NOTES.

269. *Derivatives of Fluorene. Part XII.** *2-Amino-9-bromofluorene Hydrobromide and Related Compounds.*

By T. Lloyd Fletcher and Moses J. Namkung.

With a view to synthesis of potential drugs and continuing previous work we have obtained 2-amino- and 2-acetamido-9-bromofluorene (I; R = Br, R′ = NH_2 and NHAc respectively) in good yield by heating the corresponding 9-hydroxy-compounds[1] with 48% hydrobromic acid in acetic acid at 100° for a short time; more drastic conditions were needed to provide 9-bromo-2-dimethylaminofluorene. Dickinson and Eaborn[2] failed to convert 2-aminofluorene into the bromo-compound by *N*-bromosuccinimide, and this method failed in our hands for the acetyl derivative.

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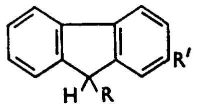
* Part XI, *J. Org. Chem.*, 1960, **25**, 1348.

[1] Pan and Fletcher, *J. Org. Chem.*, 1958, **23**, 799.

[2] Dickinson and Eaborn, *J.*, 1959, 2337.

Base converts 2-amino-9-bromofluorene into an insoluble high-melting product, presumably a bi-9-fluorenylidene derivative.



(I)

The 9-bromine atom was replaced without difficulty by reaction with pyrrolidine, morpholine, or piperidine to give the 9-substituted derivatives; and reaction with ethyl sodioacetamidomalonate gave compounds (I) in which R = $C(NHAc)(CO_2Et)_2$. Some standard derivatives of the products have been prepared. Absorption spectra are tabulated.

Experimental.—M. p.s are corrected.

2-*Amino*-9-*bromofluorene hydrobromide*. 2-Aminofluoren-9-ol (50 g., 0·255 mole) was heated in acetic acid (300 ml.) and 48% hydrobromic acid (100 ml., 0·9 mole) on a steam-bath for 30 min., during which a precipitate was formed. After cooling, this *salt* was removed and dried (83 g., 95·5%); it crystallised from acetic acid (Found: C, 46·0; H, 3·4; N, 4·2; Br, 47·1. $C_{13}H_{10}BrN,HBr$ requires C, 45·8; H, 3·3; N, 4·1; Br, 46·9%).

2-*Acetamido*-9-*bromofluorene*, m. p. 213—214° (from alcohol) (Found: C, 59·5; H, 4·2: N, 4·75. $C_{15}H_{12}BrNO$ requires C, 59·6; H, 4·0; N, 4·6%), was obtained similarly in 56·5% yield and (96% yield) by treating the amine hydrobromide with acetic anhydride on a steam-bath for 30 min.

9-*Bromo*-2-NN-*dimethylaminofluorene hydrobromide*. When 2-*NN*-dimethylaminofluoren-9-ol (10 g.) was heated at 60° with 48% hydrobromic acid (10 ml.) in acetic acid (60 ml.) for 30 min. no precipitate was obtained even after cooling. The solution was concentrated to 15 ml., a further 5 ml. of 48% hydrobromic acid were added, and the whole was set aside. Crystals which were then deposited were filtered off, washed with acetic acid (10 ml.), and dried (P_2O_5; NaOH; 1 mm.) (yield 97%). This *hydrobromide* crystallised from acetic acid (Found: C, 48·7; H, 4·2; N, 3·7; Br, 42·9. $C_{15}H_{14}BrN,HBr$ requires C, 48·8; N, 4·1; N, 3·8; Br, 43·3%).

2-*Acetamido*-9-*morpholinofluorene*. Morpholine (3·5 g.) was added dropwise to a solution of 2-acetamido-9-bromofluorene (6·04 g.) in boiling ethanol (300 ml.), the whole concentrated to 50 ml. and cooled, and the product (5·2 g., 84%) filtered off, dried, and recrystallised from methanol (charcoal); it had m. p. 234—236° alone or mixed with an authentic sample.[3]

Similarly were prepared 2-*acetamido*-9-*piperidinofluorene* (93·5% yield), m. p. 204—205° (from methanol) (Found: C, 78·1; H, 7·0; N, 9·3. $C_{20}H_{22}N_2O$ requires C, 78·4; H, 7·2; N, 9·1%), and 2-*acetamido*-9-*pyrrolidinofluorene* (100% yield), m. p. 211—212° (from methanol) (Found: C, 77·8; H, 6·9; N, 9·4. $C_{19}H_{20}N_2O$ requires C, 78·0; H, 6·9; N, 9·6%).

2-*Amino*-9-*piperidinofluorene*. 2-Amino-9-bromofluorene hydrobromide afforded 9-bromo-2-trifluoroacetamidofluorene, m. p. 180—182° alone or mixed with an authentic sample.[3] To this compound (0·89 g.) in ethanol (20 ml.) was added dropwise piperidine (0·64 g., 3 equiv.), and the mixture was boiled for 10 min. Then 2N-sodium hydroxide was added to turbidity and the whole poured into water (100 ml.). The precipitated *diamine* (100% yield) was collected and twice recrystallised from ethanol, then having m. p. 173—173·5° (Found: C, 81·7; H, 7·3; N, 11·0. $C_{18}H_{20}N_2$ requires C, 81·8; H, 7·6; N, 10·6%).

2-*Arylideneamino*-9-*morpholinofluorenes*. Equimolar amounts of 2-amino-9-morpholinofluorene and benzaldehyde were heated in a small amount of ethanol for 1 hr. and then set aside. The precipitated 2-*benzylideneamino-compound* recrystallised from methanol in needles, m. p. 156—157° (Found: C, 81·0; H, 6·0; N, 7·9. $C_{24}H_{22}N_2O$ requires C, 81·3; H, 6·2; N, 7·9%).

After a similar reaction with *p*-dimethylaminobenzaldehyde, the mixture was poured into water and made alkaline with aqueous ammonia. The precipitated gummy 2-p-*dimethylaminobenzylideneamino-compound* solidified and, recrystallised from benzene (charcoal), had m. p. 238·5—239·5° (yield, two crops, 96%) (Found: C, 78·55; H, 7·0; N, 10·3. $C_{26}H_{27}N_3O$ requires C, 78·6; H, 6·8; N, 10·6%).

Diethyl α-*acetamido*-α-(2-*acetamido*-9-*fluorenyl*)*malonate*. 2-Acetamido-9-bromofluorene (6·04 g.) in absolute ethanol (100 ml.) was added slowly to a boiling solution of diethyl acetamidomalonate (4·34 g.) and sodium (0·46 g.) in absolute ethanol (200 ml.). The mixture was concentrated to 50 ml. and cooled, and the precipitate filtered off, washed with water (to remove sodium bromide), dried (yield, 6·9 g., 79%), and crystallised from ethanol. This ester had m. p. 197—198° alone or mixed with the compound described below.

[3] Fletcher and Namkung, *J. Org. Chem.*, 1958, **23**, 680.

Absorption spectra of fluorene derivatives (I).

Substituents [a]		Ultraviolet			Infrared (mμ)		
R	R′	Concn.[b] (10^{-5}M)	$\lambda_{max.}$ [c] (mμ)	log ε	Amide N–H	Amide C=O	Others
$C_5H_{10}N$ [d]	H	3·33	307, 295, 268, 262, 230, 222	3·67, 3·79, 4·28, 4·28, 4·07, 4·31			
C_4H_8NO [e]	H	3·33	307, 295, 261, 230, 223	3·61, 3·50, 4·20, 4·22, 4·44			C–O–C 1113
C_4H_8N	NH_2	3·33	298	4·34			
$C_5H_{10}N$	NH_2	3·33	298	4·31			
C_4H_8NO	NH_2	3·33	297	4·37			C–O–C 1110
X	NH_2	3·33	297	4·33	1630	1670	Acid C=O 1760, 1730
C_4H_8N	NHAc	3·33	*307*, 294, *286*	4·22, 4·38, 4·33	1600	1660	
$C_5H_{10}N$	NHAc	3·33	*307*, 294, *286*	4·24, 4·39, 4·34	1600	1660	
C_4H_8NO	NHAc	3·33	*307*, 294, *284*	4·25, 4·40, 4·33	1600	1660	C–O–C 1115
X	NHAc	3·33	*305*, 293	4·33, 4·45	1600 1620	1665 1710	Acid C=O 1760, 1740
C_4H_8NO	$NH{\cdot}CO{\cdot}CF_3$	3·33	*310*, 295	4·27, 4·40	1620	1730	C–O–C 1110, CF_3 1200
Br	NHAc	2·5	307, 297, 252	4·37, 4·40, 4·41	1620	1680	
Br	$NH{\cdot}CO{\cdot}CF_3$	2·5	298, 252	4·25, 4·24	1620	1710	CF_3 1200
X	NO_2	3·33	330, 280	4·25, 4·17	1620	1670	Acid C=O, 1760, 1740; Aryl NO_2 1340, 1525
Br	NH_2,HBr	2·0	308, 247	4·15, 4·36			[g] N^{IV} 3050—2800sbr, 2555, 1920, 1610, 1350, 830
		3·33	*275*, 246	4·33, 4·46			
Br	NMe_2,HBr	2·0	318, 222	4·32, 4·37			[g] N^{IV} 2500, 2440, 1720
		3·33	318, *297—262*,[h] 222	4·30, 4·23 4·37			
X	H	1·0	303, *291*, *278*, 268, 232, *224*	3·59, 3·70, 4·18, 4·30, 4·13, 4·37	1625	1650	Acid C=O 1760, 1745
		2·0	303, *291*, *278*, 268, 232, *223*	3·42, 3·57, 4·12 4·24, 4·03, 4·29			
		2·25	303, *291*, *278*, 268, *253*, 232, *223*	3·63, 3·82, 4·25, 4·35, 4·14, 4·07, 4·31			
		2·5	268, 232	4·64, 4·14			
H	NH_2,HCl	—	—	—			[g] N^{IV} 3050—2750sbr, 2550, 1980, 1600, 1350, 812
C_4H_8NO	NH:CHPh	—	—	—			C–O–C 1113, C=N 1630
C_4H_8NO	$NH{:}CH{\cdot}C_6H_4{\cdot}NMe_2$-*p*		—	—			C–O–C 1113, C=N 1640, Aryl NMe_2 1370, 1235

[a] $C_5H_{10}N$ = piperidino, C_4H_8N = pyrrolidino, C_4H_8NO = morpholino, X = $C(NHAc)(CO_2Et)_2$. [b] In absolute EtOH. [c] Italicised values are for shoulders. [d] Pinck and Hilbert, *J. Amer. Chem. Soc.*, 1946, **68**, 377. [e] Bamford and Stevens, *J.*, 1952, 4675. [f] After 24 hr. absorption had increased at shorter wavelengths. [g] Jones (" Infrared Spectra of Organic Compounds: Summary Chart of Principal Group Frequencies," N.R.C. Bull. No. 6, 1959, Ottawa, Canada) gives for bonded N–H stretching in quaternary amine salts complex bands at 2900—2300 cm.$^{-1}$; Colthup (*J. Opt. Soc. Amer.*, 1950, **40**, 397) gives for amine hydrochloride 2500—2780 cm.$^{-1}$; Bellamy (" Infrared Spectra of Complex Molecules," J. Wiley and Sons Co. Inc., New York, 2nd edn., 1958, p. 259) gives NH_3 deformn. frequency near 1600 cm.$^{-1}$, symmetric mode near 1300 cm.$^{-1}$, NH_3 rocking frequency near 800 cm.$^{-1}$, and (p. 260) NH^+ 2200—1800 cm.$^{-1}$.

Diethyl α-acetamido-α-9-fluorenylmalonate * *and compounds derived from it.* After addition of 9-bromofluorene (122·5 g.) in ethanol (500 ml.) to a boiling solution of diethyl α-acetamidomalonate (108·5 g.) and sodium (11·5 g.) in absolute ethanol (600 ml.), the mixture was concentrated to 1 l. and cooled, precipitated sodium bromide was removed, and the filtrate concentrated to 300 ml. and left to cool. The precipitated *ester* (73 g., 39%) was collected; a further 67 g. (35%) were obtained by further concentration of the filtrate. Crystallisation from toluene gave material of m. p. 127—128° (Found: C, 69·4; H, 6·1; N, 3·5. $C_{22}H_{23}NO_5$ requires C, 69·3; H, 6·1; N, 3·7%).

