,6-Dimethyloxanilic acid (1·0 g.) was kept at 115° for 1 hr. The product crystallised from water in white blades (0·5 g., 65%), m. p. 175—176° (lit.,[2] 176—177°) (Found: C, 71·9; H, 7·4. Calc. for $C_9H_{11}NO$: C, 72·5; H, 7·4%), $\nu_{max.}$ 3250 (NH) and 1675 cm.$^{-1}$ (NH·CO).

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EDINBURGH PHARMACEUTICAL INDUSTRIES LTD.,
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[*Received, August 11th*, 1964.]

[3] Culvenor, *Rev. Pure Appl. Chem.*, 1953, **3**, No. 2, 97.

1194. *Aromatic Nucleophilic Substitution. Part X*. The Products of the Reactions of Alkali Halides with 1-Halogeno-2,4-dinitrobenzenes and Picryl Chloride in Anhydrous Acetone.*

By C. W. L. Bevan, J. Hirst, and E. C. Okafor.

Several years ago an investigation was started in these laboratories on the halide exchange reactions of 1-halogeno-2,4-dinitrobenzenes and picryl halides in anhydrous acetone.[1] In the picryl series, the exchange reaction between picryl chloride and chloride ions took place smoothly at $-30°$, whereas the corresponding reaction with iodide ion required a temperature of $+20°$ and the rate constants, calculated for a reversible bimolecular reaction, decreased with time. No product analysis was done in this investigation, but recently Parker and Read[2] observed that when picryl chloride and sodium iodide were refluxed in anhydrous acetone, the only product they obtained was 1,3,5-trinitrobenzene.

There is a discrepancy in the literature with regard to the Finkelstein reactions of 1-halogeno-2,4-dinitrobenzenes in anhydrous acetone. Cortier *et al.*,[3] using a conductimetric technique, studied the exchange reactions with potassium iodide and obtained the rate sequence F < Cl < Br. In the case of the fluoro-compound they state that after 10% of reaction has occurred at 109°, iodine and hydrogen fluoride are formed, but from measurements taken at less than 8% of reaction they get an order of magnitude for the rate constant of the exchange reaction. Miller and Parker[4] obtained similar results, but state that iodide does not displace fluoride from 1-fluoro-2,4-dinitrobenzene in acetone. Using lithium or potassium iodide at 121° they found that consumption of iodide always corresponded to less than 10% of reaction and after 24 hours they recovered 80% 1-fluoro-2,4-dinitrobenzene, some hydrogen fluoride, and a black tar.

In view of the above, we decided to investigate in more detail the products of these reactions and also those of the reaction of iodide ion with 1-chloro-2,4-dinitrobenzene, Miller and Parker[4] having already shown that iodide ion in acetone reacts with 1-bromo-2,4-dinitrobenzene to give 1-iodo-2,4-dinitrobenzene. The results are given below.

Reaction of Picryl Chloride with Iodide Ions.—A solution of sodium iodide (0·400M) and picryl chloride (0·08M) in anhydrous acetone was refluxed for 1·75 hr.; a 54% yield of 1,3,5-trinitrobenzene was obtained. Under identical conditions lithium iodide gave a 37% yield of the same product. Large amounts of iodine were found and mesityl oxide (identified by u.v. spectra and 2,4-dinitrophenylhydrazone, cf. Experimental section) was isolated. Control experiments established that, under the conditions used, sodium iodide in acetone did not give iodine, and sodium iodide and iodine in acetone did not produce mesityl oxide. In view of the products isolated we tentatively put forward the following mechanism for the reaction:

$$PiCl + I^- \longrightarrow PiI + Cl^-$$

$$PiI + I^- \longrightarrow Pi^- + I_2$$

$$Pi^- + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow PiH + {}^-CH_2{\cdot}CO{\cdot}CH_3$$

$$CH_3{\cdot}CO{\cdot}CH_3 + {}^-CH_2{\cdot}CO{\cdot}CH_3 \longrightarrow (CH_3)_2{\cdot}CO^-{\cdot}CH_2{\cdot}CO{\cdot}CH_3$$

$$(CH_3)_2{\cdot}CO^-{\cdot}CH_2{\cdot}CO{\cdot}CH_3 + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow (CH_3)_2(COH){\cdot}CH_2{\cdot}CO{\cdot}CH_3 + {}^-CH_2{\cdot}CO{\cdot}CH_3$$

$$(CH_3)_2C(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3 \xrightarrow{I_2} (CH_3)_2{\cdot}C{=}CH{\cdot}CO{\cdot}CH_3$$

$${}^-CH_2{\cdot}CO{\cdot}CH_3 + I_2 \longrightarrow CH_2I{\cdot}CO{\cdot}CH_3 + I^-$$

(Pi = picryl)

* Part IX, *J.*, 1963, 5868.

[1] Emovon, unpublished results.
[2] Parker and Read, *J.*, 1962, 9.
[3] Cortier, Fierens, Gilon, and Halleux, *Bull. Soc. chim. belges*, 1955, **64**, 709.
[4] Miller and Parker, *J. Amer. Chem. Soc.*, 1961, **83**, 117.

Reaction of Picryl Chloride with Chloride Ions.—After one hour at −20°, 97% of picryl chloride was recovered from solutions 0·1M in both picryl chloride and lithium chloride. The rate constant for this reaction is $5{\cdot}41 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$ at −20·5°.[5]

Reaction of 1-Chloro-2,4-dinitrobenzene with Iodide Ions.—Under the conditions used the only pure product isolated was 1-chloro-2,4-dinitrobenzene; the results are summarised in Table 1. In all the experiments, no trace of *m*-dinitrobenzene could be found.

TABLE 1.

Alkali iodide	[Chloro-compound]	Conditions	% Recovery of pure chloro-compound
NaI (0·4M)	0·08	Reflux for 1·75 hr.	75
NaI (0·15M)	0·1	9 hr. at 100°	83
LiI (0·15M)	0·1	9 hr. at 100°	74

Potassium iodide at 110° was used, the total halide concentration being estimated by Volhard's method and iodide ion with ceric sulphate. The results showed that, while the total halide concentration remained constant, after 9 hr. 9% of iodide had disappeared. A simultaneous isolation of product gave a substance of m. p. 48—54°. As attempts to separate it into components by v.p.c. and thin-layer chromatography failed, a portion was quantitatively hydrolysed with methoxide ion; estimation of total halide and of iodide showed that 9·3% of iodide was present; thus the reaction is a straightforward replacement.

The Reaction of 1-Fluoro-2,4-dinitrobenzene with Iodide Ions.—The reaction between sodium iodide and 1-fluoro-2,4-dinitrobenzene at 111° was followed by titration of iodide ion by Volhard's method and iodine with thiosulphate. Control experiments with sodium iodide in acetone showed that iodine was not produced under these conditions. The results are given in Table 2.

TABLE 2.

