

826. β -Aroylpropionic Acids. Part XIII.* The Infrared and Ultra-violet Spectra of the Products of Interaction of Grignard Reagents with Succinic Anhydrides and β -Aroylpropionic Acids and Their Esters.

By F. G. BADDAR and (MRS.) ADIBA HABASHI.

IN a previous publication¹ the action of Grignard reagents on succinic anhydrides and β -aroylpropionic acids and their esters was shown to afford $\gamma\gamma$ -diarylbutyrolactones (I), 3,3-diarylprop-2-ene-1-carboxylic acids (IV), 2,2,5,5-tetra-aryltetrahydrofurans (II), and 1,1,4,4-tetra-arylbuta-1,3-dienes (III), whose structures were established by ultraviolet spectra.² These structures have now been confirmed by infrared spectra.

The lactones (I) showed the characteristic stretching frequency for saturated γ -lactones (1780—1765 cm^{-1})^{3a} (see Table 1). This band was absent from the spectra of the tetrahydrofurans (II).

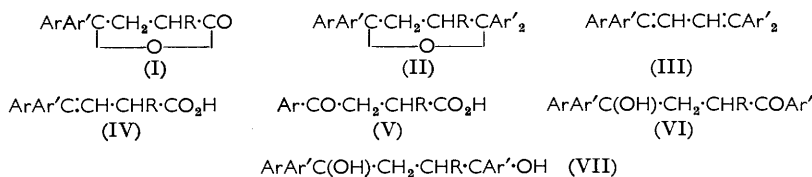
TABLE 1. Infrared maxima (cm^{-1}).

Compound	R	Ar	Ar'	Alcohol. OH	OH of CO ₂ H	C=O of sat. lactone	C=O of CO ₂ H	Ketonic C=O
1b	Me	<i>o</i> -MeO	<i>o</i> -MeO	—	—	1775vs	—	—
c	H	2-MeO-5Me	"	—	—	1770vs	—	—
e	H	2,5-(MeO) ₂	2,5-(MeO) ₂	—	—	1780vs	—	—
f	Me	"	"	—	—	1775vs	—	—
g	H	2-MeO''-5-Ph	<i>o</i> -MeO''	—	—	1765vs	—	—
h	H	2-MeO-5-C ₆ H ₄ OMe(- <i>p</i>)	"	—	—	1780vs	—	—
IVa	Me	<i>o</i> -MeO	<i>o</i> -MeO	—	2630m	—	1715vs	—
b	H	2-MeO-5-Me	"	—	2680m	—	1710vs	—
c	H	2-MeO-5-Cl	"	—	2720m	—	1710vs	—
d	H	2,5-(MeO) ₂	2,5-(MeO) ₂	—	2630m	—	1700vs	—
f	H	2-MeO-5-Ph	<i>o</i> -MeO	—	2600w	—	1720s	—
Va	Me	<i>o</i> -MeO	—	—	2660m	—	1705vs	1666vs
b	Me	2,5-(MeO) ₂	—	—	2630w	—	1705vs	1666vs
VIa	H	2-MeO-C ₁₀ H ₆ (-1)	<i>o</i> -MeO	3530*m	—	—	—	1675vs
b	Me	2,5-(MeO) ₂	2,5-(MeO) ₂	3530*m	—	—	—	1660m
VII	H	"	<i>o</i> -MeO	3530*m	—	—	—	—

* Sharp.

The propene acids (IV) showed the characteristic stretching frequencies of the C=O and O-H of the carboxyl group at 1720—1700 and 2700—2630 cm^{-1} , respectively.^{3b} The same two bands appeared in the spectra of the γ -keto-acids (V). The latter acids also showed the carbonyl stretching frequency at 1666 cm^{-1} .^{3c}

No characteristic bands appeared in the infrared spectra of the tetra-arylbuta-1,3-dienes (III), and their structure rest entirely on their ultraviolet spectra.²



The structure assigned to 1-(2,5-dimethoxyphenyl)-1,4,4-tri-*o*-methoxyphenylbutane-1,4-diol was supported by the ultraviolet spectrum,² and is now confirmed by a sharp infrared band at 3530 cm^{-1} , characteristic of the O-H group.^{3d}

The ultraviolet spectra of the γ -hydroxybutyphenones (VIa, b, and c) (Figure) threw

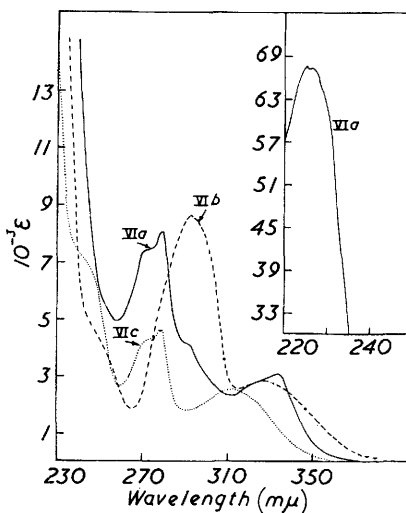
* Part XII, submitted for publication in *Egypt J. Chem.*

¹ Baddar, El-Assal, and Habashi, *J.*, 1957, 1690.

² Baddar, Habashi, and Sawiris, *J.*, 1957, 1699.

³ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1956, pp. (a) 153, (b) 140, (c) 114, (d) 84.

some light on the structures. Thus, compound (VIc) had maxima at 279 (ϵ 4610) and 313 $m\mu$ (ϵ 2520) (see Table 2) identical with those for γ -(5-chloro-2-methoxyphenyl)- γ -*o*-methoxyphenylbutyrolactone² (λ_{\max} 279 $m\mu$, ϵ 4630) and for *o*-methoxyacetophenone⁴ [λ_{\max} 305 $m\mu$, ϵ 3800], respectively. The absorption of this butyrophenone (VIc) in the region 270—280 $m\mu$ is identical with that² for the butanediol (VII) but with nearly half its absorption intensity. Similarly the band at 293 $m\mu$ (ϵ 8630) for the butyrophenone (VIb) is identical with that for $\gamma\gamma$ -di-2,5-dimethoxyphenyl- α -methylbutyrolactone² [λ_{\max} 294 $m\mu$ (ϵ 7940)], whereas the band at 327.5 $m\mu$ (ϵ 2840) is probably due to the 2,5-dimethoxyacetophenone residue [cf. λ_{\max} 333 $m\mu$ (ϵ 3640) for β -2,5-dimethoxybenzoyl- α -methylpropionic acid (Vb)] (Table 2). The inflexions at about 240 and 245 $m\mu$ in the



Ultraviolet absorption spectra of butyrophenones (VI).

absorption curves for the ketones (VIa and b) may be equivalent to the maxima at 246 and 249 $m\mu$ of *o*-methoxyacetophenone⁴ and β -2,5-dimethoxybenzoyl- α -methylpropionic acid, respectively. The absorption curve for the butyrophenone (VIa) shows the characteristic bands for naphthalene⁵ (λ_{\max} 225 and 280 $m\mu$, Table 2) with a slight bathochromic shift

TABLE 2. Ultraviolet maxima and minima ($m\mu$).

Compound	R	Ar	Ar'	λ_{\max} *	ϵ	λ_{\min}	ϵ
Vb	Me	2,5-(MeO) ₂	—	249, 333	5880, 3640	240, 275	5220, 256
VIa	H	2-MeO-C ₁₀ H ₆ (-1)	<i>o</i> -MeO	225, 273i 280, 290i 334	67610, 7440 8070, 4160 3070	258.5 313	4930 2280
b	Me	2,5-(MeO) ₂	2,5-(MeO) ₂	245i, 293 327.5	5010, 8630 2840	265.5 315	1830 2570
c	H	2-MeO-5-Cl	<i>o</i> -MeO	240i, 279 313, 274i	7290, 4610 2520, 4300	260 293	2650 1820

* = inflexion.

(5 $m\mu$) probably due to the 2'-methoxyl group. The long-wavelength band at 334 $m\mu$ is probably the summation of two superimposed bands, a strong band for *o*-methoxyacetophenone and a weak one for substituted naphthalene. However, the curves for the three butyrophenones are identical in general features, supporting assignment of similar structures to them. These structures were confirmed by infrared spectra, compounds (VIa and b) showing the characteristic stretching frequency for the carbonyl group^{3c} at 1675 and 1660 cm^{-1} , respectively, and a sharp band at 3530 cm^{-1} for the O-H group.^{3d}

⁴ Morton and Stubbs, *J.*, 1940, 1347.

⁵ Mayneord and Roe, *Proc. Roy. Soc.*, 1935, A, 152, 299.

Experimental.—Infrared spectra were kindly determined by Samuel P. Sadtler and Sons, Inc., using the potassium bromide wafer technique.

Ultraviolet spectra are for solutions in 95% alcohol, measured by a Bechmann DU quartz spectrophotometer.

No infrared maxima at the regions cited were given by the tetrahydrofurans (II) where (i) R = Me and Ar = Ar' = *o*-MeO·C₆H₄ or 2,5-(MeO)₂C₆H₃ or (ii) R = H and Ar = Ar' = 2,5-(MeO)₂C₆H₃ or Ar = 2-MeO-5-Cl·C₆H₃ and Ar' = *o*-MeO·C₆H₄; or by the butadienes (iii) where Ar = 2-MeO-5-Me·C₆H₃ or 2-methoxy-1-naphthyl and Ar' = *o*-MeO·C₆H₄.

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827. The Preparation of Aryl 2-Acetamido-2-deoxy-β-D-galactosides.

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PHENYL and *p*-nitrophenyl 2-acetamido-2-deoxy-β-D-galactosides were required as substrates for the enzyme "N-acetyl-β-galactosaminidase."¹ Difficulties were encountered in the preparation of crystalline 2-amino-2-deoxygalactose (galactosamine) hydrochloride by the methods of Jorpes and Bergstrom² or Roseman and Ludowieg,³ but a combination of the procedures of Bera, Foster, and Stacey⁴ for the preparation of chondroitin sulphate and of Gardell⁵ for the separation of hexosamine hydrochlorides gave the essential pure hydrochloride.

As in the successful use of acetochloroglucosamine (I) (2-acetamido-3,4,6-tri-*O*-acetyl-1-chloro-2-deoxy-α-D-glucose) in the synthesis of aryl 2-acetamido-2-deoxy-β-D-glucosides,⁶ and the reported lability of acetobromogalactosamine,⁷ acetochlorogalactosamine (II) (2-acetamido-3,4,6-tri-*O*-acetyl-1-chloro-2-deoxy-α-D-galactose) has been prepared and used to synthesise the required substrates by condensation with phenols in aqueous acetone under alkaline conditions (cf. Glaser and Wulwek⁸).

Our unsuccessful use of titanium tetrachloride⁹ in the preparation of acetochloroglucosamine from 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucose (unpublished results) and the successful use of mixed penta-acetates with prolonged exposure to acetic anhydride saturated with dry hydrogen chloride⁶ led to our adopting the latter procedure for the preparation of acetochlorogalactosamine.

Acetochlorogalactosamine was converted into 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-α-D-galactose hydrochloride (IV). This type of conversion is not an isomerisation (cf. Tarasiejska and Jeanloz¹⁰) but requires a molar addition of water and was first described in the case of acetobromoglucosamine.¹¹

A brief account of part of this work has been published.¹² Tarasiejska and Jeanloz¹⁰ have since reported the synthesis of acetochlorogalactosamine and its use in the preparation of alkyl 2-acetamido-2-deoxy-β-D-galactosides.

Experimental.—Infrared spectra were determined on potassium chloride pellets.

2-Amino-2-deoxy-D-galactose hydrochloride. Barium chondroitin sulphate was prepared, from dried bovine tracheal cartilage (100 g.) by the "simplified procedure" of Bera *et al.*⁴ The

¹ Heyworth, Borooh, and Leaback, *Biochem. J.*, 1957, **67**, 21P.

