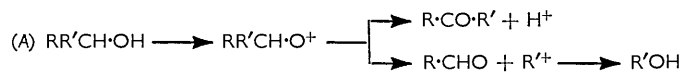


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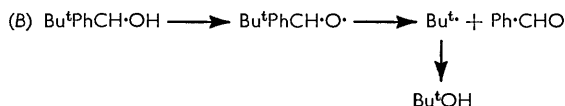
553. *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part VI.*¹ *Carbon-Carbon Bond Fission in the Oxidations of 2-Phenylethanol and α -t-Butylbenzyl Alcohol.*

By J. R. JONES and WILLIAM A. WATERS.

MOSHER and his colleagues² have directed attention to the fact that several secondary alcohols suffer some carbon-carbon bond fission when oxidised by chromic acid and have suggested that this may be due to transient oxy-cation formation (A). Hampton, Leo, and Westheimer,³ who have studied this bond fission with α -t-butylbenzyl alcohol, have



set forth evidence that an ion of chromium(v) may be effecting the bond fission process for which a mechanism (B) involving oxy-radical formation has been proposed.⁴ Since vanadium(v) may well resemble chromium(v) and is known to be a one-electron oxidant in acid solution, we have investigated the possibility of effecting carbon-carbon bond fission in oxidation of alcohols.



2-Phenylethanol has been found to be oxidised by ammonium metavanadate to benzaldehyde, benzoic acid, and formic acid under conditions in which (a) dehydration to styrene did not occur and (b) phenylacetic acid was not oxidised, whilst (c) benzyl alcohol was rapidly oxidised. Similarly α -t-butylbenzyl alcohol was oxidised mainly to benzaldehyde and benzoic acid, butyl phenyl ketone being only a minor oxidation product. This oxidation, data on which are tabulated below, is complicated by the fact that some dehydration, with rearrangement to phenyltrimethylethylene, $\text{Ph}\cdot\text{CMe}\cdot\text{CMe}_2$, occurs. This olefin is only slowly oxidised by vanadium(v), and it cannot be the immediate precursor

¹ Part V, Littler and Waters, preceding paper.

² Mosher and Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 2544; Mosher and Langerak, *ibid.*, 1949, **71**, 286; 1951, **73**, 1302.

³ Hampton, Leo, and Westheimer, *J. Amer. Chem. Soc.*, 1956, **78**, 306.

⁴ Waters, *Quart. Rev.*, 1958, **12**, 286; see also ref. 3, p. 311, footnote.

of any benzaldehyde for it would be expected to yield acetophenone⁵ which, in similar circumstances, is oxidised smoothly to benzoic acid.

This work establishes that carbon-carbon bond fission can occur when alcohols other than 1,2-glycols are oxidised by one-electron-abstracting reagents and is consistent with a mechanism of type (B). Its significance in relation to mechanisms of glycol homolysis, recently discussed by Littler and Waters,¹ is evident.

Experimental.—Oxidation of 2-phenylethanol. The alcohol, b. p. 218—219° (2 g.), together with purified chlorobenzene (10 ml.), was rapidly stirred, at 100°, with ammonium metavanadate (15 g., 1.5 equiv. for complete oxidation) dissolved in sulphuric acid (200 ml.) of the concentrations given in Table 1. After completion of the reaction the organic products were extracted into ether. Acids were removed from the extract with aqueous sodium carbonate, and the neutral remainder obtained by evaporation of ether was analysed by vapour-phase chromatography at 150° with a 187 cm. column of Apiezon grease (10% w/w) on embacil and a hydrogen-

TABLE 1. *Oxidation of 2-phenylethanol by vanadium(v).*

H ₂ SO ₄ (M)	Reaction time (hr.)	Products detected (moles %)		
		Ph·CH ₂ ·CH ₂ ·OH	Ph·CHO	BzOH
0.7	24	4	36	38
2.5	4	0	74	18
3.4	4	0	64	24

flame ionisation detector. Only benzaldehyde, starting material, and solvents were present. The sodium carbonate extract, on acidification, gave benzoic acid, m. p. and mixed m. p. 121°, and a solution that gave a strong chromotropic acid test for formic acid.

No reduction of vanadium(v) in 3.4M-sulphuric acid at 100° occurred in 8 hr. in the presence of phenylacetic acid, but oxidation of benzyl alcohol to benzoic acid was complete in a few minutes. Dehydration of 2-phenylethanol to styrene could not be detected after 8 hr. in 4.5M-sulphuric acid, under nitrogen, at 100°. Benzaldehyde was slowly oxidised at 100° by vanadium(v) in 3.4M-sulphuric acid; in 4 hr., under nitrogen, 20% of benzoic acid was formed, and under air 30%.

Oxidation of t-butylbenzyl alcohol. The alcohol,³ b. p. 118—120°/30 mm., was purified chromatographically and crystallised to m. p. 45° before use. Portions (see Table 2), mixed with chlorobenzene (10 ml.), were oxidised at 100° and then analysed by the methods given above.

TABLE 2. *Oxidation of t-butylbenzyl alcohol by vanadium(v).*

Expt. no.	Alcohol (g.)	NH ₄ VO ₃ (g.)	H ₂ SO ₄ (M)	Total vol. (ml.)	Reaction time (hr.)	Products found (moles %)				
						Alcohol	Ph·CHO	BzOH	Ph·CO·Bu ^t	Ph·CMe ₂ ·CMe ₂
1a	2	20	1.1	200	10	100	—	—	—	—
b	2	20	1.8	220	10	>95	—	—	—	—
c	2	20	2.4	240	10	5	39	24	15	6
2	1.75	15	3.4	200	4	10	36	24	15	13
3	2.0	15	4.5	200	4	0	32	48	10	10
4	0.5	10	4.5	150	3	0	0	70	—	—

t-Butyl phenyl ketone, b. p. 70—72°/0.4 mm., n_D^{25} 1.5100 (oxime, m. p. 167°), for comparison was prepared from pivaloyl chloride by the method of Ford, Thompson, and Marvel.⁶ It resisted oxidation completely in the acidity range used for the alcohol.

In expt. 4, the alcohol was first stirred for 16 hr. at 100° with 5M-sulphuric acid to convert it into the olefin Ph·CMe₂·CMe₂. Evidently this is not oxidised to benzaldehyde. In Expts. 1—3 most of the benzoic acid is formed *via* the olefin since benzaldehyde is oxidised so slightly (see above) under these conditions.

One of us (J. R. J.) thanks the D.S.I.R. for a maintenance grant.

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⁵ Dostrovsky and Samuel, *J.*, 1954, 658.

⁶ Ford, Thompson, and Marvel, *J. Amer. Chem. Soc.*, 1935, **57**, 2621.

554. *The Photochemical Oxidation of Sulphur Chloride Pentafluoride.*

By H. L. ROBERTS.