Reaction between iodide ions and 1-fluoro-2,4-dinitrobenzene in anhydrous acetone at 111°. Initial concentration of RF = 0·05M.

Time (hr.)	[I$^-$]	[I$_2$]	% Reaction	Time (hr.)	[I$^-$]	[I$_2$]	% Reaction
0	0·0482	—	—	121·5	0·0352	0·0064	27
48	0·04574	0·00122	5·2	144	0·0352	0·0064	27
74	0·03699	0·0056	23·3	168	0·0352	0·0064	27
98·5	0·0352	0·0064	27	192	0·0352	0·0064	27

From Table 2, the rate of appearance of iodine equals the rate of disappearance of iodide, consequently no iodine is trapped in the form of an organic iodo-compound. As this is taking place from 5% of reaction (and probably less) onwards, and a slow replacement reaction followed by subsequent fast reactions would require 2 moles of iodide, the figures of Cortier[3] cannot refer to the displacement reaction.

Product analysis after 42 days at 111° gave only fluoride ion and a black tar. After 74 hr., 1-fluoro-2,4-dinitrobenzene was isolated together with an orange-yellow solid. Thin-layer chromatography showed this to be a mixture of two major and two minor components, which from their R_F values were not *m*-dinitrobenzene, 1-iodo-2,4-dinitrobenzene, or 2,4-dinitrophenol. Crystallisation from acetone–methanol followed by chromatography gave a pure compound of m. p. 198–200°. This as yet unidentified substance is a polynitro-compound, $\lambda_{max.}$ 251·3 mμ, containing C, 41·9%; H, 3·0%; N, 14·6%, but no halogen.

Experimental.—Acetone. Potassium permanganate was added to "AnalaR" acetone until a pink colour persisted on prolonged refluxing. After drying ($CaSO_4$) and fractionation, the middle fraction was saturated with "Anhydrone," and anhydrous acetone distilled off as required.

[5] Ataga, unpublished results.

General method of isolation of products. After the appropriate reaction time, the mixture was cooled and poured into a large volume of ice–water. The product was filtered off and identified by m. p. and mixed m. p. with authentic samples.

Mesityl oxide from picryl chloride and sodium iodide. Picryl chloride (4 g.) and sodium iodide (12 g.) in acetone (200 c.c.) were refluxed for 1·75 hr., and the acetone then distilled off, the last traces being removed in a stream of nitrogen. At this stage a lachrymatory substance (iodoacetone?) was swept out by the nitrogen. The residue, treated with 2N-sodium thiosulphate until it no longer gave a positive test for iodine, was extracted with di-isopropyl ether. The extract had $\lambda_{max.}$ 251·3 mμ; mesityl oxide (prepared by Vogel's method [6]) $\lambda_{max.}$ 253·8 mμ (isopropyl ether); 1,3,5-trinitrobenzene $\lambda_{max.}$ 259·7 mμ (isopropyl ether). A 2,4-dinitrophenylhydrazone (0·0132 g.) prepared from the ethereal extract and purified on a bentonite–kieselguhr column had $\lambda_{max.}$ 393·7 mμ (methanol), m. p. 201·5—203°, not depressed on admixture with the 2,4-dinitrophenylhydrazone of mesityl oxide, which also showed $\lambda_{max.}$ 393·7 mμ (in methanol). A control experiment exactly as above but omitting the picryl chloride gave a di-isopropyl ether extract which had no absorption in the 250 mμ region. All spectral measurements were carried out with a Unicam S.P. 700 instrument.

Products from the reaction of 1-fluoro-2,4-dinitrobenzene and sodium iodide. Nine tubes, each containing 10 c.c. of an acetone solution 0·05M in both the fluoro-compound and iodide were left in a thermostat at 111° for 74 hr. The contents of the tubes were poured into 300 c.c. of water and left for several hours. Filtration gave an orange-yellow substance (0·1305 g.), m. p. 150—186°. Extraction of the filtrate with ether, followed by crystallisation of the extract with sodium-dried ether, gave a yellow product, liquid at room temperature, whose infrared spectrum was identical with that of 1-fluoro-2,4-dinitrobenzene. Thin-layer chromatography on silica gel of the product, m. p. 150—186°, with cyclohexane–chloroform (5:12) gave two small spots, R_F 0·119 and 0·152, and two larger spots, R_F 0·241 and 0·346. Under identical conditions the R_F values of *m*-dinitrobenzene, 1-iodo-2,4-dinitrobenzene, and 2,4-dinitrophenol are 0·600, 0·640, and 0·033. A part of this product is insoluble in chloroform. Crystallisation of this from acetone–methanol gave a substance, m. p. 198—200°, m. p. unchanged by chromatography on a silica-gel column with the above cyclohexane–chloroform mixture.

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[*Received, June 29th,* 1964.]

[6] A. I. Vogel, "Practical Organic Chemistry," Longmans, London, 3rd edn, p. 333.

1195. *A Convenient Synthesis of 3-Phenylpyrazole.*

By M. S. GIBSON and A. W. MURRAY.

A SAMPLE of 3-phenylpyrazole was recently required in connexion with other work in the pyrazole series. The behaviour of the readily available 1,1,1,3-tetrachloro-3-phenylpropane towards methanolic potassium hydroxide [1] led us to adumbrate the following scheme, in which hydroxide ion functions as base and hydrazine as nucleophile.

$$Ph{\cdot}CHCl{\cdot}CH_2{\cdot}CCl_3 \xrightarrow{OH^-} [Ph{\cdot}CH{:}CH{\cdot}CCl_3] \xrightarrow[S_N2']{NH_2{\cdot}NH_2} [Ph{\cdot}CH(NH{\cdot}NH_2){\cdot}CH{:}CCl_2]$$

$$\xrightarrow[\text{shift}]{\text{prototropic}} [Ph{\cdot}C(NH{\cdot}NH_2){:}CH{\cdot}CHCl_2 \text{ or } Ph{\cdot}C(:NNH_2){\cdot}CH_2{\cdot}CHCl_2] \longrightarrow \overline{Ph{\cdot}C{:}N{\cdot}NH{\cdot}CH{:}CH}$$

Reaction was carried out by refluxing 1,1,1,3-tetrachloro-3-phenylpropane with an excess of 99—100% hydrazine hydrate containing potassium hydroxide (4—4½ Equiv.,), and the pyrazole conveniently isolated as the picrate. Chromatography of the crystallised picrate on alumina, a procedure based on the known hydrolysis of 1-(2,4-dinitrophenyl)-pyrazole on alumina,[2] provides the easiest method of recovering the pyrazole.

[1] H. Goldwhite, M. S. Gibson, and C. Harris, *Tetrahedron*, 1964, **20**, 1649.
[2] H. P. Crocker and R. H. Hall, *J.*, 1955, 4489.

Experimental.—We thank Mr. V. Manohin for microanalysis.

