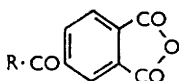


NOTES.

657. Anhydride Derivatives of Trimellitic 1,2-Anhydride.

By R. G. BARKER, K. WARD, jun., and J. W. GREEN.

FEW attempts have been made to prepare the anhydride esters of trimellitic anhydride (I), such as 4-methoxycarbonylphthalic anhydride (II). It seemed possible to prepare these esters from anhydride derivatives of (I), such as the unsymmetrical anhydrides. Bourne *et al.*¹ demonstrated that esterification reactions of carboxylic acids promoted by trifluoroacetic anhydride predominantly follow an S_N1 mechanism, *i.e.*, the formation of the unsymmetrical anhydride, followed by ionisation into a trifluoroacetate anion and acylium cation, and esterification of the highly electrophilic cation. Accordingly, two unsymmetrical anhydrides, (III) and (IV), were prepared by reaction with trifluoroacetic and acetic anhydrides. The di-anhydride (III) was not stable and disproportionated readily into trifluoroacetic anhydride and bis(trimellitic anhydride) anhydride (VI) when heated or treated with certain solvents. It reacted with alcohols and phenols under various conditions to give (I) and the alkyl or aryl trifluoroacetate and not the desired ester anhydrides of (I). These results can be explained in terms of a bimolecular reaction mechanism,² the ester being derived from the stronger acid. Any tendency towards an S_N1 reaction must be insignificant.



- | | |
|--------------------------------|--------------------------|
| (I) R = OH | (IV) R = O·CO·Me |
| (II) R = OMe | (V) R = Cl |
| (III) R = O·CO·CF ₃ | (VI) R = Trimellitoylox; |

The di-anhydride (IV) was treated with methanol. It was shown that the ester anhydride (II) can be removed from mixtures by sublimation, but in this case none could be recovered, a result which might be expected since acetic benzoic anhydride leads predominantly to acetates.³ The acids do not differ greatly in strength, but steric factors might favour the formation of (I) and acetate esters.

A path to the ester anhydrides of (I) was found through the acid chloride (V). Refluxing of a mixture of (I) in excess of thionyl chloride gave high yields of (V), although the initial

¹ Bourne, Stacey, Tatlow, and Tedder, *J.*, 1949, 2976; Bourne, Stacey, Tatlow, and Worrall, *J.*, 1954, 2006; 1958, 3268.

² Tedder, *Chem. Rev.*, 1955, **55**, 787.

³ Bailey and Chang, *J. Org. Chem.*, 1962, **27**, 1192.

product to separate in low yield was the tri-anhydride (VI). Equimolar amounts of the acid chloride and methanol reacted exothermically with evolution of hydrogen chloride. Sublimation led to a 68% recovery of the ester anhydride. This acid chloride should be a promising anhydride derivative as an esterification intermediate for the preparation of the 4-alkoxycarbonylphthalic anhydride series, mixed di-esters, and cross-linked esters. An alternative path to the ester anhydrides is through reaction with the tri-anhydride (VI); reaction with methanol led to both (I) and (II).

Experimental.—Melting points are corrected. Fluorine was determined by a Schoniger combustion⁴ with the aid of a sodium peroxide catalyst, followed by titration with ceric chloride.^{4,5} Infrared spectra were recorded on a Perkin-Elmer model 21 spectrophotometer. Molecular weights were determined from the freezing-point depression of benzene or dioxan. Anhydride equivalents were determined by reaction with morpholine followed by titration with methanolic hydrochloric acid.⁶ (The titration was followed potentiometrically rather than with the mixed indicator, which has a wide colour change with dilute solutions. Acetone was used as the solvent instead of methanol for the highly reactive anhydride of trimellitic anhydride and trifluoroacetic acid.)

Unsymmetrical anhydride (III) of trimellitic anhydride and trifluoroacetic acid. Synthesis. A solution of (I) (5.0 g., 0.026 mole) in trifluoroacetic anhydride (30 g., 0.143 mole) was refluxed for 5 hr. The hot solution was filtered, and the filtrate solidified on cooling to room temperature. After drying *in vacuo*, the unsymmetrical anhydride (III) (5.61 g., 74.8%) was obtained. On heating above the melting point (91–94°), the evolution of a gas was followed by solidification and remelting at 220°. After three recrystallisations from benzene it had double m. p. 94–96°, 223° (Found: F, 19.3, 19.5%; neut. Equiv., 73.9; anhyd. Equiv., 150; *M*, 274 ± 3. Calc. for C₁₁H₃F₃O₆: F, 19.8%; neut. Equiv., 72.05; anhyd. Equiv., 144.1; *M*, 288.1), ν_{\max} (in Nujol) 1870, 1838, 1778, and 1765 cm.⁻¹ (anhydride carbonyl).

Disproportionation. A mixture of (I) (50 g., 0.26 mole) and trifluoroacetic anhydride (67.5 g., 0.32 mole) in acetone (160 ml.), kept at room temperature for several days, yielded (VI) (25.1 g.), m. p. 224–227° (from 1,2-dichloroethane) (lit.,⁷ 220.7–224.7°) (Found: C, 58.6; H, 2.0%; neut. Equiv., 59.5; anhyd. Equiv., 128; *M*, 356 ± 10. Calc. for C₁₈H₆O₉: C, 59.05; H, 2.0%; neut. Equiv., 61.0; anhyd. Equiv., 122; *M*, 366.2), ν_{\max} (KBr) 1860, 1801, 1776, and 1737 cm.⁻¹ (anhydride carbonyl), with no carboxyl or hydroxyl absorption bands. Disproportionation also occurred in nitroethane and in ether, and on heating.

Esterification. Several esterification procedures are summarised in the Table. In most cases no attempt was made to isolate the trifluoroacetates, as the trimellitates were of primary concern.

Esterification reactions of the anhydride (III).

Solvent	Alcohol	Temp.	Identified products (%)
None	Phenol	75°	(I) 85
None	Butan-1-ol	75	(I) 83; n-butyl trifluoroacetate, 70
None	Methanol	25	(I) 87; methyl trifluoroacetate, 31
Acetone	Butan-1-ol	25	n-butyl trifluoroacetate, 54
Acetone	Phenol	25	(I) 46; (VI) 10
Acetone	<i>o</i> -Cresol	25	(I) 55; (VI) 17
Acetone	None	25	(VI) 53
Trifluoroacetic acid	Methanol	25	(I) 75
Trifluoroacetic acid	Butan-2-ol	25	(I) 79
Trifluoroacetic acid	Butan-2-ol	85	(I) 87
Trifluoroacetic acid	Octan-2-ol	25	(I) 72
Trifluoroacetic acid	Phenol	83	(I) 78; monophenyl trimellitrate, 0.2
Ether	Butan-1-ol	25	(I) 50; n-butyl trifluoroacetate, 28
Carbon tetrachloride	Phenol	75	(I) 80
<i>o</i> -Dichlorobenzene	Butan-2-ol	25	(I) 80
1,2-Dichloroethane	Butan-2-ol	25	(I) 96

⁴ Schoniger, *Mikrochim. Acta*, 1955, 123; 1956, 869.

⁵ Brunisholz and Michod, *Helv. Chim. Acta*, 1954, 37, 598.

⁶ See Johnson and Funk, *Analyt. Chem.*, 1955, 27, 1464.

⁷ Knobloch and Liao, U.S.P. 2,911,416 (1959).

Unsymmetrical anhydride of trimellitic anhydride and acetic acid. A mixture of (I) (10 g., 0.0522 mole) and acetic anhydride (81.08 g., 0.794 mole) was refluxed for 3 hr. After the removal of acetic acid (38.4 g.) and excess acetic anhydride by distillation, refrigeration induced the precipitation of what was probably a mixture (2.6 g.) of (I) and (IV). On cooling the reaction mixture to -79° and then allowing it to warm slowly crude (IV) (2.11 g.) separated. Continued cooling led to the separation of a further 0.87 g. After several recrystallisations from benzene, the unsymmetrical anhydride (IV) had m. p. $84-86^{\circ}$ (Found: C, 56.05, 55.7; H, 2.7, 2.7%; neut. Equiv., 59.3; anhyd. Equiv., 121; M , 225 ± 10 . Calc. for $C_{11}H_6O_6$: C, 56.4; H, 2.6%; neut. Equiv., 58.5; anhyd. Equiv., 117; M , 234), ν_{\max} (KBr) 1863, 1812, 1778, and 1732 cm^{-1} (C=O) with no carboxyl or hydroxyl absorption.

A solution of (IV) (1.03 g., 0.0044 mole) and methanol (0.1426 g., 0.0044 mole) in dry benzene (50 ml.) was refluxed for 18 hr. while protected from the atmosphere by a drying tube. After the distillation of 25 ml. of solvent, the solution was concentrated to dryness *in vacuo* at room temperature. Sublimation at $80^{\circ}/1-2\text{ mm.}$ for 5 days led to only 0.1 g. of sublimate, m. p. $100-145^{\circ}$. This could have contained a small amount of (II), but the major portion was probably (I).

Phthalic anhydride-4-carbonyl chloride (V). A mixture of (I) (5.0 g., 0.026 mole) in thionyl chloride (32.7 g., 0.275 mole) was refluxed for 6 hr.; hydrogen chloride was evolved. Cooling led to the separation of white crystals (0.4 g.), m. p. $219-223^{\circ}$, shown to be (VI) by mixed m. p. and anhydride equivalent. The remainder of the solution was vacuum-concentrated to dryness, leaving a product (4.4 g.), m. p. $63.5-66^{\circ}$ [80.3% based on the formation of (V)]. Recrystallisation from benzene or ether, or sublimation, led to pure (V), m. p. $65-66.5^{\circ}$ (Found: C, 51.35; H, 1.75; Cl, 16.7%; neut. Equiv., 53.5; M , 211 ± 4 . Calc. for $C_9H_2ClO_4$: C, 51.35; H, 1.45; Cl, 16.8%; neut. Equiv., 52.6; M , 210.6), ν_{\max} (KBr) 1848 and 1778 (anhydride carbonyl) and 1743 cm^{-1} (acid chloride carbonyl), with no carboxyl or hydroxyl absorption.