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* The authors thank Mr. W. H. Wetzel for some assistance in this and the following experiment.

Adding nitric acid (*d* 1·42; 76 ml.) and concentrated sulphuric acid (15 ml.) to the foregoing ester (76°, 2 g.) in acetic acid at 50° and later heating at 65° gave, by the usual working up, *diethyl α-acetamido-α-(2-nitro-9-fluorenyl)malonate* (67 g.), m. p. 183·5—184° (from ethanol) (Found: C, 61·7; H, 5·3; N, 6·6. $C_{22}H_{22}N_2O_7$ requires C, 61·9; H, 5·2; N, 6·6%).

The nitro-ester (42·6 g.) was reduced by hydrazine hydrate (25 ml.) and Raney nickel in ethanol (2·5 l.) (cf. ref. 3) to the 2-*aminofluorenyl ester* (95·5%), m. p. 173—174° (from ethyl acetate) (Found: C, 66·9; H, 5·9; N, 7·5. $C_{22}H_{24}N_2O_5$ requires C, 66·65; H, 6·1; N, 7·1%). With acetic anhydride at 100° in 5 min. this gave the above-mentioned 2-*acetamidofluorenyl ester*, m. p. 197—198° (Found: C, 65·5; H, 6·1; N, 6·7. $C_{24}H_{26}N_2O_6$ requires C, 65·7; H, 6·0; N, 6·4%).

The nitro-ester (1 g.), when boiled with sodium dichromate (10 g.) in glacial acetic acid (100 ml.) for 1 hr., gave 2-nitrofluorenone (95%), m. p. and mixed m. p. 224—224·5°.

We thank the National Cancer Institute, National Institutes of Health, U.S.P.H.S., for aiding this work, in part, with a grant (CY-1744). Microanalyses were done by Alfred Bernhardt, Microanalytical Laboratories, Mülheim (Ruhr), and by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Ultraviolet spectra were obtained on a Beckman DK-1 recording instrument. Infrared spectra were for potassium bromide discs, measured on a Beckman IR-5 instrument. We are grateful to Barbara J. Bigley and Karen Olsoe for technical assistance.

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270. *The Pyrolysis of* 1,3,5-*Trioxan.*

By W. HOGG, D. M. MCKINNON, A. F. TROTMAN-DICKENSON, and G. J. O. VERBEKE.

BURNETT and BELL [1] found that the gas-phase thermal decomposition of 1,3,5-trioxan between 272° and 347° is a homogeneous unimolecular reaction whose rate constant at pressures above 15 mm. is given by $\log k$ (sec.$^{-1}$) = 14·8 − (47,400/2·3$\boldsymbol{R}T$). At 312° the rate constant falls rapidly as the pressure is reduced to 0·1 mm. The reaction, therefore, appeared to be suitable for a test of theories of unimolecular reaction. It does not involve free radicals and occurs at comparatively low temperatures so that the effect of many inert gases could be studied.

We have re-investigated the reaction at 272°, 312°, and 347°. The first-order plots were linear for four half-lives and the final pressure was always close to three times the initial pressure, as required by the equation, $(CH_2O)_3 = 3CH_2O$. The rate constant with 20—80 mm. initial pressure was given by (22 runs) $\log k$ (sec.$^{-1}$) = 14·95 − (47,400/2·3$\boldsymbol{R}T$). Several runs were done at each of the temperatures with 5—90 mm. pressure after the reaction vessel had been packed with Pyrex tubes so as to increase the surface: volume ratio 3·3 times. The mean points were very slightly lower than those given by the Arrhenius equation, but by little more than the normal scatter. There is no evidence for a fast heterogeneous reaction. Burnett and Bell had difficulty in preparing and drying their trioxan. Frequently their final pressures were much less than three times the initial pressures. The present results are, therefore, to be preferred.

The decomposition was followed at initial pressures down to 0·1 mm. (340° and 312°) and 0·5 mm. (272°). At 340° the rate fell to one-quarter of its high-pressure value, with no sign of breaks in the plots of $\log k$ against $\log p$. The decline was much less marked at low temperatures. The A factors and activation energies at the various pressures are:

Pressure (mm.)	0·1	1	10	100
$\log A$ (sec.$^{-1}$)	11·0	12·3	14·5	15·0
E (kcal. mole^{-1})	35·6	39·5	45·8	47·4

Theories of unimolecular reaction predict such variations of Arrhenius parameters with pressure, but the observed values vary too sharply to be explained on these lines. Possibly heterogeneous processes are important at the lowest pressures and temperatures.

The variation of rate constant with pressure at 312° is compared below with that

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[1] Burnett and Bell, *Trans. Faraday Soc.*, 1938, **34**, 420.

observed by Burnett and Bell, whose determinations were rather more scattered. The present curve is less convex by an amount that is probably outside experimental error.

$\log p$ (mm.)	2	1·5	1·0	0·5	0	−0·5	−1·0
$\log k/k$: present work	0·00	−0·02	−0·08	−0·18	−0·28	−0·36	−0·47
Burnett and Bell	0·00	−0·02	−0·07	−0·12	−0·21	−0·34	−0·52

Experimental.—1,3,5-Trioxan (Eastman) was degassed and purified by bulb-to-bulb sublimation at low pressure with rejection of considerable end fractions. Different samples gave identical rate constants.

Two apparatus, to which several of the components were common, gave identical results. The second version had a Pyrex reaction vessel (385 c.c.) contained in a mercury-vapour jacket. The outer jacket was wound with heating-tape and lagged. The vessel was inclined to the horizontal so that mercury that entered accidentally from the manometers ran out again. A precise temperature was maintained in the vessel by adjustment of the pressure of the mercury-boiler. The reaction vessel was attached by 1·5 mm. capillary to the storage vessel, the vacuum-line, and three manometers. The first manometer had one arm of 2 cm. diameter and the other a 2 mm. capillary tube. The second was a butyl phthalate–mercury manometer that gave a magnification of 8·9. The third was a McLeod gauge, of 10·7 c.c. total capacity, giving multiplication factors of 24, 92, and 500 when used with a linear scale. All the taps (silicone grease), the tubing, and the McLeod were wound with electric heating-tape and kept slightly above 100°.

Thanks are offered for an Imperial Chemical Industries Fellowship held by G. J. O. V.

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271. *Polycyclic Cinnoline Derivatives. Part VII.*[1] *Benzo*[c][^{15}N]*cinnoline.*

By P. F. HOLT, B. I. HOPSON-HILL, and C. J. McNAE.

IN the study of the nitration of benzo[*c*]cinnoline, quantitative isolation of the nitro-derivatives, which is difficult, can be obviated by the method of isotopic dilution making use of nitrobenzo[*c*][^{15}N]cinnolines. A method has therefore been sought for the preparation of ^{15}N-labelled benzo[*c*]cinnoline in good yield. Benzo[*c*]cinnolines are usually prepared by reducing 2,2′-dinitrobiaryls, which are obtained from *o*-halogeno-nitroaryls by the Ullmann reaction. To this end *o*-bromo[^{15}N]nitrobenzene has been prepared,[2] but only in poor yield.

The several methods which have been described for converting biphenylbisdiazonium salts into benzo[*c*]cinnolines, by forming a diaza-link and eliminating nitrogen, offer the possibility of the introduction of nitrogen-15 from labelled nitrite, provided that the elementary nitrogen produced in the reaction is not derived solely from the external nitrogen atoms. Three of these reactions have been examined.

(*a*) Täuber[3] formed benzo[*c*]cinnoline by reducing biphenyl-2,2′-bisdiazonium salts and heating the resulting dihydrazino-compound with hydrochloric acid at 150°. The benzo[*c*]cinnoline formed from 2,2′-di[β-^{15}N]hydrazinobiphenyl dihydrochloride by this method retained only a part of the nitrogen-15, indicating that mechanisms involving both N–N and C–N fission, but mainly the former, were involved. An assay of the ^{15}N abundance in the ammonia formed in the reaction confirmed this result. As a method for the production or labelled benzo[*c*]cinnoline, it is not efficient enough for our purpose.

(*b*) Dobbie, Fox, and Gauge[4] reported that benzo[*c*]cinnoline together with carbazole was formed from biphenyl-2,2′-bisdiazonium bromide by the action of cuprous bromide, instead of the expected 2,2′-dibromobiphenyl. Mechanisms for this reaction have been suggested.[5,6] Following the procedure of Dobbie, Fox, and Gauge, we have been unable

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[1] Part VI, *J.*, 1861, 1363.

[2] McNae, unpublished result.

[3] Täuber, *Ber.*, 1896, **29**, 2270.

[4] Dobbie, Fox, and Gauge, *J.*, 1911, **99**, 1615.

[5] Saunders and Waters, *J.*, 1946, 1154; Hodgson, *J.*, 1948, 348.

[6] Saunders, " The Aromatic Diazo Compounds," Arnold, London, 1949, p. 263.

to produce either carbazole or benzo[*c*]cinnoline but have obtained 2,2′-dibromobiphenyl.

(*c*) Sandin and Cairns[7] showed that, while diazonium salts normally give arylarsonic acids with sodium arsenite, diazotised 2,2′-diaminobiphenyl gives benzo[*c*]cinnoline. Two mechanisms have been suggested for this reaction,[5] both of which involve the initial elimination of one diazonium group and the formation of the pyridazine ring from the other. Biphenyl-2,2′-bisdiazonium chloride, prepared by diazotising the amine with [^{15}N]nitrite, was decomposed with arsenite to give a cinnoline which retained half the nitrogen-15 of the nitrite. The result would be expected from either of the proposed mechanisms. This appears to be a satisfactory method of preparing benzo[*c*]cinnoline.

It is not known how far this reaction is applicable to the preparation of other labelled cinnolines. Sandin and Cairns also converted 2,2′-diamino-4,4′-dimethylbiphenyl into the corresponding cinnoline derivative and concluded that the reaction was general, but we have found it does not occur with 2-*o*-diazoniophenylnaphthalene-1-diazonium chloride.

Experimental.—Potassium [^{15}N]*nitrite.* Potassium [^{15}N]nitrite was prepared from potassium [^{15}N]nitrate by the method previously described[8] or, in better yield, by Heath's method[9] using lead powder.

2,2′-*Diaminobiphenyl.* 2,2′-Dinitrobiphenyl (3·0 g.) on catalytic reduction[10] yielded the diamine (2·0 g.; m. p. 79°; lit., 80°); alternatively, reduction by the method of More and Furst[11] yielded 1·71 g. of diamine (m. p. 77—78°) from 2·44 g.

2,2′-*Di*[β-^{15}N]*hydrazinobiphenyl dihydrochloride.* Täuber's method[3] was repeated, with potassium [^{15}N]nitrite, to obtain the dihydrazine from 2,2′-diaminobiphenyl (1·32 g.). The product was contaminated with sodium chloride.

To characterise the compound, a small sample of 2,2′-di[^{15}N]hydrazinobiphenyl was prepared by shaking the dihydrochloride with an excess of ammonia and extracting the solution with benzene. The concentrated solution gave orange-brown crystals, m. p. 103—105° (Täuber[3] gives 110°).

Benzo[c]*cinnoline from* 2,2′-*di*[β^{15}N]*hydrazinobiphenyl dihydrochloride.* The dihydrazino-compound, sealed in a tube with 20% hydrochloric acid (6 ml.), was kept at 160° ± 7° for 3 hr. (cf. Täuber,[3] 150°, 1 hr.) and the product precipitated in aqueous sodium carbonate. Microsublimation gave benzo[*c*]cinnoline, m. p. 152—153° (lit., 156°).

Benzo[c][^{15}N]*cinnoline.* 2,2′-Diaminobiphenyl (0·50 g.) was converted by Sandin and Cairns' method[7] using potassium [^{15}N]nitrite (atom % ^{15}N 32·4) into *benzo*[c][^{15}N]*cinnoline*, (0·12 g.; m. p. 154—156°). The [^{15}N]-abundance of the bisdiazonium compound was assumed to be half that of the potassium nitrite. For results see the Table.

