NOTES.

545. *The Optical Rotation of* (—)-N-1-*Phenylethylphthalamic Acid and Its Salts.*

By F. A. HART and FREDERICK G. MANN.

THE above acid (I) can be readily prepared by the interaction of phthalic anhydride and (—)-1-phenylethylamine in boiling ether, and Mann and Watson [1] record $[M]$ —130° for a 0·559% ethanolic solution. (All rotations are measured with the Na_D light, λ 5893 Å.) The acid should be of considerable value for the optical resolution of bases and appropriate salts, particularly as the (+)-acid is also available. The object of this Note is to point out that the progress of the resolution of a cation by the fractional crystallisation of its phenylethylphthalamate cannot be reliably assessed by the rotation of the salt. This is due to the fact that the order and sign of the rotation of the phthalamate ion depend both on the concentration of the solution and on the nature of the associated cation, even when the latter is itself symmetric.

This first became apparent during attempts to resolve the *As-spiro*-bis-5-chloro*iso*arsindolinium cation (II),[2] the (—)-1-phenylethylphthalamate of which, when once recrystallised from ethanol, had no detectable activity in 0·65% ethanolic solution, and

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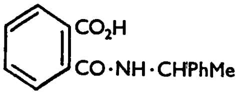
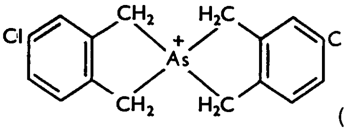
[1] Mann and Watson, *J.*, 1947, 505.

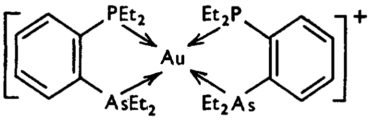
[2] Lyon, Mann, and G. H. Cookson, *J.*, 1947, 662.

when twice recrystallised had $[\alpha]$ +2·7°, $[M]$ +17° in 0·660% solution. The cation (II) in this crop was precipitated as the thiocyanate, which was inactive. In another preparation the phthalamate was recrystallised three times from ethanol, and then was again apparently inactive in 0·511% ethanolic solution. This crop when treated in ethanolic solution with picric acid deposited the arsindolinium picrate, which was inactive, but the mother-liquor showed the (—)-rotation expected of the free phthalamic acid. The reasonable deduction to draw from the optical inactivity of a salt of an optically active acid, namely, that the cation had an activity equal and opposite to that of the anion, is invalid in this case.

A more striking example is that of the (—)-*N*-1-phenylethylphthalamate of the bis-(*o*-diethylphosphinophenyldiethylarsine)aurous cation[3] (III), the initial crop of which, and the crops obtained after two and four recrystallisations, had $[\alpha]$ +10·9°, +11·7°, +12·0°, $[M]$ +116°, +125°, and +128° in 3·106, 2·603, and 1·039% ethanolic solutions respectively. The final crop gave however the inactive picrate of the cation (III).


(I)


(II)


(III)

We have therefore briefly investigated the sodium, ammonium, and potassium salts of the acid (I). These salts were not readily recrystallised in small quantities, and were therefore prepared by careful addition of the ethanolic base (1 mol.) to a cold ethanolic solution of the acid, which was then evaporated to dryness in a vacuum-desiccator at room temperature. The salts had the rotations: Na salt, 1·340% ethanolic solution, $[\alpha]$ +0·56°, $[M]$ +1·6°; NH_4 salt, 1·78% solution in aqueous ethanol (13 : 87 by vol.), $[\alpha]$ —3·65°, $[M]$ —10·5°; K salt, 1·3999 and 4·197% ethanolic solutions, $[\alpha]$ —13·8° and —21·3°, $[M]$ —42° and —66° respectively. The rotation of the potassium salt solution remained unchanged when set aside for 24 hr. at room temperature. The rotations of these salts cannot be affected by asymmetric transformation in solution.

Although a change in the order or even in the sign of the rotation of a compound with change in concentration is not uncommon (cf. 2-amino-*n*-octane hydrochloride[4]), it is unusual for such a change in the rotation of an ion to be caused by the nature of the opposite ion. We suggest tentatively that in the phthalamate ion the slight positive charge on the nitrogen atom (which is normal for amide groups) may cause an appreciable electrostatic attraction between this atom and the negative oxygen of the carboxylate ion (IV). The rotation of this " bonded " ion would very probably be different from that of the unbonded ion. It is highly probable that in solution an equilibrium would exist between these two forms, and the rather delicate electronic equilibrium which determines this would almost certainly be affected by the concentration of the solution, and by the size and nature of the cation, *i.e.*, by the intensity of the positive charge on the periphery of the cation.

An alternative explanation, namely, that the positive charge on the nitrogen atom and the consequent increase in the acidic nature of the hydrogen atom to which it is attached may promote hydrogen bonding (V), and that the equilibrium in solution is between this

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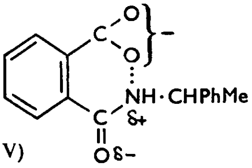
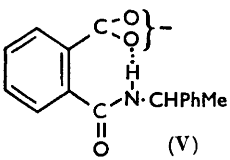
[3] Cochran, Hart, and Mann, preceding paper.

[4] Mann and Porter, *J.*, 1944, 456.

" bonded " ion and the unbonded ion, receives little support from the infrared spectrum of the carefully dried potassium salt. Dr. N. Sheppard reports: " The spectrum of this


(IV)


(V)

salt showed the following absorption bands (cm.$^{-1}$) which could be correlated with the presence of functional groups.

(*a*) –CO·NH–	3240	NH stretching frequency
	1640	C=O „ „ in amide (amide I)
	1568	NH deformation frequency (amide II)
(*b*) $-CO_2^-$	1590, 1384	Stretching vibrations of this ion

A particularly strong hydrogen bond between the NH linkage of the amide group and the $\cdot CO_2^-$ group would be expected to give an abnormally low NH stretching frequency and perhaps a high NH deformation frequency for the ·CO·NH· group. The NH stretching frequency is in fact just outside the lower limit of the generally accepted range for this vibration (3320—3270 cm.$^{-1}$);[5] the NH deformation frequency is towards the high end of the usual range (1570—1515 cm.$^{-1}$).[5] Although these observations do suggest that the NH bond is rather more strongly hydrogen-bonded than is usual in amides, the effect is not marked. The possibility cannot be ruled out that the hydrogen bonding present is that of the ordinary amide-to-amide intermolecular type rather than that of the intramolecular type (V). The spectrum of the sodium salt is virtually identical with that of the potassium salt throughout the above regions."

Experimental.—Salts of the (–)-*acid* (I). The potassium salt, prepared as above, formed deliquescent crystals, which were dried at 50°/0·01 mm. The sample used for the infrared spectrum determination was handled in a dry-box immediately after drying, and the spectrum indicated the presence of only traces of water. The elementary analysis of another portion of this sample indicated the presence of a hemihydrate, although this may have been fortuitous, in spite of the precautions taken during the analytical manipulation (Found: C, 60·5, 60·8; H, 4·7, 4·9; N, 4·4. Calc. for $C_{16}H_{14}O_3NK$: C, 62·5; H, 4·6; N, 4·6. $C_{16}H_{14}O_3NK,\frac{1}{2}H_2O$ requires C, 60·7; H, 4·7; N, 4·4%). The *sodium salt*, similarly prepared and dried, was not deliquescent (Found: C, 65·2; H, 5·0; N, 4·8. $C_{16}H_{14}O_3NNa$ requires C, 65·8; H, 4·8; N, 4·8%).

We thank the Department of Scientific and Industrial Research for a grant (to F. A. H.).

THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, January 22nd*, 1957.]

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[5] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen, London, 1954, p. 176.

546. *Compounds of Silicon. Part II.* The Reaction of Silicon Halides with Diazoalkanes.*

By R. A. Shaw.

The diazo-alkane method of alkylenation has been successfully employed with silicon tetrachloride and tetrabromide, methyltrichlorosilane,[1] and trichlorosilane,[2] $SiX_4 + CHRN_2 \longrightarrow SiX_3{\cdot}CHRX + N_2$, but with silicon tetrafluoride,[1] triethyl-,[1] trimethyl-,[2] and triphenyl-chlorosilane,[2] and tetraethoxysilane [2] it failed to give the desired organo-silicon products. Yakubovich and his co-workers [1] suggested a free-radical mechanism involving initial formation of an alkylene biradical $CHR\colon$, which then attacked the silicon–halogen bond. Seyferth [3] prefers a polar mechanism, pointing out that all metals whose halides undergo alkylenation possess available *d*-orbitals, and that a primary co-ordination step is possible.