² Jorpes and Bergstrom, *Z. physiol. Chem.*, 1936, **244**, 254.

³ Roseman and Ludowieg, *J. Amer. Chem. Soc.*, 1954, **76**, 301.

⁴ Bera, Foster, and Stacey, *J.*, 1955, 3788.

⁵ Gardell, *Acta Chem. Scand.*, 1953, **7**, 207.

⁶ Leaback and Walker, *J.*, 1957, 4754.

⁷ Stacey, *J.*, 1944, 272.

⁸ Glaser and Wulwek, *Biochem. Z.*, 1924, **145**, 514.

⁹ Baker, Joseph, Schaub, and Williams, *J. Org. Chem.*, 1954, **19**, 1786.

¹⁰ Tarasiejska and Jeanloz, *J. Amer. Chem. Soc.*, 1958, **80**, 6325.

¹¹ Micheel, van de Kamp, and Wulff, *Chem. Ber.*, 1955, **88**, 2011.

¹² Heyworth and Leaback, *Chem. and Ind.*, 1958, 1145.

Infrared spectra (max. in cm^{-1}).

Compounds	—OH and —NH region	NH_3^+X^-	O-Acyl	Amide I & II	Hydrochlorides	C-Hal stretching
(II)	3330	None	1740	1670, 1545	None	760
(I) ⁶	3250	None	1735	1640, 1540	None	755
(IV) ⁶	None	3000—2500	1750	None	2010, 1600, 1580	None
(III) ⁶	None	3000—2500	1750	None	2015, 1595, 1580	None

polysaccharide was hydrolysed with 5*N*-hydrochloric acid (500 ml.) under reflux for 20 hr. After decolorisation with charcoal the solution was concentrated *in vacuo* to about 25 ml. and neutralised with De-Acidite FF in the carbonate form. The neutral solution was concentrated *in vacuo* to about 5 ml. and applied to a column of Dowex 50-X8 (200—400 mesh; H^+ form). The column (45 × 3 cm.) was eluted with 0.3*N*-hydrochloric acid, and fractions (15 ml.) were collected at 7 min. intervals. Fractions containing pure galactosamine hydrochloride were separated from the few earlier ones containing also glucosamine hydrochloride and the few later ones containing also talosamine hydrochloride ¹³ and amino-acids. The galactosamine hydrochloride solutions were evaporated *in vacuo* to crystals (2.4 g.) which on re-crystallisation from water had m. p. 180°.

Acetochlorogalactosamine (II). A mixture of α - and β -penta-acetylgalactosamine was made by the zinc chloride method of Stacey ⁷ (yield, 63%) and 2.8 g. were dissolved and kept at room temperature for 24 hr. with acetic anhydride (12 ml.) which had been saturated at 0° with dry hydrogen chloride. The solution was cooled to 0°, re-saturated with dry hydrogen chloride, ⁶ and kept at room temperature for 14—21 days. The mixture was poured into chloroform (50 ml.), neutralised with cold saturated sodium hydrogen carbonate, and washed with water. The chloroform layer was dried (MgSO_4) and evaporated. Addition of dry ether and re-evaporation gave a crystalline product (1.3 g., 50%). Recrystallisation of *acetochlorogalactosamine* from dry ethyl acetate gave plates, m. p. 130°, $[\alpha]_D^{18} +138^\circ$ (*c* 0.7 in CHCl_3) (Found: C, 44.3; H, 5.8; N, 3.9, 4.3; Cl, 9.7. $\text{C}_{14}\text{H}_{20}\text{O}_8\text{NCl}$ requires C, 46.0; H, 5.5; N, 3.8; Cl, 9.7%). It is soluble in chloroform, acetone, acetic acid, or nitromethane but insoluble in ether or cold water. The infrared spectrum (Table) shows a close similarity to that of acetochloroglucosamine (I). ⁶

1,3,4,6-Tetra-O-acetyl-2-amino-2-deoxy- α -D-galactose hydrochloride (IV). Acetochlorogalactosamine (0.25 g.) was kept in nitromethane (5 ml.) and 2*N*-hydrochloric acid (0.012 ml.) for 2 days. Needles (0.088 g.) were filtered off and washed with nitromethane. Water (0.005 ml.), added to the filtrate, gave a second crop (0.016 g.). The *hydrochloride* decomposed at 150—190° and had $[\alpha]_D^{18} +139^\circ$ (*c* 0.3 in H_2O) (Found: C, 42.7; H, 5.9; N, 3.7; Cl, 9.3. $\text{C}_{14}\text{H}_{22}\text{O}_9\text{NCl}$ requires C, 43.8; H, 5.8; N, 3.7; Cl, 9.2%). It is soluble in water or acetic acid but insoluble in chloroform or nitromethane. The infrared spectrum (Table) is similar to that of the corresponding glucosamine compound (III). ⁶

p-Nitrophenyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy- β -D-galactoside. Acetochlorogalactosamine was condensed with *p*-nitrophenol according to Leback and Walker's directions. ⁶ Recrystallisation from ethanol gave the *tetra-acetyl derivative*, m. p. 184°, $[\alpha]_D^{20} -7^\circ$ (*c* 0.5 in acetone) (Found: C, 51.3; H, 5.1; N, 5.7. $\text{C}_{20}\text{H}_{24}\text{O}_{11}\text{N}_2$ requires C, 51.3; H, 5.2; N, 6.0%).

p-Nitrophenyl 2-acetamido-2-deoxy- β -D-galactoside.—The above compound (0.134 g.) was de-O-acetylated by shaking it in dry methanol (5 ml.) with *n*-sodium methoxide (0.1 ml.), and then keeping the mixture at 5° overnight. The crystals were filtered off, stirred with acetone, filtered off, and washed with acetone and ether. The *galactosaminide* (0.069 g., 71%) was heated *in vacuo* over P_2O_5 at 100° for 16 hr. and then had m. p. 205°, $[\alpha]_D^{20} +19^\circ$ (*c* 0.12 in H_2O) (Found: C, 47.8; H, 5.7; N, 8.3. $\text{C}_{14}\text{H}_{18}\text{O}_8\text{N}_2$ required C, 49.1; H, 5.3; N, 8.2%).

The galactosaminide is seen as a single spot (R_F 0.63) on paper chromatograms run in butan-1-ol-ethanol-water (4:1:5 by vol.; upper layer) by quenching of background fluorescence in ultraviolet light. The corresponding glucosaminide has R_F 0.65.

Phenyl 2-acetamido-2-deoxy- β -D-galactoside. Acetochlorogalactosamine, with phenol, gave crystalline phenyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy- β -D-galactoside, m. p. 165°. This product (0.6 g.) was de-O-acetylated by being kept in methanol (6.5 ml.) and chloroform (6.5 ml.) with 0.1*N*-sodium methoxide (0.5 ml.) at room temperature for 6 hr. and then at 5°

¹³ Heyworth and Walker, *Supp. Internat. Abs. Biol. Sci.*, 1958, 1—48.

overnight. The crystals were filtered off and washed with methanol to yield the galactosaminide (0.28 g. 66%), m. p. 230°.

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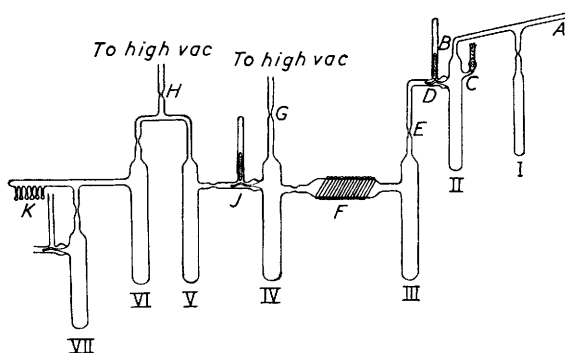
828. *The Activation of Carbon-Carbon Double Bonds by Cationic Catalysts. Part IX.¹ The Dimerisation of 1,1-Diphenylethylene in the System Benzene-Titanium Tetrachloride-Hydrogen Chloride.*

By ALWYN G. EVANS and E. D. OWEN.

DIMERISATION of 1,1-diphenylethylene in benzene-titanium tetrachloride-hydrogen chloride has been studied dilatometrically. The initial rate of dimerisation is of first order with respect to both titanium tetrachloride and hydrogen chloride, and of second order in monomer. No reaction occurs in the absence of hydrogen chloride. The product first formed is the linear dimer, 1,1,3,3-tetraphenylbut-1-ene, and this reacts further to form the cyclic dimer, 3-methyl-1,1,3-triphenylindane.

Experimental.—Titanium tetrachloride (from British Drug Houses) was refluxed over copper turnings for several days in an atmosphere of dry nitrogen, then fractionated up a 40-cm. point column, the fraction boiling at 136° being allowed to run into the high-vacuum apparatus (Fig. 1) at point *A*. A first fraction was sealed off in *I*, and the main distillate run

FIG. 1.



into *II*, which was then sealed off at *B* and *C*. The capillary at *D* was broken by the magnetic breaker, and the apparatus evacuated through *G*. After being outgassed several times, the titanium tetrachloride was distilled into *III* and the apparatus sealed off at *E*. The titanium tetrachloride was then distilled under high vacuum to and fro between *III* and *IV* over copper turnings in *F* kept at 150° by a heating spiral. The trap *IV* was then sealed off from the tube *F* and from the high-vacuum system. The rest of the apparatus was then evacuated through *H* and sealed off. The capillary *J* was broken and the titanium tetrachloride distilled *via* *V* and *VI* into the small calibrated bulbs at *K*, each of which was then sealed off. The remainder was collected and sealed off in the ampoule *VII*. The titanium tetrachloride so purified was perfectly colourless.

1,1-Diphenylethylene was purified as in Part V.² Hydrogen chloride was prepared as in Part VII.³

¹ Part VIII, Evans and Price, *J.*, 1959, 2982.

² Evans and Lewis, *J.*, 1957, 2975.

³ Evans and Lewis, *J.*, 1959, 1946.

Benzene, purified as in Part V,² was sealed off for four weeks under high vacuum in vessels fitted with magnetically operated breakers and containing sodium-potassium alloy. This is liquid at room temperature, and so presented a constant untarnished surface to the benzene, which was shaken at regular intervals.

Procedure. This was the same as described in Part VII,³ the very rigorous method A (Part V²) being used for making up all mixtures.

Results.—In the absence of hydrogen chloride, systems containing rigorously purified benzene, monomer, and titanium tetrachloride reacted at a negligible rate (see Table 1, expt.*).

TABLE 1.

10 ³ I.R.	10 ³ [HCl]	[M]	10 ³ [TiCl ₄]	Temp.	10 ³ I.R.	10 ³ [HCl]	[M]	10 ³ [TiCl ₄]	Temp.
<i>a</i> *	0	0.91	4.60	30°	1.58	2.78	0.86	4.90	55°
131	4.90	0.95	16.3	55	2.46 †	2.6	1.29	6.79	30
27.8	2.20	0.95	16.3	55	1.95 †	2.6	1.29	6.79	40
75.0	6.23	0.95	10.6	55	2.50 †	2.6	1.29	6.79	55
32.6	3.83	0.95	10.6	30	2.66	2.0	1.56	6.4	55
5.96	1.22	0.95	10.6	30	1.19	2.0	1.10	7.09	55
38.5 †	4.30	0.91	4.60	30	0.556	2.0	0.79	7.58	55
13.9	2.24	0.91	4.60	30	1.59	2.2	0.77	16.0	55
77.3	18.0	0.91	4.60	30	2.86	2.2	0.77	25.5	55
					89.4	2.2	0.77	721	55
					59.1	2.2	0.77	593	55

*†† See text. *a*, $< 8 \times 10^{-5}$. I.R. = Initial rate of formation of linear dimer (moles l.⁻¹ hr.⁻¹). All concentrations molar.