Compound decomposed	Atom % of ^{15}N	Benzo[*c*]-cinnoline, atom % of ^{15}N	Ammonia, atom % of ^{15}N	For N–N break	For C–N break
2,2′-Dihydrazinobiphenyl	17·1	6·2	—	0·37	17·1
	16·4	3·9	—	0·37	16·4
		—	27·0	32·8	0·37
Biphenyl-2,2′-bisdiazonium chloride	16·2	15·8	—	0·37	16·2

Atmospheric abundance, atom % of ^{15}N: 0·37

Two of us (B. I. H-H. and C. J. M.) acknowledge grants from the Department of Scientific and Industrial Research.

The University, Reading. [*Received, August 3rd,* 1960.]

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[7] Sandin and Cairns, *J. Amer. Chem. Soc.*, 1936, **58**, 2019.
[8] Holt and Hopson-Hill, *J.*, 1952, 4251.
[9] Heath, *J.*, 1957, 4152.
[10] Adams, Cohen, and Rees, *J. Amer. Chem. Soc.*, 1927, **49**, 1093.
[11] More and Furst, *J. Org. Chem.*, 1958, **23**, 1504.

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272. *The Reduction of Diaryl Ketones and Diarylmethanols to Diarylmethanes.*

By J. Blackwell and W. J. Hickinbottom.

A large number of nuclear substituted diphenylmethanes were required for another investigation. It was found that they could be prepared most conveniently by reduction

TABLE 1. *Diphenylmethanes prepared from substituted benzophenones.*

Subst.	B. p./mm.	n_D^{20}	Yield (%)	Found (%)			Formula	Required (%)		
				C	H	Hal.		C	H	Hal
2-Cl	157°/10 [a]	1·5889	89							
3-Cl	161°/12	1·5867	90	77·0	5·7	17·1	$C_{13}H_{11}Cl$	77·0	5·5	17·5
4-Cl	160°/11 [a]	1·5854	90	—	—	—		—	—	—
2-Br	166—167°/16 [b]	1·6100	91	—	—	—		—	—	—
3-Br	129—130°/1·0	1·6056	90	62·8	4·6	32·8	$C_{13}H_{11}Br$	63·1	4·5	32·4
4-Br	164°/14 [c]	1·6045	90	—	—	—		—	—	—
2-I	177°/12 [d]	1·6406	90	—	—	—		—	—	—
3-I	181°/12	1·6389	89	53·2	3·8	43·3	$C_{13}H_{11}I$	53·1	3·7	43·2
4-I *	M. p. 43—44° [e]	—	88	—	—	—		—	—	—
2-F	74°/0·2	1·5586	90	83·6	5·9	10·2	$C_{13}H_{11}F$	83·8	6·0	10·2
3-F	75°/0·2	1·5563	90	83·5	5·9	10·5	$C_{13}H_{11}F$	83·8	6·0	10·2
4′-Cl-3-OMe	198—199°/17	1·5798	88	72·0	5·8	15·4	$C_{14}H_{13}ClO$	72·2	5·6	15·3
2-Br-4′-Cl	129°/0·4	1·6138	90	55·1	3·8	28·1 [f]	$C_{13}H_{10}BrCl$	55·4	3·6	28·4 [f]
3-Br-4′-Cl	132—133°/0·5	1·6117	90	55·1	3·8	28·4 [g]	$C_{13}H_{10}BrCl$	55·4	3·6	28·4 [g]
4-Cl-2′-I	151—152°/0·3	1·6440	88	47·5	3·2	10·5	$C_{13}H_{10}ClI$	47·5	3·1	10·8
4-Cl-3′-I	150°/0·2	1·6428	89	47·7	3·0	11·0	$C_{13}H_{10}ClI$	47·5	3·1	10·8
4-Cl-4′-I	148°/0·2	m. p. 47°	89	47·8	3·3	10·5	$C_{13}H_{10}ClI$	47·5	3·1	10·8
4-Cl-2′-F	91—92°/0·2	1·5680	90	70·5	4·7	16·1 [h]	$C_{13}H_{10}ClF$	70·7	4·6	16·1 [h]

* Added by Soxhlet extraction. [a] Cf. Tschitschibabin and Schlesser, *J. Russ. Phys. Chem. Soc.*, 1925, **56**, 151. [b] Cf. Bergmann, *J. Org. Chem.*, 1939, **4**, 1. [c] Cf. Speer and Hill, *J. Org. Chem.*, 1937, **2**, 139. [d] Cf. Seidel, *Ber.*, 1928, **61**, 2276. [e] Cf. Akagi and Iwashige, *J. Pharm. Soc. Japan*, 1954, **74**, 610. [f] Br (Found: Cl, 12·8. Reqd.: Cl, 12·6%). [g] Br (Found: Cl, 12·6. Reqd.: Cl, 12·6%). [h] Cl (Found: F, 8·6. Reqd.: F, 8·6%).

TABLE 2. *Diphenylmethanes prepared from substituted diarylmethanols.*

Subst.	B. p./mm.	n_D^{20}	Yield (%)	Found (%)			Formula	Required (%)		
				C	H	Hal		C	H	Hal
2-Me	141°/13 [i]	1·5762 [j]	90	—	—	—		—	—	—
3-Me	139—140°/11	1·5713 [j]	90	—	—	—		—	—	—
4-Me	140°/11 [k]	1·5692 [j]	89	—	—	—		—	—	—
2-OMe †	162°/11 [l,m,t]	—	90	—	—	—		—	—	—
3-OMe	165°/13	1·5763	91	84·9	7·2		$C_{14}H_{14}O$	84·8	7·1	
4-OMe	166°/13 [n]	1·5758 [o]	90	—	—	—		—	—	—
3-OH †	183—184°/11 [u]	—	88	84·8	6·7		$C_{13}H_{12}O$	84·7	6·6	
4-F	132°/14 [p]	1·5552	90	—	—	—		—	—	—
4′-Cl-2-Me	172—173°/11	1·5842	90	77·3	6·0	16·7	$C_{14}H_{13}Cl$	77·6	6·0	16·4
4′-Cl-3-Me	169—170°/10	1·5790	89	77·8	5·8	16·3	$C_{14}H_{13}Cl$	77·6	6·0	16·4
4′-Cl-4-Me	166—167°/9 [s]	1·5840	90	77·3	6·1	16·7	$C_{14}H_{13}Cl$	77·6	6·0	16·4
4′-Cl-2-OMe	115°/0·2 [v]	1·5840 [w]	88	72·4	5·6	15·0	$C_{14}H_{13}ClO$	72·2	5·6	15·3
4′-Cl-4-OMe	191°/14 [o]	1·5827	89	—	—	—		—	—	—
2,4′-Cl_2	185°/11 [q]	1·5976	90	—	—	—		—	—	—
3,4′-Cl_2	181°/10	1·5954	89	65·5	4·3	30·3	$C_{13}H_{10}Cl_2$	65·8	4·3	29·9
4,4′-Cl_2	M. p. 56° [r]	—	88	—	—	—		—	—	—
4-Br-4′-Cl	M. p. 52°	—	88	55·2	3·8	28·4 [x]	$C_{13}H_{10}BrCl$	55·4	3·6	28·4
4′-Cl-3-F	184—185°/30	1·5669	89	70·4	4·7	16·3 [y]	$C_{13}H_{10}ClF$	70·7	4·6	16·1
4-Cl-4′-F	159°/12	1·5663	89	71·0	4·7	15·7 [z]	$C_{13}H_{10}ClF$	70·7	4·6	16·1

† Added by Soxhlet extraction. [i] Mascarelli and Pirona, *Chem. Abs.*, 1939, **33**, 9314. [j] Lamneck and Wise, *J. Amer. Chem. Soc.*, 1954, **76**, 1104. [k] von Auwers and Frühling, *Annalen*, 1921, **422**, 224. [l] Claisen, *Annalen*, 1925, **442**, 239. [m] Stoermer and Frick, *Ber.*, 1924, **57**, 27. [n] Späth, *Monatsh.*, 1913, **34**, 2007. [o] Pratt, Preston, and Draper, *J. Amer. Chem. Soc.*, 1950, **72**, 1367. [p] Lichtenberger and Thermet, *Bull. Soc. chim. France*, 1951, 318. [q] Cristol and Haller, *J. Amer. Chem. Soc.*, 1945, **67**, 2222. [r] Stephen, Short, and Gladding, *J.*, 1920, **117**, 522. [s] M. p. 26—27°. [t] M. p. 30—31°. [u] M. p. 55°. [v] M. p. 24—25°. [w] At 25°. [x] Br (Found: Cl, 12·6. Reqd.: Cl, 12·6%). [y] Cl (Found: F, 9·0. Reqd.: F, 8·6). [z] Cl (Found: F, 8·6. Reqd.: F, 8·6%).

of the corresponding diaryl ketones and diarylmethanols by lithium aluminium hydride and aluminium chloride.[1] In this Note, the preparation of 37 diarylmethanes is reported in yields of about 90%. The method thus appears to be of fairly general application; it also has the advantage of being both convenient and rapid.

Experimental.—The following modification of Brown and White's method [1] was suitable and convenient.

Aluminium chloride (0·35 mole, 46·7 g.) in ether (100 c.c.) was added to a suspension of lithium aluminium hydride (0·175 mole, 6·6 g.) in ether (10 c.c.). The substituted benzophenone or alcohol (0·10 mole) in ether was added during 10 min., and the mixture then heated under reflux for 30 min. Excess of the reagent was destroyed by adding ethyl acetate, and the mixture was poured into 20% aqueous sulphuric acid. The ether solution, after washing and drying, was evaporated, and the product isolated by any convenient method. It was necessary in some few reductions to introduce the ketone or alcohol into the reducing medium by extraction from a Soxhlet thimble. The Tables summarise our results.

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[*Received, August 3rd,* 1960.]

[1] Brown and White, *J.*, 1957, 3755; Nystrom and Berger, *J. Amer. Chem. Soc.*, 1958, **80**, 2896.

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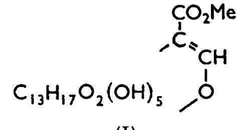
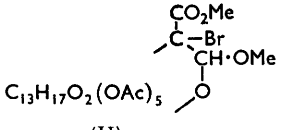
273. *Loganin. Part II.*[1] *Structural Interpretation of the Spectral Properties.*

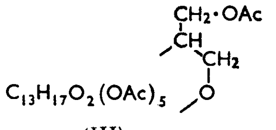
By A. J. BIRCH and J. GRIMSHAW.

THE conclusions previously [1] drawn from the infrared spectrum of loganin now appear to be erroneous; in particular the small band at 1738 cm.$^{-1}$ thought to indicate the presence of a saturated ester group must have been due to an impurity. On further examination loganin from *Strychnos lucida* R.Br. showed infrared bands at 1710 and 1650 cm.$^{-1}$ which we now assign to an $\alpha\beta$-unsaturated ester carbonyl group and an enol ether group respectively; it has an ultraviolet band at $\lambda_{\max}$ 237 mμ (log ε 4·03) in aqueous solution, attributed to an unsaturated ester group of the type shown in partial structure (I). In view of doubts expressed [2] on the identity of our original material, we believe that these spectra, together with the m. p.s and optical rotations of loganin and its penta-acetyl derivative (cf. refs. 2 and 3) establish that it is in fact loganin.

Previously [1] we interpreted the spectra to indicate the presence of an $\alpha\beta$-unsaturated carbonyl function in a five-membered ring, but this is contradicted by our inability to find the expected low-intensity absorption maximum in the region of 300 mμ. The chromophore represented in formula (I), which has been studied for synthetic compounds [4] and is present in plumierid,[5] is, however, in accord with the spectrum of loganin and its presence is supported by the result of reaction of penta-acetyl-loganin with bromine in methanol.