The present work agrees with the latter mechanism. Whilst silicon tetrachloride with diazomethane in ether with or without a copper catalyst gave chloromethyltrichlorosilane in reasonable to good yields (with boron trifluoride as catalyst only " polymethylene " was obtained), reaction in *n*-pentane was much slower and yielded only " polymethylene." The solvating power of the medium therefore exerts a powerful effect on the rate as well as on the course of this reaction. Strong inhibition of a free-radical reaction would not be expected on passing from a polar to a non-polar solvent (provided no interaction with the solvent took place), whilst reduction in rate, or complete suppression, of a heterolytic reaction in the latter solvent is acceptable.

The increase in steric screening in the series SiX_4, $SiRX_3$, SiR_2X_2, SiR_3X invoked by Yakubovich and his co-workers to account in part for the slower alkylenation [1] and hydrolysis in this series, is hardly applicable as the larger chloro- and bromo-methyl derivatives are much more reactive towards diazomethane than are the corresponding methyl compounds. The reason for the smaller reactivity of, *e.g.*, methyltrichlorosilane than of trichlorochloromethylsilane towards diazomethane arises therefore from the greater electron-density on the silicon atom in the former compound, which hinders the approach of a nucleophilic reagent.[3] Further evidence for the polar mechanism is the reaction of trichlorosilane with diazomethane,[2] which gives dichlorochloromethylsilane (*i.e.*, reaction of a Si–Cl bond) in excellent yield : in well-established free-radical reactions trichlorosilane suffers fission of its Si–H bond when it adds to olefins,[4] perfluoro-olefins,[5] or acetylenes.[6]

The homopolar and " ionic bond energies " [7] of the Si–X bonds discussed, explain many of the reported results. Whilst these figures (see Table) cannot be considered strictly quantitative, and do not permit comparisons between the two types of bond energies (because of the effects of the other groups attached to the silicon atom, and because of solvation effects), within each type they provide a reasonable qualitative order of the energies required to heterolyse or homolyse Si–X bonds. Thus whilst Si–C and Si–H bonds are weaker than the Si–Cl bond, their " ionic bond energies " are much greater than

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* Part I, *J.*, 1956, 2779.

[1] Yakubovich, Makarov, Ginsburg, Gavrilov, and Merkulova, *Doklady Akad. Nauk S.S.S.R.*, 1950, **72**, 69; *Chem. Abs.*, 1951, **45**, 2865; Yakubovich and Ginsburg, *Zhur. obshchei Khim.*, 1952, **22**, 1783; *Chem. Abs.*, 1953, **47**, 9256.

[2] Seyferth and Rochow, *J. Amer. Chem. Soc.*, 1955, **77**, 907.

[3] Seyferth, *Chem. Rev.*, 1955, **55**, 1155.

[4] Sommer, Pietrusza, and Whitmore, *J. Amer. Chem. Soc.*, 1947, **69**, 188; Barry, DePree, Gilkey, and Hook, *ibid.*, p. 2966.

[5] Haszeldine and Marklow, *J.*, 1956, 962.

[6] Burkhard and Krieble, *J. Amer. Chem. Soc.*, 1947, **69**, 2687.

[7] Eaborn, *J.*, 1950, 3077.

that of the Si–Cl bond, and thus the lack of methylenation of the Si–H bond in trichlorosilane,[2] and of the Si–C bond in, *e.g.*, methyltrichlorosilane,[1] as well, of course, as of the Si–O bond in tetraethoxysilane,[2] is readily explained.

Bond Si–X	Homopolar bond energy (kcals.) [8]	" Ionic bond energy " (kcals.) *	Bond Si–X	Homopolar bond energy (kcals.) [8]	" Ionic bond energy " (kcals.) *
Si–I	55·0	167·4	Si–C≡	75·0	222·9
Si–Br	73·5	179·0	Si–F	134·0	237·4
Si–Cl	90·3	190·3	Si–O–	106·0	242·4
Si–S–	60·9	192·7	Si–H	79·9	249·8

* Calc. from electron affinities given by Pritchard and Skinner.[9]

The reaction of trimethylchlorosilane with 9-diazofluorene has been investigated in the presence of copper bronze in ether and pyridine solutions. From the ether solution only di-9-fluorenylidene was isolated, but when pyridine was used in the hope that the more polar solvent would facilitate Si–Cl heterolysis dipyridinecupric chloride [10] and fluorenone azine were obtained. Karrer and his co-workers [11] have reported that organic and inorganic acid chlorides dissolve copper bronze at room temperature on addition of dry pyridine in a few seconds, the above-mentioned copper derivative being one of the products. This reaction provides yet another example of the similar chemical behaviour of silicon and acyl halides.[12]

Experimental.—A column of approx. six theoretical plates was employed for fractional distillation.

Ether and *n*-pentane for dissolving the silicon halides (fractionally distilled before each experiment) were dried with sodium wire. The pyridine was dried first over potassium hydroxide and then by azeotropic distillation.

Diazomethane was prepared in ether or *n*-pentane from methylnitrosourea,[13] dried, and standardised.[8]

Unless otherwise stated, yields of halogenoalkylsilanes are based on diazomethane.

Reactions of silicon tetrachloride with diazomethane. (*a*) Silicon tetrachloride (82 g., 0·48 mole) in ether (100 ml.) was cooled to −50° and diazomethane (10·9 g., 0·26 mole) in ether (500 ml.) was added dropwise (3 hr.) with stirring. A few minutes later the solution became colourless. It was allowed to warm to room temperature, kept overnight, decanted from a trace of " polymethylene," and fractionally distilled, to give silicon tetrachloride (31 g., 38%), b. p. 56—58°, and trichlorochloromethylsilane (13 g., 46%), b. p. 112—113°.

(*b*) By the same procedure, but at −78°, silicon tetrachloride (27%) and trichlorochloromethylsilane (46%) were obtained.

(*c*) By the same procedure as under (*b*), in the presence of copper bronze, silicon tetrachloride (34·5%) and trichlorochloromethylsilane (62%) were obtained.

(*d*) To a solution of silicon tetrachloride (74 g., 0·435 mole) in ether (100 ml.) at −78° were added boron trifluoride (1 ml. of N-ether solution), and then diazomethane (9·5 g., 0·225 mole) in ether (500 ml.) (1 hr.). The reaction was vigorous and " polymethylene " (1·9 g., 63%) was precipitated. The filtrate yielded silicon tetrachloride (57 g., 77%), but no trichlorochloromethylsilane.

(*e*) To a solution of silicon tetrachloride (84 g., 0·49 mole) in *n*-pentane (100 ml.) at −50° was added dropwise (3 hr.) with stirring diazomethane (6·9 g., 0·165 mole) in *n*-pentane (500 ml.). Reaction was very slow, with formation of a white precipitate. After a further 3 hr. at −50°, the solution was allowed to warm to room temperature, kept for 3 days, and then filtered with exclusion of moisture. " Polymethylene " (1·85 g., 80%) was obtained. The filtrate yielded silicon tetrachloride (66 g., 79%) but no trichlorochloromethylsilane.

[8] Gilman and Dunn, *Chem. Rev.*, 1953, **52**, 77.

[9] Pritchard and Skinner, *ibid.*, 1955, **55**, 745.

[10] Lang, *Ber.*, 1888, **21**, 1580; Cox, Sharratt, Wardlaw, and Webster, *J.*, 1936, 129.

[11] Karrer, Wehrli, Biedermann, and Vedova, *Helv. Chim. Acta*, 1928, **11**, 233.

[12] Shaw, Thesis, London, 1955; *J.*, 1956, 2779; Hughes, personal communication; Eaborn, personal communication.

[13] Arndt, *Org. Synth.*, 1947, Coll. Vol. II, p. 165.