3-*Phenylpyrazole picrate.* 1,1,1,3-Tetrachloro-3-phenylpropane[1] (8 g.) was added to a solution of potassium hydroxide (8 g.) in 99—100% hydrazine hydrate (40 ml.), and the mixture was refluxed for 15 hr., during which time potassium chloride separated. The mixture was diluted with water (200 ml.), extracted with ether (3 × 50 ml.), and the ethereal extract washed, dried ($MgSO_4$), and evaporated, yielding a brown oil. Treatment with ethanolic picric acid afforded 3-phenylpyrazole picrate (2·9 g.), which crystallised from ethanol as yellow needles, m. p. 173—175° (decomp.) (lit.,[3] 170—171°) (Found: N, 18·9. Calc. for $C_{15}H_{11}N_5O_7$: N, 18·8%).

3-*Phenylpyrazole.* (*a*) *Chromatography of 3-phenylpyrazole picrate on alumina.* A solution of 3-phenylpyrazole picrate (800 mg.) in the minimum of benzene–methanol was added to a column of alumina (Spence, Type H) packed in benzene. A large bright-yellow zone was obtained. Elution with methanol (200 ml.) furnished (i) a fast-moving brown front, (ii) a colourless fraction, and (iii) a yellow fraction. Fractions (i) and (ii) were combined and evaporated; sublimation *in vacuo* of the brown viscous residue gave 3-phenylpyrazole (190 mg.), which crystallised from n-heptane as tiny colourless rhombs, m. p. 78° (lit.,[3,4] 78°) (Found: C, 74·8; H, 5·5; N, 19·7. Calc. for $C_9H_8N_2$: C, 75·0; H, 5·55; N, 19·45%).

(*b*) *Decomposition of 3-phenylpyrazole picrate with sodium methoxide.* A solution of 3-phenylpyrazole picrate (1·35 g.) in methanol (35 ml.) was refluxed with 0·61N-methanolic sodium methoxide (15 ml.) for 5 min. under nitrogen. The solution was poured into water (100 ml.) and thoroughly extracted with ether. Evaporation of the dried ethereal solution gave a brown, oily residue which, on sublimation *in vacuo*, afforded 3-phenylpyrazole (280 mg.); crystallisation from n-heptane gave tiny off-white rhombs, m. p. and mixed m. p. with previous sample, 76—77°.

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[3] L. Knorr, *Ber.*, 1895, **28**, 688, 696.
[4] K. Bowden and E. R. H. Jones, *J.*, 1946, 953.

1196. *Synthesis and Base-catalysed Cleavage of an* N-*Acylkephalin.*

By J. J. WREN and DANUTA S. MERRYFIELD.

FOR comparison with *N*-acylethanolamine derivatives obtained from lipid extracts,[1] the *N*-acylkephalin (I; X = CO·$[CH_2]_{14}$·Me, Y = NH·CO·$[CH_2]_{14}$·Me) has been synthesised. Methanolysis[2] or hydrolysis under mild, basic conditions converted it into the expected deacylation product, DL-glycerol 1-(2-palmitoylaminoethyl hydrogen phosphate) (I; X = H, Y = NH·CO·$[CH_2]_{14}$·Me), but also, in 20% or higher yield, to *N*-(2-hydroxyethyl)-palmitamide. Thus the deacylation product appears to be highly base-labile, like the related derivatives (I; X = H, Y = NMe^{3+}) of choline[3] and [I; X = H, Y = NH·$C_6H_3(NO_2)_2$] of 2,4-dinitrophenylethanolamine.[4] That these derivatives are more labile than glycerol 1-(2-aminoethyl hydrogen phosphate)[2,3] (I; X = H, Y = NH_2) may be attributable to electron deficiency at the nitrogen atoms.

Not more than 75% of the theoretical yield of *N*-(2-hydroxyethyl)palmitamide was formed on prolonged methanolysis, although this compound is completely stable under the conditions used. Hence the deacylation product undergoes more than one cleavage reaction (cf. ref. 5).

$CH_2(OX)\cdot CH(OX)\cdot CH_2\cdot O\cdot PO(OH)\cdot O\cdot CH_2\cdot CH_2\cdot Y$ (I)

Experimental.—*Synthesis.* Palmitoyl chloride (2·5 g.) in ether (5 ml.) was added to a solution of 2,3-di-*O*-palmitoyl-DL-glycerol 1-(2-aminoethyl hydrogen phosphate) (0·25 g.) in

[1] J. J. Wren and D. S. Holub, *Biochem. J.*, 1964, **90**, 3P.
[2] G. Hübscher, J. N. Hawthorne, and P. Kemp, *J. Lipid Res.*, 1960, **1**, 433.
[3] B. Maruo and A. A. Benson, *J. Biol. Chem.*, 1959, **234**, 254; H. Brockerhoff, *J. Lipid Res.*, 1963, **4**, 96.
[4] L. W. Wheeldon and F. D. Collins, *Biochem. J.*, 1957, **66**, 435.
[5] D. M. Brown and D. A. Usher, *Proc. Chem. Soc.*, 1963, 309; G. L. Schmir and C. Zioudrou, *Biochemistry*, 1963, **2**, 1305.

anhydrous pyridine (30 ml.) and stirred (4 hr.). The resulting mixture was poured into chilled methanol (200 ml.), chilled N-hydrochloric acid was added to bring the pH to 2, and two extractions were made with chloroform. The extracts were combined, washed, and evaporated, and the residue was chromatographed on a column of Mallinckrodt silicic acid (10 g.) prepared in AnalaR chloroform. The first effluent (chloroform; 200 ml.) was rejected, and the second (5% methanol in chloroform; 200 ml.) collected and evaporated. The residue (0·36 g.), consisting of the N-*acylkephalin*, was recrystallised four times from butan-2-one and once from pure dioxan for analysis (Found: C, 68·4; H, 11·0; N, 1·7; P, 3·2. $C_{53}H_{104}NO_9P$ requires: C, 68·4; H, 11·3; N, 1·5; P, 3·3%). The pure compound had m. p. 66—67°; $\nu_{max.}$ (Nujol) at 3300, 1740, 1650, 1540, 1170, and 722 cm.$^{-1}$.

Attempted purification on Florisil. Unexpectedly, the *N*-acylkephalin could not be eluted from magnesium silicate (Florisil) as it could from silicic acid. Methanol (40%) eluted a relatively insoluble substance with a different melting point (82—124°, after recrystallisation) but a very similar infrared spectrum; the only change noted was a shift to 1070 cm.$^{-1}$ of a peak previously found at 1050 cm.$^{-1}$ (Nujol) or 1020 cm.$^{-1}$ (chloroform). Since washing with hydrochloric acid reversed the shift, and restored solubility, it was apparent that a magnesium salt was formed[6] on the column.