Methanol (0.269 g., 0.0084 mole) was added dropwise to finely divided (V) (1.75 g., 0.0083 mole). The reaction was accompanied by the evolution of heat and of hydrogen chloride and resulted in a syrup. The concentrated products from reactions conducted in neutral solvents were also syrups. The usual crystallisation techniques were unsuccessful with these syrups, but sublimation at $80^{\circ}/1-2\text{ mm.}$ led to crude 4-methoxycarbonylphthalic anhydride (II), m. p. $100-101^{\circ}$ (from ether) (lit.,⁸ m. p. $94-99^{\circ}$; lit.,⁹ $104-105$ and $100-103^{\circ}$), mixed m. p. with authentic (II) prepared by the reaction of (I) and ethereal diazomethane, $99-101^{\circ}$; ν_{\max} (KBr) 1858 and 1779 (anhydride carbonyl) and 1732 cm^{-1} (ester), and no carboxyl or hydroxyl absorption.

Esterification of (VI) and methanol. A solution of (VI) (0.89 g., 0.0024 mole) and methanol (0.0792 g., 0.0025 mole) in 1,2-dichloroethane (50 ml.) was refluxed for 18 hr. After concentrating the solution to dryness, the product (0.79 g.) was sublimed at $80^{\circ}/1-2\text{ mm.}$ for 5 days, to give (II), m. p. $88-98^{\circ}$ (0.1 g., 20.2%), m. p. $99-100^{\circ}$ (from ether) and mixed m. p. $99-101^{\circ}$. In a similar, separate reaction partial concentration of the 1,2-dichloroethane solution led to the crystallisation of (I), m. p. $162-166^{\circ}$.

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⁸ Wegscheider, Perndanner, and Auspitzer, *Monatsh.*, 1910, **31**, 1253.

⁹ Duff, Erdtman, and Harvey, *Acta Chem. Scand.*, 1954, **8**, 1073.

658. Tautomerism of 2-Iminothiazolidin-4-ones and 2-Amino-2-thiazolin-4-ones.

By A. M. COMRIE.

A RECENT study¹ of compounds formerly regarded as 2-imino-oxazolidin-4-ones (I; X = O) has revealed that, in methanol solution at least, they have the tautomeric amino-structure (II; X = O), while some closely related selenium analogues exist in the imino-form² (I; X = Se). It has been generally assumed that the sulphur analogues are 2-iminothiazolidin-4-ones³ (I; X = S), but some derivatives have been described as 2-amino-2-thiazolin-4-ones⁴ (II; X = S). Spectroscopic comparison with substances containing ultraviolet-transparent *N*-alkyl substituents and unambiguously related to structure (I) or (II) was, therefore, carried out (Table I). Absorption maxima at about 220 and 245 m μ were shown, respectively, by the model compounds (I; X = S; R = R¹ = Et or Me; R² = H, Et, or Ph; R³ = H) and (II; X = S; R = R¹ = Et or Me; R² = H, Et, or Ph; R³ = H). In the latter group, the peak at 245 m μ experienced a hypsochromic shift to 220 m μ on addition of strong acid but reappeared when the solution was neutralized. A similar shift takes place among 2-amino-2-selenazolin-4-ones² and probably results from protonation of the doubly-bonded nitrogen atom⁵ and rearrangement of the endocyclic to an exocyclic double bond, thus destroying conjugation with the ring carbonyl group.

With compounds having both nitrogen atoms unsubstituted (I or II; R = R¹ = H) and hence potentially capable of tautomerism, absorption maxima were observed at 220



and 250 m μ . Furthermore, the peak at 250 m μ could be made to undergo the same reversible changes with acid and alkali, as did the corresponding peak in the model compounds (II). The intensity of the peak at 220 m μ was, surprisingly, the same in the model compounds and compounds in which both peaks were present (see ref. 6). This may possibly be due to comparison between compounds with *N*-alkyl substituents (I; R = R¹ = Et or Me) and compounds unsubstituted on the nitrogen atoms (I; R = R¹ = H). It would appear, therefore, that both forms are present in aqueous solutions.^{6,7}

Compounds with a 5-methylene group readily formed benzylidene derivatives (Table 2). The ultraviolet spectrum of 5-benzylidene-2-iminothiazolidin-4-one (I; R = R¹ = H; R²R³ = PhCH₂) resembled that of the 3-alkyl-2-alkylimino-5-benzylidenethiazolidin-4-ones⁸ (I; R = R¹ = Et or Me; R²R³ = PhCH₂) rather than that of the 2-dialkylamino-5-benzylidene-2-thiazolin-4-ones (II; R = R¹ = Et or Me; R²R³ = PhCH₂).

Each compound showed a strong absorption band at *ca.* 1740 cm.⁻¹, indicative of a 4-carbonyl group⁹ and hence excluded tautomerism involving a hydroxyl group. In a recent examination¹⁰ of some 5-phenyl derivatives, the tautomeric form obtained depended upon the nature of the substituent on the exocyclic nitrogen atom. Thus, with a phenyl

¹ Howell, Quinones, and Hardy, *J. Org. Chem.*, 1962, **27**, 1686; Najer, Giudicelli, Menin, and Loiseau, *Compt. rend.*, 1962, **254**, 2173.

² Comrie, Dingwall, and Stenlake, *J.*, 1963, 5713.

³ Brown, *Chem. Rev.*, 1961, **61**, 463.

⁴ Durden, Stansbury, and Catlette, *J. Amer. Chem. Soc.*, 1959, **81**, 1943.

⁵ Angyal and Angyal, *J.*, 1952, 1461.

⁶ Najer, Giudicelli, and Menin, *Compt. rend.*, 1962, **254**, 2591.

⁷ Anderson and Seeger, *J. Amer. Chem. Soc.*, 1949, **71**, 340.

⁸ VanAllan, *J. Org. Chem.*, 1956, **21**, 24.

⁹ Pianka and Poulton, *J.*, 1960, 983.

¹⁰ Najer, Giudicelli, Menin, and Morel, *Bull. Soc. chim. France*, 1963, 1022.

group, the imino-form (I; $R^1 = R^2 = H$; $R = R^3 = Ph$) was obtained, whereas an alkyl or aralkyl group gave rise to the amino-form *e.g.* (II; $R^1 = R^2 = H$; $R = Me$; $R^3 = Ph$). It was also concluded that the amino-form best represented compounds in which the nitrogen atoms were unsubstituted ($R = R^1 = H$), a conclusion at variance with the present work due to assignment of the amino-structure to compounds absorbing about 220 $m\mu$.

Experimental.—2-Iminothiazolidin-4-ones (Table 1). Equimolecular quantities (0.01 mole) of α -halogeno-carboxylic acids and thiourea were refluxed in ethanol (25 ml.) for about 1 hr. The salts were isolated in 45–70% yield by concentrating the mixture or by the addition of ether, and purified by recrystallizing from ethanol or ethanol-ether. The bases were liberated by the addition of ammonia, extracted into ether, the ether removed, and the residue recrystallized from ethanol, methanol, or aqueous ethanol.

3-Alkyl-2-alkyliminothiazolidin-4-ones (Table 1). The salts were similarly obtained in 40–60% yield by condensing α -halogeno-carboxylic acids with 1,3-dialkyl-2-thioureas. The bases were isolated and purified as above.

2-Dialkylamino-2-thiazolin-4-ones (Table 1). Condensation of α -halogeno-carboxylic acids with 1,1-dimethylthiourea as before gave the salts in 60–70% yield on concentrating and cooling

TABLE I.
Ultraviolet absorption spectra for aqueous solutions.

Compound	Formula	Structure	R, R ¹ , R ² , R ³	M. p.	N (%)		$\lambda_{max.}$	
					Found	Reqd.	$m\mu$	ϵ
3-Methyl-2-methyliminothiazolidin-4-one hydrochloride ^a	C ₈ H ₈ ClN ₂ OS	I	Me, Me, H, H	— ^b	15.3	15.5	218	15,900
5-Ethyl-3-methyl-2-methyliminothiazolidin-4-one hydrobromide ^c	C ₇ H ₁₃ BrN ₂ OS	I	Me, Me, Et, H	204–205 ^d	11.2	11.1	220	13,700
3-Methyl-2-methylimino-5-phenylthiazolidin-4-one hydrochloride ^a	C ₁₁ H ₁₃ ClN ₂ OS	I	Me, Me, Ph, H	184–185	11.0	10.9	218	18,800
3-Ethyl-2-ethyliminothiazolidin-4-one ^{e, j}	C ₇ H ₁₂ N ₂ OS	I	Et, Et, H, H	88			220	12,600
3,5-Diethyl-2-ethyliminothiazolidin-4-one hydrobromide	C ₈ H ₁₇ BrN ₂ OS	I	Et, Et, Et, H	178–179	10.0	10.0	222	15,500
3-Ethyl-2-ethylimino-5-phenylthiazolidin-4-one ^{e, j}	C ₁₃ H ₁₆ N ₂ OS	I	Et, Et, Ph, H	80	11.6	11.3	220	19,200
2-Dimethylamino-2-thiazolin-4-one hydrochloride	C ₆ H ₈ ClN ₂ OS	II	Me, Me, H, H	183–184	15.2	15.5	242	18,800
2-Diethylamino-2-thiazolin-4-one ^{f, j}	C ₇ H ₁₂ N ₂ OS	II	Et, Et, H, H	— ^g			246	15,250
2-Dimethylamino-5-ethyl-2-thiazolin-4-one hydrobromide	C ₇ H ₁₃ BrN ₂ OS	II	Me, Me, Et, H	178–179	10.6	11.1	242	19,400
2-Dimethylamino-5-phenyl-2-thiazolin-4-one hydrochloride ^h	C ₁₂ H ₁₄ ClN ₂ OS	II	Me, Me, Ph, H	144–145	11.0	10.9	242	20,400
2-Iminothiazolidin-4-one hydrochloride ¹³	C ₆ H ₈ ClN ₂ OS	I and II	H, H, H, H	ca. 250			221	16,100
5-Ethyl-2-iminothiazolidin-4-one hydrobromide ⁱ	C ₆ H ₈ BrN ₂ OS	I and II	H, H, Et, H	218–219 (dec.)	12.8	12.4	250	7,200
2-Imino-5-phenylthiazolidin-4-one ¹³	C ₈ H ₈ N ₂ OS	I and II	H, H, Ph, H	243–244			220	17,000
							250	6,700
							250	18,700
							250	4,500