BISPENTAFLUROSULPHUR PEROXIDE was obtained as a by-product of the fluorination of sulphur when oxygen was present in the fluorine.¹ As a preparative technique this is of little value and it was thought that oxidation of sulphur chloride pentafluoride² might prove a more attractive route.

When sulphur chloride pentafluoride and oxygen are heated in a nickel vessel, no reaction takes place below 350° at which temperature sulphur chloride pentafluoride decomposes in the same manner as it does in the absence of oxygen.³ However, under ultraviolet irradiation two compounds, bispentafluorosulphur oxide and bispentafluorosulphur peroxide, are obtained.

Bispentafluorosulphur oxide boils at 31° and solidifies at -115°. It is stable to aqueous media either acidic or alkaline thus indicating that no fluorine-oxygen bonds are present, and unlike disulphur decafluoride it is only slowly decomposed by ultraviolet radiation. Bispentafluorosulphur peroxide is similar to the oxide in respect of its stability to aqueous media and to light.

Experimental.—Microanalyses are by Dr. A. F. Colson and the infrared absorption spectroscopy by Mr. L. H. Cross.

Thermal oxidation of sulphur chloride pentafluoride. The reaction vessel was a 600-ml. nickel tube. The sulphur chloride pentafluoride and oxygen were introduced from cylinders directly into the vessel, the relative quantities used being indicated by the pressure in the tubes; pressures up to 6 atm. were used. The reaction was followed by regular sampling, the samples being analysed by gas chromatography. No reaction was observed below 350° during 24 hr. Above this temperature, sulphur hexafluoride, sulphur tetrafluoride, and chlorine are produced in equimolar quantities. As these are the normal products of the thermal decomposition of sulphur chloride pentafluoride it is evident that oxidation had not occurred.

Photochemical oxidation of sulphur chloride pentafluoride. The apparatus used was a standard Hanovia 10-l. photochemical reaction vessel with quartz centre tube. This tube acts as a container for a Hanovia 509/12 mercury-arc tube and provides a means of circulating cooling water between the lamp and the reactants.

The vessel was first filled with a 3 : 1 (molar) mixture of sulphur chloride pentafluoride and oxygen. No reaction took place until the mercury arc was switched on, and reaction was then completed in about 6 hr. Longer periods of irradiation did not cause further reaction although both sulphur chloride pentafluoride and oxygen were still present. Possibly chlorine, now present, was absorbing the radiation necessary to maintain reaction. The contents of the vessel were condensed into a liquid-air trap and allowed to warm slowly until they were liquid. At this stage excess of iced 20% sodium hydroxide solution was added. A heavy colourless liquid settled out and was separated. This was washed with water and dried (CaCl₂ and P₂O₅). The yields obtained were variable but from a total pressure of 1 atm. in the 10-l. vessel about 25 g. of products were obtained.

On fractional distillation this liquid yielded *bispentafluorosulphur oxide*, b. p. 31° (about 75% of the total) (Found: S, 24.9; F, 69.5%; *M*, 270. S₂F₁₀O requires S, 23.7; F, 70.5%; *M*, 270), and bispentafluorosulphur peroxide, b. p. 49° (Found: *M*, 286. Calc. for S₂F₁₀O₂: *M*, 286).

Vapour pressures. These were measured with a mercury manometer connected to a bulb immersed in a cooling bath, the temperature of which was measured with a previously calibrated alcohol thermometer. For the oxide the results can be represented by $\log_{10} p = -(1375/T) + 7.40$. The boiling point found by extrapolation is 31° (in agreement with the observed value), the latent heat of vaporisation calculated from the slope is 6300 cal. mole⁻¹, and the Trouton constant is 20.7. For the peroxide, the equation is $\log_{10} p = -(1450/T) + 7.39$, the boiling point found by extrapolation is 49° (in agreement with previous workers¹), the latent heat of vaporisation is 6600 cal. mole⁻¹, and the Trouton constant 20.7.

¹ Harvey and Bauer, *J. Amer. Chem. Soc.*, 1954, **76**, 859.

² Roberts and Ray, *J.*, 1960, 665.

³ Dodd, Woodward, and Roberts, *Trans. Faraday Soc.*, 1957, **53**, 1545.

Melting point. The melting point of bispentafluorosulphur monoxide, measured with a calibrated thermocouple, was $-115^{\circ} \pm 4^{\circ}$.

Infrared absorption spectrum of bispentafluorosulphur oxide. In view of the similarity in physical properties between disulphur decafluoride and bispentafluorosulphur oxide, and the difficulty of obtaining accurate analyses on sulphur-fluorine compounds, it is of interest that the spectrum of the oxide is quite different from that of the decafluoride.³ Intense bands occur at 959 (v.s.), 920, 806, 698, ~ 600 , and 558 (v.s.) cm^{-1} .

IMPERIAL CHEMICAL INDUSTRIES LIMITED, ALKALI DIVISION RESEARCH DEPARTMENT,
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555. *The Reaction of Ruthenium and Osmium Tetroxides with Ammonia.*

By M. L. HAIR and P. L. ROBINSON.

THE reactivity of octavalent ruthenium and osmium compounds suggests that the metals are not exerting their maximum covalency and so should be able to form co-ordinate links as an acceptor, giving products of the form MO_4, PF_3 . Hair and Robinson¹ isolated the former type of complex, $\text{RuO}_4, \text{PF}_3$ and $\text{OsO}_4, \text{PF}_3$ being prepared by direct combination of phosphorus trifluoride with the tetroxides in a closed apparatus.

Ammonia might be expected to cause ruthenium and osmium to increase their covalency through combination with the tetroxides to form amines, and the compounds $\text{RuO}_4, \text{NH}_3$ and $\text{OsO}_4, \text{NH}_3$ have now been prepared and characterised. The former is exceptionally unstable and explodes at -20° , but $\text{OsO}_4, \text{NH}_3$ is quite stable and can be sublimed.

When ammonia is condensed on to ruthenium tetroxide at -30° and the vessel and its contents are allowed to warm a violent reaction occurs at about -20° , the ammonia being immediately oxidised to nitrogen and water, without, however, any evidence of the formation of oxides of nitrogen. Should the ammonia be admitted slowly to ruthenium tetroxide cooled to -30° , the solid turns red. Ammonia may be added until the composition is approximately $\text{RuO}_4, \text{NH}_3$, but addition of ammonia beyond this point or a slight raising of the temperature when this point has been reached causes explosive decomposition. Thus, though the compound can be isolated, it can be studied only below -20° .