Methanolysis (typical experiment). The *N*-acylkephalin (20·5 mg.) was dissolved in chloroform (4 ml.) and left (15 min.) in a stoppered flask at room temperature with 0·33N-methanolic sodium hydroxide (2 ml.). After acidification of the solution to pH 2 with hydrochloric acid, the product was extracted with ether and chromatographed on silicic acid as described elsewhere;[7] 1% methanol eluted methyl palmitate (12·3 mg.), 2% methanol eluted *N*-(2-hydroxyethyl)palmitamide (1·3 mg.), and 15% methanol eluted DL-*glycerol* 1-(2-*palmitoylaminoethyl hydrogen phosphate*) (4·8 mg.). More material (2·0 mg.), of the same infrared spectrum, was recovered from the aqueous phase set aside before chromatography.

This product was combined with that of a similar experiment, re-chromatographed in 5% methanol and 10% methanol (first eluate rejected), crystallised from chloroform–methanol and ether–methanol, and dried at 56°. It then had m. p. 100–101° (sintered at 93°); $\nu_{max.}$ (Nujol) at 3300 1645, 1550, 1221, 1152, 1121, 1073, 1057, 1020, 935, 777, and 721 cm.$^{-1}$ (Found: C, 55·3; H, 9·6; N, 2·9; P, 7·0. $C_{21}H_{44}O_7NP$ requires C, 55·6; H, 9·8; N, 3·1; P, 6·8%). In Benedict's assay for α-glycols[8] it consumed 97·5% of the theoretical quantity of periodic acid. It was soluble in water and polar organic solvents, and had R_F 0 on thin-layer chromatograms developed[7] as for *N*-(2-hydroxyethyl)palmitamide. It gave positive reactions for lipid (with iodine vapour), α-glycol,[9] secondary amide,[7] and phosphorus[10] on the chromatograms, but no ninhydrin reaction. It yielded *N*-(2-hydroxyethyl)palmitamide when heated (15 min.) in aqueous solution at pH 1.

THE LYONS LABORATORIES, HAMMERSMITH ROAD, LONDON, W.14. [*Received, July 3rd*, 1964.]

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[8] J. B. Martin, *J. Amer. Chem. Soc.*, 1953, **75**, 5483.
[9] J. Baddiley, J. G. Buchanan, R. E. Handschumacher, and J. F. Prescott, *J.*, 1956, 2818.
[10] J. C. Dittmer and R. L. Lester, *J. Lipid Res.*, 1964, **5**, 126.

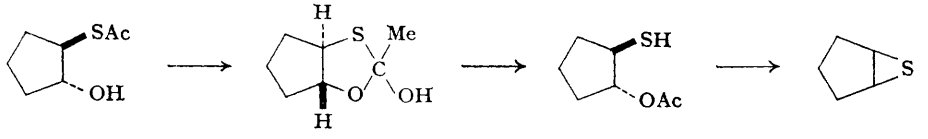
1197. *The Formation of Cyclopentene Sulphide from the Acetyl Derivatives of 2-Mercaptocyclopentanol.*

By M. KYAW and L. N. OWEN.

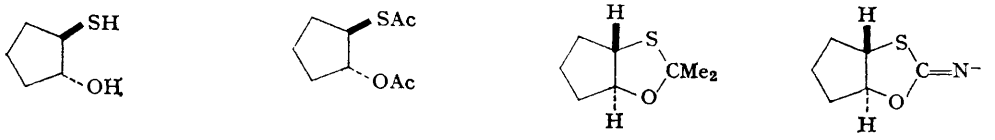
IT has been shown[1] that, in weakly alkaline solution, the normal hydrolysis of *trans*-2-acetylthiocyclopentanol (I) to 2-mercaptocyclopentanol (V) is accompanied by cyclisation to the episulphide (IV); measurements of the separate rates at which the acetyl group is lost and the thiol group is liberated were interpreted to indicate the occurrence of rearrangement, *via* the orthoacetate (II), to give *trans*-2-mercaptocyclopentyl acetate (III), which then undergoes an internal S_N2 displacement. Goodman, Benitez, and Baker[2] criticised this scheme on the grounds that the existence of the intermediate (II), possessing two *trans*-fused

[1] J. S. Harding and L. N. Owen, *J.*, 1954, 1528.
[2] L. Goodman, A. Benitez, and B. R. Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 1680.

five-membered rings, was quite improbable. They suggested that the thiolacetate (I) was much more likely to effect an intermolecular transfer of an acetyl group to another molecule of itself to form the diacetate (VI), and, in support of this contention, they showed that the latter compound gave a good yield of the episulphide when it was treated with aqueous sodium hydroxide. Although they did not imply that any intermediate was involved in the route from the diacetate, direct cyclisation is inadmissible, and the immediate precursor of the episulphide must be the monoacetate (III); that this undergoes cyclisation, was demonstrated in the earlier quantitative experiments,[1] and confirmation has now been provided by isolation of cyclopentene sulphide from it.



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



(V) (VI) (VII) (VIII)

Nevertheless, it does not follow that the reaction of the diacetate follows the route (VI) → (III) → (IV) exclusively. There is little difference between the rate of hydrolysis of a thiolacetate and that of an ordinary acetate,[3] and the diacetate (VI) would be expected to give an appreciable proportion of 2-acetylthiocyclopentanol (I) as well as the monoacetate (III). The product (I) could then be converted either into (III) by the route originally postulated,[1] or, if the alternative proposal[2] be accepted, into equal proportions of the mercapto-alcohol (V) and the original diacetate (VI).

The argument that the isomerisation of (I) to (III) cannot occur through the orthoacetate (II), is fallacious. There are several heterocyclic analogues of *trans*-bicyclo[3,3,0]octane which are easily formed under mild conditions;[4,5] the isopropylidene derivative (VII)[5] of *trans*-2-mercaptocyclopentanol (V) is a good example. Goodman and Baker[6] have indeed accepted the structure (VIII) as an intermediate in the preparation of cyclopentene sulphide by reaction of cyclopentene oxide with potassium thiocyanate. Furthermore, we now have evidence which refutes the suggestion of intermolecular acylation. If this were to occur during the alkaline hydrolysis of 2-acetylthiocyclopentanol (I), another alcohol, present in large excess, should act as a competitive acceptor for the donated acetyl group, and the route to the episulphide (IV) through the diacetate (VI) would be inhibited. Quantitative experiments, in which the thiolacetate (I) is hydrolysed in 0·05N-sodium hydroxide in aqueous dioxan, show that the addition of a twenty-fold proportion of cyclopentanol has no significant effect on the course of the reaction. Both in the presence and in the absence of the competitor, the initial rapid rise in thiol value, corresponding to the migration of the acetyl group,[1] is followed by a fall, as cyclisation occurs, to the same final value. There can, therefore, be little doubt that the migration is intramolecular.