Reaction of trimethylchlorosilane with 9-*diazofluorene.* (*a*) Excess of trimethylchlorosilane (2·5 ml.) in ether (10 ml.) was added to 9-diazofluorene [14] (0·78 g.) in ether (50 ml.). No apparent reaction occurred. After 1 hr. copper bronze (0·05 g.) was added; nitrogen evolution then lasted for 1 hr. After a further 2 hr., the solution was filtered, and the filtrate concentrated to give deep orange-red needles of di-9-fluorenylidene (0·28 g., 43%), m. p. and mixed m. p. 189—190°.

(*b*) Trimethylchlorosilane (2·5 g., 0·023 mole) was distilled into a solution of 9-diazofluorene (3·0 g., 0·0156 mole) in pure, dry pyridine (50 ml.). Copper bronze (0·5 g.) was added. Gas evolution occupied 24 hr., and the solution became dark. It was kept at room temperature for 72 hr. Decantation left a mixture of purple and blue crystals. Extraction with boiling benzene removed the purple compound, which on recrystallisation from the same solvent gave purple fluorenone azine (0·11 g., 4%), m. p. and mixed m. p. 271—272°. Blue dichroic needles of dipyridinocupric chloride (1·1 g., 48%) remained (Found: N, 9·6; Cl, 24·45; Cu, 21·4. Calc. for $C_{10}H_{10}N_2Cl_2Cu$: N, 9·6; Cl, 24·2; Cu, 21·7%). Optical, morphological, and *X*-ray examinations (for which we thank Dr. C. H. Carlisle) show that they are identical with a specimen prepared according to directions by Cox *et al.*[10]

The author is grateful to Professor W. Wardlaw, C.B.E., D.Sc., for his encouragement.

BIRKBECK COLLEGE, MALET STREET, LONDON, W.C.1. [*Received, October 12th,* 1956.]

[14] Schönberg, Awad, and Latif, *J.*, 1951, 1368.

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547. *Methyl* 3 : 6-*Anhydro*-2-O-*methyl*-α-D-" *altropyranoside* " (-*mannopyranoside*).

By A. B. FOSTER.

THE action of methanolic sodium methoxide on methyl 4 : 6-di-*O*-benzoyl-2-*O*-methyl-3-*O*-toluene-*p*-sulphonyl-α-D-altropyranoside (I) has been reported [1] to yield methyl 3 : 6-anhydro-2-*O*-methyl-α-D-altropyranoside. Reactions which involve the formation of anhydro-rings from toluene-*p*-sulphonyl derivatives usually occur with Walden inversion at the carbon atom which carries the toluene-*p*-sulphonyloxy-residue.[2] Further, a study of models shows that only four methyl 3 : 6-anhydro-D-hexopyranosides are structurally

An identical product was obtained on methylation of methyl 3 : 6-anhydro-α-D-mannopyranoside (V). There can be little doubt about the structure of the latter compound which is usually prepared by the action of alkali on 6-halogeno-6-deoxy, or 6-toluene-*p*-sulphonyl derivatives of methyl α-D-mannopyranoside.[5–7]

Experimental.—Methyl 3 : 6-*anhydro*-2-O-*methyl*-α-D-*mannopyranoside*. A solution of methyl 2-*O*-methyl-3-*O*-toluene-*p*-sulphonyl-α-D-altropyranoside {2 g., m. p. 117—118°, $[\alpha]_D$ +87° (*c*, 1·28 in $CHCl_3$). Robertson and Whitehead [1] quote m. p. 118°, $[\alpha]_D$ +88·1° in $CHCl_3$, for this compound} in methanol (60 ml.) in which sodium (0·3 g.) had been dissolved was boiled under reflux for 5 hr. Thereafter the solution was diluted with water (60 ml.), neutralised with dilute sulphuric acid, and evaporated under diminished pressure. The residue was extracted with hot chloroform (100 ml.), the extract dried ($MgSO_4$) and evaporated, and the solid residue recrystallised from chloroform–ether, giving methyl 3 : 6-anhydro-2-*O*-methyl-α-D-mannopyranoside (0·29 g., 28%) in prisms, m. p. 105—106°, $[\alpha]_D$ +103° (*c*, 1·5 in $CHCl_3$). Robertson and Whitehead [1] report m. p. 107—108°, $[\alpha]_D$ 105·1° in $CHCl_3$, for the product obtained by the action of alkali on methyl 4 : 6-di-*O*-benzoyl-2-*O*-methyl-3-*O*-toluene-*p*-sulphonyl-α-D-altropyranoside.

Methyl 3 : 6-*anhydro*-2 : 4-*di*-O-*methyl*-α-D-*mannopyranoside*. (*a*) Methyl 3 : 6-anhydro-2-*O*-methyl-α-D-mannopyranoside (1·02 g.) was added during 1 hr. to liquid ammonia (30 ml.), in which sodium (0·4 g.) had been dissolved. Methyl iodide (4 ml.) was then added during 30 min. (vigorous mechanical agitation was maintained throughout) and after a further 30 min. the ammonia was evaporated and the residue extracted several times with ether. Evaporation of the combined extracts and crystallisation of the residue from ether at −30°, with seeding, gave methyl 3 : 6-anhydro-2 : 4-di-*O*-methyl-α-D-mannopyranoside (0·5 g., 43%) as square plates, m. p. 31—32°, $[\alpha]_D$ +104·1° (*c*, 1·4 in H_2O) (Found : OMe, 46·2. $C_9H_{16}O_5$ requires OMe, 45·6%). Robertson and Whitehead obtained this compound as a syrup, $[\alpha]_D$ +69° (in $CHCl_3$).

(*b*) Methyl 3 : 6-anhydro-α-D-mannopyranoside (1·35 g., prepared by Dr. W. J. G. Jones) was methylated as in (*a*) to yield a di-*O*-methyl derivative (1·15 g., 73%), m. p. 32—33°, $[\alpha]_D$ +101·2° (*c*, 1·0 in H_2O) (Found : OMe, 46·4%). The m. p. of a mixture with the product from (*a*) was 31—32°.

The author thanks Professor F. Smith and Professor M. Stacey, F.R.S., for their interest.

Chemistry Department, The University,
Edgbaston, Birmingham, 15.

[*Received, December 27th*, 1956.]

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[6] Haskins, Hann, and Hudson, *J. Amer. Chem. Soc.*, 1946, **88**, 628.
[7] Foster, Overend, Stacey, and Vaughan, *J.*, 1954, 3367.

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548. *The Use of Equilibrium Constants to calculate Thermodynamic Quantities. Part III.* Equilibria in the System* tert.*-Butyl Bromide–*iso*Butene–Hydrogen Bromide.*

By K. E. Howlett.

Equilibria in the gaseous system *tert.*-butyl bromide–*iso*butene–hydrogen bromide were studied by Kistiakowsky and Stauffer.[1] This work has been repeated because discrepancies had been found between our earlier results [2] and those of Kistiakowsky and Stauffer for the corresponding chloride system.

Experimental.—The technique is described in Part I.[2] Glass wool is a satisfactory catalyst for attainment of equilibrium in the decomposition of *tert.*-butyl bromide. *tert.*-Butyl bromide was prepared by Bryce-Smith and Howlett's method [3] and had b. p. 72·8°, f. p. −16·3°, n_D^{25}

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* Part II, *J.*, 1955, 1784.

[1] Kistiakowsky and Stauffer, *J. Amer. Chem. Soc.*, 1937, **59**, 165.
[2] Howlett, *J.*, 1951, 1409.
[3] Bryce-Smith and Howlett, *J.*, 1951, 1141.

1·4249. It was stored in the dark at −80° when not being distilled into the reaction chamber. In order to obviate errors arising from pressure measurements on non-ideal gases, all experiments were made at pressures of 40—90 mm. at 100—210°. Under these conditions differences between fugacities and pressures are within experimental error. To facilitate comparison with the earlier work,[1] the newly observed equilibrium constants (Table 1) are calculated in atm. units, by considering *tert.*-butyl bromide to be the product of reaction.

TABLE 1.

Temp.	99·7°	100·3°	110·4°	131·5°	155·5°	210·4°
Mean K_p (atm.$^{-1}$) *	883	843	441	110	28·1	3·14
Mean error (No. of expts. in parentheses)	12(8)	14(3)	6(5)	1·6(5)	0·1(3)	0·06(3)

* Since K_p varies in a logarithmic manner with T, the mean values of K_p were obtained by averaging $\log_{10} K_p$ at each temperature.