On the introduction of hydrogen chloride a great increase in the reaction rate was observed (Table 1, expt.†). Thus hydrogen chloride is a cocatalyst. Part of a typical reaction curve is shown in Fig. 2; the volume was measured until its change with time became negligible.

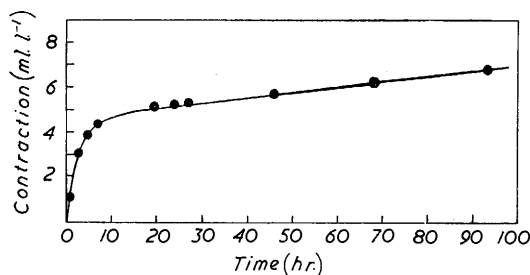


FIG. 2. Typical reaction curve for [Monomer] = 0.77, [TiCl₄] = 5.93×10^{-1} , [HCl] = 2.2×10^{-3} moles l.⁻¹, at 55°.

Various runs were stopped at different stages and the systems analysed. When 25% of the total volume change had occurred, the product consisted entirely of 1,1,3,3-tetraphenylbut-1-ene (linear dimer), and 3-methyl-1,1,3-triphenylindane (cyclic dimer) could not be detected. At 65% of the total volume change, 85% of the product was linear dimer and 15% cyclic dimer. At 95% of the total volume change, 90% of the product was cyclic dimer and 10% linear dimer.

Initial rates of reaction found from the initial slopes of the reaction curves are shown in Table 1. Since it is the linear dimer which is formed initially, they are the rates of formation of linear dimer from monomer. The initial rate does not change with temperature over the range 30° to 55° (see Table 1, expts.†), and so the activation energy E_f is zero.

Using the results of Table 1, we plotted log (initial rate) against log [initial monomer] for constant [TiCl₄] and constant [HCl]; log (initial rate) against log [TiCl₄] for constant [initial monomer] and constant [HCl]. We find the orders in monomer and TiCl₄ to be 2.2 ± 0.2 and 1.0 ± 0.1 , respectively.

We have plotted log {initial rate/([initial monomer]²[TiCl₄])} against log [HCl] and find that the order in HCl is 0.9 ± 0.1 .

Thus the initial rate of formation of linear dimer = k_f [initial monomer]²[TiCl₄][HCl]. The mean value of k_f at 30° is 2.3×10^{-2} mole⁻³ l.³ sec.⁻¹.

As for the SnCl₄-HCl system,³ and in contrast to the SnCl₄-H₂O system,² no optimum

[HCl]/[TiCl₄] ratio has been found, even though the [HCl] was increased up to 40 times that of the [TiCl₄], showing that no stable TiCl₄.HCl complex is formed.

When the colourless titanium tetrachloride is added to the benzene the resultant solution is coloured owing to complex formation between the chloride and benzene. This colour is clearly observable even for titanium tetrachloride concentrations of the order of 2×10^{-4} mole l.⁻¹.

Discussion.—In these monomer-TiCl₄-HCl-benzene systems, only linear dimer is formed at the beginning of the reaction, but later linear dimer is converted into cyclic dimer. This subsequent reaction of the linear dimer into cyclic dimer causes the volume-time curve (Fig. 2) to straighten out in the later stages.

We interpret our results in accordance with the scheme already presented in Parts VII³ and VIII,¹ where Ti replaces Sn through eqns. (1)—(4). This mechanism will account for the results if we make the same assumptions as those of Part VIII, and the initial rate of reaction will be given by the expression:

$$\begin{aligned} \text{Initial rate of formation of linear dimer} &= k_{2a}[M][MH^+TiCl_5^-] \\ &= (k_{2a}k_{1a}/k_{1b})[M]^2[TiCl_4][HCl] \end{aligned}$$

where [M] = initial monomer concentration. This expression is consistent with our results, and $(k_{2a}k_{1a}/k_{1b}) = k_{2a}K_1 = k_t$.

Values of ΔG_t^\ddagger , ΔH_t^\ddagger , and ΔS_t^\ddagger are in Table 2.

TABLE 2.

$10^3 k_t$ *	Temp.	$\Delta H_t^\ddagger = E - RT$ (kcal. mole ⁻¹)	ΔG_t^\ddagger (30°) (kcal. mole ⁻¹)	ΔS_t^\ddagger (30°) (cal. deg. ⁻¹ mole ⁻¹)
(1.3 mole ⁻³ sec. ⁻¹) 2.3	30°	0	20.1	-66
1.8	40			
2.3	55			

* k_t is expressed in terms of the number of moles l.⁻¹ of linear dimer appearing per second.

Comparison of these results with those of Parts VII and VIII shows that the change from SnCl₄-HCl to TiCl₄-HCl (*a*) does not change the mechanism of reaction; (*b*) reduces the activation enthalpy for the conversion of monomer into linear dimer from 4.1 kcal. mole⁻¹ to 0 kcal. mole⁻¹; (*c*) causes the entropy of activation to become more negative: this offsets the effect on the enthalpy of activation, and results in the value of k_t at 30° being the same for the two systems; (*d*) brings about the formation of cyclic dimer at a rate which is more comparable with that of the linear dimer formation.

The last effect is very striking.—In the case of SnCl₄-HCl, systems which gave a measurable rate for the conversion of monomer into linear dimer showed no production of cyclic dimer. A very high rate of production of linear dimer had to be obtained before the formation of cyclic dimer could be detected. In the case of TiCl₄-HCl, however, a catalyst concentration which gives a reasonable rate of formation of linear dimer also gives a reasonable rate for the production of cyclic dimer, although of course this does not begin to be measurable until the concentration of linear dimer becomes appreciable.

We thank the Royal Society for financial help. One of us (E. D. O.) thanks D.S.I.R. for a Maintenance Allowance.

829. The Structures of Potassium Trifluorocuprate(II) and Potassium Trifluorochromate(II).

By A. J. EDWARDS and R. D. PEACOCK.

SPECIMENS of the double fluorides KCuF_3 and KCrF_3 have been prepared at various times, but apart from an observation that the unit cell of KCuF_3 is non-cubic¹ no structural data have been reported. In general the compounds AMF_3 (A = NH_4 , K, Rb; M = transition metal) have the perovskite lattice, sometimes with slight modifications which may be the result of preparative difficulties, as none of the salts can be satisfactorily recrystallised from a solvent. Since Cu^{II} and Cr^{II} show a Jahn-Teller type of distortion in their simple fluorides,^{2,3} and Cu^{II} also in the complex fluoride K_2CuF_4 ,⁴ it is of interest to know whether similar distortions occur in the perovskite type of compound.

We find that KCuF_3 and KCrF_3 have tetragonal unit cells which for chemical reasons are assigned to space group $P4/mmm$. The unit cells (Table 1) contain one formula unit

TABLE 1.

	Dimensions		<i>hkl</i>	Relative intensities			
	KCuF_3	KCrF_3		KCuF_3		KCrF_3	
Unit cell size	$a_0 = 4.13 \text{ \AA}$	4.27 \AA	100	Calc. 12	Obs. 14	Calc. 8	Obs. 8
	$c_0 = 3.92 \text{ \AA}$	4.01 \AA	001	5	6	3.6	4.3
Density: obs.	3.97	3.31	110	22	24	20	15
calc.	3.96	3.39	101	42	42	36	29
$F_1 - F_1$	2.92 \AA	3.02 \AA	111	5.5	5.3	8	8
$F_1 - F_{11}$	2.85 \AA	2.93 \AA	200	29	25	28	30
Atomic positions: K at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; Cu or			002	12	14	11	12
Cr at $(0,0,0)$; $3F$ at $(0, \frac{1}{2}, 0)$; $(\frac{1}{2}, 0, 0)$;			210	2.7	3	1.6	3
$(0,0, \frac{1}{2})$.			201	2.5	3	1.5	2
			102	2.2	3	1.3	1
			211	16	13	14	16
			112	7	8	6	11
			220	8	6	8	10
			202	14	14	13	16

and are closely related to the cubic perovskite cell. In each compound the transition metal has six octahedrally disposed fluorine neighbours, but the tetragonal distortion is caused by unequal metal-fluorine bond lengths; two of the six M-F distances are shorter than the other four (Table 2). The bonds are therefore distorted in a sense opposite to

TABLE 2. Transition metal-fluorine distances in copper(II) and chromium(II) fluorine compounds (\AA).

CuF_2 2 at 2.27	KCuF_3 4 at 2.07	K_2CuF_4 4 at 2.08
4 at 1.93	2 at 1.96	2 at 1.95
CrF_2 2 at 2.43	KCrF_3 4 at 2.14	
2 at 2.01	2 at 2.00	
2 at 1.98		

that found in the large majority of Cu^{II} and Cr^{II} compounds such as the difluorides, in which there are four shorter and two longer transition metal-fluorine bonds; in fact the only other example of such a distortion is in the very recently determined structure of K_2CuF_4 in which the Cu-F bond distances are nearly identical to those found by us for KCuF_3 .

The infrared peaks for KCuF_3 and KCrF_3 ⁵ are out of sequence with those of the other

¹ Martin, Nyholm, and Stephenson, *Chem. and Ind.*, 1956, 83.

² Billy and Haendler, *J. Amer. Chem. Soc.*, 1957, **79**, 1049.

³ Jack and Maitland, *Proc. Chem. Soc.*, 1959, 232.

⁴ Knox, *J. Chem. Phys.*, 1959, **30**, 991.

⁵ Peacock and Sharp, *J.*, 1959, 5545.

transition-metal perowskites (Cr, 481; Mn, 407; Fe, 431; Co, 439; Ni, 445; Cu, 489; Zn, 437 cm.⁻¹) and in view of the present work it seems probable that they reflect the longer M-F distances only.

Experimental.—Potassium trifluorocuprate(II) is prepared by the addition of a cupric chloride solution to a boiling solution of potassium fluoride just acidified with hydrofluoric acid. It has been reported as green, blue, or white; we find that the pure compound is a white crystalline powder (Found: K, 24.6; F, 35.9. Calc. for KCuF₃: K, 24.5; F, 35.7%).

Potassium trifluorochromate(III) is obtained by the addition of solid chromous acetate to potassium hydrogen fluoride solution in the absence of air. The compound, which is pale blue, is very difficult to obtain pure because it oxidises easily when wet; our specimens always contained a little potassium fluoride (Found: K, 28.2; F, 39.4. Calc. for KCrF₃: K, 26.4; F, 38.5%).

Thin-walled Pyrex capillaries were used to hold X-ray powder samples and photographs were taken with a 19 cm. Hilger camera with filtered Cu-K_α radiation. Duplicate films were microphotometered on a Hilger instrument (Type L 451); some difficulty was encountered with KCrF₃ because of the intense background.

The calculated intensity of a powder reflection is given by the expression

$$I_c = \text{constant} \times F^2_{hkl} \cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta} \cdot pAT$$

where T is the temperature factor and the other symbols have their usual meaning. We have assumed that A and T cancel since the crystals are of moderate absorption.⁶ Scattering factors were corrected for dispersion by the K electrons. Values of the scattering factors are those of Berghuis *et al.*⁷

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⁶ Bradley, *Proc. Phys. Soc.*, 1935, **47**, 879.

⁷ Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

830. Nitration of *m*-Iodonitrobenzene.

By R. S. KAPIL.

THE nitration of *m*-iodonitrobenzene has been reported;^{1,2} the only product isolated was 4-iodo-1,2-dinitrobenzene. We have reinvestigated this reaction. Although it might give a mixture of dinitro-isomers, only 3-iodo-³ and 4-iodo-1,2-dinitrobenzene were isolated.