Goodman, Benitez, and Baker[2] failed to repeat the preparation of cyclopentene sulphide

[3] P. N. Rylander and D. S. Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 3021.
[4] S. A. Harris, R. Mozingo, D. E. Wolf, A. N. Wilson, and K. Folkers, *J. Amer. Chem. Soc.*, 1945, **67**, 2102; L. N. Owen and A. G. Peto, *J.*, 1955, 2383; S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, *J. Org. Chem.*, 1955, **20**, 1178; S. F. Birch, R. A. Dean, and E. V. Whitehead, *ibid.*, 1958 **23**, 783; H. Booth, F. E. King, K. G. Mason, J. Parrick, and R. L. St. D. Whitehead, *J.*, 1959, 1050.
[5] M. Kyaw and L. N. Owen, *J.*, 1965, 1298.
[6] L. Goodman and B. R. Baker, *J. Amer. Chem. Soc.*, 1959, **81**, 4924.

from the thiolacetate (I), but we have confirmed the earlier report.[1] The yield is lower than that from the monoacetate (III), probably because the latter, possessing a free thiol group, is more soluble in the aqueous alkaline medium.

It has been reported[7] that 2,3-epithiobutane reacts quite rapidly with iodine in hydroxylic solvents. In the quantitative experiments mentioned above, the stability of the end-point of the thiol estimation indicated that any similar reaction on cyclopentene sulphide was insignificant, and a control experiment on the pure episulphide showed that attack by iodine was very slow. In contrast, cyclohexene sulphide reacted much faster; it took up one equivalent of iodine in half an hour at room temperature, presumably to give bis-*trans*-2-iodocyclohexyl disulphide, since Stewart and Cordts[8] have shown that bishalopropyl disulphides are formed by the addition of chlorine or bromine to 1,2-epithiopropane.

Experimental.—Materials. *trans*-2-Acetylthiocyclopentanol, b. p. 70—72°/10^{-2} mm., n_D^{24} 1·5153 (Found: thiol-S, nil), and *trans*-2-mercaptocyclopentyl acetate, b. p. 96—98°/20 mm., n_D^{20} 1·4870 (Found: thiol-S, 19·0. Calc. for $C_7H_{12}O_2S$: thiol-S, 20·0%) were prepared as previously described.[1]

Cyclopentene sulphide. (i) A mixture of *trans*-2-acetylthiocyclopentanol (3·0 g.), sodium hydrogen carbonate (3·0 g.), and water (50 c.c.) was heated under reduced pressure so that slow distillation occurred with an internal temperature of 60°. Extraction of the distillate with ether gave cyclopentene sulphide (0·34 g.), b. p. 125—130°, n_D^{22} 1·5222; higher-boiling fractions contained some starting material.

(ii) A mixture of *trans*-2-acetylthiocyclopentanol (5·3 g.) and 0·5N-sodium hydroxide (70 c.c.) was shaken for 4 hr., then acidified to pH 5 with 2N-hydrochloric acid, and extracted with light petroleum (b. p. 40—60°) to give cyclopentene sulphide (0·50 g.), b. p. 125—128°, n_D^{22} 1·5225; higher-boiling fractions were also obtained.

(iii) A mixture of *trans*-2-mercaptocyclopentyl acetate (6·2 g.) and aqueous 2N-sodium hydroxide (21 c.c.) was shaken for 12 hr., and then worked-up as described under (ii), to give cyclopentene sulphide (2·3 g.), b. p. 70—73°/70 mm., n_D^{22} 1·5222.

The episulphide from each reaction was characterised by treatment with potassium methyl xanthate to give the trithiocarbonate (*trans*-4,5-cyclopentano-1,3-dithiolan-2-thione), m. p. 147°.[9]

Reactions of episulphides with iodine. (i) A solution of cyclohexene sulphide[10] (26·8 mg.) in dioxan (10 c.c.) and water (10 c.c.), containing starch, was titrated with 0·0135N-iodine, added 1 c.c. at a time as soon as the blue colour faded. After the addition of 17·0 c.c. in this way (35 min.), the uptake virtually ceased; this corresponds to 0·98 atom of iodine per mol. A similar result was obtained when the water was replaced by 2N-hydrochloric acid (20 c.c.).

(ii) Cyclopentene sulphide (58·4 mg.), titrated in dioxan (10 c.c.) and water (10 c.c.) with 0·0505N-iodine, added in 0·1-c.c. portions, took up only 0·5 c.c. (0·04 atom per mol.) in 36 min.

Alkaline deacetylations of trans-2-*acetylthiocyclopentanol.* These were carried out in 0·05N-sodium hydroxide in aqueous dioxan (1:1 by volume) at 0° by the method described earlier.[1] For the competitive experiment, the cyclopentanol was added to the medium before the acetate was introduced. The following Table shows the extent to which the acetyl group is removed and the thiol group liberated.

(*a*) *trans*-2-Acetylthiocyclopentanol (0·0113M)

t (min.)	1·8	2·5	9·0	21·0	55·0	75·0
Acetyl	0·24	0·38	0·72	0·94	1·01	1·01
Thiol	0·45	0·82	0·48	0·39	0·38	0·38

(*b*) *trans*-2-Acetylthiocyclopentanol (0·0108M) and cyclopentanol (0·20M)

t (min.)	1·2	2·3	9·5	19·3	56·0	110·0
Acetyl	0·15	0·31	0·75	0·92	1·00	1·00
Thiol	0·34	0·64	0·47	0·41	0·38	0·38

DEPARTMENT OF CHEMISTRY, IMPERIAL COLLEGE, LONDON, S.W.7.

[*Received, September 7th,* 1964.]

[7] G. K. Helmkamp and D. J. Pettitt, *J. Amer. Chem. Soc.*, 1960, **25**, 1754.
[8] J. M. Stewart and H. P. Cordts, *J. Amer. Chem. Soc.*, 1952, **74**, 5880.
[9] S. M. Iqbal and L. N. Owen, *J.*, 1960, 1030.
[10] C. C. J. Culvenor, W. Davies, and K. H. Pausacker, *J.*, 1946, 1050.

1198. *Synthesis of Sudachitin and Demethoxysudachitin.*

By H. H. Lee and C. H. Tan.

Sudachitin[1] and demethoxysudachitin,[2] flavones from *Citrus sudachi*, are, respectively, 4′,5,7-trihydroxy-3′,6,8-trimethoxyflavone and 4′,5,7-trihydroxy-6,8-dimethoxyflavone. Our interest in the light-absorption of such 5,7-dihydroxy-flavonoids in the presence of sodium acetate, and the availability of 4-benzyloxy-2-hydroxy-3,5,6-trimethoxyacetophenone,[3] led us to synthesize the two trihydroxy-flavones for spectral studies (see Table).

Light-absorption of flavones in various solvents [$\lambda_{max.}$ (mμ); log ε in parentheses].