(I)


(II)


(III)

The methyl ether bromide (II) obtained was to be expected from the chemistry of plumierid [5] and aucubin,[6] both of which contain an enol ether group. The methyl ether bromide possesses no absorption maximum between 210 and 300 mμ and one broad absorption

[1] Part I, Birch and Smith, *Austral. J. Chem.*, 1956, **9**, 234.
[2] Mertz and Lehmann, *Arch. Pharm.*, 1957, **290**, 543.
[3] Mertz and Krebs, *Arch. Pharm.*, 1937, **275**, 217.
[4] Bader, *Helv. Chim. Acta*, 1953, **28**, 215; Korte and Buchel, *Angew. Chem.*, 1959, **71**, 709.
[5] Halpern and Schmid, *Helv. Chim. Acta*, 1958, **41**, 1109.
[6] Grimshaw and Juneja, *Chem. and Ind.*, 1960, 656.

band due to double-bond stretching vibrations (ester groups) at 1745 cm.$^{-1}$, thus establishing the relation between the enol ether and the ester group. The difficulty experienced[1,2,3] in hydrogenating the double bond of loganin is also in accord with structure (I) since similar difficulty was encountered with plumierid.[5]

In view of doubts expressed[2] we have confirmed the finding that loganin is the methyl ester of an acid. Alkaline hydrolysis produced loganic acid[1] (norloganin[2]), isolated as the penta-acetyl derivative, $\lambda_{max.}$ 230 mμ (log ε 4·0 in ethanol), $\nu_{max.}$ 3200 (very broad), 1750, 1715, and 1645 cm.$^{-1}$. Brief treatment with methyl iodide and silver oxide re-formed loganin penta-acetate, previously[1] also re-formed by the action of diazomethane. The product of reaction of loganin with lithium in liquid ammonia, isolated as its hexa-acetyl derivative,[1] also supports the formula (I) and the derivative can be assigned the partial structure (III). It shows no infrared absorption due to hydroxyl, has a band at 1740 cm.$^{-1}$ (OAc), and no absorption maximum in the ultraviolet region (210—300 mμ).

It seems clear that the acetaldehyde reported as formed on the ozonolysis of penta-acetyl-loganin[1] in fact came from the ethyl acetate used as solvent, and loganin does not[2] contain an ethylidene residue. Loganin, $C_{17}H_{26}O_{10}$, must contain, in addition to the expanded unit shown (I), a glycoside group, a further hydroxyl group, a carbocylic ring, an ether ring, and a methyl group attached to carbon. In view of the chemical relationship of loganin to plumierid[5] and the occurrence of loganin in *Strychnos* species[7] and aucubin in *Buddleia* species,[8] both belonging to the family of Loganiaceæ, we suggest a biogenetic and therefore structural relation between these compounds. On this basis it is possible to indicate several likely structures for loganin, but we prefer to reserve discussion of these until more experimental evidence is available.

Experimental.—Infrared spectra are quoted for Nujol mulls.

Methylation of penta-acetyl-loganic acid. Penta-acetyl-loganic acid (20 mg.) was dissolved in methyl iodide (3 ml.) and refluxed over silver oxide (30 mg.) for 90 min., then the mixture was diluted with ether and filtered. The filtrate was washed with sodium hydrogen carbonate solution and water and dried (Na_2SO_4), and the solvent removed. The residue crystallised from ethyl acetate–light petroleum (b. p. 60—80°) as needles (15 mg.), m. p. 140—141° undepressed on admixture with loganin penta-acetate, m. p. 141—142°. The two samples showed the same infrared spectrum.

Penta-acetyl-loganin methyl ether bromide (II). Loganin penta-acetate (60 mg.), dissolved in methanol (5 ml.), was cooled to 0° and bromine (16 mg.) in methanol (1·5 ml.) slowly added. The solution was decolorised and gradually deposited needles, m. p. 130—145°. Recrystallisation from ethyl acetate–light petroleum (b. p. 60—80°) afforded *penta-acetyl-loganin methyl ether bromide* as stout needles, m. p. 158—161° (Found: C, 47·5; H, 5·55; Br, 11·5; OMe, 8·9. $C_{28}H_{39}BrO_{16}$ requires C, 47·2; H, 5·5; Br, 11·3; 1OMe, 8·7%).

This work was carried out during the tenure (by J. G.) of an I.C.I. Fellowship. We are indebted to Dr. E. Ritchie for a gift of loganin.

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[7] Dunstan and Short, *Pharm. J. Trans.*, 1883, **14**, 1025; Anet, Hughes, and Ritchie, *Austral. J. Chem.*, 1953, **6**, 58.

[8] Paris and Chaslot, *Ann. pharm. franç.*, 1955, **13**, 648.

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274. *Reactions of Organic Azides. Part X.*[1] *The Schmidt Reaction with 3′-Oxoindeno(2′,1′-2,3)thiophen: the Structure of the Product.*

By C. L. ARCUS and G. C. BARRETT.

3′-OXOINDENO(2′,1′-2,3)THIOPHEN (I) with hydrazoic acid in trichloroacetic and sulphuric acid at 55° gave material which, on sublimation and recrystallisation from nitrobenzene, yields a single product.[1] Possible structures are thieno(2′,3′-3,4)-2-quinolone (II), formed by migration of the phenylene ring, or the isoquinolone isomer formed by migration of

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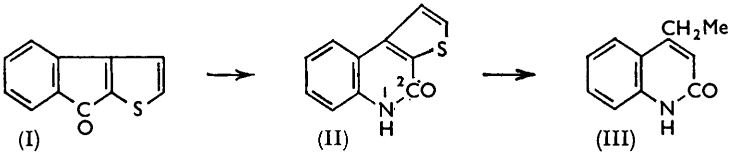
[1] Part IX, Arcus and Barrett, *J.*, 1960, 2098.

the thieno-ring. The compound was largely unchanged after being heated with aqueous potassium permanganate, even at 250°; but with Raney nickel it was reductively desulphurised to 4-ethylcarbostyril[2] (III) and therefore has structure (II). Migration of the phenylene group is analogous to the migration of phenyl during the Schmidt reaction with 2-benzoylthiophen.[3]



(I) (II) (III)

Experimental.—M. p.s are corrected.

Thieno(2′,3′-3,4)-2-quinolone (0·30 g.; m. p. 281°) was heated with potassium permanganate (2·97 g.) in water (30 ml.) during 3 hr. The purple mixture was filtered hot; after being suspended in water saturated with sulphur dioxide, the solid (0·20 g.) had m. p. 278—280°, not depressed by the starting material. The filtrate, after saturation with sulphur dioxide, was cooled and a trace of white solid, m. p. > 280°, was filtered off. The filtrate was acidified with sulphuric acid; ether-extraction yielded a buff solid (0·07 g.), m. p. 178—181°, which contained nitrogen and sulphur but was not further investigated.

An identical mixture, heated at 250° for 3½ hr. and treated as above, returned the starting material, m. p. and mixed m. p. 279—281°.

Raney nickel " C "[4] (1·0 g.) and the thienoquinolone (0·10 g.) were heated under reflux in *m*-xylene (25 ml.) during 6 hr. Evaporation of the filtered mixture yielded 4-ethylcarbostyril (0·07 g.; m. p. 188—190°), that had m. p. 194·5—195·5° after recrystallisation from heptane, addition to alumina in benzene, and elution with benzene containing 10% of ether (Found: C, 75·7; H, 6·15; N, 8·1. Calc. for $C_{11}H_{11}NO$: C, 76·3; H, 6·4; N, 8·1%). This product was identical with 4-ethylcarbostyril, m. p. 197·5° (mixed m. p. 197°; same infrared spectrum), prepared by Wöhnlich's method[2] (Found: C, 76·0; H, 6·6; N, 8·3%).

We thank the Department of Scientific and Industrial Research for a maintenance grant (to G. C. B.) and Imperial Chemical Industries Limited for participation in a grant.

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[*Received, August 4th,* 1960.]

[2] Wöhnlich, *Arch. Pharm.*, 1913, **251**, 535.
[3] Badger, Howard, and Simons, *J.*, 1952, 2849.
[4] Hurd and Rudner, *J. Amer. Chem. Soc.*, 1951, **73**, 5157.

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275. *Isobutyl and t-Butyl Derivatives of 2-Methoxynaphthalene.*

By R. T. Ferris and D. Hamer.

Isobutylphenols can most satisfactorily be prepared by the Claisen rearrangement of 1-methylallyl phenyl ethers, followed by the reduction of the isobutenylphenol so obtained.[1] We have used this method to prepare 1-isobutyl-2-naphthol and then methylated it to give 1-isobutyl-2-methoxynaphthalene (m. p. 27°). Cahen[2] has reported the preparation of an " isobutylnerolin " by the reaction of isobutyl bromide with nerolin and aluminium chloride in carbon disulphide. A substance with m. p. 66° was obtained, but subsequent work on this type of reaction has suggested that the product might be a t-butyl rather than an isobutyl derivative.[3] Some later work by Bromby, Peters, and Rowe,[4] and by Tsukervanik and Tambortseva,[5] failed to resolve the course of this reaction or the nature of Cahen's product.

We therefore prepared 2- (m. p. 35°) and 3-methoxy-1-t-butylnaphthalene (m. p. 67°)

[1] Bartz, Miller, and Adams, *J. Amer. Chem. Soc.*, 1935, **57**, 371.
[2] Cahen, *Bull. Soc. chim. France*, 1898, **19**, 1007.
[3] Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3276.
[4] Bromby, Peters, and Rowe, *J.*, 1943, 144.
[5] Tsukervanik and Tambovtseva, *Bull. Univ. Asie centrale*, 1938, **22**, 221; *Chem. Abs.*, 1940, **34**, 4729.

and 1-isobutyl-2-methoxynaphthalene (m. p. 27°). The first was prepared by the Friedel–Crafts reaction of t-butyl chloride and nerolin. The second was made by treating 1-bromo-2-methoxynaphthalene with t-butyl chloride and aluminium chloride, the bromine atom then being removed through the Grignard derivative. The isobutyl compound was prepared by using the Claisen rearrangement referred to above. When 1-methylallyl naphthyl ether was distilled under reduced pressure, it rearranged to 1-isobutenyl-2-naphthol. This was reduced to the isobutyl compound and finally converted with dimethyl sulphate into 1-isobutyl-2-methoxynaphthalene.

A comparison of these products with the report of Cahen (or with the substance isolated by following his procedure) shows that the " isobutylnerolin " which he isolated was 3-methoxy-1-t-butylnaphthalene. It also appears that the orientation of the t-butyl group is very dependent on the reaction conditions.

Experimental.—2-Methoxy-1-t-butylnaphthalene was prepared by the normal Friedel–Crafts reaction between nerolin, t-butyl chloride, and aluminium chloride in ligroin (b. p. 60°). When recrystallised it had m. p. 35° (Found: C, 84·0; H, 8·3. Calc. for $C_{15}H_{18}O$: C, 84·1; H, 8·4%).

3-*Methoxy*-1-*t-butylnaphthalene*. 1-Bromo-2-methoxynaphthalene was first prepared by heating nerolin (20 g.) and *N*-bromosuccinimide (9 g.) in carbon tetrachloride (50 ml.) for 8 hr. under reflux.[6] The product recrystallised from ligroin, yielding 10 g. of the bromo-compound. Conversion into 1-bromo-2-methoxy-4-t-butylnaphthalene was accomplished by the Friedel–Crafts reaction : 1-bromo-2-methoxynaphthalene (11·9 g.), t-butyl chloride (4·6 g.), and aluminium chloride (0·22 g.) were heated under reflux in ligroin (15 ml.) for 3 hr. When isolated and recrystallised, 7 g. of product were obtained, having m. p. 78—80° (Found: C, 61·3; H, 5·9; Br, 27·0. Calc. for $C_{15}H_{17}BrO$: C, 61·5; H, 5·8; Br, 27·3%). Finally the 1-bromo-group was removed through hydrolysis of the Grignard derivative. The product from above (7 g.) was dissolved in ether (25 ml.) and reacted with magnesium turnings (0·66 g.) in ether (30 ml.). The resulting solution was heated, hydrolysed, and then distilled under reduced pressure; 3 g. of 3-methoxy-1-t-butylnaphthalene, m. p. 67°, were obtained (Found: C, 83·8; H, 8·2. Calc. for $C_{15}H_{18}O$: C, 84·1; H, 8·4%). The same product was obtained by carrying out the reaction as described by Cahen.

1-*Methylallyl* 2-*naphthyl ether*. Naphthol (72 g.), 1-methylallyl chloride (45 g.), and potassium carbonate (70 g.) were refluxed in acetone (75 g.) for 22 hr. with stirring. Water (100 ml.) was then added and the product taken up in ether. This solution was washed with 10% sodium hydroxide solution, then with water, and dried with potassium carbonate. After evaporation of the solvent and purification of the product, 28 g. of 1-*methylallyl* 2-*naphthyl ether* were obtained, with m. p. 49° (Found: C, 84·5; H, 7·2. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%).