^a Base, m. p. 71–72° (Found: N, 19.8. C₈H₈N₂O₂S requires N, 19.4%); *picrate*, m. p. 180–181° (from methanol) (Found: N, 18.3. C₁₁H₁₁N₃O₆S requires N, 18.8%). ^b Darkens about 180°. ^c Base, m. p. 22–24° (Found: N, 16.0. C₇H₁₂N₂O₂S requires N, 16.3%); *picrate*, m. p. 140–141° (from methanol) (Found: N, 17.2. C₁₃H₁₃N₃O₆S requires N, 17.45%). ^d Base, m. p. 95–96° (Found: N, 12.9. C₁₁H₁₃N₂O₂S requires N, 12.7%); *picrate*, m. p. 146–147° (from methanol) (Found: N, 16.0. C₁₇H₁₃N₃O₆S requires N, 15.6%). ^e *Picrate*, m. p. 178° (from methanol) (Found: N, 14.8. C₁₃H₁₃N₃O₆S requires N, 14.7%). ^f *Picrate*, m. p. 131–132° (from methanol) (Found: N, 17.3. C₁₃H₁₃N₃O₆S requires N, 17.5%). ^g n_D^{20} 1.5621 (Found N, 16.4. Calc. for C₇H₁₂N₂O₂S: N, 16.3%). ^h Base, m. p. 134–135° (from aqueous methanol) (Found: N, 13.0. C₁₁H₁₃N₂O₂S requires N, 12.7%). ⁱ Base, m. p. 207–208° (from aqueous ethanol) (Found: N, 19.3. Calc. for C₆H₈N₂O₂S: N, 19.4%). (lit.¹⁴ gives m. p. 200°). ^j In presence of an equivalent amount of hydrochloric acid.

the mixture. 2-Diethylamino-2-thiazolin-4-one was prepared from thioglycolic acid and diethylcyanamide.¹¹

5-Benzylidene derivatives (Table 2). Heating equimolecular quantities of benzaldehyde and the thiazolidin-4-one or 2-thiazolin-4-one in ethanol containing a few drops of 20% sodium hydroxide till the smell of benzaldehyde was very faint (*ca.* 2 min.) gave the 5-benzylidene derivative in 40–50% yield on cooling and adding water till the mixture was cloudy. The precipitate was purified by crystallization from ethanol, methanol, or aqueous ethanol.

¹¹ Schubert, Ger. P. 930,563/1955.

¹² Allen and VanAllan, *Org. Synth.*, 1955, **3**, 751.

¹³ Dodson and Turner, *J. Amer. Chem. Soc.*, 1951, **73**, 4517.

¹⁴ Andreasch, *Monatsh.*, 1887, **8**, 418.

TABLE 2.

Compound	Formula	Structure	R, R ¹ , R ² R ³	M. p.	N (%)	
					Found	Reqd.
5-Benzylidene-3-methyl-2-methyliminothiazolidin-4-one	C ₁₃ H ₁₂ N ₂ OS	I	Me, Me, PhCH:	113—114°	11.8	12.1
5-Benzylidene-3-ethyl-2-ethyl-iminothiazolidin-4-one ¹⁶	C ₁₄ H ₁₆ N ₂ OS	I	Et, Et, PhCH:	74		
5-Benzylidene-2-dimethylamino-2-thiazolin-4-one ^a	C ₁₂ H ₁₂ N ₂ OS	II	Me, Me, PhCH:	90—91	11.7	12.1
5-Benzylidene-2-diethylamino-2-thiazolin-4-one	C ₁₄ H ₁₆ N ₂ OS	II	Et, Et, PhCH:	96—97	10.45	10.8
5-Benzylidene-2-iminothiazolidin-4-one ¹⁴	C ₁₀ H ₈ N ₂ OS	I	H, H, PhCH:	290		

^a *Picrate*, m. p. 198—200° (from methanol) (Found: N, 15.2. C₁₈H₁₈N₅O₈S requires N, 15.2%).

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¹⁶ Libermann, Himbert, and Hengl, *Bull. Soc. chim. France*, 1948, 1120.

659. Gas-chromatographic Analysis and Separation of Straight-chain Isomeric Halogeno-octanes.

By P. N. GATES, W. GERRARD, and E. F. MOONEY.

GAS-LIQUID chromatography (g.l.c.) has aided the revelation of the remarkable prevalence of rearrangement of the alkyl group in the formation of halogeno-alkanes by the reactions between inorganic halides and the esters of inorganic acids.¹ The separation of the 1-, 2-, 3-, and 4-halogeno-octanes is an apposite example, because of the close boiling points of the 2-, 3-, and 4-isomers, and because of the extensive reports on the correlation between reaction mechanisms and optical activity effects in the 2-substituted octane systems.

To establish an analytical method each isomer had first to be isolated pure; this also

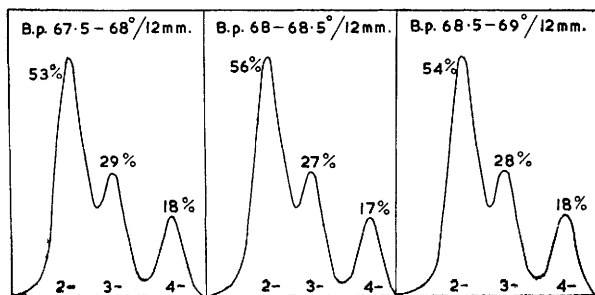


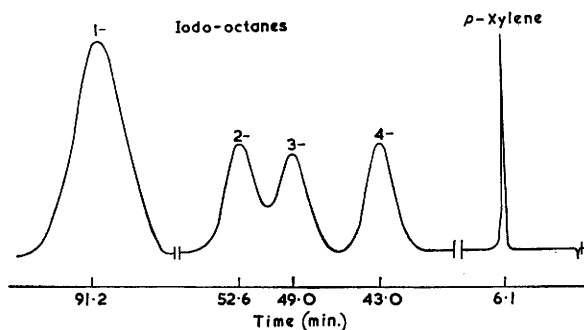
FIG. 1. Chromatography of three different fractions of commercial 2-bromo-octane on 10% diethyl (+)-tartrate on Celite at 44°.

involved the separation of the isomerically pure alcohol, from which the halides were prepared, and the establishment of the isomeric purity of the halogeno-alkanes and aldehydes used to prepare the alcohols.

¹ Cooper and Gerrard, *Chem. and Ind.*, 1961, 320; Cook, Coulson, Gerrard, and Hudson, *ibid.*, 1962, 1506; Gerrard, Hudson, and Murphy, *J.*, 1962, 1099; Charalambous, Frazer, and Gerrard, *J.*, 1963, 826; Gerrard and Hudson, *J.*, 1963, 1059.

Distillation did not always permit the isolation of pure isomers; *e.g.*, the chromatograms of fractions of commercial 2-bromo-octane are given in Fig. 1, which shows that there is no significant change in isomeric composition. Isomerically pure specimens of the halogeno-octanes were therefore obtained by passing a selected distillation fraction down

FIG. 2. Separation of isomeric iodo-octanes, using 10% dibutyl (+)-tartrate on Celite column.



the "preparative" scale g.l.c. column. These pure specimens were used (a) to show that no isomerism occurs on the column, (b) to establish the analytical procedure, and (c) for infrared and nuclear magnetic studies which will be reported elsewhere, since rotational isomerism requires detailed infrared analysis, and n.m.r. studies have shown anomalous

Relative retention times of isomeric straight-chain octane derivatives, $C_8H_{17}X$.

	OH	OH	Cl	Br	I
1-Isomer	15.2	21.6	4.07	7.06	16.4
2-Isomer	6.97	9.92	2.37	4.73	8.65
3-Isomer	5.64	7.93	2.19	4.36	8.06
4-Isomer	5.25	7.43	1.98	3.88	7.08
Column	P.E.G. 400	D.B.T.	D.B.T.	D.B.T.	D.B.T.
Column temp.	78°	76°	50°	63°	67°
Argon flow (ml./min.)	50	60	54	55	55
Internal marker (taken as 1.00)	<i>o</i> -Xylene	<i>p</i> -Xylene	<i>p</i> -Xylene	<i>p</i> -Xylene	<i>p</i> -Xylene

shielding in all but the 1-halogeno-isomers. The relative retention times of the alcohols and halides are given in the Table, and a chromatogram of a mixture of the iodides is given in Fig. 2, which shows, as does Fig. 1, the difficulty in resolving the secondary isomers.

Experimental.—*Preparative scale g.l.c.* The column was 4 ft. in length with a nominal $\frac{1}{2}$ " bore and was packed with 85—100 mesh Celite impregnated with the appropriate stationary phase; a Griffin and George katharometer was used to follow the emergence of the fractions.