In the *tert.*-butyl bromide–*iso*butene–hydrogen bromide system, our results agree closely with those of Kistiakowsky and Stauffer. The combined results can therefore be summarised by the method detailed in " Handbuch der Physik "[4] in the form

$$\log_{10} K_p = (18850 \pm 140)/4{\cdot}575T - (8{\cdot}12 \pm 0{\cdot}06)$$

Thus ΔH_{415} is 18,850 cal. mole^{-1} and ΔS_{415} is 37·14 where 415° K is the mean temperature at which observations were made. By combining ΔH with $\Delta H_f{}^\circ{}_{415}$ for hydrogen bromide * (−8·40 kcal. mole^{-1}) and $\Delta H_f{}^\circ{}_{415}$ for *iso*butene[5] (−4·93 kcal. mole^{-1}), $\Delta H_f{}^\circ{}_{415}$ for *tert.*-butyl bromide is calculated to be −32·18 kcal. mole^{-1}. Similarly, by combining ΔS_{415} with $S^\circ{}_{415}$ for hydrogen bromide[6] (49·78) and $S^\circ{}_{415}$ for *iso*butene[7] (78·19), $S^\circ{}_{415}$ for *tert.*-butyl bromide is found to be 90·83.

Sheppard[8] has assigned the fundamental vibration frequencies (excluding internal rotational modes) for *tert.*-butyl bromide, and Williams and Gordy[9] have deduced from its microwave absorption a value for the two (equal) large moments of inertia (I_B and I_C) of the molecule. The other moment (I_A) was calculated in Part II. From the results the statistical entropy of the rigid molecule can be calculated and hence the entropy due to hindered rotation (S_{hr}) may be deduced by comparison with the value 90·83 obtained above. This entropy can be used in conjunction with the reduced moment of inertia (I_m) of each methyl group and Pitzer and Gwinn's tables[10] to determine the potential (V) hindering free rotation of each methyl group. The relevant figures are: Moments of inertia (g. cm.^{2} × 10^{40}): I_A, 185·0; I_B, 412·1; I_C, 412·1; I_m, 5·251: Entropy components at 415° K: S_v 13·77; S_{t+r} 68·33; S° 90·83; S_{hr} 8·73; $V = 3100$ cal. mole^{-1}. The value of the hindering potential is clearly of the correct order of magnitude. It has therefore been used in the calculation of some of the thermodynamic functions for *tert.*-butyl bromide over the temperature range 298—700° K (see Table 2).

TABLE 2. *Entropies, specific heats, and heats of formation in the gas phase.*

Temp. (K)	298·16°	400°	500°	600°	700°
S°	80·52	89·55	97·77	105·4	112·5
$C_p{}^\circ$	27·88	34·15	39·48	43·97	47·78
$\Delta H_f{}^\circ$ (kcal. mole^{-1})	−30·48	−31·99	−33·09	−33·88	−34·43

Further, as indicated in Part II, the results can be used to deduce a value

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* The value appropriate to 25° given by Partington (" An Advanced Treatise on Physical Chemistry," Longmans, London, 1949), corrected by means of Kirchhoff's equation.

[4] " Handbuch der Physik," Springer, Berlin, 1928, Vol. 3, Chap. 13.

[5] Kilpatrick, Prosen, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 559.

[6] Gordon and Barnes, *J. Chem. Phys.*, 1933, **1**, 692.

[7] Kilpatrick and Pitzer, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 163.

[8] Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 527.

[9] Williams and Gordy, *J. Chem. Phys.*, 1950, **18**, 994.

[10] Pitzer and Gwinn, *ibid.*, 1942, **10**, 428.

of 59·6 kcal. mole^{-1} at 25° for the bond dissociation energy of the C–Br bond in *tert.*-butyl bromide; and comparison with the data for the rate constants for unimolecular decomposition [11] of *tert.*-butyl bromide gives the rate constants for homogeneous bimolecular addition of hydrogen bromide to *iso*butene to be $k = 10^{7.4} \exp(-24{,}000/\mathbf{R}T)$ l. mole^{-1} sec.$^{-1}$

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[11] Harden and Maccoll, *J.*, 1955, 2454.

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549. *Chromatography of Polynitronaphthylamines.*

By E. R. WARD and P. R. WELLS.

LARSON and HARVEY [1] found that mixtures of nitroanilines and mixtures of certain isomeric substituted nitroanilines could be separated quantitatively by chromatography. Hunter [2] (cf. Larson and Harvey [1]) suggested that these results could be explained in relation to the possibility of the occurrence of intramolecular hydrogen bonding, and the relative stability of the resulting structure. As Hoyer [3] found, among isomers the one which can form a chelated hydrogen-bonded structure is most weakly adsorbed.

We now find that this method, with minor modifications, can be applied successfully to the separation of mixtures of di- and/or tri-nitronaphthylamines, but fails with all mixtures of mononitronaphthylamines so far examined (cf. Dean,[4] and Ward and Coulson [5]). Mixtures of related compounds, *e.g.*, 7-nitro-1-naphthylamine and 2 : 4-dibromo-7-nitro-1-naphthylamine, have also been so separated. Most of our mixtures arose from the hydrolysis of nitrated *N*-acylnitronaphthylamines and the method has made it possible to determine the relative proportions of isomers arising in such nitrations. Furthermore we have separated completely mixtures which contain one or more isomers in relatively small concentration, *e.g.*, that of dinitronaphthylamines arising from the mononitration of *N*-acetyl-3-nitro-2-naphthylamine. Since the hydrolysis product invariably contains appreciable amounts of side-products (in the case of hydrolysed-polynitro-*N*-phthaloylnaphthylamines possibly half the material) two chromatographic treatments are usually required, the first removing side-products (which are usually much more strongly adsorbed) and crudely separating the mixture, the second yielding pure nitro-amines. The separations of polynitronaphthylamines are much facilitated by there usually being appreciable differences in the colours of the products.

Although we agree with Hunter [2] that chelation is a major factor we also find that others must be taken into account. Thus separations 1, 2, 3, and 11 are explained completely by chelation (steric inhibition of chelation intervening in 11) but against this there is the outstanding case of the failure to separate the chelated 2-nitro-1-naphthylamine from the non-chelated 4-nitro-1-naphthylamine. Furthermore the chelated 1 : 6-dinitro-2-naphthylamine (separation 7) is more strongly adsorbed than the two 6 : *x*-dinitro-2-naphthylamines which cannot possibly be more chelated and are almost certainly not chelated. Solubility differences should account for the separation of dinitronaphthylamines from trinitronaphthylamines (separations 8, 9, and 10) and must certainly intervene in other cases (*e.g.*, 14). Separations 4, 6, and 12 might be explained by differences in basicity, chelation effects being absent or being taken as equivalent. In separation 5 it

[1] Larson and Harvey, *Chem. and Ind.*, 1954, 45.
[2] Hunter, " Progress of Stereochemistry," Butterworths, London, 1954, Vol. 1, p. 232.
[3] Hoyer, *Z. Electrochem.*, 1950, **54**, 413.
[4] Dean, Thesis, London, 1952.
[5] Ward and Coulson, *J.*, 1954, 4541.

is reasonable to assume that the least strongly adsorbed compound, 1 : 3-dinitro-2-naphthylamine, is the most strongly chelated of the three and that the other dinitronaphthylamines are separable by virtue of differences in basicity.

Experimental.—General procedure. The method followed was largely that of Larson and Harvey. The hydrolysed nitration products were usually dissolved in benzene but, where they were not readily soluble, mixtures of benzene and ethyl acetate were employed, thus restricting the volume of the initial solution. The columns were developed to produce separate coloured bands with benzene or benzene–ethyl acetate in varying proportions, each band was then separately eluted in several fractions with similar solvents (the concentration of ethyl acetate usually being progressively increased according to the observed rate of elution). The composition of each fraction was judged by the colour of the solid obtained by evaporation, m. p., and mixed m. p. Where required selected fractions were bulked together and rechromatographed to give a complete separation. In one case satisfactory elution was obtained with benzene–ethanol but in general ethanol was not a satisfactory eluant since it tended to elute side-products which normally remained at the top of the column with the alternative solvents. As frequently reported,[1, 4, 6] we found acetone to be an unsatisfactory solvent.