In 1-iodo-2,3-dinitrobenzene the nitro-group in position 2 is mobile and reacts with alcoholic ammonia to give 2-iodo-6-nitroaniline. The observation agrees with that of Hodgson and Smith⁴ who isolated under similar conditions 2-methyl-6-nitroaniline from 2,3-dinitrotoluene. 4-Iodo-1,2-dinitrobenzene behaves normally with hydrazine hydrate, giving mainly 5-iodo-2-nitrophenylhydrazine.

Experimental.—Nitration of *m*-iodonitrobenzene. To a cooled suspension of *m*-iodonitrobenzene (10 g.) in concentrated sulphuric acid (42 c.c.; d 1.82), fuming nitric acid (28 c.c.; d 1.5) was added dropwise with vigorous shaking, the temperature being kept below 10°.

¹ Jacobson, Fertsch, and Heubach, *Annalen*, 1898, **303**, 339.

² Ullmann and Bielecki, *Ber.*, 1901, **34**, 2179.

³ Wender, *Gazzetta*, 1889, **19**, 231.

⁴ Hodgson and Smith, *J.*, 1933, 500.

The mixture was heated on a water-bath for 2 hr., then poured on crushed ice. The solid mass on repeated crystallization from ethanol gave 4-iodo-1,2-dinitrobenzene as yellow plates, m. p. 74° (Found: I, 42.9. Calc. for $C_6H_3O_4N_2I$: I, 43.2%).

The mother-liquor deposited needles of 3-iodo-1,2-dinitrobenzene, which recrystallized as pale yellow needles (0.7 g.), m. p. 138° (lit.,³ 138°), from ethanol (Found: I, 43.0%).

Action of alcoholic ammonia on 1-iodo-2,3-dinitrobenzene. The iododinitrobenzene (1 g.) in ethanol was refluxed with alcoholic ammonia for 2 hr. On cooling, 2-iodo-6-nitroaniline separated in orange-red needles, m. p. 108° (Found: I, 47.9. $C_6H_5O_2N_2I$ requires I, 48.1%).

Action of hydrazine hydrate on 4-iodo-1,2-dinitrobenzene. The iododinitrobenzene (1 g.) in ethanol was treated with 2 equiv. of cold hydrazine hydrate solution. 5-Iodo-2-nitrophenylhydrazine was filtered off after 1 hr., and recrystallized from ethyl acetate in orange-red needles (0.6 g.), m. p. 150° (Found: I, 45.3. $C_6H_6O_2N_3I$ requires I, 45.5%). It formed an *acetyl derivative*, lemon-yellow needles, m. p. 228° (from ethanol) (Found: I, 39.5. $C_8H_8O_2N_3I$ requires I, 39.6%), a *diacetyl derivative*, lemon-yellow needles or plates m. p. 172° (from ethanol) (Found: I, 34.8. $C_{10}H_{10}O_4N_3I$ requires I, 35.0%), a *propionyl derivative*, lemon-yellow needles, m. p. 162° (from ethanol) (Found: I, 37.7. $C_9H_{10}O_3N_3I$ requires I, 37.8%), and a *benzoyl derivative*, pale yellow needles, m. p. 200° (from ethanol) (Found: I, 33.1. $C_{13}H_{10}O_3N_3I$ requires I, 33.2%).

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831. *The Preparation of 2-Nitroacetophenone from o-Nitroaniline, and the Synthesis of 2-Phthalimidoacetophenone.*

By J. MALCOLM BRUCE and R. IAN FRYER.

SEVERAL methods¹ have been used for the preparation of 2-nitroacetophenone, but the extension of Beech's procedure² to this compound has not previously been described. Diazotised *o*-nitroaniline with acetaldehyde semicarbazone gave 9% of 2-nitroacetophenone semicarbazone, and with acetaldoxime gave, after hydrolysis of the intermediate oxime, 24% of 2-nitroacetophenone.

For another study, an *NN*-diacyl derivative of 2-aminoacetophenone was required. Atkinson *et al.*³ reported that 2-diacetamidoacetophenone resulted when the amine was boiled with acetic anhydride, but in our hands this yielded only the monoacetyl derivative. Addition of a catalyst caused extensive decomposition. However, 2-phthalimidoacetophenone was obtained by treating the amine with phthalic anhydride in *NN*-dimethylformamide or acetic acid, but it was more conveniently prepared by cyclisation of 2-*o*-carboxybenzamidoacetophenone.⁴

Experimental.—Solvents were removed on the water-bath, where necessary under reduced pressure (water-pump). M. p.s are corrected.

2-Nitroacetophenone Semicarbazone. *o*-Nitroaniline (13.8 g.) in 6% hydrochloric acid (125 c.c.) was diazotised with sodium nitrite (7 g.) in water (15 c.c.), treated with sodium acetate (5.5 g.) in water (15 c.c.), and added during 15 min. below the surface of a stirred solution of acetaldehyde semicarbazone (15 g.), sodium acetate hydrate (54 g.), copper sulphate (5 g.), and sodium sulphite hydrate (0.8 g.) in water (140 c.c.) at 10–20°. The mixture was stirred

¹ (a) Kiang, Mann, Prior, and Topham, *J.*, 1956, 1319; (b) Reynolds and Hauser, *Org. Synth.*, 1950, 30, 70, and references cited therein; Emerson, Heyd, Lucas, Stevenson, and Wills, *J. Amer. Chem. Soc.*, 1947, 69, 706.

² Beech, *J.*, 1954, 1297.

³ Atkinson, Simpson, and Taylor, *ibid.*, p. 165.

⁴ Bogert and Nabenhauer, *J. Amer. Chem. Soc.*, 1924, 46, 1702.

for 2 hr., then filtered, and the solid was washed with water, dried *in vacuo*, and extracted successively with boiling benzene (150 c.c.) and ethanol (150 c.c.). On being cooled the latter solution deposited a solid from which, by repeated crystallisation from ethanol, the *semicarbazone* (2 g., 9%) was obtained as bright yellow needles, m. p. 210—211° undepressed on admixture with material prepared from authentic ^{1a} 2-nitroacetophenone (Found: C, 48.9; H, 4.6; N, 25.3. C₉H₁₀O₃N₄ requires C, 48.7; H, 4.5; N, 25.2%).

2-Nitroacetophenone. *o*-Nitroaniline (27.6 g.) was diazotised as above, sodium acetate (17.5 g.) in water (30 c.c.) was added, and the solution was neutralised to Congo Red with hydrochloric acid. Solutions of acetaldoxime (18 g.) in water (30 c.c.), and of copper sulphate (10 g.), sodium sulphite hydrate (1.6 g.), and sodium acetate hydrate (130 g.) in water (120 c.c.), were then added simultaneously, the former below the surface, during 1 hr., and the mixture was neutralised to Congo Red, treated with concentrated hydrochloric acid (225 c.c.), and refluxed for 3 hr. Distillation in steam afforded an oil which was isolated by extraction with ether, washed with aqueous 5% sodium hydroxide, and distilled to give the nitro-ketone (8 g., 24%), b. p. 170—176°/25 mm. The semicarbazone had m. p. and mixed m. p. 209—210°.

2-Acetamidoacetophenone. 2-Aminoacetophenone ^{1a} (1.35 g.) was refluxed with acetic anhydride (5 c.c.) for 1½ hr., the solvent was removed, and the residue was distilled at 0.01 mm. (bulb-to-bulb, bath at 110°) to give an oil from which, by crystallisation from aqueous ethanol, the derivative (1.0 g.) was obtained as needles, m. p. 75° (lit.,⁵ 76°) (Found: C, 67.9; H, 6.3; N, 7.8. Calc. for C₁₀H₁₁O₂N: C, 67.8; H, 6.2; N, 7.9%). Addition of sodium acetate or (+)-camphor-10-sulphonic acid caused extensive decomposition. Atkinson *et al.*³ report m. p. 84—86° for 2-diacetamidoacetophenone.

2-Phthalimidoacetophenone. (a) A solution of 2-aminoacetophenone (1.35 g.) and phthalic anhydride (1.48 g.) in *NN*-dimethylformamide (10 c.c.) was heated at 100° for 1 hr., stirred, and refluxed for 2 hr., and the solvent was removed. The residue was extracted with cold benzene (20 c.c.), and the soluble material was distilled at 0.01 mm. (bulb-to-bulb, bath at 200°) to give a yellow oil which, on being crystallised from benzene-light petroleum (b. p. 40—60°), afforded the *ketone* (0.85 g., 32%) as blades, m. p. 134.5—135° (Found: C, 72.4; H, 4.3; N, 5.4. C₁₆H₁₁O₃N requires C, 72.5; H, 4.2; N, 5.3%). A yield of 38% was obtained when the amine and the anhydride were refluxed together for 5 hr. with sodium acetate (4 g.) in acetic acid (20 c.c.). The *2,4-dinitrophenylhydrazone*, orange blades from butan-1-ol, had m. p. 226° (Found: C, 59.1; H, 3.5; N, 15.7. C₂₂H₁₅O₆N₃ requires C, 59.3; H, 3.4; N, 15.7%).

(b) A mixture of 2-*o*-carboxybenzamidoacetophenone⁴ (25.5 g.), sodium acetate (40 g.), and acetic acid (300 c.c.) was stirred and refluxed for 5 hr., solvent (200 c.c.) was removed, and the residue, after being cooled to 50°, was added to water (600 c.c.). The suspension was stirred for 3 hr., then filtered, and the solid was washed with water, dried, and sublimed at 130°/0.01 mm. Crystallisation of the sublimate from light petroleum (b. p. 100—120°) afforded the *ketone* (15.3 g., 64%), m. p. and mixed m. p. 134—135°.

One of us (R. I. F.) thanks Dr. L. Hellberg for discussions.

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⁵ Davey and Gwilt, *J.*, 1957, 1008.

832. *The Relation between the Heat and Volume of Mixing.*

By J. S. ROWLINSON and A. R. MATHIESON.

MATHIESON¹ has recently proposed equations for the calculation of the heat of mixing from the volume of mixing of a binary mixture. His key equation, (12), relates the derivatives with respect to composition of ΔH and ΔV , where these are the differences of the molar heat and volume of the mixture and those of separated components at the same

¹ Mathieson, *J.*, 1958, 4444.

pressure and temperature. It can be most simply derived from the usual rules of partial differentiation, as follows:

$$\left(\frac{\partial \Delta H}{\partial x}\right)_{\Delta V, T} = \left(\frac{\partial \Delta H}{\partial x}\right)_{P, T} + \left(\frac{\partial \Delta H}{\partial P}\right)_{x, T} \left(\frac{\partial P}{\partial x}\right)_{\Delta V, T}$$

$$\left(\frac{\partial P}{\partial x}\right)_{\Delta V, T} = - \left(\frac{\partial \Delta V}{\partial x}\right)_{P, T} / \left(\frac{\partial \Delta V}{\partial P}\right)_{x, T}$$

whence

$$\left(\frac{\partial \Delta H}{\partial x}\right)_{P, T} = \left(\frac{\partial \Delta H}{\partial x}\right)_{\Delta V, T} + \left(\frac{\partial \Delta H}{\partial P}\right)_{x, T} \left(\frac{\partial \Delta V}{\partial x}\right)_{P, T} / \left(\frac{\partial \Delta V}{\partial P}\right)_{x, T} \quad (12)$$

It was suggested¹ that $(\partial \Delta H / \partial x)_{\Delta V, T}$ may be neglected if ΔH is proportional to ΔV at a given pressure and temperature. This condition is necessary but not sufficient. Let $\Delta H(P, T, x) = A(P, T) \cdot \Delta V(P, T, x)$ where A is a constant of proportionality that is independent of x at a given P and T . Then

$$\left(\frac{\partial \Delta H}{\partial x}\right)_{\Delta V, T} = \Delta V \left(\frac{\partial A}{\partial x}\right)_{\Delta V, T}$$

$$= -\Delta V \left(\frac{\partial A}{\partial P}\right)_T \left(\frac{\partial \Delta V}{\partial x}\right)_{P, T} / \left(\frac{\partial \Delta V}{\partial P}\right)_{x, T}$$

This is zero only if A is independent of pressure. In general A is a function of pressure, and is certainly so for the statistical models cited,¹ for which this term in eqn. (12) is the larger and is of opposite sign to the term retained. Any value of this equation without this term must therefore be justified experimentally.