1-*Isobutyl*-2-*methoxynaphthalene*. The above isobutenylnaphthol (20 g.) was hydrogenated in dry ethanol (150 ml.) over platinum oxide (0·2 g.) under pressure in a rocking autoclave at 20°. From the resultant solution 15 g. of 1-isobutyl-2-naphthol were obtained (m. p. 34°). This naphthol was shaken in alkali with dimethyl sulphate (6·3 g.). 1-*Isobutyl*-2-*methoxy-naphthalene* was filtered off, washed, and recrystallised twice, giving 5 g. of product, m. p. 27° (Found: C, 83·9; H, 8·3. $C_{15}H_{18}O$ requires C, 84·1; H, 8·4%).

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[*Received, August 25th*, 1960.]

[6] Buu-Hoï, *Annalen*, 1944, **556**, 1.

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276. O^2,3'-*Cyclouridine*.

By R. LETTERS and A. M. MICHELSON.

PREVIOUS attempts to convert 3'-*O*-toluene-*p*-sulphonyluridine (I) into the cyclonucleoside (II) by using a number of bases were unsuccessful[1] despite the fact that both 3',5'-di-*O*-methanesulphonylthymidine and 3'-deoxy-3'-iodothymidine readily gave O^2,3'-cyclonucleoside derivatives.[2] A general method for the preparation of cyclonucleosides from the appropriate methanesulphonyl or toluene-*p*-sulphonyl derivative is now described.

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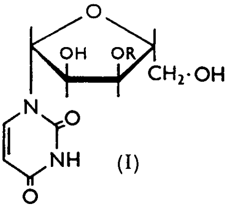
[1] Brown, Parihar, Todd, and Varadarajan, *J.*, 1958, 3028.

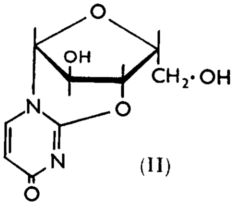
[2] Michelson and Todd, *J.*, 1955, 816.

Sodium t-butoxide (1 mol.) converted 5′-*O*-methanesulphonylthymidine completely into the cyclonucleoside, *O*^{2},5′-cyclothymidine[2] which had been obtained previously only by way of the 5′-deoxy-5′-iodonucleoside. 3′-*O*-Toluene-*p*-sulphonyluridine[1] with sodium t-butoxide in dimethylformamide gave three products that were detected by paper chromatography. The major product, purified by counter-current distribution, closely resembled *O*^{2},2′-cyclouridine in its paper-chromatographic, paper-electrophoretic, and light-absorption properties (cf. Table 1); it was not oxidised by sodium metaperiodate and we conclude that it is *O*^{2},3′-cyclouridine (II).



(I)

R = *p*-$C_6H_4Me{\cdot}SO_2$



(II)

3′-*O*-Toluene-*p*-sulphonyluridine with sodium hydroxide gave 3-β-D-xylofuranosyluracil.

TABLE 1. *Light-absorption properties of cyclonucleosides.*

Solvent:	95% EtOH		Water		0·01N-HCl		0·01N-NaOH	
	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)
O^2,2′-Cyclouridine	249, 223	237	250, 222	239	250, 221	234	253, 224	237
O^2,3′-Cyclouridine	230	—	246, 230	240	246, 230	240	253, 225	240
O^2,5′-Cyclothymidine ...	244	221	250	223	252	224	253	226

Experimental.—O^2,3′-*Cyclouridine.* To a solution of 3′-*O*-toluene-*p*-sulphonyluridine[1] (440 mg., 1 mmole) in dimethylformamide (25 c.c.) was added sodium t-butoxide (4 c.c. of an 0·5M-solution in t-butyl alcohol), and the mixture was kept at 100° for 2 hr. Solvent was then removed under reduced pressure and the residue washed with anhydrous ether and then submitted to counter-current distribution (70 transfers) in ethyl acetate and water. The major product was present in the first two tubes, the contents of which were evaporated to dryness. The residue was dissolved in 95% ethanol. Addition of ether precipitated O^2,3′-*cyclouridine* as an amorphous powder which was collected and dried (135 mg., 56%). Traces of sodium toluene-*p*-sulphonate were removed by shaking an aqueous solution of the compound with a mixture of acidic and basic ion-exchange resins. Pure *O*^{2},3′-cyclouridine crystallised from ethanol–ether as needles (Found: N, 11·7. $C_9H_{10}N_2O_5,H_2O$ requires N, 11·5%). Light absorption: in H_2O, $\lambda_{max.}$ 246, 230 mμ (ε 5780, 6900), $\lambda_{min.}$ 240 mμ (ε 5420); in 0·01N-HCl, $\lambda_{max.}$ 246, 230 mμ (ε 5660, 6965), $\lambda_{min.}$ 240 mμ (ε 5250); in 0·01N-NaOH, $\lambda_{max.}$ 253, 225 mμ (ε 5430, 5780), $\lambda_{min.}$ 240 mμ (ε 4905).

5′-O-*Methanesulphonylthymidine.* Methanesulphonyl chloride (1·5 mol.) was added to 3′-*O*-acetylthymidine[3] (0·41 g.) in pyridine (5 c.c.), and the solution kept at 0° overnight. Water (1 c.c.) was then added, the mixture evaporated to dryness, and a solution of the residue in chloroform was washed successively with 0·1N-sulphuric acid, aqueous sodium hydrogen carbonate, and water, then dried (Na_2SO_4), and evaporated. This residue was dissolved in 95% ethanol (10 c.c.), saturated ethanolic ammonia (10 c.c.) was added, and the mixture was left at 0° overnight. Solvent was removed and the final residue recrystallised from ethanol to give 5′-O-*methanesulphonylthymidine* (290 mg.), m. p. 149° (Found: N, 8·7. $C_{11}H_{16}N_2O_7S$ requires N, 8·8%).

Action of sodium t-butoxide on 5′-O-*methanesulphonylthymidine.* Sodium t-butoxide (0·2 c.c. of an 0·5M-solution in t-butyl alcohol; 0·1 mmole) was added to a solution of 5′-*O*-methanesulphonylthymidine (32 mg., 0·1 mmole) in dimethylformamide (1·8 c.c.), and the mixture kept at 100° for 2 hr. Paper chromatography and paper electrophoresis showed complete conversion into *O*^{2},5′-cyclothymidine, identical with an authentic specimen.

Paper chromatography and paper electrophoresis (*Table* 2). Ascending chromatograms on

[3] Michelson and Todd, *J.*, 1953, 951.

TABLE 2.

	R_F A	R_F B	R_F C	Electrophoresis (cm.)
O^2,2'-Cyclouridine	0·16	0·28	0·60	−2
O^2,3'-Cyclouridine	0·16	0·26	0·60	0
Uridine	0·20	0·30	0·60	16
3-β-D-Arabinofuranosyluracil	0·25	0·35	0·63	4·5
3'-*O*-Toluene-*p*-sulphonyluridine +0·1N-NaOH at 100° for 2 hr.	0·35	0·44	0·63	5·5
3'-*O*-Toluene-*p*-sulphonyluridine	0·85	0·86	0·89	4·5

Whatman no. 1 paper were used with solvent systems: A, butan-1-ol–water (86 : 14); B, butan-1-ol–acetic acid–water (4 : 1 : 5); C, propan-2-ol–aq. 1% $(NH_4)_2SO_4$ (2 : 1). Electrophoresis was carried out on Whatman no. 1 paper with 0·02M-borate buffer, and a voltage gradient of 20 v/cm. for 1½ hr. Migrations toward the anode are tabulated.

With the exception of uridine, all compounds listed gave a negative result with the periodate–Schiff's spray reagent.[4]

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[4] Buchanan, Dekker, and Long, *J.*, 1950, 3162.

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277. *The Preparation of Some 2-Substituted 9-Diazofluorenes.*

By KEITH D. WARREN.

THIS note describes the preparation, by the method of Nenitzescu and Solomonica,[1] of a number of 2-substituted 9-diazofluorenes (Table 1). Preparation of the corresponding hydrazones (Table 2) led, in four cases, to two products, each of which was oxidised to the same diazo-compound.

TABLE 1. 2-*Substituted* 9-*diazofluorenes.*

Subst.	Yield (%)	M. p.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
NO_2	55	expl. ~180°	66·15	2·9	18·0	$C_{13}H_7N_3O_2$	65·8	2·95	17·7
NH_2 *	70	137·5 † [b]	—	—	—	$C_{13}H_9N_3$	—	—	—
F	73	93·5—94·5	—	—	13·3	$C_{13}H_7FN_2$	—	—	13·3
Cl	65	126·5—127·5 †	68·8	3·3	12·2	$C_{13}H_7ClN_2$	68·8	3·1	12·3
Br	65	138—139 †	57·75	2·9	10·4	$C_{13}H_7BrN_2$	57·6	2·6	10·3
I	69	145·5—146·5 †	49·3	2·4	8·75	$C_{13}H_7IN_2$	49·05	2·2	8·8
OH	15	197—200 ‡	74·8	4·2	13·5	$C_{13}H_8N_2O$	75·0	3·9	12·5
OMe	56	126—127 †	75·6	4·5	12·7	$C_{14}H_{10}N_2O$	75·7	4·5	12·6
OEt	66	118—119	76·4	5·1	11·9	$C_{15}H_{12}N_2O$	76·3	5·1	11·9
CN	80	(117—118) 126—127	77·3	3·5	19·3	$C_{14}H_7N_3$	77·4	3·25	19·3

* Not new. † Melts with decomp. ‡ Decomp. without melting.
[a] Rapid heating: slow heating, decomp. 140—142°. [b] Bennett and Noyes (*Rec. Trav. chim.*, 1929, **48**, 895) give 137°. [c] Two crystal forms.

Experimental.—M. p.s are corrected.

Hydrazones. The appropriate ketone was heated under reflux with a slight excess of 100% hydrazine hydrate solution, in alcohol. The product was recrystallised from the minimum volume of that solvent.

Diazo-compounds. The hydrazone was shaken with yellow mercuric oxide (excess) and anhydrous sodium sulphate for 4 hr. in anhydrous ether containing ethanolic potassium hydroxide. The product from the ethereal solution was recrystallised from low-boiling light petroleum.

2-*Ethoxyfluorenone.* 2-Hydroxyfluorenone (9 g.) and sodium hydroxide (2·5 g.) in "AnalaR" acetone (280 ml.) were heated under reflux for 1 hr., ethyl bromide (7·85 g.) being added during 15 min. and heating continued for 24 hr. After filtration and reduction to 50 ml., the solution was poured into 10% aqueous sodium hydroxide (1·5 l.). The resulting solid, after recrystallisation from alcohol (charcoal) and chromatography in benzene on neutral alumina, gave 2-*ethoxyfluorenone* as light orange needles (from light petroleum), m. p. 94·5—95° (3·5 g., 38%) (Found: C, 80·6; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·35; H, 5·4%).

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[1] Nenitzescu and Solomonica, *Org. Synth.*, Coll. Vol. II, p. 496.

TABLE 2. *2-Substituted fluorenone hydrazones.*

Subst.	Yield (%)	M. p.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
NO_2 *	65	228—230° ‡ [a]	65·4	3·6	17·3	$C_{13}H_9N_3O_2$	65·3	3·8	17·6
NH_2 *	82	206—207 [b]	—	—	—	$C_{13}H_{11}N_3$	—	—	—
F	69	176—177 †	—	—	13·35	$C_{13}H_9FN_2$	—	—	13·2
Cl	72	131—132	68·6	3·9	11·9	$C_{13}H_9ClN_2$	68·3	3·9	12·2
Br	80	126—127 ‡	57·4	3·4	10·2	$C_{13}H_9BrN_2$	57·1	3·3	10·3
I	71	161·5—163·5	49·0	2·9	8·95	$C_{13}H_9IN_2$	48·75	2·8	8·75
		141·5—143 ‡	—	—	—	,,	—	—	—
OH *	51	205—207 ‡ [c]	—	—	—	$C_{13}H_{10}N_2O$	—	—	—
OMe	52	136·5—138	74·8	5·2	12·7	$C_{14}H_{12}N_2O$	75·0	5·4	12·5
		97—100	—	—	—	,,	—	—	—
OEt	67	155—157 †	75·4	5·6	11·75	$C_{15}H_{14}N_2O$	75·6	5·9	11·8
		145—147	—	—	—	,,	—	—	—
CN	65	209—211 †	76·5	4·25	19·0	$C_{14}H_9N_3$	76·7	4·1	19·2
		180—182 †	—	—	—	,,	—	—	—

*†‡ See Table 1. [a] Gerhardt (*Monatsh.*, 1920, **41**, 199) gives m. p. 214°. [b] Bennett and Noyes (footnote *b*, Table 1) give 209°. [c] Gerhardt (footnote *a*) gives m. p. 201—202°.