When ammonia is slowly admitted to osmium tetroxide, a smooth reaction begins at -25° in which one molecule of ammonia is taken up by the tetroxide, leading to a yellow product. This may be entirely $\text{OsO}_4, \text{NH}_3$ provided the temperature is kept low enough. When allowed to warm, the material separates into two parts; the more volatile portion, which can easily be removed under vacuum, proves to be $\text{OsO}_4, \text{NH}_3$. It condenses to an orange solid. The residue is osmiamic acid, HO_3OsN , presumably formed by the decomposition of the ammine:



Some of the decomposition may take place at the time of the reaction with ammonia if the temperature is allowed to rise, for the proportion of osmiamic acid is dependent on the temperature of preparation, more being formed at higher temperatures.

Previously osmiamic acid has been known only in solution. The sodium, potassium, zinc, mercury, and ammonium salts have been known for many years, potassium osmiamate being first prepared by the action of concentrated ammonia on a solution of osmium tetroxide in strong potash.²

The ultraviolet absorption spectrum of osmiamic acid shows a well-defined, characteristic peak at 2235 Å. That this absorption band is ascribable to the osmiamate ion was

¹ Hair and Robinson, *J.*, 1958, 106.

² Brizard, *Ann. Chim. Phys.*, 1900, 21, 373.

established by the fact that potassium osmium solution gives a very similar spectrum incorporating the characteristic peak. The osmium tetroxide complex with ammonia exhibits a completely different spectrum, the peak occurring at 2460 Å.

When treated with concentrated hydrochloric acid, potassium osmium was converted into the pink nitridochloride, K_2OsNCl_5 .³ Osmiamic acid dissolved in concentrated hydrochloric acid to give a red solution, presumably of the pentachloronitrido-osmic acid, H_2OsNCl_5 . Both solutions had identical ultraviolet spectra with a strong peak at 2291 Å.

An account of the reactions of these tetroxides with other donor molecules and of the infrared spectra of the compounds will be published later.

This work was carried out during the tenure of a Salters' Scholarship (M. L. H.).

KING'S COLLEGE, NEWCASTLE UPON TYNE.

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³ Sidgwick, "Chemical Elements and their Compounds," Oxford University Press, p. 1508.

556. *Interaction between Thionyl Halides and Alkoxytrimethylsilanes.*

By B. R. CURRELL, M. J. FRAZER, and W. GERRARD.

MUTUAL replacement of alkoxy (or aryloxy) by halogen attached to phosphorus, sulphur, silicon, or boron is related to the electron density on the oxygen. The alkoxy-silane-boron trichloride mixture¹ reacts quickly:



The nucleophilic function of oxygen in the chlorosilane is reduced by the presence of chlorine, and the electrophilic function of boron in the dichloroborate is reduced by the alkoxy group, so that further replacement between these two is noticeably slower, although there is a drift towards the tri-*n*-butyl borate, that will not react with silicon tetrachloride.² Similar results have been found for tri-*n*-butyl phosphite and boron trichloride² or silicon tetrachloride,² for triphenyl phosphite and boron halides,³ and for certain other systems. Reactions of trialkyl⁴ and triaryl phosphates⁵ with boron halides (Cl, Br), and of trialkyl phosphates⁶ with silicon tetrachloride, follow entirely different courses, which do not give a mixture of chloro-esters.

Trimethylneopentylloxysilane and thionyl chloride react rapidly at room temperature to give the stable neopentyl chlorosulphinate.⁷ Alkoxytrimethylsilanes, $RO \cdot SiMe_3$ ($R =$ alkyl of ordinary reactivity such as Bu^a , Bu^i , Bu^s) (1 mol.), readily gave the alkyl chlorosulphinate with 1 mol. of thionyl chloride, and the dialkyl sulphite with 0.5 mol., showing that in this system the chlorosulphinate is reactive enough to react with the alkoxytrimethylsilane, although it cannot do so with tetra-*n*-butoxysilane.⁸ This means that the four alkoxy groups result in a lower electrophilic power of silicon, as compared with the inductive influence of three methyl groups together with the effect of one alkoxy in the alkoxytrimethylsilane. The inductive effect of the three methyl groups is also illustrated by the much slower reaction of sulphites with chlorotrimethylsilane than with silicon tetrachloride.

The most convenient method for the preparation of bromosulphinates is the reaction of the alkoxytrimethylsilane with thionyl bromide, because neither hydrogen bromide nor

¹ Gerrard and Strickson, *Chem. and Ind.*, 1958, 860.

² Chainani, Gerrard, Honey, and Lindsay, unpublished work.

³ Frazer, Gerrard, and Patel, *Chem. and Ind.*, 1959, 90, 728.

⁴ Gerrard and Griffey, *Chem. and Ind.*, 1959, 55.

⁵ Frazer, Gerrard, and Patel, *J.*, 1960, 726.

⁶ Gerrard and Jeacocke, *Chem. and Ind.*, 1959, 704.

⁷ Gerrard and Tolcher, *J.*, 1954, 3640.

⁸ Currell, Frazer, Gerrard, Haine, and Leader, *J. Inorg. Nuclear Chem.*, 1959, 12, 45.

pyridinium bromide is involved, and it is these substances which usually catalyse the decomposition of the ester during the distillation.

Experimental.—*Alkoxytrimethylsilanes and thionyl chloride.* The ester (0.1 mole), prepared in the presence of pyridine (Bu^t) or in the absence of base ^a (Bu^t, Bu^s, C₆H₁₃-CHMe), was added dropwise to thionyl chloride (0.1 mole), at room temperature. Next morning, a mixture of the chlorosilane, alkyl chloride, and thionyl chloride was removed at 20 mm., and the chlorosulphinate was distilled. Compounds thus prepared are in Table 1. There was considerable

TABLE 1.

R in Me ₃ Si-OR	Me ₃ SiCl, yield (%)	RO·SO·Cl				Found (%) ^a	
		Yield (%)	B. p./mm.	n _D (t)	Cl	S	
Bu ⁿ ^b	69.5	43.2	50—52°/14	1.4550 (20°)	20.9	19.6	
Bu ⁿ	75.6	57.2	60—68°/25	1.4535 (21°)	22.1	20.1	
Bu ^t	95.8	80.5	58—62°/20	1.4530 (20°)	21.3	20.2	
Bu ^s	97.2	69.5	58—60°/20	1.4535 (21°)	21.7	19.9	

^a Calc. for C₄H₉O₂ClS: Cl, 22.7; S, 20.4%. Prepared with pyridine.

decomposition into 2-chloro-octane and octene during the distillation of the 1-methylheptyl chlorosulphinate; but the chlorosilane was obtained in 71% yield.

When thionyl chloride (1 mol.) was added to the ester (2 mol.), a similar procedure afforded the dialkyl sulphite (see Table 2).

TABLE 2.

R in Me ₃ Si-OR	Me ₃ SiCl, yield (%)	(RO) ₂ SO				S (%)	
		Yield (%)	B. p./mm.	n _D (t)	Found	Calc.	
Bu ⁿ	32.6 ^a	88.0	112—115°/15	1.4280 (27°)	16.1	16.4	
Bu ^s	82.3	90.5	90—92°/18	—	15.6	16.4	
C ₆ H ₁₃ CHMe ...	66.2	66.2	117—119°/0.2	1.4426 (20°)	11.1	10.8	

^a Many fractionations were required to separate this from alkyl chloride.