Since either ΔV or $T(\partial \Delta V / \partial T)_{P, x}$ may be the greater, Mathieson's eqn. (15) allows ΔH to be positive or negative for positive ΔV , as is required.

However, for the system cyclohexane-carbon tetrachloride the sign of

$$(\partial P / \partial \Delta V)_{T, x} (\partial \Delta H / \partial P)_{T, x}$$

has been overlooked and the apparent agreement for this system is fortuitous.¹ For the other three non-polar systems considered,¹ $T(\partial \Delta V / \partial T)_{P, x} > \Delta V$ and the agreement stands. The disagreement for cyclohexane-carbon tetrachloride may be connected with the unusual variation² of $(\partial \Delta V / \partial T)_{P, x}$ with x . For the other systems, even ethanol-water, this has a maximum value at some intermediate value of x around 0.5, but for cyclohexane-carbon tetrachloride it is roughly linear in x , passing through zero at about $x = 0.6$. Further experimental evidence exists in favour of eqn. (12), with $(\partial \Delta H / \partial x)_{\Delta V, T}$ neglected. Scatchard³ has derived equations $(\Delta E)_V = \Delta V / \beta$ and

$$(\Delta H)_P = (\Delta V / \beta) [1 + T(\partial V / \partial T) / V - \Delta V (1 + d \ln \beta / dT) / 2V]$$

which closely resemble Mathieson's eqn. (15) when $\beta = \beta_0$, and they have been tested by Meares⁴ who found good agreement for a wide range of mixtures of butane-1,3-diol diacetate with other esters.

No general relation between ΔH and ΔV has been sought from classical thermodynamics, as restrictive conditions have been imposed,¹ the validity of which can only be determined by comparison with experiment.

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² Wood and Gray, *J. Amer. Chem. Soc.*, 1952, **74**, 3729.

³ Scatchard, *Trans. Faraday Soc.*, 1937, **33**, 160.

⁴ Meares, *ibid.*, 1949, **45**, 1066.

833. *Chlorine Hydrate.*

By K. W. ALLEN.

Chlorine hydrate has a formula $\text{Cl}_2 \cdot 7.27 \pm 0.17\text{H}_2\text{O}$.

CHLORINE HYDRATE has been investigated often since Davey deduced that it is a compound.¹ Faraday analysed it and concluded that it should be represented as $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$.² Roozeboom³ determined the saturated vapour pressure-temperature relationships from -10° to $+16^\circ$ and carried out a series of analyses from which he concluded that the formula was $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$. Much recent work has used Roozeboom's results. Further analyses have been reported by Bouzat and Azinieres⁴ and Anwar-Ullah⁵ all of which led to the formula $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$.

There have been several thermodynamic discussions, all using essentially a Hess's law type of calculation. Of these, the most significant⁶ concludes that the formula should be $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, but this depends entirely upon Roozeboom's data.³

More recently, consideration of clathrate compounds has led to a fuller understanding of the gas hydrates and particularly of chlorine hydrate. They are now explained as a regular framework of water molecules containing voids or holes large enough to contain gas molecules. Two separate structures have been described to account for gas hydrates (*e.g.*, chlorine, sulphur dioxide, methyl chloride) with a cell-constant of 12 Å, and the liquid hydrates (*e.g.*, ethyl chloride, chloroform) with a cell-constant of 17.2 Å. Each of these contains holes of two different sizes. The unit cell of the gas hydrate structure contains 46 water molecules and provides two small and six medium holes, while that of the liquid hydrate contains 136 water molecules and provides sixteen small and eight large holes.^{7,8} For a particular gas hydrate, depending largely upon the size of the gas molecule, there are four possibilities: medium holes all filled; medium and small holes all filled; all medium and some small holes filled; some medium and some small holes filled.

For chlorine hydrate, von Stackelberg *et al.*⁸ assumed a formula $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and explained this as due to a 96% filling of all the holes. Pauling and Marsh⁹ compared the X-ray diffraction patterns measured for chlorine hydrate with those calculated for the general gas-hydrate structure, assuming different ways of filling the holes. They deduced that chlorine molecules occupy the medium holes only and none of the small holes, and consequently they predicted a composition corresponding to $\text{Cl}_2 \cdot 7\frac{2}{3}\text{H}_2\text{O}$.

Further understanding of this compound depends upon a precise knowledge of its actual composition, which we have now established.

The value 7.27 ± 0.17 found for the ratio of water to chlorine molecules does not correspond exactly to the filling of the medium holes as suggested by Pauling and Marsh,⁹ for which the value is 7.67. It is even further from the value 6.0 used by von Stackelberg⁸ which approximates to filling all medium and small holes.

In view of Pauling and Marsh's results,⁹ it seems certain that the structure involves filling of all the medium holes together with a few of the small holes with chlorine molecules. If 20% of the small holes are filled, a structure and composition consistent with the experimental result is obtained. This proposition is further supported by the calculated value for the density which is 1.29 g./ml. for this structure (1.26 g./ml. for $6\text{Cl}_2 \cdot 46\text{H}_2\text{O}$; 1.40 g./ml. for $8\text{Cl}_2 \cdot 46\text{H}_2\text{O}$; 1.38 g./ml. for $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$). The experimental value, reported by von Stackelberg *et al.*,⁸ is 1.29 ± 0.02 g./ml.

¹ Davey, *Phil. Trans.*, 1811, **101**, 30.

² Faraday, *Quart. J. Science, Literature, and Arts*, 1823, **15**, 71.

³ Roozeboom, *Rec. Trav. chim.*, 1884, **3**, 59; 1885, **4**, 65.

⁴ Bouzat and Azinieres, *Bull. Soc. chim. France*, 1924, **35**, 545.

⁵ Anwar-Ullah, *J.*, 1932, 1172.

⁶ Ivan Harris, *Nature*, 1943, **151**, 309.

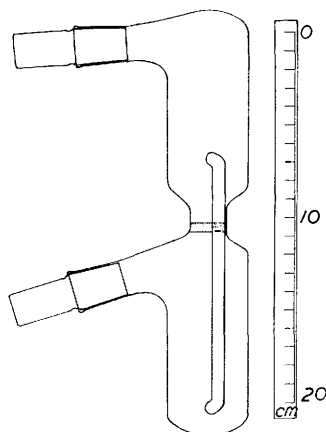
⁷ Clausen, *J. Chem. Phys.*, 1951, **19**, 259, 662, 1425.

⁸ von Stackelberg *et al.*, *Z. Electrochem.*, 1954, **58**, 25, 40, 99, 104, 162.

⁹ Pauling and Marsh, *Proc. Nat. Acad. Sci. U.S.A.*, 1952, **38**, 112.

EXPERIMENTAL

To avoid having to dry the crystals of chlorine hydrate, which had been a source of constant difficulty and error in all previous analytical work, Schreinmakers' wet-residue method was used.¹⁰ Chlorine hydrate was prepared by passing a stream of chlorine gas at atmospheric pressure through dilute solutions of calcium chloride (5–14% of CaCl_2) at 0° . Because the crystals are very feathery and difficult to separate adequately from the mother-liquor, this was done in a special equilibrium apparatus which consisted of two glass bulbs separated by a coarse sintered-glass disc (Figure). Chlorine was passed in through the upper opening. It went through the side tube and bubbled up through the solution. Excess of gas escaped from the



lower opening to waste. When a fair quantity of solid hydrate had formed, the openings were closed with glass-stoppers lubricated with "Fluorube" grease. The whole apparatus was kept in ice for several days, with occasional shaking to attain equilibrium, then inverted so that the solid was filtered off on the sintered disc, and left inverted in ice for several hours to allow the solid to drain. Portions of the solid were transferred with a dry fork made of very fine glass rod to tared weighing bottles containing saturated potassium iodide solution. Samples of the liquid were transferred with an all-glass hypodermic syringe fitted with a glass needle to similar weighing bottles. From this stage all the samples were analysed in the same way. After re-weighing, the samples were transferred to beakers and the iodine which had been liberated by the free chlorine was titrated with 0.05N-sodium thiosulphate and sodium starch glycollate indicator. Then the calcium chloride was determined gravimetrically in these

solutions by precipitation as calcium oxalate, ignition to calcium carbonate, and weighing.

Since in each case the wet solid of known total composition is a mixture of liquid of known composition and dry solid, the composition of the dry solid can be found. Usually this is done by graphical extrapolation on an equilateral triangle, but in this instance the intersections were too acute for this method to be sufficiently accurate. The results were plotted on rectangular co-ordinates and the extrapolations were all calculated algebraically.

Sixteen conjugate pairs of liquid and wet solid were analysed and the compositions of dry solids were calculated. The final value for the composition of chlorine hydrate was $35.15 \pm 0.54\%$ of chlorine. This corresponds to a formula $\text{Cl}_2, 7.27 \pm 0.17\text{H}_2\text{O}$.

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LONDON, E.C.1.

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¹⁰ Schreinmakers, *Z. phys. Chem.*, 1893, **11**, 75.

834. *The Ionisation Potential of NH.*

By R. I. REED and W. SNEDDEN.

THE latent heat of the sublimation of carbon and the heat of atomisation of nitrogen are not independent quantities¹ and the preferred value² of $L(\text{C}) = 7.386$ ev leads to $D(\text{N-N}) = 9.67$.³ It is accordingly of interest to examine, by electron-impact methods already described,² certain of the bond-dissociation energies in ammonia. The experimental results, which are more extensive than those hitherto obtained are in the Table.

¹ Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1954, p. 165.

² Reed and Snedden, *Trans. Faraday Soc.*, 1958, **54**, 949.

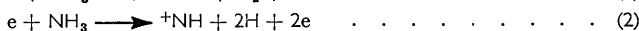
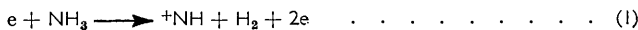
³ Franklin and Field, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press Inc., New York, 1957, p. 270.

It appears that Mann, Hustrulid, and Tate's⁴ earlier method has yielded an average value for $A(^+NH)$ and only the excited states of the nitrogen ion for $A(^+N)$.

Species	NH	N
Appearance potential (ev \pm 0.1)	17.1, 21.6	22.6, 24.1, 26.65, 28.6
" " " (ev \pm 0.5, ref. 4)	19.4	25.0, 28.1
Ionisation potential (ev \pm 0.05)	13.10	—

There is already good evidence for the value of the first bond-dissociation energy obtained by electron-impact studies upon ammonia,⁴ and also by the pyrolysis of hydrazine⁵ and benzylamine,⁶ the values being 4.50 ev, 4.34 ev, and 4.51 ± 0.08 ev respectively—in good agreement.

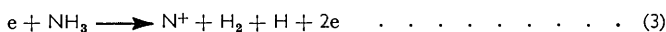
Our work has shown two appearance potentials for the ^+NH ion 4.5 ± 0.2 ev apart. Such a difference, which corresponds to the dissociation energy of molecular hydrogen, suggests that this ion is obtained by the two reaction processes:



the second being associated with the value of 21.6 ± 0.1 ev.