Flavone	In 95% EtOH	In 0·02M-NaOEt	In EtOH–NaOAC	In EtOH–$AlCl_3$	In EtOH–HCl
4′,5,7-Trihydroxy-3′,6,8-trimethoxyflavone (Sudachitin)	283 (4·15) 349 (4·08)	‡	285§ 323 400	259 293 365	250 (infl. 3·99) 282 (4·06) 349 (4·19)
4′,5,7-Trihydroxy-6,8-dimethoxyflavone (Demethoxysudachitin)	283 (4·33) 337 (4·33)	285 328 385	285§ 306 (infl.) 344 (infl.) 396	265 (infl.) 295 (infl.) 310 352	283 (4·38) 338 (4·47)
4′,7-Dibenzyloxy-3′,5,6,8-tetramethoxyflavone	251 (4·32)* 271 (4·31) 334 (4·45)				
4′,7-Dibenzyloxy-5,6,8-trimethoxyflavone	272 (4·49)† 325 (4·65)				

* Reported for 3′,4′,5,6,7,8-hexamethoxyflavone (nobiletin), 248 (4·34), 271 (4·28), and 333 (4·45) (L. J. Swift, *J. Org. Chem.*, 1960, **25**, 2067).

† Reported for 4′,5,6,7,8-pentamethoxyflavone (tangeretin), 272 (4·30) and 324 (4·46) (G. H. Stout and V. F. Stout, *Tetrahedron*, 1961, **14**, 296).

‡ Decomposed before absorption could be determined.

§ Spectrum determined immediately after addition of sodium acetate.

As with lucidin and 5,7-dihydroxy-6,8-dimethoxyflavone,[3] the positions of Band II of sudachitin and demethoxysudachitin are not appreciably affected by the presence of a weak base, although the two flavones themselves are unstable in alkaline solution.

Experimental.—M.p.s. were determined on a Kofler hot-stage apparatus. Ultraviolet spectra were measured with a Perkin–Elmer Model 137UV spectrophotometer. Microanalyses were by Mrs. H. K. Tong (Singapore).

	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
4,4′-Dibenzyloxy-2-hydroxy-3,5,6-trimethoxychalcone	95—96°	$C_{32}H_{30}O_7$	73·0	5·8	73·0	5·7
4,4′-Dibenzyloxy-2-hydroxy-3′,3,5,6-tetramethoxychalcone	95—97	$C_{33}H_{32}O_8$	71·3	5·95	71·2	5·8
4′,7-Dibenzyloxy-5,6,8-trimethoxyflavone	132·5—133·5	$C_{32}H_{28}O_7$	73·2	5·5	73·3	5·4
4′,7-Dibenzyloxy-3′,5,6,8-tetramethoxyflavone	158—160	$C_{33}H_{30}O_8$	71·6	5·5	71·5	5·45
4′,5,7-Trihydroxy-6,8-dimethoxyflavone (Demethoxysudachitin)*	277—279 (lit.,[2] 271—273)	$C_{17}H_{14}O_7$	61·9	4·6	61·8	4·3
4′,5,7-Trihydroxy-3′,6,8-trimethoxyflavone (Sudachitin)†	241—243 (lit.,[1] 239·5—240·5)	$C_{18}H_{16}O_8$	60·0	4·8	60·0	4·5

* Triacetate, m. p. 192—194° (lit.,[2] 188—190°) (Found: C, 60·3; H, 4·6. Calc. for $C_{23}H_{20}O_{10}$: C, 60.5; H, 4·4%). † Trimethyl ether (nobiletin), m. p. and mixed m. p. 136·5—137·5°.

[1] T. Horie, M. Masumura, and S. Okumura, *Bull. Chem. Soc. Japan*, 1961, **34**, 1547; *J. Chem. Soc. Japan*, 1962, **83**, 468.

[2] T. Horie, H. Shimoo, M. Masumura, and S. Okumura, *J. Chem. Soc. Japan*, 1962, **83**, 602.

[3] H. H. Lee and C. H. Tan, *J.*, 1965, 2743.

Preparation of chalcones and flavones. The chalcones were prepared by reaction of 4-benzyloxy-2-hydroxy-3,5,6-trimethoxyacetophenone with 4-benzyloxybenzaldehyde[4] or 4-benzyloxy-3-methoxybenzaldehyde[5] in ethanolic sodium hydroxide solution. The flavones were obtained by oxidative cyclization of the corresponding chalcones with selenium dioxide in pentan-1-ol. Sudachitin and demethoxysudachitin were isolated from the hydrolysis of their dibenzyl ethers with boiling concentrated hydrochloric acid in aqueous acetic acid (1:1) for 2 hr.

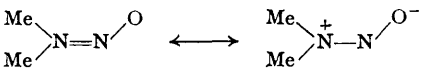
UNIVERSITY OF MALAYA, KUALA LUMPUR. [*Received, November 10th*, 1964.]

[4] R. Stoermer and F. Wodarg, *Ber.*, 1928, **61**, *B*, 2323.
[5] R. M. Anker, A. H. Cook, and I. M. Heilbron, *J.*, 1945, 917.

1199. *Internal Rotation in Dimethylnitrosamine.*

By D. J. BLEARS.

PURE liquid dimethylnitrosamine shows, up to 90°, a clearly defined doublet in its 60 Mc./sec. n.m.r. spectrum. Looney *et al.*[1] suggested that the primary contributions to the electronic structure are the resonance forms (I) and (II).



(I) (II)

Observation of two methyl resonances indicates that the configuration is probably planar with the methyl groups "fixed" in different environments owing to the partial double-bond character of the N–N bond which arises from overlap between the *p*-orbitals of the two nitrogen atoms.

The difference in chemical shift between the two methyl groups can be ascribed to electric-field effects[2] between the oxygen atom and the methyl groups situated at different distances from the oxygen atom. In such a field effect the lower-field and higher-field resonances may be assigned to the CH_3 groups *cis* and *trans*, respectively, to the oxygen atom.[1]

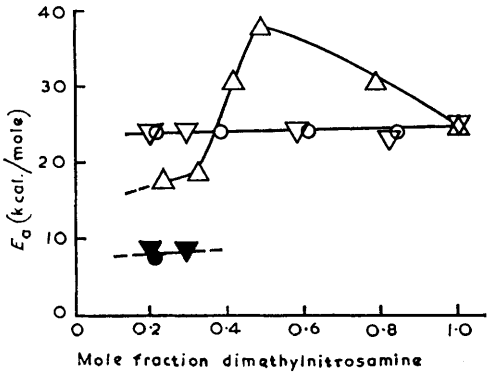
Arrhenius plots of the rate constant against $1/T$ (°c) yield the activation energy, E_a, hindering rotation about the N–N partial double bond. The rate constants[3] have been derived from the partial collapse of the methyl resonances with rising temperature, using the Bloch equations[4] modified for kinetic effects. Numerical solutions due to Lee[5,6] have been used. These equations give the rate constant in terms of the minimum to maximum v-mode intensity ratio ($I_{min.}/I_{max.}$) and the separation to separation at infinitely slow exchange ratio ($\delta\omega_e/\delta\omega$). The ratio $I_{min.}/I_{max.}$ shows a reasonable sensitivity over a good range of rate constants, k. Changes in the $\delta\omega_e/\delta\omega$ ratio correspond to small changes in k over the range of interest, and hence the former ratio is expected to give the most reliable estimate of E_a. For both ratios the most reliable k values occur when their curves have intermediate slopes.[6]