Alkoxy silanes and chlorosulphinates. Equimolecular amounts of the reactants were heated under reflux at 80° for the time stated, with the results in Table 3.

TABLE 3.

R in Me ₃ Si-OR	Time (hr.)	(RO) ₂ SO			
		Yield (%)	B. p./mm.	n _D (t)	Found: S (%)
Bu ⁿ	7	85.3	103—105°/13	1.4310 (20°)	15.9
Bu ^t	12	89.0	86—88°/10	1.4269 (19°)	16.8

Chlorotrimethylsilane and dialkyl sulphites. The reactants (0.1 mole) were heated under reflux at 80° for 80 hr. Results are in Table 4.

TABLE 4.

R in (RO) ₂ SO	Me ₃ Si-OR, yield (%)	Recovery (%)	(RO) ₂ SO		
			B. p./mm.	n _D (t)	Found: S (%)
Bu ⁿ	—	88.0	116—118°/20	1.4305 (20°)	15.9
Bu ⁿ ^a	17.0 ^a	69.5	115—117°/20	1.4300 (20°)	16.1
Bu ^t	—	88.0	91—92°/12	1.4265 (20°)	15.6
Bu ^t ^a	12.9 ^b	65.8	100—102°/20	—	16.9
Bu ^s	32.8 ^c	20.3	86—88°/15	1.4250 (21°)	15.5

^a C₅H₉N₂HCl (0.3 g.) added. ^b B. p. 121—123°, n_D²⁰ 1.3930. ^c B. p. 111—112°, n_D²⁵ 1.3850. B. p. 109—111°, n_D²⁰ 1.3885, d₄²⁰ 0.772.

Chlorotrimethylsilane and alkyl chlorosulphinates. A mixture of the reactants (0.1 mole of each) was held at 25° for 9 days. n-Butyl chlorosulphinate (91.5%), b. p. 57—60°/18 mm., n_D²⁰ 1.4580 (Found: Cl, 22.1; S, 20.0%), and isobutyl chlorosulphinate (88%), b. p. 52—54°/20 mm., n_D²⁰ 1.4540 (Found: Cl, 22.0; S, 19.3%), were separately recovered.

Thionyl bromide and alkoxytrimethylsilanes. The ester (1 mol.) was added to thionyl bromide ¹⁰ (1 mol.) at room temperature. A mixture of bromotrimethylsilane and alkyl

⁹ Currell and Gerrard, *Chem. and Ind.*, 1958, 1289.

¹⁰ Frazer and Gerrard, *Chem. and Ind.*, 1954, 280.

bromide was removed at 20 mm. n-Butyl bromosulphinate (66.5%). b. p. 82°/12 mm., n_D^{20} 1.4980 (Found: Br, 36.2. Calc. for $C_4H_9O_2BrS$: Br, 38.0%), and isobutyl bromosulphinate (76.0%), b. p. 80–82°/15 mm., n_D^{20} 1.5020 (Found: Br, 39.0%), were separately obtained; but the s-butyl ester could not be isolated.

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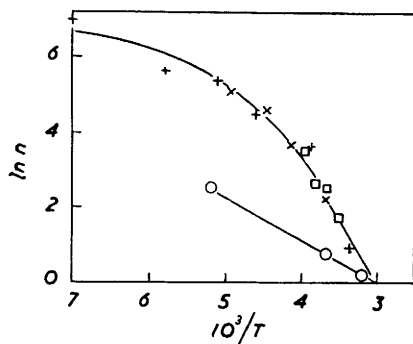
557. Polymerisation Ceiling Temperatures of Some Substituted Styrenes.

By A. R. MATHIESON.

For polymerisations having an equilibrium propagation, Dainton and Ivin¹ have shown that there is a ceiling temperature (T_c) above which no high polymer can be formed, and at which the free energy of polymerisation becomes zero:

$$T_c = \Delta H_p / (\Delta S^\circ + R \ln [M]) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ΔH_p , ΔS° , $[M]$ are respectively the enthalpy and entropy of polymerisation, and the monomer concentration. The effect of temperature on the degree of polymerisation (n),



Effect of temperature on the degree of polymerisation of α -methylstyrene.

Catalysts: \circ , CCl_3CO_2H ;³ $+$, $AlCl_3$;⁸
 \times , H_2SO_4 ;⁷ \square , BF_3 -ether.¹²

for ionic polymerisations with normal bimolecular propagation and unimolecular termination only, is given by

$$\ln (1/n) = E_n/RT + \ln (1/[M]) + \text{Const.} \quad . \quad . \quad . \quad . \quad (2)$$

where E_n is the difference of the activation energies of propagation and termination. When $T = T_c$, $n = 1$. For the standard state of $[M] = 1$, T_c depends only on ΔH_p and ΔS° , and ΔH_p is influenced by steric hindrance to polymerisation, loss of resonance stabilisation, branching, and end-effects.²

Ionic dimerisations and polymerisations of substituted styrenes have been interpreted in terms of equilibrium propagations,³⁻⁵ and linearity of $\ln (1/n)$ in $\ln (1/[M])$ and in $1/T$ has been established for the ionic polymerisation of α -methylstyrene.^{3,6} To calculate the ceiling temperatures, equation (2) was used for the polymerisations and the equilibrium constants at various temperatures for the dimerisations (T_c is here defined as the temperature at which the free energy of dimerisation becomes zero). The results, given in the Table, confirm that T_c is independent of the catalyst and of the solvent. For α -methylstyrene use of equation (2) gives the same result as a direct measurement of T_c ,^{3,6} and here

¹ Dainton and Ivin, *Trans. Faraday Soc.*, 1950, **46**, 331.

² Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York, 1953, pp. 249–256.

³ Brown and Mathieson, *J.*, 1958, 3563.

⁴ Evans, Jones, Jones, and Thomas, *J.*, 1956, 2757.

⁵ Brackman and Plesch, *J.*, 1958, 3563.

⁶ McCormick, *J. Polymer Sci.*, 1957, **25**, 488.

T_c is substantially the same for the formation of high⁶ or of very low^{3,7,8,9} polymer. This result is due to the similarity of ΔH_p for high and low polymer for α -methylstyrene (-8.42 kcal. mole⁻¹ for $n = \infty$, -8.28 kcal. mole⁻¹ for $n = 3$ ^{3,10}). For this substance, increase of $-\Delta H_p$ with decrease of n due to reduction of steric hindrance¹⁰ is compensated by the increased importance of the cyclised substituted indane end-groups at lower values of n .³ The Figure shows that for this monomer the plots of $\ln n$ against $1/T$ fall approximately on the same line for three catalysts out of four, and that the linearity probably does not extend to very high degrees of polymerisation (this is not certain because for sulphuric acid and aluminium chloride catalysis values of n have been obtained from intrinsic viscosities by using a formula valid for low values of n ¹¹).