No.	Mixture in order of elution			Ratio *	Solvents †		
					Orig.	Develop.	Eltn.
1	2 : 5-$(NO_2)_2$-1	4 : 5-$(NO_2)_2$-1		1 : 2	C 3 : 1	C 3 : 1	C 1 : 1, B
2	2 : 7-$(NO_2)_2$-1	4 : 7-$(NO_2)_2$-1		1 : 2	A	D 4 : 1	D 4 : 1, D 4 : 1
3	3 : 8-$(NO_2)_2$-1	3 : 5-$(NO_2)_2$-1		1 : 1	A	C 9 : 1	C 9 : 1, C 3 : 2
4	3 : 8-$(NO_2)_2$-2	3 : 5-$(NO_2)_2$-2		1 : 1	C 9 : 1	C 6 : 1	C 4 : 1, C 1 : 1
5	1 : 3-$(NO_2)_2$-2	3 : 8-$(NO_2)_2$-2	3 : 6-$(NO_2)_2$ 2	15 : 3 : 2	A	A	A; C 8 : 1, C 5 : 1; B
6	4 : 8-$(NO_2)_2$-2	4 : 5-$(NO_2)_2$-2		1 : 1	C 6 : 1	C 3 : 1	C 1 : 1, C 1 : 1
7	6 : x-$(NO_2)_2$-2 ‡	6 : y-$(NO_2)_2$-2	1 : 6-$(NO_2)_2$-2	2 : 1 : 9	C 9 : 1	C 3 : 1	C 3 : 1, C 3 : 1, C 3 : 1
8	2 : 5-$(NO_2)_2$-1	2 : 4 : 5-$(NO_2)_3$-1		1 : 1	C 2 : 1	C 2 : 1	C 2 : 1, C 2 : 1
9	2 : 7-$(NO_2)_2$-1	2 : 4 : 7-$(NO_2)_3$-1		3 : 4	A	A	C 4 : 1, C 2 :1
10	2 : 7-$(NO_2)_2$-1	4 : 7-$(NO_2)_2$-1	7 : x : x-$(NO_2)_3$-1 §	1 : 4 : 4	C 9 : 1	C 9 : 1	C 9 : 1, C 9 : 1, C 3 : 1
11	1 : 3 : 5-$(NO_2)_3$-2	1 : 3 : 8-$(NO_2)_3$-2		19 : 16	A	C 9 : 1	C 9 : 1, C 4 : 1
12	1-Br-3-(NO_2)-2	3-(NO_2)-2		1 : 1	A	A	C 8 : 1, C 5 : 1
13	2 : 4-Br_2-7-(NO_2)-1	7-(NO_2)-1		7 : 1	A	C 9 : 1	C 9 : 1, C 9 : 1
14	1-Br-3-(NO_2)-2	1 : 6-Br_2-3(NO_2)-2		1 : 1	A	A	A, C 4 : 1

* Approximate ratio of components of mixture as isolated from the column.

† A Benzene, B ethyl acetate, C benzene–ethyl acetate in proportions (v/v) indicated, D benzene–ethanol. The eluting solvents are given in the order in which they eluted the respective amines.

‡ x and y are probably 4 or 8. § Probably 4 : 5 : 7-trinitro-1-naphthylamine.

The following mixtures of nitronaphthylamines could not be separated: 2-nitro-1-naphthylamine and 4-nitro-1-naphthylamine, 5-nitro-2-naphthylamine and 8-nitro-2-naphthylamine, 3-nitro-1-naphthylamine and 4-nitro-2-naphthylamine. *N*-Acetyl-2 : 3-dinitro-1-naphthylamine could not be separated from *N*-acetyl-3 : 4-dinitro-1-naphthylamine, but 3 : 4-dinitro-1-naphthylamine and *N*-acetyl-2 : 3-dinitro-1-naphthylamine were readily separated.

The authors thank Dr. T. M. Coulson, B.Sc., who made the initial experiments, J. Pierce, M.Sc., and A. Hardy, M.Sc., for experimental assistance, and the Department of Scientific and Industrial Research for a maintenance grant (to P. R. W.).

LEICESTER COLLEGE OF TECHNOLOGY AND COMMERCE,
LEICESTER.
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[6] Fuhrmann, *J. Recherches Centr. nat. Recherche sci., Labs Bellevue (Paris)*, 1953, No. 25, pp. 257, 258; *Chem. Abs.*, 1954, **48**, 7983.

550. *2-Acetamido-2-deoxy-*D*-galactitol* ("N*-Acetyl-*D*-galactosaminol*").

By W. R. C. Crimmin.

This note records the preparation and characterisation of 2-acetamido-2-deoxygalactitol (*N*-acetylgalactosaminol), which was required as a reference compound in structural studies of oligosaccharides derived from blood-group mucopolysaccharides.[1] 2-Acetamido-2-deoxy-D-sorbitol (*N*-acetyl-D-glucosaminol) was prepared by catalytic hydrogenation of 2-acetamido-2-deoxy-α-D-glucopyranose [2] but the corresponding aminodeoxygalactitol has not been described. Sodium borohydride [3] was used for reduction of 2-acetamido-2-deoxy-α-D-galactopyranose; the crystalline galactitol was isolated in reasonable yield and was further characterised as the penta-*O*-acetyl derivative.

Experimental.—*2-Acetamido-2-deoxy-*D*-galactitol.* Sodium borohydride (0·5 g.) in water (20 ml.) was added slowly with occasional shaking to 2-acetamido-2-deoxy-α-D-galactopyranose (0·8 g.) in water (15 ml.) at 0°. The mixture was kept at 0° for 30 min. and at room temperature for 2 hr. Excess of borohydride was then destroyed with 4N-hydrochloric acid. The solution was concentrated *in vacuo* and the borate removed as the methyl ester by distillation.[4] The residue was dissolved in water, and de-ionised with Biodeminrolite resin (carbonate form). The solution was again concentrated, and the residue crystallised from water–acetone (1 : 1 v/v) by addition of light petroleum to incipient crystallisation. The product (400 mg.) had m. p. 174—176°, $[\alpha]_D = -42°$ (*c* 0·353 in H_2O) (Found: C, 42·8; H, 7·7; N, 6·2. $C_8H_{17}O_6N$ requires C, 43·0; H, 7·7; N, 6·3%). Paper chromatographic analysis in pyridine–ethyl acetate–water–acetic acid (5 : 5 : 3 : 1 v/v) showed a single component having the same R_F value as 2-acetamido-2-deoxygalactopyranose and a positive reaction to periodate–benzidine [5] reagent but a negative one to benzidine [6] and ninhydrin [7] reagents.

*Penta-*O*-acetyl derivative.* 2-Acetamido-2-deoxygalactitol (80 mg.) was acetylated with sodium acetate–acetic anhydride. Crystallisation from methanol gave *2-acetamido-1 : 3 : 4 : 5 : 6-penta-*O*-acetyl-2-deoxy-*D*-galactitol* (60 mg.), m. p. 176—178°, $[\alpha]_D = +15°$ (*c* 0·532 in $CHCl_3$) (Found: *O*-acetyl,[8] 49·7. $C_{18}H_{27}O_{11}N$ requires 49·7%).

Hydrochloride. The galactitol (50 mg.) in N-hydrochloric acid (6·5 ml.) was heated in a sealed ampoule for 5 hr. The solution was taken to dryness and gave an uncrystallisable syrup, $[\alpha]_D = -9°$ in water. Chromatographic analysis on paper showed a single component having the same R_F value as 2-amino-2-deoxygalactose hydrochloride; while giving positive reactions to periodate–benzidine, ninhydrin, and silver nitrate–sodium hydroxide [9] reagents the hydrochloride was negative to aniline–diphenylamine [10] reagent.

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[1] Côté and Morgan, *Nature*, 1956, **178**, 1171.
[2] Karrer and Meyer, *Helv. Chim. Acta*, 1937, 20, 626.
[3] Whelan and Morgan, *Chem. and Ind.*, 1955, 1449.
[4] Khym, Zill, and Cheniae, *J. Amer. Chem. Soc.*, 1953, **75**, 1339.
[5] Cifonelli and Smith, *Analyt. Chem.*, 1954, **26**, 1132.
[6] Bacon and Edelman, *Biochem. J.*, 1951, **48**, 114.
[7] Toennies and Kola, *Analyt. Chem.*, 1951, **23**, 823.
[8] Wolfrom, Konigsberg, and Soltzberg, *J. Amer. Chem. Soc.*, 1936, **58**, 490.
[9] Trevelyan, Proctor, and Harrison, *Nature*, 1950, **166**, 444.
[10] Buchan and Savage, *Analyst*, 1952, **77**, 401.