The available test for the presence of excess of kinetic energy² suggests that it is absent, and, the production of all the fragments in their electronic ground states being assumed, $D(NH-H) = A(^+NH) - I(NH) - D(NH_2-H) + D(H-H)$ can be written for eqn. (1), and the same expression less the final term $D(H-H)$ for (2). Substituting the measured values and $D(NH_2-H) = 4.50$ ev, we obtain the energy 4.0 ± 0.15 ev in each case.

A similar examination of the appearance potentials of the N^+ ion from ammonia gave four values which are considered to result from two fragmentations:



in which all the fragments are formed in their electronic ground states, and two in which the N^+ ion is formed in the 1D state. These considerations lead to four equations for $D(N-H)$ of which

$$D(N-H) = A(N^+) = I(N) - D(NH_2-H) - D(NH-H) + D(H-H)$$

$$\text{and} \quad D(N-H) = A(^*N^+) - I(N) - D(NH_2-H) - D(NH-H) + e$$

are two, $^*N^+$ representing the electronically excited nitrogen ion. Substitution of the previously determined bond energies and the spectroscopic quantities $I(N) = 14.477$ ev⁷ and $E_e = N(^3P) \longrightarrow N(^1D) = 1.90$ ev⁸ gives $D(N-H) = 3.7 \pm 0.25$ ev, 3.67 ± 0.25 ev, 3.7 ± 0.25 ev, and 3.7 ± 0.25 ev. A spectroscopic determination of $D(N-H) = 3.8$ ev⁸ has already been made, and the present values are in good agreement. This quantity together with the heats of atomisation of nitrogen and hydrogen allow the evaluation of $\Delta H_i(NH, g) = 3.57$ ev, a figure previously obtained by Altshuller.⁹ Combining this quantity with $\Delta H_i(NH_2, g) = 1.76$ ev, we obtain the bond-dissociation energy $D(NH-H) = 4.07$ ev. This agrees well with the present electron-impact value, suggesting that $I(NH) = 13.10 \pm 0.05$ ev is probably correct. The ionisation potentials of the iso-electronic species are $I(O) = 13.61$ ev¹⁰ and $I(CH_2) = 11.9 \pm 0.1$ ev.¹¹

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[Received, June 15th, 1959.]

⁴ Mann, Hustrulid, and Tate, *Phys. Rev.*, 1940, **58**, 340.

⁵ Szwarc, *Proc. Roy. Soc.*, 1949, *A*, **198**, 267.

⁶ *Idem*, *ibid.*, p. 285.

⁷ Moore, Nat. Bur. Stand. Circular No. 467, 1949.

⁸ Pannetier and Gaydon, *J. Chim. phys.*, 1951, **48**, 221.

⁹ Altshuller, *J. Chem. Phys.*, 1954, **22**, 1947.

¹⁰ Nier and Hanson, *Phys. Rev.*, 1936, **50**, 722.

¹¹ Langer, Hipple, and Stevenson, *J. Chem. Phys.*, 1954, **22**, 1836.

835. *Hydrolysis of Isopropylideneglycerol Esters of Fatty Acids.*

By L. HARTMAN.

FOR the preparation of pure α -monoglycerides of fatty acids the classical method of Fischer *et al.*¹ based on the acylation of isopropylideneglycerol is regarded as most reliable and convenient.² The only difficulty is encountered in the removal of the blocking group, which is accomplished by hydrolysis with mineral acids. This hydrolysis requires varying conditions depending on the molecular weight of the fatty acids and induces partial splitting of the low-molecular monoglycerides into glycerol and fatty acids. Some isomerisation to β -monoglycerides also appears possible in view of recent findings³ that there exists an equilibrium between the 1- and the 2-ester, involving 8—10% of the latter. Aqueous acetic acid⁴ is well suited for the hydrolysis of isopropylideneglycerol esters of C_2 — C_5 acids, but the hydrolysis becomes increasingly difficult with the homologous acids, and impracticable from nonanoic acid onward. Boric acid, used successfully by Martin⁵ in the removal of the benzylidene group from 2-acyl-1,3-benzylideneglycerols, was found in the present work to be a convenient reagent in the hydrolysis of isopropylideneglycerol esters. This acid is known to form esters with glycerol which are readily decomposed on contact with water. Thus cleavage of isopropylideneglycerol esters with boric acid, followed by treatment with water, leads to α -monoglycerides. The main difficulty was the selection of a suitable co-solvent for boric acid and the esters. Triethyl borate used by Martin⁵ is difficult to prepare and, moreover, was not particularly effective in this instance. Dioxan, several alcohols, and other solvents were tried with varying success and finally 2-methoxyethanol was selected as most convenient. Contrary to expectation the hydrolysis with boric acid and hydrochloric acid produced similar amounts of impurities in the case of high-molecular esters, and no saving in the purification of the crude product could be achieved. Nevertheless, the procedure described below may be found a convenient alternative to the classical method because of the greater ease of operation, particularly for esters of acids of medium chain length (C_8 — C_{12}), the hydrolysis of which requires otherwise special precautions. Monocaproin represents about the limit of the usefulness of the proposed procedure. Monoglycerides of C_2 — C_5 acids, which are increasingly soluble in water, are best prepared by hydrolysis with aqueous acetic acid.⁴

Experimental.—Isopropylideneglycerol esters of highly purified fatty acids were prepared by the classical method as modified by Daubert *et al.*⁶ After the evaporation of solvents used they were dried in a vacuum-desiccator, and aliquot parts were hydrolysed to monoglycerides. A few examples are given below.

α -Monostearin. Isopropylideneglycerol stearate (4 g., 0.01 mole) and finely powdered boric acid (6.2 g., 0.1 mole) were heated with 2-methoxyethanol (20 ml.) on a boiling-water bath for 30 min. A small amount of boric acid remained undissolved. The mixture was taken up in ether and washed three times with water, the ethereal solution was dried (Na_2SO_4), most of the solvent was evaporated, and the product was dried first in the air and finally in a vacuum-desiccator. The yield of crude monoglyceride was 3.6 g. (theoretical); it had m. p. 78—79°, acid value 4.7, and α -monoglyceride content by the periodate method⁷ 89.8%. After two crystallisations from ether pure α -monostearin, m. p. 81—81.5°, was obtained. Crude monostearin prepared by hydrolysis with hydrochloric acid had m. p. 79—80°, acid value 2.8, and α -monoglyceride content 91.3%. Determination of β -monoglycerides in both crude products by the method of Brokaw *et al.*⁸ gave no definite results since perchloric acid used as the isomeris-

¹ Fischer, Bergmann, and Bärwind, *Ber.*, 1920, **53**, 1589.

² Malkin and Bevan, in "Progress in the Chemistry of Fats and Other Lipids," Pergamon Press, London, 1957, Vol. IV, p. 66.

³ Martin, *J. Amer. Chem. Soc.*, 1953, **75**, 5483.

⁴ Baer and Fischer, *ibid.*, 1945, **67**, 2031.

⁵ Martin, *ibid.*, 1953, **75**, 5482.

⁶ Daubert, Fricke, and Longenecker, *ibid.*, 1943, **65**, 2142.

⁷ Pohle and Mehlenbacher, *J. Amer. Oil Chemists' Soc.*, 1950, **27**, 54.

⁸ Brokaw, Perry, and Lyman, *ibid.*, 1955, **32**, 194.

ation reagent hydrolysed some of the residual isopropylidenglycerol ester. It seems, however, that neither product contained appreciable amounts of the β -isomer.

In practice drying of isopropylidenglycerol ester and isolation of the crude monoglyceride can be omitted.

α -Monolaurin. Crude monolaurin prepared in 97% yield by using similar molar proportions and conditions had m. p. of 58—59°, acid value 8.4, and α -monoglyceride content 87.7%. After crystallisation from a mixture of ether and light petroleum the m. p. rose to 62—63°.

α -Monocaprylin. The crude product had m. p. of 34.5—35.8°, acid value 12.2, and α -monoglyceride content 87.6%. After several crystallisations from light petroleum the m. p. was 39.5—40.5° and the α -monoglyceride content 100.9%. (No m. p. for racemic α -monocaprylin could be found in the literature. The m. p. of the optically active L- α -monoglyceride had been reported as 28—30°.*)

α -Monocaproin. Isopropylidenglycerol hexanoate (4.6 g., 0.02 mole), boric acid (6.2 g., 0.1 mole), and 2-methoxyethanol (20 ml.) were heated at 100° for 30 min. The mixture was taken up in 5% aqueous sodium hydrogen carbonate and extracted three times with ether. The syrup remaining after evaporation of the ether was purified by extraction with light petroleum in which the monoglyceride is difficultly soluble. After a final crystallisation from ether-light petroleum (1 : 3) at -20° the m. p. was 18.5—19.5° (lit.,⁹ 19.4°) and the α -monoglyceride content 99.4%.

Thanks are expressed to Miss J. M. Monnie for technical assistance.

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WELLINGTON, NEW ZEALAND. [Received, June 22nd, 1959.]

⁹ Daubert, Spiegl, and Longenecker, *J. Amer. Chem. Soc.*, 1943, **65**, 2144.

836. *A Deuterium Isotope Effect in the Oxidation of Cyclohexanol by Cerium(IV).*

By J. S. LITTLER.

THERE is a primary kinetic isotope effect in the oxidation of cyclohexanol and 1-deuterio-cyclohexanol by quinquivalent vanadium in acid solutions.¹ As the existence of such an effect in the oxidation of an alcohol by another one-electron oxidant had not been observed, the oxidation of the above alcohols by ceric sulphate has now been studied. A kinetic isotope effect $k_H/k_D = 1.9$ has been found, indicating that this reaction also proceeds by a mechanism that requires participation of the C-H bond in the rate-determining process.

Ardon,² who studied the oxidation of ethanol by cerium(IV) in perchloric acid, deduced a rate equation

$$\frac{d[\text{Ce}^{\text{IV}}]}{dt} = \frac{kK[\text{Ce}^{\text{IV}}][\text{alcohol}]}{1 + K[\text{alcohol}]}$$

indicating that a Ce^{IV} -alcohol complex is formed with a stability constant $K = 4.3$ and a decomposition rate constant $k = 67 \times 10^{-4} \text{ sec.}^{-1}$ at 20°. Our results fit a similar equation in which $K = 13.0$ and $k = 1.38 \times 10^{-4} \text{ sec.}^{-1}$ at 50°. Here K is the apparent constant based on the total concentration of cerium(IV), though in fact several ceric sulphate complexes may be reacting species.^{3,4}

As in the case of the oxidation by vanadium, the existence of the isotope effect indicates that the oxidation step probably involves one-electron transfers within a cyclic alcohol- Ce^{IV} complex as in eqn. (1), but the low value of k_H/k_D (cf. $k_H/k_D = 3.6$ for V^{V} in HClO_4 and 4.5 in H_2SO_4) shows the possibility of concurrent oxidation by an acyclic mechanism such

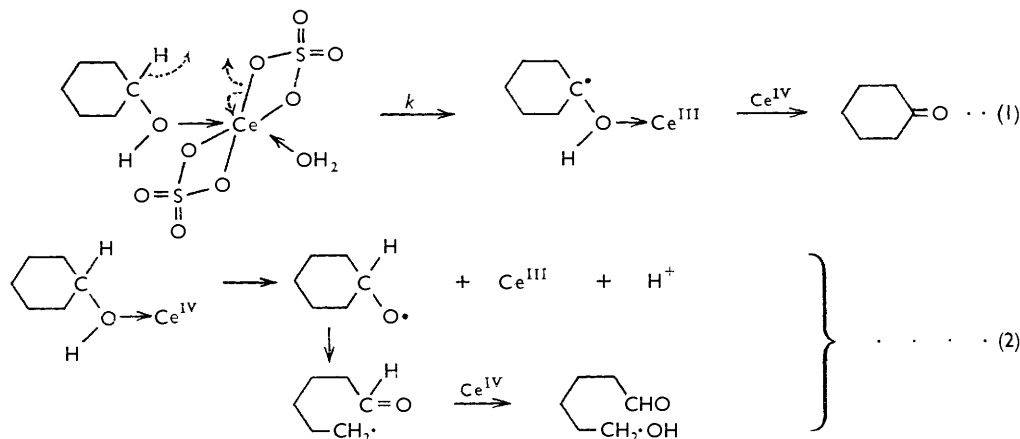
¹ Littler and Waters, *J.*, 1959, 4046.