It seems that *para*-substitution does not markedly increase the steric hindrance to polymerisation. Steric effects are not the only influences on T_c , as α -phenylstyrene has a higher value of T_c than α -methylstyrene, and *para*-substitution in α -phenylstyrene markedly alters T_c . Clearly, the presence of electron-releasing substituents increases T_c ,

Monomer	Catalyst	Solvent	T_c	Ref.
α -Methylstyrene	$\text{CCl}_3 \cdot \text{CO}_2\text{H}$	$\text{C}_2\text{H}_5\text{Br}$	$60^\circ \pm 1^\circ$	<i>a</i>
"	†	Tetrahydrofuran	61 ± 1	<i>c</i>
"		H_2SO_4	60 ± 2	<i>d</i>
"		$\text{C}_2\text{H}_5\text{Cl}$	~ 60	<i>e</i>
<i>p</i> -Bromo- α -phenylstyrene *	$\text{CCl}_3 \cdot \text{CO}_2\text{H}$	C_6H_6	92 ± 3	<i>f</i>
α -Phenylstyrene *	"	"	107 ± 2	<i>b</i>
"	*	$\text{Pr}^i \cdot \text{NO}_2$	104 ± 18	<i>g</i>
"	*	$\text{CCl}_3 \cdot \text{CO}_2\text{H}$	107 ± 2	<i>b</i>
<i>pp'</i> -Dimethyl- α -phenylstyrene *	"	$\text{C}_2\text{H}_5 \cdot \text{NO}_2$	106 ± 4	<i>b</i>
<i>p</i> -Methoxy- α -phenylstyrene *	"	C_6H_6	157 ± 13	<i>b</i>
<i>pp'</i> -Dimethoxy- α -phenylstyrene *	"	"	188 ± 28	<i>b</i>

* Dimerisations. † T_c directly measured.

a, Brown and Mathieson, *J.*, 1958, 3563. *b*, Evans, Jones, Jones, and Thomas, *J.*, 1956, 2757. *c*, McCormick, *J. Polymer Sci.*, 1957, 25, 488. *d*, Heiligmann, *J. Polymer Sci.*, 1951, 6, 155. *e*, Hersberger, Reid, and Heiligmann, *Ind. Eng. Chem.*, 1945, 37, 1073; Jordan and Mathieson, *J.*, 1952, 621. *f*, Evans, Jones, and Thomas, *J.*, 1958, 4563. *g*, Evans, Jones, and Thomas, *J.*, 1957, 2095.

in the Table the monomers being given in order of increased electron-releasing power of the substituents. Direct comparison of T_c for α -methylstyrene and α -phenylstyrene is difficult because when formed at normal temperatures the dimer and low polymers of α -methylstyrene are mixtures of saturated cyclised and unsaturated linear forms,³ whereas the results quoted for α -phenylstyrene refer to the formation of linear unsaturated dimer only, higher catalyst concentrations being needed to produce the saturated cyclised form,¹² irreversibly.

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⁷ Heiligmann, *J. Polymer Sci.*, 1951, 6, 155.

⁸ Hersberger, Reid, and Heiligmann, *Ind. Eng. Chem.*, 1945, 37, 1073; Jordan and Mathieson, *J.*, 1952, 621.

⁹ Worsfold and Bywater, *J. Amer. Chem. Soc.*, 1957, 79, 4917.

¹⁰ Roberts and Jessup, *J. Res. Nat. Bur. Stand.*, 1951, 46, 11.

¹¹ Jordan and Mathieson, *J.*, 1952, 2345.

¹² Evans and Price, *J.*, 1959, 2982.

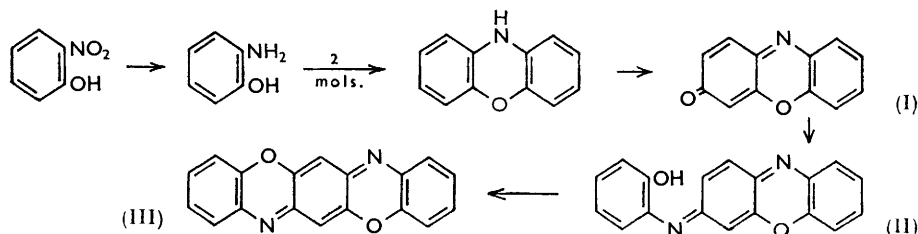
558. *The Mechanism of Formation of Benz[5,6]-[1,4]-oxazino-[2,3-a]phenoxazine from o-Nitrophenol.*

By M. KHALIFA.

THE mechanism shown in the annexed formulæ was suggested earlier¹ to account for the formation of benz[5,6]-[1,4]-oxazino[2,3-a]phenoxazine (III) as a by-product on fusion of *o*-nitrophenol with potassium hydroxide. We have confirmed this by preparing the compound from (a) *o*-aminophenol and (b) 3-phenoxazone (I).

¹ Khalifa and (in part) Linnell, *J. Org. Chem.*, 1959, 24, 853.

Fusion of *o*-aminophenol with potassium hydroxide caused a vigorous reaction which was difficult to control. Under less vigorous conditions—potassium hydroxide in boiling benzene or heating with sodium ethoxide at 200–220°—*o*-aminophenol was recovered



unchanged. However, use of ethanolic potassium hydroxide led directly to the pentacyclic product (III). Secondly, phenoxazine was oxidised by ferric chloride to phenoxazone² (I) and this was condensed with *o*-aminophenol; the intermediate product, presumably (II), yielded the benzoxazinophenoxazine (III) on oxidation with ferric chloride.

Experimental.—(a) *o*-Aminophenol (10 g.) and powdered potassium hydroxide (10 g.) were refluxed in ethanol (50 ml.) for 30 hr., then set aside for 4 days; ammonia was evolved. The mixture was acidified with acetic acid and the excess of acid was neutralised with sodium hydrogen carbonate. Overnight a brownish-red solid (4.5 g.) was deposited which on vacuum-sublimation gave *o*-aminophenol, m. p. and mixed m. p. 174° (2.3 g.), and then garnet-red needles (0.5 g.) of the product (III), soluble in benzene with a green fluorescence, giving a deep blue colour with concentrated sulphuric acid, and subliming at about 265°/1 atm. (lit., 241°,³ ca. 250°⁴).

(b) Phenoxazine (1.9 g.) in boiling glacial acetic acid (20 ml.) was oxidised by ferric chloride (7 g.) for about 10 min., then cooled. *o*-Aminophenol (1.1 g.) was added and the whole was kept overnight and oxidised again by heating it with ferric chloride (4.5 g.). The mixture was then diluted with water, neutralised with sodium carbonate, and acidified with hydrochloric acid before extraction with benzene. The benzene extract, on being dried (Na₂SO₄) and distilled, gave 2 g. of a solid which on vacuum-sublimation gave a brownish-red sublimate followed by a pure sublimate of the product (III) (1.6 g.).