Analytical apparatus. This was based upon the Pye Argon Chromatograph, except that radium-D sealed sources were used in the detector, the gas-flow was measured by a Rotameter, and the column temperature was controlled by a Fielden electronic unit. Diethyl (+)-tartrate $\alpha_D^{17} + 13.48^\circ$ ($l = 1$), dibutyl (+)-tartrate (D.B.T.), $\alpha_D^{17} + 11.11^\circ$ ($l = 1$) (Eastman Kodak), and polyethylene glycol (P.E.G. 400) were found to be the best stationary phases, and were used without further purification. Celite (85—100 mesh) was impregnated with stationary phase (10% w/w) in the conventional manner, and the column packed by adding small portions of the prepared Celite and tapping the column on the floor until the level of the Celite remained constant. The average efficiency of columns prepared in this way was *ca.* 600 theoretical plates per foot.

For the analysis of the octanols, polyethylene glycol (P.E.G. 400)² and dibutyl (+)-tartrate were used, and gave satisfactory separations, although octan-3- and -4-ol were not completely resolved.

² Kallina and Kuffner, *Monatsh.*, 1960, **91**, 289.

Additional data. The identity of each pure isomer RX (X = OH, Cl, Br, I) was checked by chemical analysis (C, H, Hal), b. p., n_D^{20} , and d_4^{20} . Octan-3-ol was prepared from n-pentylmagnesium bromide and propionaldehyde,³ the fraction of b. p. 168—174° being purified on the 10% P.E.G. 400 column at 80°. Octan-4-ol was prepared from n-butylmagnesium bromide and n-butyraldehyde,³ the fraction of b. p. 170—174° being similarly purified. Known procedures were adapted for the preparation of the following halogeno-octanes which were purified on the 10% dibutyl (+)-tartrate column at the temperature shown in parentheses: 3-Cl (80°),⁴ 4-Cl (80°),⁴ 2-Br (90°),⁵ 3-Br (90°),⁵ 4-Br (90°).⁵ 2-, 3-, and 4-Iodo-octane were prepared as for 2-iodo-octane,⁶ and were obtained isomerically pure by ordinary distillation.

NORTHERN POLYTECHNIC, HOLLOWAY ROAD, LONDON N.7.

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³ Dorough, Glass, Gresham, Malone, and Reid, *J. Amer. Chem. Soc.*, 1941, **63**, 3100.

⁴ French and Gerrard, *J.*, 1949, **3326**.

⁵ Frazer, Gerrard, Machell, and Shepherd, *Chem. and Ind.*, 1954, 931.

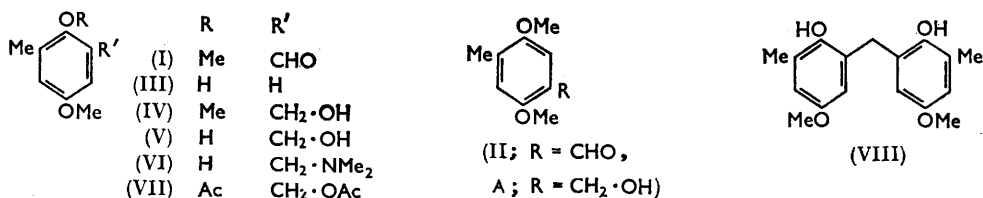
⁶ Berlak and Gerrard, *J.*, 1949, **2309**.

660. *Synthesis of 2,5-Dimethoxy-3-methylbenzaldehyde and 2,5-Dimethoxy-4-methylbenzaldehyde.*

By A. A. R. SAYIGH, HENRI ULRICH, and M. GREEN.

OF the two required isomeric aldehydes, 2,5-dimethoxy-3-methylbenzaldehyde (I) and 2,5-dimethoxy-4-methylbenzaldehyde (II), the latter was synthesised from 2,5-dimethoxytoluene by a Gattermann reaction; but this and several other direct methods failed to convert 4-methoxy-2-methylphenol (III) into the corresponding aldehyde. Compound (I) was finally prepared by oxidation with selenium dioxide¹ of 3-hydroxymethyl-2,5-dimethoxytoluene (IV), which was synthesised by two different procedures.

By the Lederer–Manasse reaction,² with formaldehyde and calcium hydroxide in water, 4-methoxy-2-methylphenol (III) was converted into 2-hydroxymethyl-4-methoxy-6-methylphenol (V) which gave compound (IV) on methylation. The alcohol (V) partially decomposed during distillation under reduced pressure to an uncharacterised phenolic material. From the reaction of *o*-toluquinol and formaldehyde followed by methylation, Euler and his co-workers³ isolated a compound (A) to which they assigned the structure



(IV) on the basis of its conversion into a 2,5-dihydroxymethylbenzoic acid which depressed the melting point of 2,5-dihydroxy-4-methylbenzoic acid prepared by the Kolbe reaction. The compound (A) was not found by us to be the same as our product (IV) and we have

¹ Weygand, Kinkel, and Tietjen, *Chem. Ber.*, 1950, **83**, 394; Astin, Newman, and Riley, *J.*, 1933, 391.

² Manasse and Lederer, *Ber.*, 1894, **27**, 2409; Lederer, *J. prakt. Chem.*, 1894, (2), **50**, 225; Helfer, *Helv. Chim. Acta*, 1924, **7**, 995; Moran, Schreiber, Engel, Behn, and Yamins, *J. Amer. Chem. Soc.*, 1952, **74**, 127.

³ von Euler, Adler, and Caspersson, *Arkiv Kemi, Min., Geol.*, 1942, **16A**, No. 11, 1.

identified it as 4-hydroxymethyl-2,5-dimethoxytoluene by obtaining the aldehyde (II) from its oxidation with selenium dioxide, and 2,5-dimethoxy-4-methylbenzoic acid⁴ by alternative oxidation procedures. By this result the structural assignment of the aldehyde (II) is also confirmed.

The second synthesis of compound (IV) was of poor yield. It involved a Mannich reaction of compound (III) with formaldehyde and dimethylamine⁵ yielding 2-dimethylaminomethyl-4-methoxy-6-methylphenol (VI), which, when heated with acetic anhydride,⁶ gave 2-acetoxy-5-methoxy-3-methylbenzyl acetate (VII). This was hydrolysed with alkali and compound (IV) was obtained by methylation of the hydrolysate. A by-product of this reaction was bis-(2-hydroxy-5-methoxy-3-methylphenyl)methane (VIII), which may have arisen from the reversible decomposition of 2-hydroxymethyl-4-methoxy-6-methylphenol (V) to give 4-methoxy-2-methylphenol (III) and formaldehyde, followed by the condensation of compound (III) with compound (V) or with an intermediate arising from compound (V) by loss of a molecule of water.

Experimental.—2,5-Dimethoxy-4-methylbenzaldehyde (II). (a) This compound was synthesised in 89.6% yield from 2,5-dimethoxytoluene, hydrogen cyanide, and aluminium chloride, according to the standard Gattermann procedure;⁷ it had b. p. 111—116°/0.9 mm., m. p. 85—86° (Found: C, 66.7; H, 6.9. Calc. for C₁₀H₁₂O₃: C, 66.65; H, 6.7%).

(b) To compound (A)³ (18.2 g.), m. p. 74.5—75°, dissolved in benzene (60 ml.), finely powdered selenium dioxide (5.5 g.) was added and the suspension was azeotropically distilled until the formation of water stopped. Distillation of the residue under reduced pressure gave 2,5-dimethoxy-4-methylbenzaldehyde (11.5 g., 63.8%), m. p. 84—85°, having an infrared spectrum identical with that of the material obtained in (a), and causing no depression of its melting point.

2-Hydroxymethyl-4-methoxy-6-methylphenol (V). Calcium oxide (28 g.) was added gradually to a suspension of 4-methoxy-2-methylphenol (138 g.) in water (800 ml.) and 37% formalin (81 g.) under nitrogen. The mixture was shaken until solution was complete and then kept overnight. The solution solidified when shaken; it was diluted with water and acidified with acetic acid, and the oily phenol was extracted with ether. The extract, after being washed with sodium hydrogen carbonate solution and water and dried (Na₂SO₄), was evaporated. Distillation of the product (137.5 g.) under reduced pressure caused extensive decomposition. The distillate of 2-hydroxymethyl-4-methoxy-6-methylphenol, b. p. 136—140°/1 mm., had m. p. 58—59° after crystallisation from isohexane (Found: C, 64.2; H, 6.9. Calc. for C₉H₁₂O₃: C, 64.3; H, 7.2%).

3-Hydroxymethyl-2,5-dimethoxytoluene (IV). (a) To a solution of crude compound (V) (137.5 g.) in acetone (200 ml.) were added anhydrous potassium carbonate (115 g.) and methyl iodide (125 g.). The solution boiled, and boiling under reflux was continued for 18 hr., then the solution was poured into a large volume of water, and the precipitated oil extracted with ether. The extract was washed with 2N-sodium hydroxide solution and repeatedly with water, then dried (Na₂SO₄) and distilled in a vacuum to give a main fraction, b. p. 109—116°/0.6 mm., *n*_D²⁴ 1.5327—1.5344, of slightly impure 3-hydroxymethyl-2,5-dimethoxytoluene [98.2 g., 54% based on (III)] (Found: C, 64.2; H, 7.9. Calc. for C₁₀H₁₄O₃: C, 65.9; H, 7.7%).

(b) To a mixture of compound (III) (20 g.) and 23% dimethylamine (29 g.) was added 37% formalin (13 g.) dropwise with stirring and cooling to keep the temperature below 20°. After it had been stirred for 2 hr. the mixture was extracted with benzene and the extract dried (Na₂SO₄) and evaporated to give crude 2-dimethylaminomethyl-4-methoxy-6-phenol (VI) which was heated under reflux with boiling acetic anhydride (50 g.). This solution was then diluted with water and extracted with benzene, the extract washed with water, sodium carbonate, and then water, the benzene was evaporated, and the residue (VII) hydrolysed in boiling aqueous methanolic sodium hydroxide for 3 hr. This alkaline solution was acidified and extracted with ether. From this extract impure (VIII), m. p. 126—130°, was obtained. The alkaline solution

⁴ Gilman, Swiss, Willis, and Yeoman, *J. Amer. Chem. Soc.*, 1944, **66**, 798; Inouyel, *Pharm. Bull. (Japan)*, 1954, **2**, 359; Posternak, Huguenin, and Alcalay, *Helv. Chim. Acta*, 1956, **39**, 1564.