2-*Cyanofluorenone*. This was prepared according to Dickinson and Eaborn's method; it formed yellow-brown needles (from light petroleum, then alcohol), m. p. 182—183° (lit.,[2] 173°). The identity of the product was established by acid-hydrolysis to fluorenone-2-carboxylic acid (yield 83%).

Except for the fluorine-containing compounds, analyses were by Mr. J. M. L. Cameron and his staff.

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[2] Dickinson and Eaborn, *J.*, 1959, 2337.

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278. *Kinetics of the Alkaline Hydrolysis and Bromination of Bromoform.*

By R. P. BELL and M. H. FORD-SMITH.

IN studying the bromination of acetaldehyde and acetone in aqueous alkali, giving bromoform, we have made some kinetic measurements on the subsequent bromination and hydrolysis of bromoform. The alkaline hydrolysis of the haloforms in aqueous dioxan has been studied extensively by Hine and his co-workers.[1] They find that the rate of deuterium exchange is very much greater than the rate of hydrolysis under the same conditions, and on this basis propose the mechanism:

$$\text{(i)}\quad CHBr_3 + OH^- \rightleftharpoons CBr_3^- + H_2O \ \text{(Fast)}$$

$$\text{(ii)}\quad CBr_3^- \longrightarrow CBr_2 + Br^- \ \text{(Rate-determining)}$$

$$\text{(iii)}\left\{\begin{array}{l} CBr_2 + 2OH^- \longrightarrow CO + H_2O + 2Br^- \\ CBr_2 + 3OH^- \longrightarrow HCO_2^- + H_2O + 2Br^- \end{array}\right\}\text{(Fast}$$

The analogous species CCl_2 is believed to occur in the thermal decomposition of chloromethanes.[2] We have found that bromoform reacts slowly with alkaline aqueous hypobromite solution according to the equation $CHBr_3 + BrO^- \longrightarrow CBr_4 + OH^-$, carbon tetrabromide (m. p. 49°) being deposited in good yield. The experiments described below show that the reaction is of zero order with respect to hypobromite, and of first order with respect to both bromoform and hydroxide ions: the second-order velocity constant at 25·2° is $3{\cdot}1 \pm 0{\cdot}3 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$. The hydrolysis of bromoform has been studied under the same conditions, giving a velocity constant $2{\cdot}7 \pm 0{\cdot}1 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$, *i.e.*, the velocities of the two processes are the same within experimental error. Hypobromite does not react with formate ion or with carbon monoxide under these conditions, so that the rate-determining step in the bromination of bromoform must also be reaction

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[1] Hine, Dowell, and Singley, *J. Amer. Chem. Soc.*, 1956, **78**, 479; Hine, Burske, Hine, and Langford, *ibid.*, 1957, **79**, 1406.

[2] Shilov and Sabirova, *Zhur. fiz. Khim.*, 1960, **34**, 860.

(ii) above, followed by the rapid reaction $CBr_2 + BrO^- + Br^- + H_2O \longrightarrow CBr_4 + 2OH^-$. It thus appears that the species CBr_3^- does not react rapidly with hypobromite.

Experimental.—Bromoform was distilled under reduced pressure and stored in the dark, freshly prepared aqueous solutions being used. Hypobromite solutions were prepared by dissolving bromine in an excess of sodium hydroxide, and were estimated iodometrically. In the kinetic measurements the initial concentrations were $[OH^-] = 0{\cdot}1$—$0{\cdot}5$M, $[OBr^-] = 0{\cdot}0022$M, $[CHBr_3] = 0{\cdot}001$—$0{\cdot}003$M. The reaction was followed by measuring the absorption due to hypobromite ion with a S.P. 500 Unicam spectrophotometer (1 cm. silica cell in holder at $25{\cdot}2° \pm 0{\cdot}1°$). Hypobromite was found to have maximum absorption at 3300 Å with $\varepsilon = 301 \pm 0{\cdot}5$ (mean of 15 measurements): this is in good agreement with the measurements by Farkas and Klein [3] ($\lambda = 3300$ Å, $\varepsilon = 300$) but differs from those by Anbar and Dostrovsky [4] ($\lambda = 3330$ Å, $\varepsilon = 180$). There is no appreciable absorption at this wavelength by bromoform, carbon tetrabromide, bromide, or hydroxide. The concentration of hydroxide ions does not change significantly during an experiment, and plots of log $[CHBr_3]$ against time were linear, showing that the reaction is of zero order with respect to hypobromite and of first order with respect to bromoform. The second-order constants were obtained by dividing the slopes of these plots by $0{\cdot}434[OH^-]$; the mean of six experiments was $k = 3{\cdot}1 \pm 0{\cdot}3 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$.

The rate of hydrolysis was measured under the same conditions, but with the omission of hypobromite, the reaction being followed by the absorption due to bromoform. This has a maximum at $\lambda = 2205$ Å ($\varepsilon = 1900$), but this wavelength could not be used because of strong absorption by bromide and hydroxide. Measurements were made at 2550 or 2650 Å, and the concentration of bromoform remaining assumed proportional to $D_t - D_\infty$, where D is the optical density. The mean of three experiments was $k = 2{\cdot}7 \pm 0{\cdot}1 \times 10^{-4}$ l. mole sec.$^{-1}$. This value differs little from that obtained by Hine *et al.*[1] ($3{\cdot}2 \times 10^{-4}$) for alkaline hydrolysis in 67% aqueous dioxan.

The rather large experimental error in these velocity constants is due to slight decomposition or evaporation of bromoform solutions, and deposition of solid carbon tetrabromide or evolution of carbon monoxide in the later stages of the reaction.

We thank the Department of Scientific and Industrial Research for a Research Studentship awarded to M. H. F.-S.

PHYSICAL CHEMISTRY LABORATORY, OXFORD. [*Received, September 27th*, 1960.]

[3] Farkas and Klein, *J. Chem. Phys.*, 1948, **16**, 886.
[4] Anbar and Dostrovsky, *J.*, 1954, 1105.

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279. *Preparation of Polychlorobenzylamines.*

By J. S. MORLEY.

THE mono-, five of the six possible di-, five of the six possible tri-, 2,3,4,5-tetra-, and 2,3,4,5,6-penta-chlorobenzylamines have been prepared in good yield from the corresponding chlorobenzyl bromides or chlorides by way of the quaternary salts, $(Ar{\cdot}CH_2{\cdot}C_6H_{12}{\cdot}N_4)^+X^-$, formed with hexamine. Conversion of these salts into benzylamines [1,2] was smooth with 4 or more molar proportions of a strong acid. When less acid or a weaker acid was used, conversion into benzaldehydes occurred [3] except where two *o*-chloro-substituents were present. In these cases only benzylamines were formed even on boiling the salts in water.[4]

Experimental.—*Preparation of toluenes.* 2,6-Dichlorotoluene was available commercially. The following toluenes were prepared by recorded methods: 2,3-,[5] 2,5-dichloro-,[6] 2,3,6 ,[7]

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[1] Delépine, *Bull. Soc. chim. France*, 1895, **13**, 358.
[2] Galat and Elion, *J. Amer. Chem. Soc.*, 1939, **61**, 3585.
[3] Sommelet, *Compt. rend.*, 1913, **157**, 852.
[4] Cf. Angyal, Morris, Rassack, and Waterer, *J.*, 1949, 2704.
[5] Marvel, Overberger, Allen, Johnston, Saunders, and Young, *J. Amer. Chem. Soc.*, 1946, **68**, 861.
[6] Crauw, *Rec. Trav. chim.*, 1931, **50**, 772.
[7] Brimelow, Jones, and Metcalfe, *J.*, 1951, 1208.

Benzylamines.

Subst.	Base, b. p./mm.	Hydrochloride (m. p.)	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
o-Cl	219°/749 [a]		86							
m-	226—228°/749 [b]		95							
p-	222—224°/765 [c]		85							
2,3-Cl_2	136—140°/18	266—267° [l]	100	39·2	3·8	6·7	$C_7H_7NCl_2,HCl$	39·6	3·8	6·6
2,4-	132°/20 [d]	279—280 [e,m]	89	39·6	3·7	6·3				
2,5-	124—126°/13	259—260 [l]	99	39·6	3·8	6·3				
2,6-	117°/10	237—238 [f]	93	39·9	3·8	6·6				
3,4-	137—139°/15 [g]	239—240 [h,n]	87	40·1	3·8	6·8				
2,3,5-Cl_3	M. p. 59—59·5° [p]		91	39·5	2·8	6·8	$C_7H_6NCl_3$	40·0	2·9	6·7
2,3,6-	146—147°/10 [i]		95	40·4	2·9	6·7				
2,4,5-	M. p. 59—60° [p]		85	39·8	2·9	6·7				
2,4,6-	M. p. 62—63° [j,p]	247—248 [k]	89	39·5	2·7	6·6				
3,4,5-		271—272 [n]	80	33·6	2·9	5·4	$C_7H_6NCl_3,HCl$	34·0	2·9	5·7
2,3,4,5-Cl_4	M. p. 90—91° [p]	>300 [n]	46	33·9	1·9	5·8	$C_7H_5NCl_4$	34·3	2·0	5·7
2,3,4,5,6-Cl_5	M. p. 139—140° [p]		43	30·2	1·5	4·9	$C_7H_4NCl_5$	30·1	1·4	5·0

[a] Graymore and Davies (*J.*, 1945, 293) give b. p. 220°/775 mm. [b] Graymore and Davies (*loc. cit.*) give b. p. 226°/760 mm. [c] Graymore and Davies (*loc. cit.*) give b. p. 218—224°/775 mm. [d] Sasa (*J. Soc. Org. Synthet. Chem., Japan*, 1954, **12**, 24) gives b. p. 127—132°/21·5—22 mm.; Surrey and Lesher (*J. Amer. Chem. Soc.*, 1956, **78**, 2573) give b. p. 140°/122 mm. [e] Sasa (*loc. cit.*) gives m. p. 262—263°; Surrey and Lesher (*loc. cit.*) give m. p. 282·1—284·3°; Speziale and Hamm (*J. Amer. Chem. Soc.*, 1956, **78**, 2556) give m. p. 270—272°. [f] Angyal, Morris, Rassack, and Waterer (*J.*, 1949, 2704) give m. p. 237—238°. [g] Surrey and Lesher (*loc. cit.*) give b. p. 139—140°/17 mm. [h] Speziale and Hamm (*loc. cit.*) give m. p. 237—239°. [i] The base slowly crystallised. One recrystallisation from light petroleum gave colourless prisms, m. p. 43—44°. Brimelow, Jones, and Metcalfe (*J.*, 1951, 1208) give b. p. 144°/12 mm. and m. p. 43—44°. [j] Graf, Perathoner and Tatzel (*J. prakt. Chem.*, 1936, **146**, 88) give m. p. 62°. [k] Graf, Perathoner, and Tatzel (*loc. cit.*) give m. p. 247°. [l] Crystallised from ethanol–ether. [m] Crystallised from ethanol. [n] Crystallised from water. [p] Colourless prisms or needles from light petroleum.

2,4,5-,[7] and 3,4,5-trichloro-,[8] 2,3,4,5-tetrachloro-,[9] 2,3,4,5,6-pentachloro-.[10] 2,3,5-Trichlorotoluene was obtained in 90% yield from 2-amino-3,5-dichlorotoluene (a by-product in the manufacture of 2-amino-5-chlorotoluene) by the Sandmeyer reaction. 2,4,6-Trichlorotoluene was prepared from 3-amino-2,4,6-trichlorotoluene[8] as follows: A suspension of the finely divided amine (1 mole) in 6N-hydrochloric acid (4 moles) was diazotised at 0—10° with a concentrated aqueous solution of sodium nitrite (1·1 moles). The filtered diazonium solution was treated with 50% (w/w) hypophosphorous acid (15 moles) in a 10-l. beaker and the mixture was left at room temperature overnight. Pure 2,4,6-trichlorotoluene (75% yield), m. p. 32—33°, separated and was collected and dried at room temperature.