551. *Influence of* ortho-*Substituents on the Stretching Frequencies of Side-chain Carbonyl Groups in Substituted Benzenes.*

By D. G. O'Sullivan and P. W. Sadler.

Nucleophilic reactions, and certain other properties, of the side chain of a substituted benzene are influenced by *meta-* or *para*-substituents in a manner which can be related to the σ-values [1] of the latter substituents. The effect of an *ortho*-substituent is complicated, steric and field factors being superimposed, to varying extents, on polar effects. Attempts to determine polar effects of *ortho*-substituents, and consequently to assess the magnitude of other influences producing specific *ortho*-effects, always involve the adoption of some basic assumption which, although plausible, is never certain. Thus McDaniel and Brown [2] assumed that proton-acceptance by certain substituted pyridines provides a nearly ideal reference system for the estimation of purely polar contributions of *ortho*-substituents, and Taft,[3] following earlier work by Ingold,[4] assumed that the ratio of rate constants of base- to acid-catalysed hydrolysis of benzoic esters depends on polar factors only.

A simple connection often exists between certain infrared frequencies and polar effects.[5] Carbonyl frequencies are linearly dependent on the σ-values of *meta-* and *para*-substituents in benzenoid compounds,[6] and parallel monotonic sequences with σ-values also exist for the stretching frequencies of the amino-, hydroxy-, and nitro-groups.[7] Although the number of compounds listed is small, the data presented in the annexed Table indicate a regularity in the frequency patterns for various series of *ortho*-substituted benzenoid compounds. The magnitudes of the frequency shifts [ν(subst.) — ν(unsubst.)] depend on the basic structures as follows: hydroxyiminoacetanilides < isatins (β-CO frequencies) < benzoic acids < acetanilides, isatins, (α-carbonyl frequencies) < anthranilic acids. Effects of *ortho-* as well as *meta-* and *para*-substituents can be transmitted through an NH group attached to a benzene ring.[8]

Substituent factors and carbonyl frequencies [a] (*cm.*$^{-1}$) *of* ortho-*substituted benzenoid compounds.*

Subst.	NH_2	Me	H	F	I	Br	Cl	CF_3	NO_2
σ_p [1]	−0·660	−0·170	0·0	0·062	0·276	0·232	0·227	0·551	0·778
pK_a [b]	6·68	5·97	5·17	−0·44	1·82	0·90	0·72	—	—
E_σ [c]	—	0·0	—	—	0·38	0·38	0·37	—	0·95
E_s [d]	—	0·0	—	—	−0·20	0·01	0·18	—	−0·71
σ [e]	—	−0·080	0·0	—	—	—	0·325	—	0·650
Benzoic acids	1673	—	1706	1708	1712	1713	1713	—	1719
Acetanilides	—	1683	1685	—	1693	—	1694	—	1703
Hydroxyiminoacetanilides	—	1678	1680	1681	1682	1683	1683	1686	1685
Anthranilic acids	—	—	1673	—	1700	1700	1692	—	—
Isatins (β-CO group) [f]	—	1731	1740	—	1741	1745	1745	1750	—
,, (α-CO group) [g]	—	1755	1755	1755	1761	1763	1765	1768	1772

[a] In chloroform. [b] Values for pyridines.[2] [c] Taft polar factors.[3] [d] Taft steric factors.[3] [e] Mamalis and Rydon σ-values.[9] [f] Substituent in position 4. [g] Substituent in position 7.

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[1] Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 188; Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[2] McDaniel and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 3757.

[3] Taft, *ibid.*, 1952, **74**, 3122; 1953, **75**, 4231.

[4] Ingold, *J.*, 1930, 1032.

[5] Bellamy, *J.*, 1955, 4221.

[6] Flett, *Trans. Faraday Soc.*, 1948, **44**, 767; Davison, *J.*, 1951, 2456; Fuson, Josien, and Shelton, *J. Amer. Chem. Soc.*, 1954, **76**, 2526; O'Sullivan and Sadler, *J.*, 1956, 2202; Kellie, O'Sullivan, and Sadler, *J.*, 1956, 3809.

[7] Ingraham, Corse, Bailey, and Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297; Kross and Fassel, *ibid.*, 1956, **78**, 4225.

[8] O'Sullivan and Sadler, *J. Org. Chem.*, 1956, **21**, 1179.

The Table shows that the frequencies increase with increasing *para*-σ-values. The fluoro-substituent spoils an otherwise possible correlation with the p*K*'s of pyridine bases.[2] In general, the shifts increase with increase in Taft's polar-displacement constants for *ortho*-groups,[3] but the relation is not linear. No correlation exists with Taft's steric parameters.[3]

Approximate linear dependence exists between the frequency shifts and the σ-values for *ortho*-groups suggested by Mamalis and Rydon.[9] The latter values were obtained from rate measurements on the alkaline hydrolysis of substituted benzoyloxyethyldimethylsulphonium iodides, and specific *ortho*-effects are reputed to be absent as the point of attack is well removed from the benzene ring. Good internal correlations exist between the infrared data of the different series. Thus plotting frequency shifts for acetanilides, hydroxyiminoacetanilides, and isatins against those of benzoic acids provides sets of points that lie on, or close to, a family of straight lines, one for each series of compounds. The results presented here are too limited to warrant statistical treatment, but suffice to suggest that more searching investigations might provide a useful reference system for the general study of *ortho*-effects.

Experimental.—In each series of compounds, the spectra were determined consecutively, under identical conditions, by using a Perkin-Elmer 21 double-beam recording spectrometer fitted with a rock-salt prism.

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[9] Mamalis and Rydon, *Nature*, 1950, **166**, 404.

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552. *The H_0 Acidity Scale in Aqueous Perchloric Acid.*

By T. G. Bonner and J. C. Lockhart.

Although aqueous perchloric acid is readily available in concentrations up to 72% w/w, the H_0 acidity function has not been measured above 64% $HClO_4$. Hammett and Deyrup [1] did not proceed beyond this point because of the danger of explosion; they also found that some indicators, which were stable in concentrated sulphuric acid, decomposed irreversibly in solutions of perchloric acid.

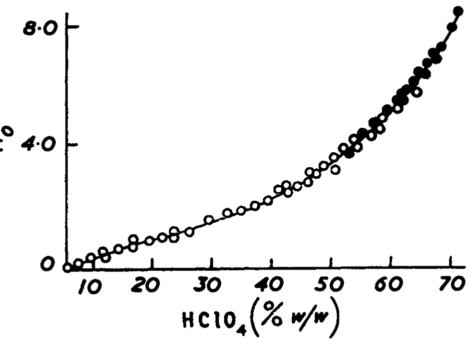
2 : 4-Dinitro-1-naphthylamine is not attacked by perchloric acid up to 72% concentration and is thus a suitable indicator for extending the H_0 scale. Indicators which had to be rejected were benzylideneacetophenone, which decomposed on irradiation with the ultraviolet light used in the spectrophotometric analysis of its solutions, and 2 : 4-dinitrodiphenylamine which, although behaving normally in concentrated sulphuric acid to give a pale yellow solution, appeared to decompose in perchloric acid, to a deep brown solution similar to that reported [1] for 4-nitrodiphenylamine.

The indicator base used by Hammett and Deyrup in their region of highest acidity was 2 : 4-dinitroaniline, but few measurements were reported for it. It has now been more extensively investigated over the range 50—62% $HClO_4$, and a new pK_a value (—4·36) evaluated for it on the basis of Hammett's pK_a value of —3·18 for 2 : 4-dichloro-6-nitroaniline.[1, 2] The measurements of the ionisation ratios [B]/[BH$^+$] now reported for 2 : 4-dinitroaniline and 2 : 4-dinitro-1-naphthylamine permit the calculation of accurate values of the acitity function H_0 over the range 50—71% $HClO_4$ from the usual equation $H_0 = \mathrm{p}K_a + \log [\mathrm{B}]/[\mathrm{BH}^+]$, where [B] and [BH$^+$] represent the concentrations of the un-ionised

[1] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.
[2] Hammett and Paul, *ibid.*, 1934, **56**, 827.