⁵ Decombe, *Compt. rend.*, 1933, **197**, 258.

⁶ Bruson and Mullen, *J. Amer. Chem. Soc.*, 1941, **63**, 271.

⁷ Gattermann, *Annalen*, 1907, **357**, 313; for details see "Organic Reactions," Vol. IX, p. 54.

containing compound (V), was methylated (dimethyl sulphate), acidified with hydrochloric acid, and extracted with ether. On evaporation of the extract two fractions were obtained, (i) b. p. 113—118°/1 mm., $n_D^{22.5}$ 1.5350 (3.1 g.), having an infrared spectrum identical with that of the material prepared in (a); (ii) b. p. 205°/0.9 mm., m. p. 135—137° after crystallisation from n-hexane (4.2 g.). The latter was identified as *bis*-(2-hydroxy-5-methoxy-3-methylphenyl)-methane (VIII) (Found: C, 71.0; H, 7.2. Calc. for $C_{17}H_{20}O_4$: C, 70.8; H, 7.0%).

2,5-Dimethoxy-3-methylbenzaldehyde (I). Finely powdered selenium dioxide (30 g.) was added to a solution of compound (IV) (95.8 g.) in benzene (100 ml.), and the suspension azeotropically distilled until the formation of water was complete (3.5 g. of water collected). The residue was distilled under reduced pressure and after a fore-run of red oil (6.2 g.), 2,5-dimethoxy-3-methylbenzaldehyde (71.5 g., 75%), b. p. 89—91°/0.5 mm., m. p. 40—41°, was collected. It crystallised from ligroin as white needles, m. p. 42° (Found: C, 66.7; H, 6.7. Calc. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.7%).

(A. A. R. S. and H. U.) THE CARWIN COMPANY, NORTH HAVEN, CONNECTICUT, U.S.A.
(M. G.) POLAROID CORPORATION, CAMBRIDGE,
MASSACHUSETTS, U.S.A.

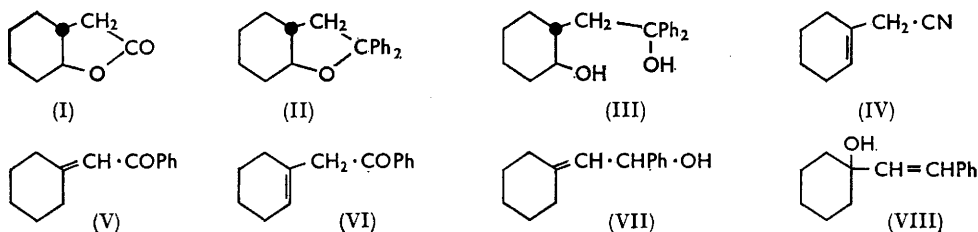
[Received, October 21st, 1963.]

661. Attempts at a New Synthesis of Phenanthrenes.

By JOSEPH KLEIN and ERNST D. BERGMANN.

UNSUCCESSFUL experiments are described to develop a general synthesis of phenanthrenes from a cyclohexane derivative which carries a suitable aryethyl bridge. Phillips and Chatterjee¹ studied the reaction of *trans*-2-hydroxycyclohexylacetic acid lactone (I) and aromatic compounds in the presence of aluminium chloride; however, a mixture of 2-, 3-, and 4-aryl-substituted cyclohexylacetic acids was obtained. Expecting that the reaction of compound (I) with arylmagnesium halides would proceed less ambiguously, we treated it with phenylmagnesium bromide. The ether (II) and the diol (III) were obtained. Similar reactions of lactones are known.² The *cis*-isomer of lactone (I) gave the *cis*-isomer of ether (II); obviously, there is no change of configuration.

Reaction of cyclohex-1-enylacetonitrile (IV) with phenylmagnesium bromide gave the acetophenone (V) in 26% yield. This is known to exist in a dynamic equilibrium with compound (VI),³ which would appear suitable for the desired cyclisation. 1-Naphthylmagnesium bromide, analogously, gave the acetophenone.



However, cyclisation of compound (V) with phosphoric-formic acid or with aluminium chloride was unsuccessful. The secondary alcohol (VII), obtained from compound (V) by reduction with lithium aluminium hydride, yielded, under the same conditions, the

¹ Phillips and Chatterjee, *J. Amer. Chem. Soc.*, 1958, **80**, 1360, 1911.

² See, e.g.: Weizmann and Bergmann, *J. Amer. Chem. Soc.*, 1938, **60**, 2647; Shriner and Sharp, *J. Org. Chem.*, 1939, **4**, 575.

³ Farrow and Kon, *J.*, 1926, 2128.

formate of the isomeric tertiary alcohol (VIII); its structure follows from the infrared (1740 cm^{-1}) and the ultraviolet spectra (284 $\text{m}\mu$ ($\log \epsilon$ 3.65)). Acetylation of alcohol (VII) gave equally the acetate of alcohol (VIII). [That compound (VII) had the above structure was shown by its re-oxidation to compound (V) with chromic acid in pyridine]. The acetate of alcohol (VIII), on treatment with either phosphoric acid-formic acid or aluminium chloride in carbon disulphide, gave polymer.

Experimental.—*Cyclohexylideneacetophenone* (V). A solution of cyclohex-1-enylacetonitrile (IV) ⁴ (12.1 g.) in anhydrous ether (40 ml.) was added dropwise to a Grignard solution, prepared from magnesium (7.2 g.), bromobenzene (51 g.), and ether (120 ml.). The solution was refluxed for 4 hr., cooled, and poured into ice-sulphuric acid. The ethereal layer was washed with dilute acid and water and distilled, yielding the ketone (V) (2.2 g.), b. p. 130—132°/1 mm.).

The aqueous layer was refluxed for 10 hr. and extracted with benzene. Distillation of the benzene layer yielded a second crop (3 g.) of ketone (V) (the total yield was 26%); ν_{max} 1680 cm^{-1} , λ_{max} (in EtOH) 242 $\text{m}\mu$ ($\log \epsilon$ 4.10).⁵ The ketone gave a 2,4-dinitrophenylhydrazone, m. p. 163—164°.⁶

α -*Cyclohexylidene-1-acetonaphthone* was obtained similarly. The aqueous layer gave, after 10 hr. of extraction, the ketone (2 g.; 8%), b. p. 190°/0.8 mm., λ_{max} (in EtOH) 304 $\text{m}\mu$ ($\log \epsilon$ 3.90), ν_{max} 1680 cm^{-1} (Found: C, 86.0; H, 7.3. $\text{C}_{18}\text{H}_{18}\text{O}$ requires C, 86.4; H, 7.2%). The ketone gave a 2,4-dinitrophenylhydrazone, m. p. 188—190°.

2-*Cyclohexylidene-1-phenylethanol* (VII). A solution of compound (V) (20 g.) in ether (60 ml.) was added dropwise to a suspension of lithium aluminium hydride (1.2 g.) in ether (100 ml.). The mixture was refluxed for 1 hr., cooled, and treated dropwise with 10% hydrochloric acid. Distillation of the ethereal layer gave the alcohol (VII) (16.5 g.; 82%), b. p. 137—139°/2 mm.; λ_{max} (in EtOH) 284 $\text{m}\mu$ ($\log \epsilon$ 3.54), ν_{max} 3440 cm^{-1} (Found: C, 83.5; H, 8.7. $\text{C}_{14}\text{H}_{18}\text{O}$ requires C, 83.2; H, 8.9%).

Acetate of Compound (VIII). Acetic anhydride (12 ml.) was added to a solution of the alcohol (VII) (10 g.) in pyridine (25 ml.). The solution was left overnight at room temperature, then poured on to ice-hydrochloric acid. Benzene was added and the organic layer washed with 10% hydrochloric acid, 10% aqueous sodium carbonate, and water. Distillation gave the acetate (11.3 g.; 93%), b. p. 133—135°/2 mm., λ_{max} (in EtOH) 284 $\text{m}\mu$ ($\log \epsilon$ 3.65), ν_{max} 1740 cm^{-1} (Found: C, 79.1; H, 7.9. $\text{C}_{16}\text{H}_{20}\text{O}_2$ requires C, 78.7; H, 8.2%).

Formate of Compound (VIII). A mixture of compound (VII) (6 g.), formic acid (10 ml.), and phosphoric acid (3 ml.) was heated on the water-bath for 5 hr., ice was added, and the product was extracted with benzene. The benzene solution was washed with 10% sodium carbonate solution and water. Distillation gave the formate (2.5 g.; 37%), b. p. 125°/1 mm.; λ_{max} (in EtOH) 285 $\text{m}\mu$ ($\log \epsilon$ 3.70), ν_{max} 1725 cm^{-1} (Found: C, 78.6; H, 8.1. $\text{C}_{15}\text{H}_{18}\text{O}_2$ requires C, 78.3; H, 7.8%).

When the formate (2 g.) was heated with palladium-charcoal (1 g.) for 2 hr. at 230—250°, then for 30 min. at 300°, and the benzene solution of the product filtered and distilled, dibenzyl (1 g.), b. p. 120°/2 mm., m. p. 49—50° (from ethanol), was obtained.