The author thanks Professor Y. M. Abou-Zeid of this Faculty for facilities.

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² Cf. Kehrman and Saager, *Ber.*, 1903, **36**, 477; 1902, **35**, 341.

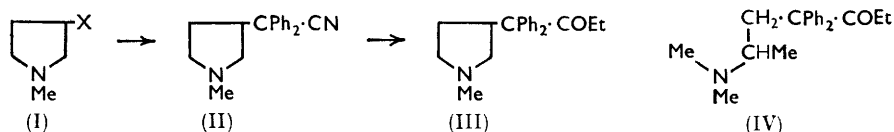
³ Fischer, *J. prakt. Chem.*, 1879, **19**, 320.

⁴ Seidel, *Ber.*, 1890, **23**, 185.

559. *Synthesis of 1-(1-Methylpyrrolid-3-yl)-1,1-diphenylbutan-2-one.*

By D. E. AMES.

1-METHYLPYRROLIDIN-3-OL (I; X = OH), now readily accessible,¹ was converted into the chloro-amine (I; X = Cl) which was condensed with diphenylacetonitrile and potassium



t-butoxide to give α -1-methylpyrrolidin-3-yl- α -diphenylacetonitrile (II). With ethylmagnesium bromide, this yielded the ketone (III). A similar sequence of reactions converted 1-phenethylpyrrolidin-3-ol into the *N*-phenethyl analogue of ketone (III). These

¹ Lunsford, Ward, Pallotta, Tusing, Rose, and Murphey, *J. Med. Pharm. Chem.*, 1959, **1**, 73; Cavalla, Davoll, Dean, and Temple, unpublished work.

compounds have been tested by Dr. C. V. Winder (Parke, Davis and Co., Detroit) who reports that amino-ketone (III) shows lower analgesic activity than amidone² (IV) and that the *N*-phenethyl compound is inactive.

Experimental.—3-Chloro-1-methylpyrrolidine. A solution of 1-methylpyrrolidin-3-ol (60 g.) in chloroform (180 c.c.) was stirred at -5° to 0° while thionyl chloride (55 c.c.) was added during 30 min. The mixture was refluxed (bath 100°) for 1.5 hr., then cooled in ice-water while an ice-cold solution of potassium hydroxide (54 g.) in water (300 c.c.) was added. The organic layer was separated and washed with water (10 c.c.) as rapidly as possible, dried (Na_2SO_4), and fractionally distilled through a short Fenske column, to give the chloride¹ (64 g., 89%), b. p. $55-58^{\circ}/50$ mm.

α -1-Methylpyrrolidin-3-yl- $\alpha\alpha$ -diphenylacetone nitrile. Diphenylacetone nitrile (63 g.) was added to potassium (13 g.) dissolved in *t*-butyl alcohol (400 c.c.), and the solution stirred under reflux (bath 120°) while the chloride (38 g.) was added gradually and for a further 1 hr. After most of the solvent had been removed by distillation, the cooled residue was treated with water (300 c.c.) and ether (300 c.c.). The separated organic layer was extracted with 2*N*-hydrochloric acid (500 c.c.; 100 c.c.), and the acid extracts were basified with 10*N*-sodium hydroxide (150 c.c.). Isolated with ether, the nitrile (33.5 g.) had b. p. $160-165^{\circ}/0.2$ mm., n_D^{20} 1.5798, m. p. $73-76^{\circ}$ (Found: C, 82.2; H, 7.2; N, 9.9. $\text{C}_{19}\text{H}_{20}\text{N}_2$ requires C, 82.6; H, 7.3; N, 10.1%).

1-(1-Methylpyrrolidin-3-yl)-1,1-diphenylbutan-2-one. The nitrile (10 g.) in ether (50 c.c.) was added to ethylmagnesium bromide (from magnesium, 2.2 g.) in ether (50 c.c.), and the mixture was stirred for 1 hr. After addition of toluene (50 c.c.), ether was removed and the residue stirred under reflux (bath 120°) for 16 hr. Concentrated hydrochloric acid (60 c.c.) and water (100 c.c.) were added and the imine was hydrolysed by heat (bath 130°) for 30 min. The separated toluene layer was extracted with 2*N*-hydrochloric acid, and the combined acid solutions were basified with aqueous ammonia. The ketone (3.5 g.), isolated with ether and purified by repeated distillation, had b. p. $153^{\circ}/0.2$ mm., n_D^{20} 1.5704 (Found: C, 81.6; H, 8.1; N, 5.0. $\text{C}_{21}\text{H}_{25}\text{ON}$ requires C, 82.0; H, 8.2; N, 4.6%). The picrate formed prisms, m. p. $176-177^{\circ}$, from methanol-acetone (Found: C, 60.8; H, 5.4; N, 10.4. $\text{C}_{27}\text{H}_{28}\text{O}_8\text{N}_4$ requires C, 60.4; H, 5.3; N, 10.4%).

1-Phenethylpyrrolidin-3-ol. 1,4-Dichlorobutan-2-ol (43 g.) and phenethylamine (109 g.) were heated together (bath 150°) for 3 hr. After addition of 2*N*-sodium hydroxide (500 c.c.), the solution was extracted with ether (300 c.c.) and toluene (100 c.c.), and the extracts were washed with water and dried (Na_2SO_4). Repeated fractional distillation gave the pyrrolidinol (42 g.), b. p. $103-105^{\circ}/0.2$ mm., n_D^{20} 1.5397 (Found: C, 75.7; H, 8.8; N, 7.2. $\text{C}_{12}\text{H}_{17}\text{ON}$ requires C, 75.4; H, 9.0; N, 7.3%).

α -1-Phenethylpyrrolidin-3-yl- $\alpha\alpha$ -diphenylacetone nitrile. The alcohol was converted into the chloride, and the crude material (33 g.; b. p. $105-108^{\circ}/0.5$ mm.) was condensed with diphenylacetone nitrile as in the previous example. The nitrile (11.5 g.) formed prisms, m. p. $109-111^{\circ}$, from ether-ethyl acetate (Found: C, 85.3; H, 7.2; N, 7.5. $\text{C}_{20}\text{H}_{26}\text{N}_2$ requires C, 85.2; H, 7.2; N, 7.7%).