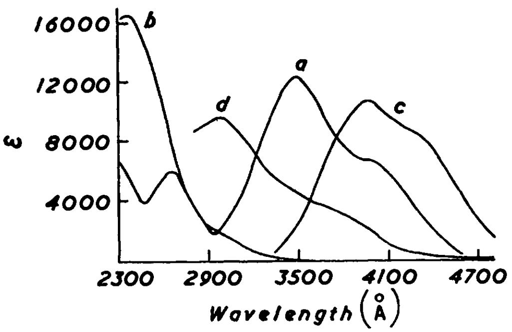
and ionised forms of the indicator in a medium of acidity H_0, and K_a the acidity constant of the acid BH$^+$. These values are given in the Table. Fig. 1 shows that H_0 values for acids stronger than 61% perchloric acid form a curve continuous with that previously reported for acids below this strength.

FIG. 1.



○ Data from Hammett and Deyrup.[1]
● Present work.

FIG. 2.



a 2 : 4-Dinitroaniline in 45·6% HClO$_4$.
b 2 : 4-Dinitroaniline in 70·0% HClO$_4$.
c 2 : 4-Dinitro-1-naphthylamine in 44·2% HClO$_4$.
d 2 : 4-Dinitro-1-naphthylamine in 72·0% HClO$_4$.

2 : 4-Dinitroaniline (pK_a = −4·36)			2 : 4-Dinitro-1-naphthylamine (pK_a = −6·37)			2 : 4-Dinitro-1-naphthylamine (pK_a = −6·37)		
HClO$_4$ (%)	log [B]/[BH$^+$]	$-H_0$	HClO$_4$ (%)	log [B]/[BH$^+$]	$-H_0$	HClO$_4$ (%)	log [B]/[BH$^+$]	$-H_0$
49·6	1·27	3·09	59·6	1·25	5·12	67·3	−0·60	6·97
50·3	0·80	3·56	61·4	0·90	5·47	67·5	−0·69	7·06
53·0	0·55	3·81	62·0	0·84	5·53	68·3	−0·87	7·24
54·2	0·31	4·05	62·7	0·58	5·79	70·2	−1·58	7·95
55·5	0·04	4·32	64·0	0·25	6·12	71·3	−2·09	8·46
57·2	−0·28	4·64	65·0	−0·03	6·40			
59·5	−0·78	5·14	65·3	−0·05	6·42			
62·2	−1·25	5·61	66·4	−0·39	6·76			

Experimental.—Materials. 2 : 4-Dinitroaniline was crystallised from alcohol to a constant spectrum, $\varepsilon_{\text{max.}}$ = 12,300 at 3480 Å in dilute aqueous perchloric acid ($\varepsilon_{\text{max.}}$ = 12,800 at 3480 Å has been reported in aqueous sulphuric acid [3]), and had m. p. 180°. 2 : 4-Dinitro-1-naphthylamine was prepared by nitration of acetnaphthalide in acetic acid and hydrolysis of the dinitro-derivative.[4] The brown product was boiled with charcoal and crystallised from alcohol to a constant spectrum, $\varepsilon_{\text{max.}}$ = 10,600 at 3960 Å in dilute aqueous perchloric acid; it had m. p. 244°.

Absorption spectra. These were measured on a Hilger " Uvispek " spectrophotometer and the indicator ionisation ratio was obtained from the equation $[\mathrm{B}]/[\mathrm{BH^+}] = (\varepsilon_{\mathrm{BH^+}} - \varepsilon)/(\varepsilon - \varepsilon_{\mathrm{B}})$, where $\varepsilon_{\mathrm{BH^+}}$ and ε_{B} are the extinction coefficients at any selected wavelength of the ionised and un-ionised forms of the indicator respectively, and ε is the extinction coefficient at the same wavelength for a particular medium containing the concentrations [B] and [BH$^+$] of the two forms. The absorption spectra of the ionised and un-ionised forms of 2 : 4-dinitroaniline and 2 : 4-dinitro-1-naphthylamine in perchloric acid are shown in Fig. 2. As the absorption curves were very slightly displaced to higher wavelengths with increasing acidity of the media, [B]/[BH$^+$] was calculated at several different wavelengths on either side of the peak, and the mean value taken.

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[3] Bartlett and McCollum, *ibid.*, 1956, **78**, 1441.
[4] Morgan and Evens, *J.*, 1919, 1126.

553. 2-*Nitro*-1-*naphthoic Acid.*

By R. D. Topsom and J. Vaughan.

2-Nitro-1-naphthaldehyde and 2-nitro-1-naphthoic acid, previously unreported, have been prepared from 2-nitro-1-methylnaphthalene *via* 2-nitro-1-naphthylpyruvic acid. 2-Nitro-1-methylnaphthalene was obtained by Veselý *et al.*[1] in low yield by a lengthy procedure; we obtained it by a satisfactory 3-stage process.

We first prepared 4-bromo-1-methylnaphthalene in 28% yield from 1-methylnaphthalene by sulphonation and subsequent bromination, reported [2] to be desirable in order to avoid unwanted by-products arising from direct bromination.[3, 4] We found, however, that a commercial "pure" grade of 1-methylnaphthalene on direct bromination, gave an almost theoretical yield of 4-bromo-derivative. This was nitrated at the 2-position and then debrominated by Edwards and Stewart's method.[5] Attempts to oxidise 1-methyl-2-nitronaphthalene gave mixtures of polycarboxylic acids; however, condensation with a large excess of ethyl oxalate at <0° gave the potassium derivative of ethyl 2-nitro-1-naphthylpyruvate, and oxidation of the derived acid gave a mixture of 2-nitro-1-naphthaldehyde and 2-nitro-1-naphthoic acid. This hindered acid was purified by taking advantage of its resistance to esterification. It may be esterified through its silver salt but fails to yield an anilide by the normal method.

In the condensation with ethyl oxalate under reflux in the absence of a large excess of ester, the main product was 1 : 2-di-(2-nitro-1-naphthyl)ethane (cf. ref. 6).

In other methods investigated, 2-nitro-1-bromonaphthalene failed to react with a Grignard reagent and with *n*-butyl-lithium, and oxidation of 3-nitroacenaphthene gave only very low yields of 2-nitronaphthalic acid, making subsequent mercuration and decarboxylation impracticable.

Experimental.—4-*Bromo*-1-*methylnaphthalene*. Bromine (38 ml.) in carbon tetrachloride (200 ml.) was added during 2 hr. at −7° to a stirred solution of 1-methylnaphthalene (100 g. of Light's "pure") in carbon tetrachloride (250 ml.) containing small amounts of iron powder and iodine. Stirring was continued for a further 1 hr. at −7° and the mixture was then left for 2 hr. as the temperature rose. Excess of bromine was removed by treatments with 2N-sodium hydroxide and with water. Solvent was removed at atmospheric pressure and a fraction, b. p. 179—180°/27 mm., was collected. Redistillation gave 4-bromo-1-methylnaphthalene (145 g., 93%), b. p. 170—171°/20 mm.

4-*Bromo*-1-*methyl*-2-*nitronaphthalene*. The method of Veselý *et al.*[7] gave variable yields, the best (*ca.* 35%) being obtained by addition of nitrating acid to 4-bromo-1-methylnaphthalene. The 2-nitro-product was obtained as pale yellow crystals, m. p. 122° after repeated recrystallisation from light petroleum (b. p. 60—80°) and ethanol.

1-*Methyl*-2-*nitronaphthalene*. 4-Bromo-1-methyl-2-nitronaphthalene (10 g.), cuprous oxide (7·5 g.), acetic anhydride (5·2 ml.), and dry, freshly distilled pyridine (40 ml.) were refluxed for 1·5 hr., then poured into 5% acetic acid (500 ml.). After 12 hr. the solid was filtered off and extracted with light petroleum (5 × 100 ml.; b. p. 60—80°). Removal of solvent yielded crystals, which were further extracted with light petroleum, then recrystallised twice from ethanol. The 1-methyl-2-nitronaphthalene was obtained as yellow crystals (4·0 g. 57%), m. p. 56°.