Oxidation of 2-cyclohexylidene-1-phenylethanol (VII). A solution of compound (VII) (3.4 g.) in pyridine (10 ml.) was added to chromic acid (3.5 g.) in pyridine (35 ml.), and the mixture left at room temperature overnight. Ice and benzene were then added, and the mixture was acidified with hydrochloric acid. The excess of chromic acid was destroyed by sodium bisulphite. The benzene layer was washed with 10% hydrochloric acid and water. Distillation gave the ketone (V) (2 g.), b. p. 145—147°/2 mm.; λ_{max} (in EtOH) 242 $\text{m}\mu$ ($\log \epsilon$ 4.00), ν_{max} 1680 cm^{-1} .

Reaction of phenylmagnesium bromide with the cis-lactone (cis-I). (a) *Equimolecular amounts* (inverse addition). A Grignard solution from magnesium (1.7 g.), bromobenzene (12 g.), and ether (50 ml.) was added dropwise during 1 hr. to a cooled solution of compound (cis-I) ⁷ (9.5 g.) in anhydrous ether (50 ml.). The solution was refluxed for 3 hr., then poured on ice-hydrochloric acid. The ether layer was washed with 10% sodium carbonate and water. Distillation gave unchanged compound (cis-I) (6.7 g.; 56%), b. p. 140—145°/30 mm., a fraction (1.5 g.)

⁴ *Org. Synth.*, **31**, 25.

⁵ Braude, Jones, Sondheimer, and Toogood, *J.*, **1949**, 607.

⁶ Marvel and Walton, *J. Org. Chem.*, **1942**, **7**, 88.

⁷ Klein, *J. Org. Chem.*, **1958**, **23**, 1209.

b. p. 150—165°/2 mm.; ν_{\max} 1680 cm^{-1} , and finally *cis-perhydro-2,2-diphenylbenzofuran* (*cis-II*) (4 g.), b. p. 185—190°/2 mm., m. p. 99—100°, showing no carbonyl absorption (Found: C, 86.6; H, 8.0. $\text{C}_{20}\text{H}_{22}\text{O}$ requires C, 86.3; H, 7.9%).

(b) *With excess of phenylmagnesium bromide.* A solution of compound (*cis-I*) (4.7 g.) in ether (30 ml.) was added dropwise to a Grignard reagent prepared from magnesium (2.4 g.), bromobenzene (17 g.), and ether (50 ml.). The solution was refluxed for 2 hr., then worked up as before. Distillation gave compound (*cis-II*) (8 g.; 85%) b. p. 180—185°, m. p. 99—100°.

Reaction of phenylmagnesium bromide with the trans-lactone (I). When the preceding reaction (excess of the Grignard reagent) was repeated with compound *trans-I*,⁸ concentration and repeated recrystallization from benzene–light petroleum gave *trans-2-2'-hydroxycyclohexyl-1,1-diphenylethanol* (III) (1.8 g.; 19%), m. p. 143—144° (Found: C, 81.1; H, 8.1. $\text{C}_{20}\text{H}_{24}\text{O}_2$ requires C, 81.0; H, 8.1%); ν_{\max} 3450 and 3200 cm^{-1} . Distillation of the mother-liquor gave the *trans-perhydro-2,2-diphenylbenzofuran* (*trans-II*) (7 g.; 70%), b. p. 165—170°/0.5 mm., m. p. 80° (from ethanol) (Found: C, 86.1; H, 8.2. $\text{C}_{20}\text{H}_{22}\text{O}$ requires C, 86.3; H, 7.9%).

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⁸ Newman and VanderWerf, *J. Amer. Chem. Soc.*, 1945, **67**, 233.

662. A Convenient Procedure for the Preparation of Analytical Samples of Solids.

By T. C. OWEN.

THE frustrations attendant upon the preparation by crystallisation of small samples of solid organic substances sufficiently pure for microanalysis are well known. This note describes a simple, inexpensive apparatus and a convenient method of crystallisation, which has the advantages of: convenience; exclusion of atmospheric dust and moisture; elimination of transfer losses; obviation of crystallisation on the filter and evaporation of volatile solvents during hot filtration to remove insoluble impurities and absorbents; spontaneous warming and condensation of moisture in materials and apparatus cooled below room temperature are greatly reduced; fresh apparatus is not required for each crystallisation.

Experimental.—Apparatus. The apparatus, shown in the Figure, consists of two similar crystallisation tubes (*S* and *R*) and a centre piece (*C*). Dry seals between the three pieces are by means of ground flanges (1–1, 2–2) held together by spring clamps. Each piece is constructed from tubes about 10 mm. in bore bearing ground flanges available commercially.* It is convenient to have several crystallisation tubes (*S*, *R*). Filtration is through a hard filter paper circle (3) (2 cm. dia.) sandwiched in the joint 1–1 of the Figure. Atmospheric moisture may be excluded by simple desiccant tubes attached to the side arms 4 and 5 and dust by plugs of absorbent cotton in the side arms.

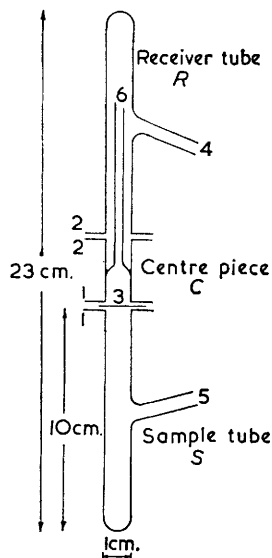
Procedure.—(a) Separation of insoluble impurities and treatment with absorbents. A sample of suitable size and solvent to a level at least 1 cm. below the side arm are placed in the sample tube (*S*). The tube is loosely stoppered and solution effected by heat; the stopper then is replaced by a filter paper (3) and the apparatus assembled as shown in the Figure. The assembly is inverted and transfer of filtrate to the receiver tube (*R*) effected by gentle suction at the side arm (4) of (*R*) or, better, especially with volatile solvents or hot solutions, by slight pressure at the side arm (5).

Treatment with an absorbent may be done in tube (*S*), which is loosely stoppered, and the

* Quickfit and Quartz flat flanges joints FG10 and clamps JC28 are convenient.

solution heated before the tube is attached to the centre piece and receiver. Two thicknesses of filter paper at 1-1 are desirable for filtration after treatment with absorbents.

(b) *Crystallisation, filtration and washing.* The receiver tube used in the previous operation now contains the clear filtrate and constitutes the sample tube (S) of the Figure. As the sample remains in this tube during any subsequent operation, transfer losses and exposure to atmospheric moisture and dust are eliminated. The other pieces are removed and the sample tube covered (a portion of a microscope slide is convenient) and crystallisation initiated by the



usual methods (cooling, seeding, etc.). The cover is replaced by a filter paper and the centre piece and receiver clamped in position. The assembly is inverted, and the mother-liquor transferred to the receiver by suction or pressure at the appropriate side arm as before. The receiver is detached, emptied, and rinsed with solvent, and filtrates may be combined for recovery of solute. The centre-piece assembly of the sample tube is returned to the orientation shown in the Figure, washing solvent introduced through the side arm (5) and/or the axial tube (6) of the centre piece and the suspension suitably agitated. The receiver is replaced, the apparatus inverted, and solvent removed by suction or pressure at (4) or (5) as before. Solvent for recrystallisation is introduced through (5) and (6) after the receiver has been removed and emptied, and the sample is brought into solution; the whole operation of crystallisation and washing is repeated as often as necessary.

After the final crystallisation and washing the mat of crystals invariably adheres to the filter paper. The centre piece assembly is detached and the ground surface (1) of the sample tube, to which the filter paper usually clings, is tapped on a clean sheet of paper. The filter paper drops off together with the adhering mass of crystals, which is transferred as a mat to the appropriate container for drying. With hygroscopic samples, drying is effected directly in the sample tube, the centre piece being removed and replaced by a glass cover and the side arm (5) connected to a vacuum line.

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663. Reductions of Iodonitrobenzenes with Sodium Stannite and Other Agents.

By BRIAN T. NEWBOLD and STEPHEN R. BAIG.

GABRIEL¹ reduced *m*- and *p*-iodonitrobenzene to the di-iodoazoxybenzenes, using alcoholic potassium hydroxide, and Baeyer² reported that *o*-iodonitrobenzene was reduced to *o*-iodoaniline by stannous chloride and hydrochloric acid at low temperature. Iodonitrobenzenes have also been reduced with magnesium and methanol,³ hydrazine and Raney nickel,⁴ zinc dust and sodium hydroxide,⁵ reducing sugars,⁶ and potassium borohydride.⁷ The object of the present work was to reduce the three isomeric idonitrobenzenes with sodium stannite, sodium arsenite, sodium 2-hydroxyethoxide, and 1,4-naphthaquinone in methanolic sodium hydroxide. Some results are given in the Table.

Reductions of idonitrobenzenes.

Compound (g.)	Agent (g.)	NaOH (g.)	H ₂ O (ml.)	Solvent * (ml.)	Time	Temp.	Products (%)			
							Rec. nitro-	Azoxy-	Amine	
<i>o</i> -Iodonitrobenzene										
5.0	SnCl ₂ (6.2)	4.8	50	A (50)	$\frac{3}{4}$ hr.	Reflux	28.0	28.8 ^a	Nil	
10.0	" (12.4)	10.0	110	A (100)	$\frac{3}{4}$ hr.	"	Nil	30.0 ^a	"	
"	As ₂ O ₃ (6.25)	"	37	B (17)	3 hr.	61°	4.5	Nil ^b	"	
"	Na (1.2)	—	—	C (20)	12 min.	Boiled	Nil	" ^b	"	
				D (20)						
25.0	NQ † (0.5)	20.0	—	B (250)	22 hr.	Reflux	"	" ^b	"	
<i>m</i> -Iodonitrobenzene										
10.0	SnCl ₂ (12.4)	10.0	50	A (100)	$\frac{3}{4}$ hr.	"	4.5	86.3	"	
"	As ₂ O ₃ (6.25)	"	37	B (17)	3 hr.	61°	1.8	87.4	"	
"	Na (1.2)	—	—	C (20)	5 min.	Boiled	20.8	30.3	"	
				D (20)						
25.0	NQ † (0.5)	20.0	—	B (250)	22 hr.	Reflux	Nil	2.3 ^b	"	
<i>p</i> -Iodonitrobenzene										
5.0	SnCl ₂ (6.2)	3.2	100	A (150)	2 hr.	"	70.0	10.2	"	
10.0	As ₂ O ₃ (6.25)	10.0	37	A (100)	3 hr.	61°	26.0	Nil ^b	10.0	
				B (30)						
"	Na (1.2)	—	—	C (20)	6 min.	Boiled	91.0	" ^b	Traces	
				D (450)						
5.0	NQ † (1.0)	48.0	—	B (850)	22 hr.	Reflux	Nil	" ^c	2.0	

* A, Acetone; B, methanol; C, ethylene glycol; D, ethanol. † NQ, naphthaquinone.