² Ardon, *J.*, 1957, 1811.

³ Hardwick and Robertson, *Canad. J. Chem.*, 1951, **29**, 828.

⁴ Mino, Kaiserman, and Rasmussen, *J. Amer. Chem. Soc.*, 1959, **81**, 1494.

as (2), corresponding to that suggested by Bawn and White⁵ for the oxidation of alcohols by the much more vigorous oxidant cobalt(III).



Results.—The kinetic measurements were made titrimetrically as in ref. 1. k is the first-order constant, calculated from initial rates of oxidation; the initial organic products are

Oxidation of cyclohexanol and 1-deuterocyclohexanol by Ce^{IV} at 50°.

$$[\text{H}_2\text{SO}_4] = 0.24\text{M}; [\text{Ce}^{\text{IV}}] = 0.0218\text{N}.$$

	Cyclohexanol				1-Deutero- cyclohexanol
[Alcohol]	0.3054	0.2036	0.1018	0.0160	0.0826
$10^4 k$ (sec. ⁻¹)	1.085	1.005	0.78	0.605	0.382

further oxidised and accelerate the reduction of Ce^{IV}, but this was expected.² If $1/k$ is plotted against $1/[\text{alcohol}]$ for the H-alcohol, a good straight line is obtained, showing Ardon's equation to be valid. The point for the D-alcohol is well away from the curve, showing its slower oxidation.

I thank Dr. W. A. Waters, F.R.S., for his interest and encouragement and the Salters' Company for a Scholarship.

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[Received, June 22nd, 1959.]

⁵ Bawn and White, *J.*, 1951, 343.

837. *Aspects of Stereochemistry. Part XIV.* Addition of Hypobromous Acid to Δ^1 -Steroids.*

By H. B. HENBEST and R. A. L. WILSON.

THE reactions of 5α -cholest-1-ene (I) and 5α -cholest-1-en- 3β -ol (V) with peracids give respectively the α -epoxide (II) by normal rear attack and the β -epoxide (V).^{1,2} The unusual course of the latter reaction has been discussed, the suggestion being made that hydrogen-bonding occurs between the 3β -hydroxyl group of the steroid and the peracid molecule during the reaction.²

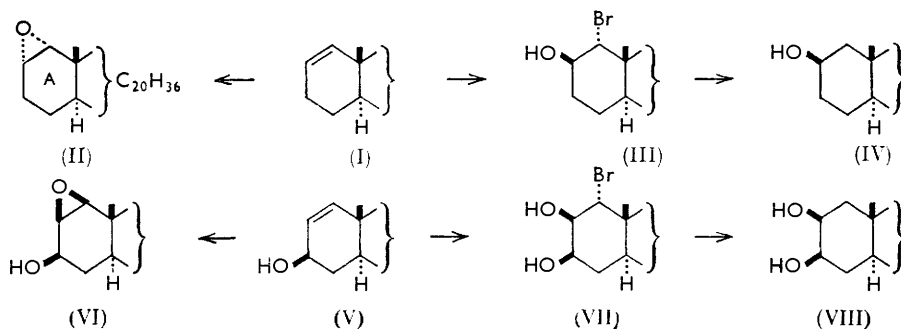
* Part XIII, Henbest and McElhinney, *J.*, 1959, 1834.

¹ Henbest and Wilson, *J.*, 1956, 3289.

² *Idem*, *J.*, 1957, 1958.

It was of interest to find out if other electrophilic reagents might also add to the double bond of the allylic alcohol (V) in an unusual fashion. Additions of hypobromous acid to the compounds (I and V) are now reported, the reactions being carried out in aqueous *t*-butyl alcohol containing *N*-bromosuccinimide and perchloric acid.

One bromohydrin (75% yield) was obtained from the parent 5 α -cholest-1-ene (I). Its structure (III) was established by reduction with sodium and ammonia to the known 2 β -alcohol (IV). The formation of the bromohydrin (III) presumably occurs *via* a 1 α ,2 α -bromonium ion that opens to the diaxial product on reaction with water.



Reaction of the allylic alcohol (V) under the same conditions gave 5 α -cholest-1-en-3-one (36%) and a bromohydrin (60%), whose structure (VII) was proved by reduction to the known 2 β ,3 β -diol (VIII). The ketone and bromohydrin were separated by chromatography on neutral alumina; use of alkaline alumina gave 1 β ,2 β -epoxycholestan-3 β -ol (VI) instead of the bromohydrin. The formation of the bromohydrin (VII) from the allylic 3 β -alcohol (V) is best explained as proceeding through a 1 α ,2 α -bromonium ion. The course of the reaction provides no evidence for the intermediate production of a 1 β ,2 β -bromonium ion, analogous to the formation of the 1 β ,2 β -epoxide (VI), as this would have led to a 2 β -bromo-1 α ,3 β -diol.

Experimental.—M. p.s were determined on a Kofler block. Rotations were measured for chloroform solutions. P. Spence alumina (Grade H) was used for chromatography; dilute acetic acid was used to neutralize and deactivate the alumina.³

1 α -Bromo-5 α -cholestan-2 β -ol (III). *N*-Bromosuccinimide (50 mg.) in aqueous *t*-butyl alcohol (30 c.c.; 5% of water), and *n*-perchloric acid (0.5 c.c.), were added in succession to a solution of 5 α -cholest-1-ene (0.1 g.) in aqueous *t*-butyl alcohol (20 c.c.) at 0°. The solution was kept at 0° for 16 hr. The steroid was then isolated with ether. *1 α -Bromo-5 α -cholestan-2 β -ol* (95 mg.) was obtained as needles, m. p. 113—116° (from acetone), $[\alpha]_D +40^\circ$ (Found: C, 69.5; H, 10.3. C₂₇H₄₇OBr requires C, 69.35; H, 10.1%).

The bromohydrin (50 mg.), in ether (30 c.c.) and methanol (1 c.c.), was added dropwise to a stirred solution of sodium (0.2 g.) in liquid ammonia (50 c.c.) and ether (30 c.c.). After an hour the steroid was isolated with ether. Crystallization from acetone gave 5 α -cholestan-2 β -ol (20 mg.), m. p. and mixed m. p. 151—154°, $[\alpha]_D +35^\circ$.

1 α -Bromo-5 α -cholestan-2 β ,3 β -diol (VII). Solutions of 5 α -cholest-1-en-3 β -ol (1 g.) in aqueous *t*-butyl alcohol (50 c.c.; 5% of water), and *N*-bromosuccinimide (0.5 g.) in aqueous *t*-butyl alcohol (30 c.c.; 5% of water), were mixed at 0° and *n*-perchloric acid (2 c.c.) was added. The solution was kept at 0° for 16 hr. The steroid was then isolated with ether. Chromatography on neutral, deactivated alumina (100 g.) gave cholest-1-en-3-one (0.36 g.) (eluted with benzene, 200 c.c.), m. p. and mixed m. p. 97—99°, and *1 α -bromo-5 α -cholestan-2 β ,3 β -diol* (0.76 g.) (eluted with 700 c.c. of 9 : 1 benzene-ether), m. p. 186—188° [from light petroleum (b. p. 60—80°)], $[\alpha]_D +35^\circ$ (Found: C, 66.7; H, 9.8%. C₂₇H₄₇O₂Br requires C, 67.05; H, 9.8%).

In another experiment, the product was chromatographed on normal alumina (100 g.).

³ Farrar, Hamlet, Henbest, and Jones, *J.*, 1952, 2657.

Elution with benzene (400 c.c.) gave 5 α -cholest-1-en-3-one (0.31 g.), m. p. and mixed m. p. 97—100°; elution with ether (500 c.c.) gave 1 β ,2 β -epoxy-5 α -cholestan-3 β -ol (VI) (0.5 g.), m. p. and mixed m. p. 173—176° (from acetone) (Found: C, 80.4; H, 10.6. Calc. for C₂₇H₄₆O₂: C, 80.6; H, 11.5%).

The bromo-diol (0.2 g.) in ether (50 c.c.) and methanol (1 c.c.) was added slowly to a stirred solution of sodium (0.5 g.) in liquid ammonia (1 l.) and ether (30 c.c.). After 1.5 hr., the steroid was isolated with ether. Crystallization from acetone gave 5 α -cholestane-2 β ,3 β -diol (VIII) (0.1 g.), m. p. and mixed m. p. 173—176°, $[\alpha]_D^{20} + 30^\circ$.

1 β ,2 β -Epoxy-5 α -cholestan-3 β -yl Methanesulphonate. Methanesulphonyl chloride (0.6 c.c.) was added to a solution of 1 β ,2 β -epoxy-5 α -cholestan-3 β -ol (0.7 g.) in pyridine at 0°. The mixture was kept at 20° for 16 hr., then the ester was isolated with ether. It (0.7 g.) had m. p. 133—136° (from methanol), $[\alpha]_D^{20} + 176^\circ$ (Found: C, 70.0; H, 10.1. C₂₈H₄₈O₄S requires C, 69.95; H, 10.05%).

We thank the Department of Scientific and Industrial Research for financial assistance (to R. A. L. W.) and Messrs. E. S. Morton and H. Swift for analyses.

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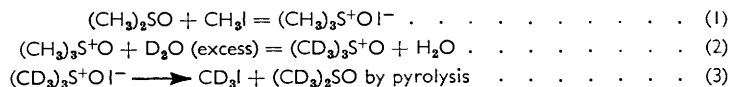
[Received, June 22nd, 1959.]

838. Rapid, Simple, and Inexpensive Preparation of [²H₃]Methyl Iodide and [²H₆]Dimethyl Sulphoxide.

By F. A. COTTON, J. H. FASSNACHT, W. D. HORROCKS, jun., and N. A. NELSON.

FULLY deuterated methyl iodide and dimethyl sulphoxide, especially the former, are useful. The former is a common starting material in the preparation of compounds containing [²H₃]methyl groups; the latter is an unusually good solvent for most classes of organic compound except aliphatic hydrocarbons, and for use in proton magnetic resonance spectroscopy.¹ Its usefulness would be enhanced by ready availability and cheapness. The usual method of preparing [²H₃]methyl iodide involves four steps, *viz.*, (1) deuteration of malonic acid followed by (2) decarboxylation to yield [²H₄]acetic acid, then (3) conversion of this into the silver salt and (4) Hunsdiecker decarboxylation by heating with iodine. We have been unable to find any method in the literature for the preparation of the sulphoxide.

This note describes a quicker, more convenient, and therefore cheaper method of preparing [²H₃]methyl iodide, yielding also [²H₆]dimethyl sulphoxide. The method was suggested by Kuhn and Trischmann's observation² that trimethyloxosulphonium iodide (Me₃S⁺O I⁻), easily made by addition of methyl iodide to dimethyl sulphoxide, could be pyrolysed smoothly back to these substances, and Smith and Winstein's observation³ that trimethyloxosulphonium nitrate readily exchanges with neutral deuterium oxide. Actually, we find that exchange between the iodide and water occurs rapidly only in slightly basic solution. Our reactions are thus:



If only the methyl iodide is required, the sulphoxide can be recycled.