2-*Nitro*-1-*naphthylpyruvic acid*. A solution of potassium ethoxide [from potassium (2·5 g.), ethanol (10 ml.), and ether (10 ml.)] was added at 0° to stirred, freshly distilled diethyl oxalate

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[1] Veselý, Štursa, Olejníček, and Rein, *Coll. Czech. Chem. Comm.*, 1929, **1**, 493.
[2] Fieser and Steligman, *J. Amer. Chem. Soc.*, 1939, **61**, 137.
[3] Mayer and Sieglitz, *Ber.*, 1922, **55**, 1835.
[4] Robinson and Thompson, *J.*, 1932, **135**, 2015.
[5] Edwards and Stewart, *Chem. and Ind.*, 1952, 472.
[6] Mayer and Oppenheimer, *Ber.*, 1916, **49**, 2137.
[7] Veselý, Štursa, Olejníček, and Rein, *Coll. Czech. Chem. Comm.*, 1930, **2**, 145.

(75 ml.). After 15 min. 2-nitro-1-methylnaphthalene (11·5 g.) was added with stirring, during 30 min. at 0°. Stirring was continued for 30 min. and the mixture then kept at −10° for 24 hr. Filtration and washing with chilled ether gave the potassium derivative of *ethyl 2-nitro-1-naphthylpyruvate* as a deep red solid. Treatment for 12 hr. with 0·5N-hydrochloric acid (250 ml.), filtration, and two recrystallisations from ethanol afforded the light yellow ester (11 g., 62%), m. p. 110·5° (Found: C, 63·0; H, 4·65; N, 5·0. $C_{15}H_{13}O_5N$ requires C, 62·7; H, 4·5; N, 4·9%).

The ester (5 g.) was stirred into a warm solution of potassium hydroxide (1 g.) in dry ethanol (30 ml.). After dissolution of solid material, water (200 ml.) was added and after 2 hr. the mixture was acidified with dilute hydrochloric acid. Filtration and two recrystallisations from 30% aqueous acetic acid furnished yellow *2-nitro-1-naphthylpyruvic acid* (3·8 g.), m. p. 179° (Found: C, 60·9; H, 3·6; N, 5·4. $C_{13}H_9O_5N$ requires C, 60·2; H, 3·5; N, 5·4%).

Oxidation. The acid (3 g.) was dissolved in a solution of sodium hydroxide (0·96 g.) in water (120 ml.). To this stirred solution was added, during 10 min., a solution of potassium permanganate (2·4 g.) in water (250 ml.) and stirring was continued for 30 min. Manganese dioxide was removed and the supernatant liquid was acidified before extraction with ether. Extraction of the ether layer with sodium hydrogen carbonate solution and acidification of this gave crude 2-nitro-1-naphthoic acid (1·5 g.), m. p. 120—130°. The solid from evaporation of the ether layer was recrystallised (charcoal) from light petroleum (b. p. 60—80°) and twice recrystallised from methanol, to give *2-nitro-1-naphthaldehyde* (0·5 g., 21%) as yellow needles, m. p. 119° (Found: C, 65·9; H, 3·6; N, 6·9. $C_{11}H_7O_3N$ requires C, 65·7; H, 3·5; N, 7·0%). The *semicarbazone* had m. p. 279° (Found: N, 21·5. $C_{12}H_{10}O_3N_4$ requires N, 21·7%).

The crude acid was refluxed for 4 hr. in ethanol (20 ml.) under a constant stream of dry hydrogen chloride. Charcoal was added before filtration and the residue from the evaporated filtrate was taken up in ether. Extraction with sodium hydrogen carbonate and acidification gave the still impure acid (1·0 g.), m. p. 187—195°. Extraction with hot 30% aqueous ethanol and three recrystallisations from 30% ethanol then gave pure, pale yellow *2-nitro-1-naphthoic acid* (0·6 g., 24%), m. p. 202° (Found: C, 61·0; H, 3·3; N, 6·3. $C_{11}H_7O_4N$ requires C, 60·8; H, 3·25; N, 6·45%). The pale yellow *ethyl ester*, obtained from the silver salt and ethyl iodide and purified by recrystallisation from ethanol, had m. p. 92° (Found: C, 63·4; H, 4·8; N, 5·8. $C_{13}H_{11}O_4N$ requires C, 63·6; H, 4·5; N, 5·7%).

2-Nitro-1-naphthoic acid was also obtained in 50% yield (m. p. 199°) from the aldehyde by oxidation with potassium permanganate in aqueous acetone.

1 : *2-Di-(2-nitro-1-naphthyl)ethane.* 2-Nitro-1-methylnaphthalene (3 g.) and diethyl oxalate (2 ml.) were added to a solution of sodium ethoxide (from 0·75 g. of sodium in 20 ml. of ethanol). After 20 minutes' refluxing, the mixture was added to water (100 ml.). The solid was washed with hot ethanol, and two recrystallisations from chlorobenzene furnished 1 : *2-di-(2-nitro-1-naphthyl)ethane* (1·5 g.) as bright yellow flakes, m. p. 232° (Found: C, 70·9; H, 4·5; N, 7·5. $C_{22}H_{16}O_4N_2$ requires C, 70·9; H, 4·3; N, 7·5%), insoluble in most common organic solvents.

We acknowledge the help of Mr. F. R. H. Gerhard in the initial work on 2-nitro-1-methylnaphthalene. Analyses were carried out in the microanalytical laboratory (Dr. A. D. Campbell) of the University of Otago.

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554. *The Pyrolysis of Hexafluoroethane.*

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THE possibility has been explored of obtaining a pyrolytic value for the dissociation energy $D(CF_3-CF_3)$; this quantity is still not known with any accuracy.[1-3] Hexafluoroethane was pyrolysed in a flow system with toluene in the usual way,[4] in the temperature range

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[1] Dibeler, Reese, and Mohler, *J. Res. Nat. Bur. Stand.*, 1956, **57**, 113.

[2] Farmer, Henderson, Lossing, and Marsden, *J. Chem. Phys.*, 1956, **24**, 348.

[3] Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Chem. and Ind.*, 1955, 896.

[4] Clark and Pritchard, *J.*, 1956, 2136.

846—1019°. The upper part of this range represents the limit of the toluene-carrier technique because of the difficulty of removing toluene decomposition products from the reaction vessel at sufficient speed and because of the deposition of coke in the reaction zone and tar in the exit tube. Two sets of experiments were performed in which different methods of analysis were employed to determine the ratio of $CF_3H : C_2H_6$ in the products: infrared absorption spectrometry and mass spectrometry. The measurements were made on the fraction which was involatile at −195° but volatile at −80°; however, with mass-spectrometric analysis, a much more careful sampling was necessary because butadiene and/or butenes were formed (from the toluene) which interfered with the peak at 51 used for the estimation of CF_3H, and a further distillation at about −165° to −170° was necessary to prevent this interference. The results from both sets of measurements were the same: the rate constant for the decomposition $C_2F_6 \longrightarrow 2CF_3\cdot$ up to 960°, was $k \approx 10^8 \exp(-50{,}000/\boldsymbol{R}T)$ sec.$^{-1}$ after which it became apparently independent of temperature. The reaction is probably heterogeneous, but we could not test this by packing the vessel because it is difficult to maintain a free flow of gas through the restricted space in the packed zone; but even if the reaction were to prove homogeneous, one could not regard the observed activation energy as a measure of the dissociation energy in view of the abnormal frequency factor with which it is associated.

As an alternative approach, it would be interesting to compare the decompositions of $PhCH_2{-}CH_3$ and $PhCF_2{-}CF_3$, which would not involve such high temperatures, but it is not feasible [5] to make the latter substance in sufficient quantities; some experiments with its precursor $PhCCl_2{\cdot}CF_3$ yielded no relevant information since the initial process apparently involved the fission of a C–Cl bond (substantial quantities of hydrogen chloride were produced). We conclude therefore that the pyrolytic approach to the C–C dissociation energy in hexafluoroethane is unsuitable, although more information on the nature of its pyrolysis might be obtained by using methane instead of toluene as a carrier gas.

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[5] Simons and Herman, *J. Amer. Chem. Soc.*, 1943, **65**, 2064.