Preparation of benzyl halides. *o*- and *p*-Chloro- and 2,4- and 3,4-dichlorobenzyl chloride, and *m*-chlorobenzyl bromide were available commercially. The following benzyl bromides were prepared by adding bromine (1·05 mole) dropwise to the corresponding toluenes (1·0 mole) (temperature as stated) at a rate compatible with the rate of absorption of the bromine, and then distilling the product under reduced pressure (figures in parentheses are temperature of reaction, b. p. of product, and % yield respectively): 2,3- (140—160°; 140—144°/31 mm.; 74), 2,5- (140—160°; 134—138°/14 mm.; 72), and 2,6-dichloro- (160—170°; 133—135°/10 mm.; 96), 2,3,5- (140—160°; 150—160°/12 mm.; 90), 2,3,6- (140—160°; 156—160°/10 mm.; 91), 2,4,5- (140—160°; 158—160°/10 mm.; 36), 2,4,6- (160—165°; 146—150°/11 mm.; 87), 3,4,5-trichloro- (160—165°; 154—170°/9 mm.; 89), 2,3,4,5-tetrachloro- (150—160°; 180—190°/13 mm.; 68), 2,3,4,5,6-pentachloro- (230°; 204—210°/13 mm.; 94). The crude distilled products (usually highly lachrymatory, low-melting, colourless solids) were used without further purification. 2,3,4,5,6-*Pentachlorobenzyl bromide* separated from ethanol or light petroleum (b. p. 60—80°) in colourless plates, m. p. 116—117° (Found: C, 24·9; H, 0·6. $C_7H_2BrCl_5$ requires C, 24·5; H, 0·6%).

Preparation of benzylamines. Solutions of the appropriate crude benzyl bromide or chloride (1 mole) and hexamine (1·1 mol.) in chloroform were mixed, and the mixture was left at room temperature for 18—24 hr. The benzyl hexammonium salt was collected, washed with chloroform, dried at 40°, then added to 6N-hydrochloride acid (4·4 mol.). The mixture was shaken for 5 min. at room temperature, heated rapidly to the b. p. and steam-distilled until no more

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[8] Cohen and Dakin, *J.*, 1902, **81**, 1337.
[9] Cohen and Dakin, *J.*, 1906, **89**, 1453.
[10] Fichter and Glantzstein, *Ber.*, 1916, **49**, 2473.

formaldehyde distilled over. The benzylamine hydrochloride (contaminated with a little of the benzylamine hydrobromide when a benzyl bromide was used as starting material) separated on cooling or occasionally during the steam-distillation. The benzylamine could be isolated as such by cold filtration without appreciable loss of yield. However, it was usually more convenient to add the hot solution from the steam-distillation to stirred 40% aqueous sodium hydroxide and ice and then to isolate the base by filtration or by extraction with ether. Yields in the Table refer to distilled or once-crystallised material. The hydrochlorides were prepared by adding ether saturated with hydrogen chloride to a solution of the base in acetone, or by recrystallisation of the crude hydrochloride isolated directly from the reaction in methanol-ether saturated with hydrogen chloride.

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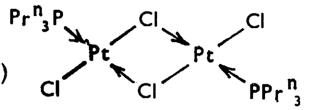
280. *Thiocyanato-bridged Complexes of Platinum*(II).

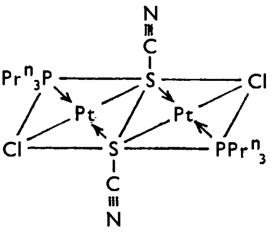
By J. CHATT and F. A. HART.

THE two isomeric forms of dichlorodithiocyanatobis(tripropylphosphine)diplatinum, $[Pt_2Cl_2(SCN)_2(PPr^n{}_3)_2]$, have been briefly described and their structures have been discussed.[1-3] This Note gives a fuller account of the preparation and properties of these compounds and describes two isomeric tetrathiocyanato-complexes, $[Pt_2(SCN)_4(PPr^n{}_3)_2]$.

When di-μ-chlorodichlorobis(tripropylphosphine)diplatinum (I) is treated in cold acetone solution with two molecular proportions of potassium thiocyanate, yellow α-$[Pt_2Cl_2(SCN)_2(PPr^n{}_3)_2]$ is obtained; the same reaction, carried out in the boiling solvent, gives the pale greenish-yellow β-compound. These compounds are dimeric in boiling benzene and non-electrolytes in nitrobenzene. The small dipole moments in benzene solution (α-compound, 1·57 D; β-compound, 1·36 D) correspond to *trans*-configuration. The only chemically reasonable structures consistent with these facts and with the infrared spectra are (II), (III), and (IV).

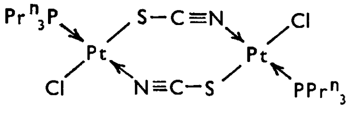
(I)

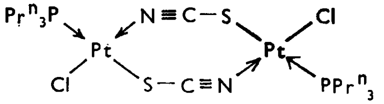




(II)

(III)





(IV)

X-Ray crystallography shows that the α-isomer has structure (III),[3,4] and that the β-isomer has structure (IV).[5] It had previously been assumed that the thiocyanato-bridge was of the type shown in (II) corresponding to the very stable mercapto-bridge —S(R)⇾,[6] but it now seems probable that in the great majority of bridged complex thiocyanates, bridging takes place through both the sulphur and the nitrogen atoms. There is no established example where bridging occurs only through the sulphur atom, but in crystalline $AgSCN(PPr^n{}_3)$ it has been shown that the thiocyanate group links three silver atoms, two through sulphur and one through nitrogen.[7]

We were originally[1] unable to detect isomerism in the tetrathiocyanate

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[1] Chatt and Hart, *Nature*, 1952, 673.
[2] Chatt and Duncanson, *Nature*, 1956, 997.
[3] Chatt, Duncanson, Hart, and Owston, *Nature*, 1958, 43.
[4] Owston and Rowe, *Acta Cryst.*, 1960, **13**, 253.
[5] Bland and Owston, personal communication.
[6] Chatt and Hart, *J.*, 1953, 2363.
[7] Turco, Panattoni, and Frasson, *Nature*, 1960, **187**, 772.

$[Pt_2(SCN)_4(PPr^n_3)_2]$, but have now identified two isomers, a yellow α-compound and a white β-compound. The isomerism does not, however, appear to be of the same type as in the dithiocyanato-compounds. In solution, each is converted into a mixture of the two forms. The β-compound has been obtained pure, but the α-compound only as a mixture with the β-compound. The dipole moment of the β-compound is about 2·8 D, which is consistent with a structure analogous to (III) or (IV), the increase of moment over the dithiocyanate complexes being due to free rotation of the terminal thiocyanato-groups. As equilibrium with the α-isomer is reached after 19 hr., the apparent moment rises to 4·9 D, indicating that the α-isomer has a *cis*-configuration, but its exact structure is uncertain.

Experimental.—*α-Di-μ-thiocyanatodichlorobis(tripropylphosphine)diplatinum.* A solution of the tetrachloro-compound (I) (5 g.) in acetone (300 c.c.) was treated at −2° with a solution of potassium thiocyanate (1.14 g., 2 mol.) in acetone (20 c.c.). The solution was evaporated to dryness at 12 mm. The residue was dissolved in chloroform (14 c.c.), the solution filtered, and precipitation effected by ether (85 c.c.). The yellow crystalline product was collected (4·70 g., 89%) and had m. p. 151—154° (decomp.; immersion at 135°). A further precipitation from chloroform–ether followed, and the product was dissolved in warm benzene (120 c.c.), from which it slowly crystallised as yellow prisms on addition of light petroleum (b. p. 80—100°; 120 c.c.). This product had m. p. 144—152° (decomp.; immersion at 135°), unchanged by another similar crystallisation, which gave 2·31 g. of the pure *compound* (Found: C, 27·1; H, 4·7; N, 3·3%; *M*, ebullioscopically in 2·37% benzene solution, 857; in 3·69% solution, 932. $C_{20}H_{42}Cl_2N_2P_2Pt_2S_2$ requires C, 26·8; H, 4·7; N, 3·1%; *M*, 898). In the infrared spectrum, ν_{CN} occurred at 2162 cm.$^{-1}$.

β-Di-μ-thiocyanatodichlorobis(tripropylphosphine)diplatinum. A boiling solution of the tetrachloro-compound (I) (5 g.) in acetone (75 c.c.) was treated with a boiling solution of potassium thiocyanate (1·14 g., 2 mol.) in acetone (15 c.c.). The solution was boiled under reflux for 16 hr., then concentrated to half volume, filtered, and cooled. The *product* (4·79 g.) recrystallised from acetone (225 c.c.) as pale lemon-yellow prisms (2·76 g.), m. p. 167·5—169°. Again recrystallised from acetone, they had m. p. 174·5—175·5° (immersion at 170°), unchanged by further recrystallisation (Found: C, 26·7; H, 4·7; N, 3·3%; *M*, ebullioscopically in 3·08% benzene solution, 922; in 5·17% solution, 920).

α- and β-Di-μ-thiocyanatodithiocyanatobis(tripropylphosphine)diplatinum. (*a*) Preparation from the tetrachloro-compound (I). A solution of compound (I) (2 g.) in acetone (50 c.c.) was treated with a solution of potassium thiocyanate (1·00 g., 4·4 mol.) in acetone (60 c.c.), boiled under reflux for 1 hr., and evaporated to dryness at 12 mm. The residue was taken up in chloroform (25 c.c.), filtered, boiled under reflux for 2 hr., and finally concentrated to 10 c.c. Ether (6 c.c.) was added to the cooled solution, giving pale yellow crystals (1·02 g.), m. p. 180—183° (decomp.). A further quantity (0·26 g.) of this material was obtained from the mother-liquor. These two products were dissolved in chloroform (5 c.c.) and precipitated as crystals by addition of ether (10 c.c.). This purification was repeated twice, giving 0·67 g. of product, m. p. 172—179° (immersion at 170°), which was the pale yellow mixed α- and β-tetrathiocyanato-compounds (Found: C, 28·0; H, 4·6; N, 6·0%; *M*, ebullioscopically in 0·42% chloroform solution, 853; in 0·80% solution, 869. Calc. for $C_{22}H_{42}N_4P_2Pt_2S_4$: C, 28·0; H, 4·5; N, 5·9%; *M*, 943). This sample was quickly extracted with chloroform (2 c.c.) and then shaken for 4 hr. with ethyl methyl ketone (3 c.c.); the residue (0·44 g.), m. p. 189—190·5°, was the more-slowly soluble white *β-tetrathiocyanato-compound* (Found: C, 28·2; H, 4·6; N, 6·3%; *M*, in 1·42% ethyl methyl ketone solution, 965). The pure β-compound showed peaks in the infrared spectrum due to ν_{CN} at 2182 and 2105 cm.$^{-1}$, and the mixed α- and β-compounds also had a peak at 2166 cm.$^{-1}$.

(*b*) Preparation from the α-dithiocyanate (III). A suspension of compound (III) (0·528 g.) in acetone (50 c.c.) and benzene (5 c.c.) was shaken with a solution of potassium thiocyanate (0·114 g., 2 mol.) in acetone (5 c.c.). The complex dissolved and the solution was allowed to evaporate to dryness during 24 hr. The residue, after being washed with water and dried, was divided into halves. One was crystallised from chloroform–ether, giving the mixed α- and β-tetrathiocyanato-compounds, m. p. 175·5—178° (immersion at 160°), identified by mixed m. p. with the compound prepared as in (*c*) below, by nitrogen analysis (Found: N, 5·75%), and by its infrared spectrum, which included peaks at 2182 and 2166 cm.$^{-1}$, the former being the stronger. The second half was boiled in chloroform (3 c.c.) for 3 hr. before precipitation by ether (10 c.c.). This treatment gave a product, m. p. 176·5—179° (immersion at 160°), identified as mixed α- and β-tetrathiocyanates by its infrared spectrum, the band at 2182 due to the β-isomer being in this case weaker than that at 2166 cm.$^{-1}$.