^a M. p. 148—149° (lit.,⁸ 148°). ^b Tars formed. ^c Azobenzene (7.7%).

o-Iodonitrobenzene is particularly difficult to reduce because it is not very stable in alkaline medium and the nitro-group is sterically hindered. It decomposes in the presence of alcoholic potassium hydroxide¹ and is not reduced by magnesium and methanol.³ With zinc dust and sodium hydroxide it gives azobenzene owing to deiodination,⁵ and reduction with hydrazine and Raney nickel⁴ gives *o*-iodoaniline. Cook and Jones⁸ prepared 2,2'-di-iodoazoxybenzene from *o*-iodonitrobenzene by means of sodium stannite, but did not attempt to isolate any other products. We reduced *o*-iodonitrobenzene with this

¹ Gabriel, *Ber.*, 1876, **9**, 1405.

² Baeyer, *Ber.*, 1905, **38**, 2760.

³ Keirstead, *Canad. J. Chem.*, 1953, **31**, 1064.

⁴ Leggetter and Brown, *Canad. J. Chem.*, 1960, **38**, 2363.

⁵ Newbold, *J.*, 1961, 4260.

⁶ Newbold and LeBlanc, *J. Org. Chem.*, 1962, **27**, 312.

⁷ Shine and Mallory, *J. Org. Chem.*, 1962, **27**, 2390.

⁸ Cook and Jones, *J.*, 1939, 1311.

agent under similar conditions, but the mixture was steam-distilled. 2,2'-Di-iodoazoxybenzene was obtained in improved yield, and *o*-iodo-nitrobenzene and -aniline were sometimes isolated. Reduction is not successful if the sodium stannite solution is not clear and freshly prepared, and also if the *o*-iodonitrobenzene is not treated rapidly with this agent. Attempted reductions with sodium stannite in excess alkali led to considerable decomposition, and only tars, and sometimes traces of *o*-iodoaniline, were formed.

King⁹ synthesised 2,2'-di-iodoazoxybenzene by electrochemical reduction of *o*-iodoxy-nitrobenzene and *o*-iodosonitrobenzene, and claimed that it was a new compound and also that all attempts at independent synthesis failed. 2,2'-Di-iodoazoxybenzene has also been prepared by reduction of *o*-iodonitrobenzene with glucose and maltose in alkaline medium.⁶ In this work, attempts were made to reduce *o*-iodonitrobenzene with the other agents mentioned above, but tars were invariably the only product, probably owing to the elevated temperature and the alkaline medium.

Reduction of *m*-iodonitrobenzene with magnesium and methanol,³ reducing sugars,⁶ and potassium borohydride in ethanol⁷ gives 3,3'-di-iodoazoxybenzene, which we prepared in excellent yield from *m*-iodonitrobenzene by reduction with sodium stannite and sodium arsenite in alkaline medium. Reduction with sodium 2-hydroxyethoxide gave a 30% yield. Tadros *et al.*¹⁰ reduced *m*-chloro- and *m*-bromo-nitrobenzene with this agent and obtained the dihalogenated azoxybenzenes. There is no steric effect in *m*-iodonitrobenzene and it is quite stable in alkaline medium, factors which render reduction more facile than in the case of *o*-iodonitrobenzene. Sogn¹¹ reported that nitrobenzene was reduced by 1,4-naphthaquinone in methanolic sodium hydroxide, to give hydrazobenzene, azobenzene, and some aniline. We applied this agent to *m*-iodonitrobenzene under similar conditions, except that the mixture was steam-distilled and the remaining mixture acidified to precipitate the products. A small yield of 3,3'-di-iodoazoxybenzene was obtained.

Reduction of *p*-iodonitrobenzene with sodium stannite yielded 4,4'-di-iodoazoxybenzene, whereas sodium arsenite gave *p*-iodoaniline in 10% yield. When sodium 2-hydroxyethoxide was employed only traces of *p*-iodoaniline resulted, and treatment with 1,4-naphthaquinone gave *p*-iodoaniline and azobenzene. The formation of azobenzene is significant because it indicates that deiodination takes place. Previous work⁵ showed that *p*-iodonitrobenzene is also reduced to azobenzene by zinc dust and sodium hydroxide.

Experimental.—The isomeric iodonitrobenzenes used were of reagent grade. Similar procedures were employed for the reduction of the iodonitrobenzenes, and one example of each method is described. Products were identified by mixed m. p., and by infrared spectroscopy with a Perkin-Elmer Infracord 137 B spectrophotometer.

Reduction of p-iodonitrobenzene with sodium stannite. Stannous chloride dihydrate (6.20 g.) was mixed with water (50 ml.) to form a slurry which was added to a solution of sodium hydroxide (3.20 g.) in water (50 ml.). The resulting clear solution of sodium stannite was added rapidly to a solution of *p*-iodonitrobenzene (5.0 g.) in acetone (50 ml.), and the mixture refluxed for 1 hr. Acetone (100 ml.) was then added and the mixture refluxed for 1 hr. Steam-distillation gave a distillate which was acidified with hydrochloric acid to give *p*-iodonitrobenzene (40.0%), m. p. 171—173° (from ethanol-benzene) (lit.,¹² 172—173°). The filtrate was made alkaline with sodium hydroxide but no *p*-iodoaniline was isolated. The residue left after steam-distillation was extracted with ethanol-benzene, to give 4,4'-di-iodoazoxybenzene (10.2%), m. p. 199—200° (from ethanol) (lit.,¹ 199.5°). Further extraction with benzene gave *p*-iodonitrobenzene (30.0%), m. p. 172—174°.

Reduction of m-iodonitrobenzene with sodium arsenite. Arsenic trioxide (6.25 g.) was mixed with water (7 ml.) to form a thick paste which was added to a solution of sodium hydroxide (10.0 g.) in water (30 ml.), to give a colourless solution of sodium arsenite. This was added in

⁹ King, *J. Org. Chem.*, 1961, **26**, 3323.

¹⁰ Tadros, Ishak, and Bassil, *J.*, 1959, 627.

¹¹ Sogn, U.S.P. 2,831,893 (1958).

¹² "Handbook of Chemistry and Physics," Chemical Rubber Co., Hodgman, Weast, and Selby, Cleveland, Ohio, 1960—1961, 42nd edn.

portions to a solution of *m*-iodonitrobenzene (10.0 g.) in methanol (17 ml.), and the whole vigorously stirred and heated at 61° for 3 hr. Steam-distillation gave *m*-iodonitrobenzene (1.8%), m. p. 37.5° (lit.,¹³ 38.5°). The residue from steam-distillation was filtered off and washed with water, to give 3,3'-di-iodoazoxybenzene (87.4%), m. p. 119.5—120° (lit.,¹⁴ 120—121°).

Reduction of m-iodonitrobenzene with sodium 2-hydroxyethoxide. To a solution of sodium 2-hydroxyethoxide, prepared by dissolving sodium (1.2 g.) in ethylene glycol (20 ml.), was added a solution of *m*-iodonitrobenzene (10.0 g.) in ethanol (20 ml.), and the mixture boiled for 5 min. Steam-distillation gave *m*-iodonitrobenzene as a liquid (20.8%) (identified by infrared analysis). The residue from steam-distillation was treated as described above, and yielded 3,3'-di-iodoazoxybenzene (30.3%).

Reduction of p-iodonitrobenzene with 1,4-naphthaquinone. To 1,4-naphthaquinone (1.0 g.) and sodium hydroxide (48.0 g.) in methanol (100 ml.), a solution of *p*-iodonitrobenzene (5.0 g.) in methanol (750 ml.) was added during 0.5 hr. The mixture was refluxed for 22 hr. and steam-distilled. The acidified distillate gave azobenzene (7.7%), m. p. 64—66° (from ethanol). The alkaline filtrate yielded *p*-iodoaniline (2.0%), m. p. 60—62° (lit.,¹² 62.8°). The mixture left after steam-distillation was acidified, and gave a brown residue (0.44 g.), m. p. >300°. This was recrystallised from ethanol, but the infrared spectrum showed that it was probably polymeric.

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¹³ Heilbron, "Dictionary of Organic Compounds," Oxford University Press, 1953, Vol. III, p. 36.

¹⁴ Gore and Wheeler, *J. Amer. Chem. Soc.*, 1956, **78**, 2160.

664. Reactions of Cobalt(III) Compounds and the Magnitude of the Cobalt(III)/Cobalt(II) Standard Potential in Aqueous Solution.

By D. A. JOHNSON and A. G. SHARPE.