1-(1-Phenethylpyrrolidin-3-yl)-1,1-diphenylbutan-2-one. The foregoing nitrile (11 g.) was added in portions to ethylmagnesium bromide (from magnesium, 3.3 g.) in ether (100 c.c.). Toluene (50 c.c.) was added to increase the solubility of the nitrile and the mixture was stirred under reflux for 2 hr. After addition of more toluene (30 c.c.), the ether was distilled away and the residue stirred and heated (bath 120°) for 48 hr. Water (150 c.c.) and concentrated hydrochloric acid (100 c.c.) were added, and the mixture was refluxed for 4 hr., then basified and treated with ammonium chloride solution. Isolated with ethyl acetate, the ketone (7.2 g.) had b. p. $227-230^{\circ}/0.2$ mm., n_D^{20} 1.5938 (Found: C, 84.9; H, 7.7; N, 3.9. $\text{C}_{23}\text{H}_{31}\text{ON}$ requires C, 84.6; H, 7.9; N, 3.5%).

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² Easton, Gardner, and Stevens, *J. Amer. Chem. Soc.*, 1947, **69**, 2941, and references there cited.

560. *The Interaction of Cyanide and Hydroxyl Ions with a Cobalt(III) Complex.*

By D. A. L. HOPE and J. E. PRUE.

A RECENT suggestion¹ that, contrary to previous beliefs, cyanide ion may be a better nucleophilic reagent than hydroxide ion for substitutions in cobalt(III) complexes, is supported by some kinetic measurements made in 1954.

In an investigation of the effect of ions of opposite charge on the optical rotatory power of the 1,9-bis-salicylideneamino-3,7-dithianonancobalt(III) ion² (which carries a single positive charge), it was found that in the presence of ferrocyanide ions the rotation decreased with time. Our suspicion that this was due to the entry of cyanide ions into the cobalt complex was confirmed by the observation that in the presence of excess of potassium cyanide the rotation of the complex falls to zero with an associated change in the absorption spectrum. Kinetic measurements were made at 25° on 5.28×10^{-5} M-solutions of the (+)-complex in potassium cyanide solutions of concentration $1-6 \times 10^{-3}$ M. In each experiment the change of the logarithm of the specific rotation of the complex with time was linear, and the reaction is therefore of first order with respect to the complex ion. The slopes of the graphs, which give the first-order rate constants, were proportional to the potassium cyanide concentration, so the reaction is also of the first order with respect to the cyanide ion. The second-order rate constant found for reaction between the complex ion and the cyanide ion was 7×10^{-2} sec.⁻¹ l. mole⁻¹ (a small correction was applied for hydrolysis of the cyanide ion). Similar behaviour was observed in sodium hydroxide solutions and the rate constant found was 5×10^{-3} sec.⁻¹ l. mole⁻¹. The rate constant for reaction of the complex ion with the cyanide ion is therefore about 14 times greater than that for reaction with the hydroxide ion.

We thank Dr. F. P. Dwyer for the gift of the cobalt complex, and the British Rayon Research Association for the award of a research scholarship to one of us (D. A. L. H.).

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¹ Nagarajaiah, Sharpe, and Wakefield, *Proc. Chem. Soc.*, 1959, 385.

² Dwyer, Gill, Gyarfás, and Lions, *J. Amer. Chem. Soc.*, 1952, **74**, 4188.

561. *2-Pyrrolidino- and 2-Piperidino-purine.*

By GERSHON LEVIN and MEIR TAMARI.

4-AMINO-5-NITROSPYRIMIDINES have been converted into purines by Bredereck and Edenhofer¹ in a single step by dissolving the reducing agent (sodium dithionite) in a mixture of formamide and formic acid. For biological testing, certain 2-aminopurines were required whose synthesis involved 5-nitropyrimidines as intermediates. We have observed that the one-step procedure can conveniently be applied to 4-amino-5-nitropyrimidines; the yield of the purines is twice that obtained when the diamine is isolated and then cyclised with formamide.

Experimental.—4-Amino-5-nitro-2-pyrrolidinopyrimidine. 4-Amino-2-chloro-5-nitropyrimidine² (5 g.) and pyrrolidine (15 g.) were refluxed in ethanol (15 ml.) for 1 hr., then kept at 0° overnight. The precipitate (4.5 g., 75%) of product crystallised from butan-1-ol in flat, yellow prisms, m. p. 223° (Found: C, 45.8; H, 5.4. C₈H₁₁N₅O₂ requires C, 45.9; H, 5.3%). At pH 8.0, the compound shows absorption maxima at 223, 276, and 369 mμ.

2-Pyrrolidinopurine. 4-Amino-5-nitro-2-pyrrolidinopyrimidine (0.7 g.) was stirred in formamide (10 ml.) and formic acid (1 ml.) at 110°. When sodium dithionite (3.5 g.) was added in portions, gas was evolved and the mixture soon became homogeneous. After 10 min., the

¹ Bredereck and Edenhofer, *Chem. Ber.*, 1955, **88**, 1306.

² Brown, *J. Appl. Chem.*, 1952, **2**, 239.

temperature was raised to 190° for 30 min. After cooling, the addition of water (20 ml.) precipitated a small amount of sulphur, which was filtered off. The filtrate, when kept overnight at 0°, deposited the yellowish product (0.45 g.), which formed colourless prisms when dissolved in 5% aqueous sodium hydroxide and reprecipitated therefrom by glacial acetic acid. It (0.31 g., 48%) then had m. p. 265° (Found: C, 57.1; H, 5.7; N, 37.1. $C_9H_{11}N_5$ requires C, 57.1; H, 5.8; N, 37.0%). It had λ_{max} 228 and 341 m μ at pH 3, 225, 251, and 335 m μ at pH 8, and 230 and 333 m μ at pH 11; it had R_F 0.83 in 17 : 1 : 2 EtOH-H₂O-AcOH (solvent A) or 7 : 2 : 1 EtOH-pyridine-H₂O (solvent B); it gave a blue fluorescence under light of λ 255 m μ .

4-Amino-5-nitro-2-piperidinopyrimidine, prepared as above in 80% yield, had m. p. 153° and λ_{max} 224, 279, and 370 m μ (pH 8.0) (Found: C, 48.5; H, 5.8; N, 31.9. $C_9H_{13}N_5O_2$ requires C, 48.4; H, 5.8; N, 31.4%).

2-Piperidinopurine, obtained in 51% yield as above, formed colourless, elongated prisms, m. p. 175° (Found: C, 58.7; H, 6.6; N, 34.5. $C_{10}H_{13}N_5$ requires C, 59.1; H, 6.4; N, 34.4%). It had λ_{max} 230 and 340 m μ at pH 3, 225, 252, and 331 m μ at pH 8, and 230 and 320 m μ at pH 11; it had R_F 0.89 in solvent (A) and 0.86 in solvent (B); it gave a blue fluorescence in light of λ 255 m μ .

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562. Constituents of *Bacopa monnieri* (L) Pennell.

By IVOR BROWN and M. MARTIN-SMITH.