(*c*) Preparation from the β-dithiocyanate (IV). A suspension of the β-dithiocyanate (0·23 g.) in acetone (8 c.c.) was shaken with a solution of potassium thiocyanate (0·050 g., 2 mol.) in acetone (2 c.c.). The complex at once dissolved and the mixture was stored at 15° for 69 hr. (if the prolonged storage is neglected, only a small yield is obtained). It was then allowed to evaporate to dryness, and the residue was crystallised from chloroform–ether, giving cream-coloured crystals (0·16 g.), m. p. 172·5—174° (immersion at 160°). These were the mixed α- and β-tetrathiocyanato-compounds, identified by analysis (Found: C, 28·0; H, 4·6%) and by infrared spectrum which included peaks at 2182 and 2166 cm.$^{-1}$, the former being the stronger.

Conductivities in nitrobenzene solution. The four thiocyanato-compounds described above are non-electrolytes in nitrobenzene solution.

Dipole moments. These were measured as described previously,[6] except that a platinum-plated glass cell of *ca.* 8 c.c. capacity was used in the dielectric-constant determinations of the tetrathiocyanato-compounds. These were carried out by using very dilute solutions because of insolubility, which also made it impossible to determine the density and refractivity terms in the case of the tetrathiocyanato-compounds; these were estimated, very probably with small error. It is impossible to make a precise allowance for the atom polarisation of metallic complexes; this quantity depends upon the type of complex, and in the present work the value ${}_{A}P = 15\%$ of ${}_{E}P$ is used. Measurements are recorded in the Table: ω is the weight fraction of solute, $\Delta\varepsilon = \varepsilon_S - \varepsilon_B$ where ε_S = dielectric constant of solution, ε_B = dielectric constant of benzene; and similarly for Δv and Δn, where v = specific volume and n = refractive index of the solution.

$10^3\omega$	$10^3\Delta\varepsilon$	$10^3\Delta n$	$-\Delta v/\omega$	${}_{T}P$	${}_{E}P$	${}_{O}P$	μ
α-$Pt_2Cl_2(SCN)_2(PPr^n{}_3)_2$, yellow.							
7·983	6·383	0·523					
7·113	5·505						
			0·60	279	194	56	1·66
β-$Pt_2Cl_2(SCN)_2(PPr^n{}_3)_2$, pale greenish-yellow.							
6·640	4·569						
10·064	7·502						
11·445		0·8004					
			0·61	264	195	40	1·40
β-$Pt_2(SCN)_4(PPr^n{}_3)_2$, white.							
0·761	1·05,* 2·45 †						
0·915	1·41,* 3·12 †						
				412 *	214	166 *	2·8 *
				739 †	214	493 †	4·9 †

* Extrapolated to zero time. † After 19 hr.

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281. *Some Observations on Rhodium–Olefin Complexes.*

By M. A. Bennett and G. Wilkinson.

In a previous paper,[1] complexes formed by norbornadiene (bicyclo[2,2,1]hepta-2,5-diene) with platinum(II), palladium(II), rhodium(I), and ruthenium(II) were described, and it was suggested that their structures were analogous to those of the corresponding complexes formed by cyclo-octa-1,5-diene.[2] Further evidence for the existence of halogen bridges in the binuclear complex of norbornadiene with rhodium(I), $[C_7H_8RhCl]_2$, is now provided. The compound reacts smoothly in the cold with a number of ligands, giving mononuclear complexes according to the reaction:

$$[C_7H_8RhCl]_2 + 2L \longrightarrow 2C_7H_8RhClL$$

Analytical data and m. p.s for some of these complexes are given in the Table. This

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[1] Abel, Bennett, and Wilkinson, *J.*, 1959, 3178.
[2] Chatt and Venanzi, *J.*, 1957, 4735.

" bridge-splitting " reaction has previously been noted for the corresponding cyclo-octa-1,5-diene complex of rhodium(I),[2] and for binuclear olefin complexes of platinum(II) and palladium(II) which are believed to contain halogen bridges.[3]

L in compound C_7H_8RhClL	Appearance	M. p.	Found C (%)	Found H (%)	Found N, P, As or Sb (%)	Found *M*	Required C (%)	Required H (%)	Required N, P, As or Sb (%)	Required *M*
p-Toluidine	Flaky yellow crystals	187—189° *	49·5	5·1	4·0	—	49·8	5·1	4·1	—
Ph_3P	Fine yellow crystals	163—164	60·9	5·0	6·4	487	60·1	4·7	6·3	493
Ph_2MeP	Orange crystals	>150 *	55·5	5·3	—	—	55·8	4·9	—	—
Ph_3As	Orange crystals	183 *	55·5	4·9	14·5	527	55·9	4·3	14·0	537
Ph_3Sb	Red crystals	>100 *	52·1	4·4	—	—	51·4	4·0	—	—

* With decomp.

The new *complexes* are fairly stable in solution in organic solvents, although the triphenylstibine compound decomposes readily in hot solvents and could not be recrystallised. It may be noted that in the corresponding series of cyclo-octa-1,5-diene complexes with P, As, and Sb as donor atoms, only the triphenylphosphine compound was stable enough to be isolated, and this is in agreement with other evidence that norbornadiene is notably more powerful than cyclo-octa-1,5-diene in its complex-forming properties.

Attempts to obtain norbornadiene complexes of rhodium(III) by addition of bromine to the mononuclear rhodium(I) compounds were unsuccessful; compounds were obtained which contained no co-ordinated olefin, as indicated by the infrared spectrum. Although rhodium(III) is isoelectronic with ruthenium(II), which is now known to form olefin complexes,[1,4] the increased positive charge and decreased size of the cation presumably contract the metal orbitals sufficiently to prevent good overlap between them and those of the olefin.

The high-resolution nuclear magnetic resonance spectrum of the recently prepared cyclo-octatetraene complex of rhodium(I), $[C_8H_8RhCl]_2$,[1] shows two main peaks at $\tau =$ 5·8 and 4·3 (measured on a Varian spectrometer at 56·4 cycles in carbon disulphide solution, relative to tetramethylsilane as internal reference), each peak showing some poorly resolved fine structure. This is in contrast to cyclo-octatetraene itself, in which the tub-form is believed to be present,[5] and to $C_8H_8Fe(CO)_3$, in which the ring may be planar,[6] since both show only one proton resonance (at τ 5·48 and 6·49, respectively). Clearly, the tub-form of cyclo-octatetraene must be present also in $[C_8H_8RhCl]_2$, and co-ordination from two non-conjugate double bonds is obviously sufficient to differentiate between the protons in the 8-membered ring. The same is probably true of $C_8H_8PtI_2$ [7] and $C_8H_8RuCl_2$,[4] but these compounds were not sufficiently soluble in organic solvents for measurement of nuclear magnetic resonance. The result shows that, even though the olefin formally supplies four π-electrons in each case, there is a notable difference in bonding between cyclo-octatetraene and the metal in $C_8H_8Fe(CO)_3$ on the one hand, and $[C_8H_8RhCl]_2$ and also π-$C_5H_5CoC_8H_8$—which has also been shown recently [8] to have two proton resonance lines for the C_8H_8 residue—on the other.

Experimental.—Norbornadienerhodium(I) chloride (0·3 g.) in dichloromethane (10 ml.) was treated with the stoicheiometric quantity of the ligand in the same solvent, and the mixture shaken for 15 min. Solvent was removed at 20°/15 mm.; the yellow or orange crystals were recrystallised from ethanol or 1 : 1 benzene–light petroleum (b. p. 40—60°) and vacuum-dried. The *p*-toluidine compound was obtained analytically pure after the crude product had been washed with ether (3 × 15 ml.) and vacuum-dried.

Cyclo-octatetraenerhodium chloride was prepared as previously described,[1] except that the temperature of the reactants was kept between 0° and 50°, instead of at room temperature. This gave higher yields of the complex and prevented deposition of rhodium metal.

[3] Chatt, Vallarino, and Venanzi, *J.*, 1957, 2496, 3413.

[4] Bennett and Wilkinson, *Chem. and Ind.*, 1959, 1516.

[5] Bastiansen, Hedberg, and Hedberg, *J. Chem. Phys.*, 1957, **27**, 1311, and references quoted therein.

[6] Manuel and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 366; Nakamura and Hagihara, *Bull. Chem. Soc. Japan*, 1959, **32**, 880; Rausch and Schrauzer, *Chem. and Ind.*, 1959, 957; Cotton, *J.*, 1960, 400.

[7] Jensen, *Acta Chem. Scand.*, 1953, **7**, 868.

[8] Nakamura and Hagihara, *Bull. Chem. Soc. Japan*, 1960, **33**, 425.

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282. *Polarographic Behaviour of* 2-*Methyl*-1,2-*di*-3′-*pyridylpropan*-1-*one.*

By M. J. ALLEN and J. VIKIN.

RECENTLY the polarographic estimation of 2-methyl-1,2-di-3′-pyridylpropan-1-one [1] has been described.[2] However, the investigators reported one wave which they attributed to the carbonyl group. As it has been demonstrated that pyridine and pyridine-containing compounds give a reduction wave it was decided to re-investigate the polarographic behaviour of this compound under conditions similar to those used by the previous workers.

The half-wave potentials, the diffusion currents, and the effect of increasing pH on these were essentially the same as reported. However, a second wave was obtained which, contrary to the behaviour of the first, became more negative only in the buffers of pH 6 and 8. Also, as has been observed with other pyridine compounds,[3] the diffusion current of the second wave decreases with increasing pH.

To eliminate the possibility that this second wave might be due to a second reduction process at the carbonyl group, the polarographic reduction of 2-methyl-1,2-di-3′-pyridylpropan-1-ol was investigated in the buffer of pH 2·2. In this experiment only one wave was observed. Its half-wave potential was the same as the second wave obtained with the ketone. The diffusion currents, however, were slightly lower. In all cases, the diffusion currents increased linearly with concentration.

Starka and Buden reported the first wave to represent a 2-electron change which no doubt represents reduction of the carbonyl to an alcohol. Coulometric analysis of the second wave shows a 4-electron change which may indicate the reduction of one double bond in each of the pyridine rings.

Experimental.—McIlvains's buffers or 0·1N-lithium chloride was used as the supporting electrolyte. The dilutions were made from a standard stock solution of 0·001M-2-methyl-1,2-di-3′-pyridylpropan-1-one in the appropriate electrolyte and 0·001M-2-methyl-1,2-di-3′-pyridylpropan-1-ol.

A Leeds and Northrup Type E Electro-Chemograph was used to obtain automatically recorded data. An H-type polarographic cell containing a centrally fused disc was used. One side of this cell contained the standard calomel reference electrode. At a reservoir height of 47·4 cm., $t = 4{\cdot}0$ sec. and $m = 1{\cdot}69$ mg. sec.$^{-1}$. The solution was deaerated by passing a stream of nitrogen through it for 5 min. before the recording.

Results are tabulated.

Polarographic data (id, μA) *in McIlvain buffers.*

Ketone concn. (10^{-4}M)	pH 2·2	pH 4·0	pH 6·0	pH 8·0	Alcohol concn. (10^{-4}M)	id (μA)
1	0·28, 2·18	0·42, 1·97	0·55, 1·53	0·69, 0·71	1	2·01
2	0·53, 4·22	0·81, 3·67	1·03, 2·93	1·17, 1·42	2	3·58
3	0·83, 6·20	1·25, 5·61	1·53, 4·23	1·76, 2·28	3	5·31
4	1·25, 8·10	1·63, 7·27	1·84, 5·17	2·14, 3·15	4	7·14
5	1·60, 9·68	2·21, 8·69	2·39, 5·79	2·63, 4·03	5	8·36
$E_{\frac{1}{2}}$ (v)	−0·759, −1·229	−0·850, −1·222	−1·000, −1·303	−1·151, −1·483	$E_{\frac{1}{2}}$ (v)	−1·194

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[1] Allen and Cohen, *J. Amer. Electrochem. Soc.*, 1959, **106**, 451; Bencze and Allen, *J. Amer. Chem. Soc.*, 1959, **81**, 4015.

[2] Starka and Buden, *J. Pharm.*, 1960, **12**, 175.

[3] Kolthoff and Laingane, " Polarography," Interscience, Publ. Inc., New York, 1952, pp. 812—815.