The activation energy for pure dimethylnitrosamine, calculated using the $I_{min.}/I_{max}$ ratio, is 25 ± 5 kcal./mole, with a frequency factor $\nu_0 = 1{\cdot}6 \times 10^{11}$ sec.$^{-1}$. This is in good agreement with the value of Looney *et al.*[1] of 23 kcal./mole and $\nu_0 = 7 \times 10^{12}$ sec.$^{-1}$ recorded at 40 Mc./sec. The lower temperature of methyl-group coalescence ($\sim 183°$) is to be expected at the

[1] Looney, Phillips, and Reilly, *J. Amer. Chem. Soc.*, 1957, **79**, 6136.
[2] Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.
[3] Loewenstein and Connor, *Z. Elektrochem.*, 1963, **67**, 3, 280.
[4] Block, *Phys. Rev.* 1946, **70**, 460.
[5] Lee, "Aplication of Nuclear Magnetic Resonance to Internal Motion—Rotational Isomeric Interconversion," personal communication.
[6] Lee, "Hindered Rotation about B–N Bonds," paper presented at the Symposium on High Resolution N.M.R. Spectroscopy, Boulder, Colorado, 1962.

lower radio-frequency. The free energy of activation calculated from the theory of absolute reaction rates, assuming a transmission coefficient of 0·5, is 25 kcal./mole, the same as that obtained by Phillips *et al.*[3,7] The entropy of activation is −1·1 e.u.

The behaviour of the activation energy in the solvents 1-chloronaphthalene, phenyl cyanide, and ethylene glycol is shown in the Figure.



Variation of activation energy with concentration in 1-chloronaphthalene, phenyl cyanide, and ethylene glycol.

$I_{min.}/I_{max.}$ { ○, 1-chloronaphthalene; ▽, phenyl cyanide; △, ethylene glycol.

$\delta\omega_e/\delta\omega$ { ▼, phenyl cyanide; ●, 1-chloronaphthalene.

In dilute solutions the changes in the $\delta\omega_e/\delta\omega$ ratio give activation energies of 7·4 kcal./mole in 0·21 mole fraction dimethylnitrosamine in 1-chloronaphthalene, and 8·4 kcal./mole for E_a in 0·20 mole fraction dimethylnitrosamine in phenyl cyanide. An extrapolated value for pure dimethylnitrosamine is ~ 10 kcal./mole, which is markedly less than that obtained from the alternative ratio using the same spectra and covering the same temperature range. As noted previously, ratio changes corresponding to small k changes will yield low values for the activation energy. Also, the fact that the observed change in the $I_{min.}/I_{max.}$ ratio is greater than that for the $\delta\omega_e/\delta\omega$ ratio taken from the same spectrum will give the more reliable value for E_a.

The approximately constant value of E_a with dilution in 1-chloronaphthalene and phenyl cyanide implies that solute–solvent interactions are unimportant in these solvents. In ethylene glycol a maximum is observed in E_a as a function of concentration. This is indicative of solute–solvent interaction of which similar concentration-dependent interactions have been found by Woodbrey and Rogers[8] in *NN*-disubstituted amides in dibromomethane. Since there is an appreciable contribution from structure (II), hydrogen bonding between this polar form and the solvent could be expected to stabilize the former, in which increased electron density at the N–N partial double bond leads to a higher activation energy. This type of interaction is compatible with the self-dimerization postulated by Looney *et al.*,[1] and with the infrared evidence of Haszeldine and Mattinson.[9] The maximum value of E_a occurs at mole fraction 0·5, which suggests that the interaction involves a 1:1 complex arising from the competition between hydrogen-bond formation between the solvent and dimethylnitrosamine, and dimerization of the latter.

Experimental.—Dimethylnitrosamine was prepared[10] by the action of nitrous acid on dimethylamine hydrochloride, and had b. p. 140° (under slightly reduced pressure). Infrared spectra were identical with those in the literature.[1,6] Solvents were commercial samples purified by vacuum-distillation and dried over Drierite.

The room-temperature n.m.r. spectrum recorded under high spectrometer gain showed the absence of impurity. A similar spectrum recorded on a sealed sample left standing for two months

[7] Phillips, Looney, and Spaeth, *J. Mol. Spectroscopy*, 1957, **1**, 35.
[8] Woodbrey and Rogers, *J. Amer. Chem. Soc.*, 1962, **84**, 13.
[9] Haszeldine and Mattinson, *J.*, 1955, **4**, 4172.
[10] *Org. Synth.*, Coll. Vol. II, 211.

showed only traces of decomposition which would have been considerable in the presence of acidic impurity.

All samples were sealed under a high vacuum, and spectra were recorded using a Varian A 60 spectrometer equipped with a variable temperature controller. The dimethylnitrosamine spectrum consists of two sharp methyl resonances chemically shifted by 46 c./sec. and situated 202 c./sec. downfield from tetramethylsilane as internal standard. This value for the shift between the two methyl groups is consistent with the value of 19 c./sec. obtained[1] at 30 Mc./sec.

I thank Dr. J. Lee for the loan of one of his Mercury programmes, and the D.S.I.R. for the award of a research studentship.

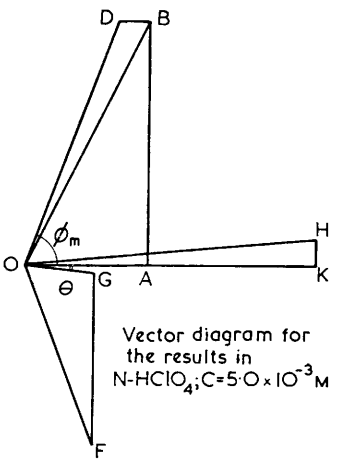
DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF MANCHESTER. [*Received, April 21st*, 1964.]

1200. *The Faradaic Impedance due to Reduction of Tervalent Bismuth at the Dropping-mercury Electrode.*

By A. A. MOUSSA and H. M. SAMMOUR.

RECENTLY, we reported values for the standard rate-constant, k, of the system $Bi^{III} \rightleftharpoons Bi^{0}(Hg)$ in various media from faradaic-impedance measurements at the dropping-mercury electrode;[1] a substitution method based on the simple equivalent circuit[2] was employed. Though the results obtained were highly consistent and agreed with those previously published, the observed values of the two components R_r and $1/\omega C_r$ leading to them, showed marked deviation, not only in magnitude, but also in the direction of change with frequency, from that expected theoretically. In this Note we show that the discrepancy should not invalidate the simple equivalent circuit adopted, and that the deviations could be the result of possible angle errors in the components of the measuring circuit; the k values reported, nevertheless, should retain their significance.