AN investigation of *Bacopa monnieri* (L) Pennell (syn. *Herpestis monniera* and *Monniera cuneifolia*; family Scrophulariaceæ), a plant employed in Ayurvedic medicine under the name Brahmi, was undertaken because of reports that it contains physiologically active alkaloids of unknown constitution.^{1,2} The dried plant was kindly provided for us by Glaxo Laboratories Ltd., and its identity confirmed by Drs. F. Fish, Royal College of Science and Technology, Glasgow, and G. Taylor, Royal Botanic Gardens, Kew. This material proved to contain only 0.002—0.003% of total basic material, consisting of a mixture of at least four compounds, as shown by paper chromatography. As the quantity of bases was so small, detailed chemical and pharmacological investigations of them were not possible. This note records the characterisation of the other constituents isolated. The presence of these compounds was not reported by the earlier workers and we were unable to confirm the presence of the sterol-like compound of m. p. 75—76° recorded by them.²

Extraction with cold light petroleum gave a paraffin hydrocarbon fraction corresponding to n-triacontane in melting point and elemental composition. Application of gas-liquid chromatography as described by Eglinton *et al.*,³ however, showed it to consist predominantly of C₂₇, C₂₉, and C₃₁ hydrocarbons with smaller amounts of the C₂₈, C₃₀, and C₃₂ homologues. As gas-liquid chromatography cannot be relied upon to separate normal and isoalkanes⁴ the mixture was also subjected to mass-spectrographic analysis. The results indicated that if iso-compounds were present it was only in trace amounts. A complex mixture of aliphatic carboxylic acids was also obtained from the petroleum extracts.

Cold chloroform extracted betulinic acid, which has been previously found in Scrophulariaceæ.⁵ Its identity was confirmed by conversion into betulin and comparison with an authentic specimen. Extraction with water or ethanol gave sodium chloride

¹ Bose and Bose, *J. Indian Med. Ass.*, 1931, **1**, 60; Steinmetz, "Codex Vegetabilis," Amsterdam, 1957; Chopra, "Indigenous Drugs of India," 2nd edn., Dhur, Calcutta, 1958, p. 341.

² Basu and Walia, *Indian J. Pharm.*, 1944, **6**, 84; Basu and Pabrai, *Quart. J. Pharm. Pharmacol.*, 1947, 137.

³ Eglinton, Hamilton, Hodges, and Raphael, *Chem. and Ind.*, 1959, 955.

⁴ Carruthers and Johnstone, *Nature*, 1959, **184**, 1131.

⁵ Retzlaff, *Arch. Pharm.*, 1902, **240**, 561; Maurer, Meier, and Reiff, *Ber.*, 1939, **72**, 1870; Barton and Jones, *J.*, 1944, 659.

and a bitter glycosidic fraction from which no crystalline components resulted after chromatography employing a variety of systems. No well-defined products resulted on hydrolysis with acid or base or with the enzymes emulsin and β -glucosidase. Both the infrared and the ultraviolet spectra of the crude glycoside indicated the absence of steroid cardiac glycosides, which are known to occur in some members of the Scrophulariaceae, e.g., *Digitalis* spp. Extraction of the plant with cold water afforded D-mannitol.

Experimental.—M. p.s were taken on a Kofler block.

Alkaloids. The crude basic material was best isolated by the procedure previously described.² The yield ranged from 20 to 30 mg. per kg. The gummy material was chromatographed on Whatman No. 1 filter-paper sheet, with water saturated with butanol-acetic acid (9:1) as solvent. Four spots were located by their white fluorescence under ultraviolet light⁶ (R_F 0.95, 0.85, 0.7, and 0).

Hydrocarbon fraction. The green residue resulting from the extraction of 20 lb. of finely ground plant material with light petroleum (b. p. 60–80°; 14 l.) was exhaustively extracted with boiling ethanol, to yield a white solid (2.0 g.). This was shaken in light petroleum (b. p. 60–80°) with 4N-sodium hydroxide. The precipitated sodium salts were removed and 0.8 g. of neutral material reclaimed from the organic layer. This was treated with dinitrophenylhydrazine hydrochloride in ethanol to remove traces of material showing infrared carbonyl absorption, and the solution was filtered through alumina (Brockmann grade V). There resulted 0.4 g. of material showing only paraffinic absorption and forming plates, m. p. 65.5–66.5°, from ethyl acetate. Gas-liquid chromatography, with n-hexacosane as standard, showed it to be a mixture of heptacosane, octacosane, nonacosane, triacontane, hentriacontane, and dotriacontane. Mass-spectrographic analysis confirmed this result.

The sodium salts obtained above were reconverted into the acids with 6N-hydrochloric acid, giving a wax, of m. p. 69–71°. A portion was methylated with diazomethane; gas-liquid chromatography showed fourteen components.

Betulinic acid. A cold chloroform extract (3 l.) of 500 g. of the plant material exhausted with light petroleum was reduced in volume to 30 ml. and shaken with 4N-sodium hydroxide. The precipitated sodium salt was collected and the acid regenerated. Crystallisation from ethanol, followed by sublimation, gave material (1.5 g.) of m. p. 302–305°, $[\alpha]_D^{25} + 7^\circ$ (c 1.98 in pyridine) {Robertson *et al.*⁷ report for betulinic acid, m. p. 316–318°, $[\alpha]_D^{25} + 7.9^\circ$ (in pyridine)} (Found: C, 79.3; H, 10.7. Calc. for $C_{30}H_{48}O_3$: C, 78.9; H, 10.6%). The methyl ester, prepared with excess of ethereal-ethanolic diazomethane, formed needles (from ethanol), m. p. 224–225°, $[\alpha]_D^{25} + 6^\circ$ (c 1.95 in pyridine) {lit.,⁷ m. p. 223–224°, $[\alpha]_D^{25} + 8^\circ$ (in pyridine)} (Found: C, 78.9; H, 10.6. Calc. for $C_{31}H_{50}O_3$: C, 79.1; H, 10.6%).

Reduction of the ester by lithium aluminium hydride afforded betulin, identical with authentic material (infrared, mixed m. p.).

D-Mannitol. The residue (10 g.) from an aqueous extract of 500 g. of finely ground plant material was filtered through alumina (Brockmann grade V; 100 g.) in butanol saturated with water. The initial 700 ml. of eluant which contained glycosidic material was rejected. The next 900 ml. on evaporation to dryness and after removal of sodium chloride, afforded D-mannitol (1.1 g.), m. p. 166.5–167° (from ethanol) (lit.,⁸ m. p. 166°) (Found: C, 39.8; H, 7.2. Calc. for $C_6H_{14}O_6$: C, 39.6; H, 7.7%). There was no mixed m. p. depression and the infrared spectrum was correct.

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⁶ Munier and Macheboeuf, *Bull. Soc. Chim. biol.*, 1949, **31**, 1144.

⁷ Robertson, Soliman, and Owen, *J.*, 1939, 1267.

⁸ Fischer, *Ber.*, 1890, **23**, 383.