A sequence of the same type will probably yield [1,1-²H₂]ethyl iodide from which various [1,1-²H₂]ethyl derivatives, some possibly of use in structural determinations by microwave spectroscopy, may be obtained.

¹ Slomp and McGarvey, *J. Amer. Chem. Soc.*, 1959, **81**, 2200; also unpublished work in this laboratory.

² Kuhn and Trischman, *Annalen*, 1958, **611**, 117.

³ Smith and Winstein, *Tetrahedron*, 1958, **3**, 317.

Experimental.— $[^2\text{H}_9]$ Trimethyloxosulphonium iodide. Trimethyloxosulphonium iodide² (38 g.) was dissolved in 170 ml. of 99.5% deuterium oxide at 80–100°, and 50 mg. of anhydrous potassium carbonate were added. The solution was heated on a steam-bath for 1 hr., then cooled to 0° for at least 2 hr. before the precipitate was filtered off. The solid was equilibrated twice more by the same procedure to give 33.4 g. (88%) of product.

$[^2\text{H}_3]$ Methyl iodide and $[^2\text{H}_6]$ dimethyl sulphoxide. In a small pear-shaped flask connected through a short Vigreux column to an ice-cooled trap and a liquid-nitrogen trap in series, the whole being connected to a water aspirator through a drying tower, 33.4 g. of $[^2\text{H}_9]$ trimethyloxosulphonium iodide was heated to 200°/20 mm. After 2 hr., during which a small amount of liquid distilled, the crystalline mass melted and rapidly decomposed. Distillation of the material in the first receiver gave 8.9 g. of crude $[^2\text{H}_3]$ methyl iodide (collected at atmospheric pressure) and 9.45 g. (80%) of $[^2\text{H}_6]$ dimethyl sulphoxide, b. p. 88°/24 mm. The yellow colour which frequently forms in the latter liquid can be removed by gentle warming with a little solid sodium thiosulphate followed by distillation from barium oxide. The crude $[^2\text{H}_3]$ methyl iodide and the material in the liquid nitrogen-cooled trap were combined and distilled, giving 17.6 g. (84%) of $[^2\text{H}_3]$ methyl iodide, b. p. 41°.

Both products had 99.0–99.2% deuteration.

This work was supported in part by the U.S. Atomic Energy Commission. We thank Professor K. Biemann and Dr. J. Seibl for mass-spectrographic analyses.

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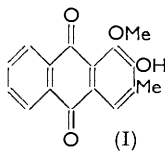
839. Naturally Occurring Quinones. Part III.* A Synthesis of Digitolutein.

By J. C. LOVIE and R. H. THOMSON.

DIGITOLUTEIN is a yellow pigment found in the leaves of the foxgloves, *Digitalis lutea* Linn.¹ and *D. purpurea* Linn.² Degradative studies by Janot *et al.*³ established that the structure was 3-methylalizarin 1-methyl ether (I), and we have now confirmed this by synthesis.

3-Methylalizarin has previously been obtained from 2-hydroxy-3-methylanthraquinone (itself obtained by a two-step condensation of *o*-cresol and phthalic anhydride) by direct,⁴ or indirect,^{3,5} hydroxylation. We find 3-methylalizarin can be conveniently synthesised on a small scale in one step by condensation of 3-methylcatechol with phthalic anhydride in fused aluminium chloride-sodium chloride. Sublimation of the crude product gives 3-methylalizarin adequate for further synthesis. Acetylation in the presence of boroacetic anhydride afforded 3-methylalizarin 2-acetate which was converted, by methylation and subsequent hydrolysis, into 3-methylalizarin 1-methyl ether, identical with natural digitolutein.

An attempt to synthesise 1,2,6,8-tetrahydroxy-3-methylanthraquinone, one of the pigments of *Rhamnus alaternus* Linn.,⁶ by a similar condensation of 3-methylcatechol with 3,5-dimethoxyphthalic anhydride failed. Interaction of these compounds under normal Friedel-Crafts conditions was also unsuccessful owing to the instability of the anhydride which was decarboxylated to 3,5-dimethoxybenzoic acid.



* The papers, J., 1949, 1277 and 1951, 1237, are regarded as Parts I and II of this series.

¹ Adrian and Trillat, *Compt. rend.*, 1899, **129**, 889.

² Paris, *Compt. rend.*, 1954, **238**, 932.

³ Janot, Chabasse-Massonneau, de Graeve, and Goutarel, *Bull. Soc. chim. France*, 1955, 108.

⁴ Mitter and Sen, *J. Indian Chem. Soc.*, 1928, **5**, 631.

⁵ Mitter and Pal, *J. Indian Chem. Soc.*, 1930, **7**, 259.

⁶ Briggs, Jacombs, and Nicholls, *J.*, 1953, 3069.

Experimental.—*3-Methylalizarin.* An intimate mixture of 3-methylcatechol (2.5 g.) and phthalic anhydride (3 g.) was stirred into a molten mixture of anhydrous aluminium chloride (50 g.) and sodium chloride (10 g.) at 120°. The temperature was raised rapidly to 180—200°, and kept there for 5—10 min. with continuous stirring. After some cooling, the melt was poured on ice (500 g.) and concentrated hydrochloric acid (500 ml.). The brown precipitate was dried and then sublimed at 150°/0.05 mm. The red sublimate (m. p. 221—222°) of 3-methylalizarin was not further purified.

3-Methylalizarin 1-methyl ether. 3-Methylalizarin (1 g.) and boroacetic anhydride (2 g.) were refluxed in acetic anhydride (12 ml.) for 5 min., and the red solution left to cool. Next day the reddish-brown acetate-boroacetate was collected, washed with dry ether, and then decomposed by stirring it in cold water for several hours. The resulting *3-methylalizarin 2-acetate* was crystallised from alcohol (charcoal), forming long yellow needles, m. p. 196—197° (Found: C, 68.6; H, 4.1; Ac, 15.4. $C_{17}H_{12}O_5$ requires C, 68.9; H, 4.1; Ac, 14.5%). The above acetate (0.3 g.) in dry acetone (30 ml.) was refluxed with methyl iodide (2 ml.) and silver oxide (2 g.) for 11 hr., more methyl iodide (2 ml.) and silver oxide (2 g.) being added after 6 hr. After filtration and removal of the solvent, the residual *3-methylalizarin 2-acetate 1-methyl ether* was crystallised from alcohol, giving long yellow needles, m. p. 204° (Found: C, 69.4; H, 4.6. $C_{18}H_{14}O_5$ requires C, 69.7; H, 4.5%). Hydrolysis³ of the ether acetate with methanolic potassium hydroxide afforded *3-methylalizarin 1-methyl ether* which crystallised from methanol in yellow needles, m. p. 219° not depressed on admixture with a sample of natural digitolutein, m. p. 218—219° (lit.,³ corrected m. p. 222°) (Found: C, 71.5; H, 4.7. $C_{16}H_{12}O_4$ requires C, 71.6; H, 4.5%). The natural and synthetic materials had identical ultraviolet and infrared spectra.

We are indebted to Professor M.-M. Janot for a specimen of digitolutein, to Dr. H. F. Bondy for a sample of 3-methylcatechol, and to Dr. V. C. Farmer for the infrared spectra in potassium bromide discs.

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840. The Skraup Test for Pyridine-2-carboxylic Acids.

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THE red colour produced by the interaction of solutions of ferrous salts with various pyridine-2-carboxylic acids was first observed by Skraup,¹ and was subsequently used as a test for this group of compounds. Ley *et al.*² prepared the complex ferrous salts of picolinic, pyrazine-3,5-dicarboxylic, and quinoxaline-2,3-dicarboxylic acid, all of which showed a low-intensity absorption maxima at *ca.* 5000 Å.

In order to put this test on a firmer basis the visible and ultraviolet absorption spectra of pyridine-mono- and -di-carboxylic acids in aqueous-methanolic ferrous ammonium sulphate were examined. All the acids with one carboxyl group adjacent to the nitrogen atom, and none of the others, gave a low-intensity absorption band in the region of 4000 Å. The absorption at longer wavelengths observed in the case of pyridine-2,6-dicarboxylic acid may be caused by this acid's acting as a terdentate ligand. Quinaldic acid and pyridine-2,4,5-tricarboxylic acid gave coloured solutions with the ferrous ammonium sulphate solution although no new maxima were observed. The colour is apparently caused by the broadening of the base of the normal absorption bands of the acids. Phenanthridine-6-carboxylic acid gave a purplish precipitate with the ferrous solution, and no colour was given by 2-methylimidazole-4,5-dicarboxylic acid. The maxima at 4400 Å and 5100 Å reported³ for ferrous complexes of the type $[FeX_3]^-$ obtained from picolinic and quinaldic acid were not observed.

¹ Skraup, *Monatsh.*, 1886, **7**, 212.

² Ley, Schwarte, and Münnich, *Ber.*, 1924, **57**, 349.

³ Shinra, Yoshikawa, Kato, and Nominzo, *J. Chem. Soc. Japan*, 1954, **75**, 44.

The extinction coefficients of the coloured species can only be evaluated if their composition and stability constants are known and so only the optical densities (O.D.) are recorded as a qualitative supplement to the test. Decreasing the pH of the picolinic

Absorption spectra of pyridine acids and their iron complexes.

Pyridine-carboxylic acid	$\lambda_{\max.}$ (\AA) ($\epsilon \times 10^{-3}$) in aq. MeOH			Iron complexes		
	Alone	Acidified *	Basified †	Pyridine molality	$\lambda_{\max.}$ (\AA)	O.D.
-2-	2645 (5.2) 2125 (5.9)	2645 (7.4) 2100 (4.1)	2630 (0.87)	4.79×10^{-4}	3980	0.66
-3-	2625 (3.6) 2120 (6.6)	2635 (4.9) 2170 (4.9)	2625 (3.0)			
-4-	2610 (3.3) 2130 (6.0)	2700 (4.4) 2175 (6.4)	2665 (2.3)	5.17×10^{-4}	3990	0.66
-2,3-	2740 (3.7)	2680 (4.1)	2685 (3.3)			
-2,4-	2580 (2.3) 2190 (4.3)	2600 (3.0) 2220 (3.4)	2595 (1.9)	3.68×10^{-4}	4100	0.18
-2,5-	2725 (7.1) 2230 (9.25)	2700 (7.6) 2260 (9.1)	2700 (6.0)			
-2,6-	2700 (6.1) 2190 (7.1)	2705 (4.45) 2235 (7.4)	2700 (4.4)	4.36×10^{-4}	4612	0.81
-3,4-	2635 (3.7)	2615 (4.6)	2645 (2.5)			
-3,5-	2685 (3.0)	2660 (3.8)	2690 (2.7)	3.07×10^{-4}	4141	0.31
-2,4,5-	2750 (1.1)	2180 (8.6) 2760 (1.1)	2720 (0.89)			

* With sulphuric acid.

† With sodium hydroxide.

acid-ferrous ammonium sulphate solution mentioned in the Table from 4.6 to 1.4 by the use of a hydrochloric acid-sodium acetate buffer caused the optical density of the solution to drop from 0.66 to 0.02 at the wavelength of maximum absorption. The position of the maximum was unaltered.

Experimental.—Ultraviolet absorption spectra were measured on a Cary recording spectrophotometer. The acids were examined in water containing methanol (10% v/v). The coloured complexes were produced by adding freshly prepared aqueous ferrous ammonium sulphate hexahydrate (0.5 ml. of 0.174M) to the pyridine-acid in 50% aqueous methanol (10 ml.), and the optical densities of the resulting solutions were measured in 4 cm. cells.

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⁴ Tittensor and Wibberley, *J.*, 1958, 3161.