By analysing vectorially the experimentally observed quantities C_m (peak capacity), R_m (peak resistance), C_d (double-layer capacity), and R_s (solution resistance), C_r and $1/\omega C_r$ values, and consequently k, were obtained and compared with previous ones. The procedure was as usual.[3] Vector OA (see Figure) is drawn equivalent to R_m; AB perpendicular to it and



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[1] Moussa and Sammour, *J.*, 1960, 2151.
[2] Randles, *Discuss. Faraday Soc.*, 1947, **1**, 11; Grahame, *J. Electrochem. Soc.*, 1952, **99**, no. 12, 371 C.
[3] Delahay, "New Experimental Methods in Electrochemistry," Interscience Publishers Ltd., London, 1954, p. 167.

equivalent to $1/\omega C_m$. R_S is subtracted; OD then gives the impedance of faradaic impedance shunted by the double-layer capacity. At an angle $= \phi_m$ vector OF is drawn equivalent to the admittance 1/OD; and FG equivalent to the admittance ωC_d is subtracted;* the difference OG determines the faradaic admittance. The corresponding impedance OH, drawn at an angle $= \theta$, is then decomposed to vectors HK and OK, which determine $1/\omega C_r$ and R_r, respectively. The results so obtained, together with those previously obtained by the substitution method (in brackets) are given below; for the various quantities involved in these calculations the reader is referred to the original paper.[1]

Frequency (c./sec.)	R_r (ohms)	$1/\omega C_r$ (ohms)	$k \times 10^3$ (cm./sec.)
(A) N-$HClO_4$; $C = 5{\cdot}0 \times 10^{-3}$M			
1000	648 (637)	60 (48)	0·37 (0·37)
$C = 3{\cdot}0 \times 10^{-3}$M			
1000	852 (1060)	338 (101)	0·70 (0·38)
3000	793 (1700)	144 (770)	0·56 (0·38)
N-$HClO_4$ made 10^{-3}N with respect to HCl; $C = 1{\cdot}0 \times 10^{-3}$M			
1000	468 (480)	31 (80)	2·5 (2·6)
$C = 3{\cdot}0 \times 10^{-3}$M			
1000	190 (187)	20 (37)	2·7 (2·4)
3000	200 (224)	22 (147)	1·9 (2·4)
(B) N-HCl; $C = 5{\cdot}0 \times 10^{-5}$M			
1000	132 (130)	114 (124)	1200 (3600)
3000	71 (72)	50 (53)	1040 (1200)
(C) N-HNO_3; $C = 1{\cdot}0 \times 10^{-3}$M			
1000	357 (330)	37 (16)	3·4 (3·5)
3000	332 (420)	34 (32)	3·6 (2·8)
$C = 2{\cdot}0 \times 10^{-3}$M			
1000	167 (167)	16 (15)	3·6 (3·6)
3000	165 (169)	20 (24)	3·7 (3·8)
4000	168 (194)	23 (44)	3·7 (3·7)
$C = 3{\cdot}0 \times 10^{-3}$M			
1000	115 (106)	13 (12)	3·6 (3·9)
3000	107 (103)	14 (15)	3·9 (4·2)
4000	106 (112)	10 (25)	3·8 (4·2)
0·8N-$HClO_4$ + 0·2N-HNO_3; $C = 2{\cdot}0 \times 10^{-3}$M			
1000	664 (648)	126 (114)	1·0 (1·0)
3000	530 (635)	180 (252)	1·5 (1·3)
0·6N-$HClO_4$ + 0·4N-HNO_3; $C = 2{\cdot}0 \times 10^{-3}$M			
1000	314 (346)	30 (37)	1·9 (1·8)
3000	334 (390)	25 (68)	1·8 (1·7)
0·4N-$HClO_4$ + 0·6N-HNO_3; $C = 2{\cdot}0 \times 10^{-3}$M			
1000	225 (250)	32 (neg.)	2·5 (2·2)
3000	250 (200)	25 (neg.)	2·5 (2·8)
(D) N-H_2SO_4; $C = 1{\cdot}9 \times 10^{-3}$M			
1000	315 (315)	47 (15)	2·1 (1·8)
3000	297 (300)	20 (7)	2·0 (1·9)
4000	312 (330)	48 (5)	2·1 (1·7)

As shown by these results, the agreement between the R_r and $1/\omega C_r$ values obtained by the two methods may be considered as satisfactory in general. The better agreement between the k values is obviously the outcome of the fact that the difference $R_r - 1/\omega C_r$ is determined largely by R_r, which is always too large compared with $1/\omega C_r$ in most of the media used. It will be further noticed that, by the vector method, direction of change with frequency is normalised in several cases. Adoption of the simple equivalent circuit seems therefore to be fully justified, and it has been further substantiated recently[4] for processes with k-values lower than 10^{-2} cm./sec.

In tracing the effect of angle errors, the procedure was as follows: of the experimentally measured quantities on our bridge over the frequency range employed, C_d and R_s are the

* In the vector diagram of reference 3, vector FG seems to be added and not subtracted.

[4] Matsuda and Delahay, *J. Phys. Chem.*, 1960, **64**, 332; Matsuda, *ibid.*, p. 339.

least to be doubted. By using these, together with the corresponding R_r and $1/\omega C_r$ values, as obtained by substitution, and proceeding vectorially in a reverse direction to that described before, we calculated C_m and R_m values and compared them with those observed experimentally. Representative results for cases where abnormal direction of change with frequency was at a maximum and a minimum, are shown below (observed values are given in brackets).

Medium	Frequency (c./sec.)	C_m (μF)	R_m (ohms)
(A) N-$HClO_4$; $C = 3{\cdot}0 \times 10^{-3}$M	1000	0·68 (0·680)	82·5 (83)
	3000	0·64 (0·644)	31 (34)
(C) N-HNO_3; $C = 2{\cdot}0 \times 10^{-3}$M	1000	1·90 (1·93)	132 (130)
	3000	0·85 (0·840)	54 (56)
	4000	0·79 (0·778)	41 (45)

As indicated by the results, while for C_m the calculated values agree excellently with the experimental, R_m is noticeably lower, particularly at higher frequencies. This is most probably the result of an inductive effect that is inherent in the block model used in the substitution method, and it would be expected to increase with frequency. The influence of such an effect in vitiating the results will depend on the circuit characteristics. Thus, in medium (A) above, at 3000 c./sec., R_r and $1/\omega C_r$ were computed vectorially for different R_m values; the results were as follows:

R_m (ohms)	29	30	(31)	32	33
R_r (ohms)	2640	2200	(1700)	1390	1180
$1/\omega C_r$ (ohms)	1130	940	(770)	440	110

These results show how sensitive R_r and $1/\omega C_r$ would be to induction effects. However, except for the extremely odd R_m value of 29 ohms, in this case, the difference $R_r - 1/\omega C_r$ that determines k, is almost constant in spite of the wide variations of the values.

We conclude that, in performing impedance measurements at the dropping-mercury electrode, it is absolutely necessary to consider angle errors carefully before any conclusions about the properties of the faradaic impedance, even with the simple equivalent circuit, are drawn.

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