It has been accepted for many years that the cobalt(III) ion is one of the most powerful oxidising agents known in aqueous media, and that the $\text{Co}^{3+}/\text{Co}^{2+}$ standard potential is about +1.8 v.¹⁻⁶ Recently, however, Rotinyan, Kheifets, and Nikolaeva⁷ have criticised the measurements on which this value was based, and Kheifets *et al.* have deduced from studies⁸ of the equilibrium between cobalt(III) hydroxide and a solution containing cobalt(III) and cobalt(II) sulphates at pH 2.2—2.6 in the presence of air that the true standard potential is as low as +1.3 v. Since this calculation involves the assumption that $\text{Co}^{3+}(\text{aq.})$ is the only cobalt(III) species present in the solution, its validity must be considered doubtful; there is strong evidence for the formation of CoOH^{2+} and binuclear species in dilute solutions of cobalt(III) in weakly acidic perchlorate media,^{9,10} and complexing by sulphate ion also occurs.^{11,12} Comparison of the $\text{Co}^{3+}/\text{Co}^{2+}$ system with other

¹ Oberer, Dissertation, Zurich, 1903.

² Jahn, *Z. anorg. Chem.*, 1908, **60**, 292.

³ Lamb and Larson, *J. Amer. Chem. Soc.*, 1920, **42**, 2024.

⁴ Noyes and Deahl, *J. Amer. Chem. Soc.*, 1937, **59**, 1337.

⁵ Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, 1952.

⁶ Charlot, "Oxidation-Reduction Potentials," Pergamon, 1958.

⁷ Rotinyan, Kheifets, and Nikolaeva, *Zhur. neorg. Khim.*, 1961, **6**, 21 (transl., p. 10).

⁸ Kheifets, Rotinyan, and Kozich, *Zhur. obshechi Khim.*, 1959, **29**, 1052.

⁹ Baxendale and Wells, *Trans. Faraday Soc.*, 1957, **53**, 800.

¹⁰ Sutcliffe and Weber, *Trans. Faraday Soc.*, 1956, **52**, 1225; *J. Inorg. Nuclear Chem.*, 1960, **12**, 281.

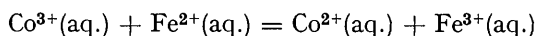
¹¹ Hargreaves and Sutcliffe, *Trans. Faraday Soc.*, 1955, **51**, 786.

¹² Sutcliffe and Weber, *Trans. Faraday Soc.*, 1961, **57**, 91.

redox systems provides firm support for the higher value. Thus, 0.1M-solutions of cobalt(III) sulphate in 4N-sulphuric acid have been found to oxidise chloride to chlorine, and manganese(II) sulphate to the manganese(III) state or, in the presence of silver ion, to permanganate. Competitive electrolytic oxidation of solutions of cobalt(II) and cerium(III) perchlorates in 2N-, 4N-, 6N-, or 8N-perchloric acid (using a rotating platinum anode at 6 v and 1 amp., below 10°) shows that in each case the cerium(III) is oxidised first; conversely, 0.1M-cobalt(III) perchlorate oxidises cerium(III) perchlorate at all these acidities, for which the Ce^{4+}/Ce^{3+} formal potential is reported to be 1.71, 1.75, 1.82, and 1.87 v, respectively.¹³ When 0.1M-cobalt(III) perchlorate is added to 0.1M-silver nitrate in dilute nitric acid, there is substantial oxidation of the latter to a dirty lemon-yellow solution containing silver(II); E for the Ag^{2+}/Ag^+ system under these conditions has been given as +1.93 v.¹⁴ On the other hand, considerable oxidation of cobalt(II) perchlorate in 4N-perchloric acid occurs when ozonised oxygen is passed through the solution at 0°; E^0 for the reaction $O_3 + 2H^+ + 2e = O_2 + H_2O$ has been estimated from thermal data to be +2.07 v.⁵

These experiments, however, relate to non-standard conditions in which preferential complexing of one oxidation state and hydrogen-ion activity may both be important. Some independent confirmation of the high Co^{3+}/Co^{2+} standard potential (which is well above that required for the liberation of oxygen from dilute mineral acids) is desirable, and we have sought to obtain this by a thermochemical method.

The instability of solutions of simple cobalt(III) compounds severely restricts the choice of conditions under which reasonably accurate measurements can be made on a reaction of established stoichiometry, and we have had to be satisfied with 4N-perchloric acid at 15° as a working medium. In this medium, the heat of the reaction



was found to be $\Delta H = -26.3$ kcal. The close similarity in size, mass, and charge of the pairs of ions involved indicates that the entropy change for the reaction should be very small, though there is an increase of 3.1 cal. deg.⁻¹ in the magnetic entropy,⁵ arising from the fact that only $Co^{3+}(aq.)$ in 4N-perchloric acid is a low-spin species.¹⁵ Complexing by perchlorate must be considered, but it is only a substantial *difference* in the complexing of Fe^{3+} and Co^{3+} , or of Fe^{2+} and Co^{2+} , under identical conditions, that would appreciably affect ΔE^0 , the difference between the standard potentials of the Fe^{3+}/Fe^{2+} and Co^{3+}/Co^{2+} systems. Nuclear magnetic resonance studies¹⁶ suggest that complexing by perchlorate in acidic media is no more than slight for Fe^{2+} , Fe^{3+} , and Co^{2+} , and although there is evidence for the existence of $FeClO_4^{2+}$, the formation constant is small.¹⁷ It may also be noted that both the heats and entropies of complexing of Fe^{3+} and Co^{3+} by hydroxyl ion are nearly identical.^{10,18}

The free-energy change derived from the changes in heat content and magnetic entropy for our reaction leads to $\Delta E^0 = 1.18$ v at 15°. If this value is combined with that of +0.745 v for the formal Fe^{3+}/Fe^{2+} potential in 0.5N-perchloric acid at the same temperature (calculated from the data of Connick and McVey,¹⁹ who used conditions closest to ours), the formal Co^{3+}/Co^{2+} potential is obtained as +1.93 v. Comparison with the Fe^{3+}/Fe^{2+} system suggests that the true standard potential at 25° would be about 0.02 v higher. In view of the assumptions that we have made, and the experimental difficulties involved (which account for the rather low degree of consistency of our results), we would

¹³ Smith and Getz, *Ind. Eng. Chem., Analyt.*, 1938, **10**, 191.

¹⁴ Noyes, DeVault, Coryell, and Deahl, *J. Amer. Chem. Soc.*, 1937, **59**, 1326.

¹⁵ Friedman, Hunt, Plane, and Taube, *J. Amer. Chem. Soc.*, 1951, **73**, 4028.

¹⁶ Klanberg, Hunt, and Dodgen, *Inorg. Chem.*, 1962, **2**, 139.

¹⁷ Sykes, *Chem. Soc. Special Publ.*, 1954, No. 1, p. 64; *J.*, 1959, 2473.

¹⁸ Milburn, *J. Amer. Chem. Soc.*, 1957, **79**, 537.

¹⁹ Connick and McVey, *J. Amer. Chem. Soc.*, 1951, **73**, 1798.

not expect a higher degree of accuracy than about ± 0.1 v for our estimated value, $E^0 = +1.95$ v at 25° ; it is, however, worth pointing out that an error of 0.1 v in E^0 would correspond to one of 2.3 kcal. in ΔH^0 , or of 8 cal deg.⁻¹ in ΔS^0 , and that the formation of a more stable perchlorate complex by Co(III) than by Fe(III) would raise the value of E^0 .

Experimental.—Solutions of cobalt(III) perchlorate were prepared by electrolysis, in an apparatus essentially similar to that described by Palmer,²⁰ of 0.4M-cobalt(II) perchlorate in perchloric acid of concentration 4.08N, to allow for the loss of hydrogen ions during hydrolysis. Towards the end of the three-hour electrolysis, the temperature of the solution was steadily raised (by increasing the current) to ca. 11° . The cooling-bath was then removed, the current switched off, and stirring continued for 10 min. by means of the rotating platinum anode. This removed any oxidising gases, and a blank experiment showed that the solution obtained by electrolysis of the perchloric acid solution had no oxidising action on potassium iodide.

The heats of reaction were measured in a well-lagged Dewar flask of about 600 ml. capacity; temperatures were measured by means of a Beckmann thermometer, and the water-equivalent of the calorimeter and its contents was determined electrically after each reaction. Before each experiment, the calorimeter contained 300 ml. of 0.125M-ferrous perchlorate solution in 4N-perchloric acid; 120 ml. of cobalt(III) perchlorate solution, prepared as above, was pipetted into an inlet tube leading to a thin-walled pear-shaped glass bulb placed in the ferrous perchlorate solution, and the two solutions were allowed to reach thermal equilibrium. At zero time, 20 ml. of the cobalt(III) solution was withdrawn from the inner bulb and run into excess of potassium iodide solution, the iodine liberated being determined with thiosulphate; simultaneously, the bulb was broken by means of a glass rod. Corrections were made for the slow gain of heat from the surroundings and for the small heat of dilution of the cobalt(III) perchlorate solution. After each experiment, the excess of ferrous iron was determined, using 0.25M-dichromate solution, and it was shown that the ratio Co(III) reduced : Fe(II) oxidised was 1.00 ± 0.02 . In five experiments, the heat of the reaction (ΔH) was found to be -26.0 , -27.8 , -25.8 , -24.8 , and -27.1 kcal., giving a mean value for ΔH of -26.3 kcal.

We thank the D.S.I.R. for a Studentship (to D. A. J.).

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²⁰ Palmer, "Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954.

665. Nitrate-derivatives of Substituted Iodosobenzenes.

By W. E. DASENT and L. E. SHARMAN.

DASENT AND WADDINGTON¹ showed that the reaction of iodosobenzene diacetate with nitric acid gave the oxygen-bridged μ -oxo-dinitratodiphenyl-di-iodine, $\text{Ph}\cdot\text{I}(\text{O}\cdot\text{NO}_2)\cdot\text{O}\cdot(\text{O}\cdot\text{NO}_2)\cdot\text{I}\cdot\text{Ph}$, and not iodosobenzene dinitrate, $\text{PhI}(\text{NO}_3)_2$, as reported² previously. We now describe the reactions of the diacetates of *m*-nitro-, *p*-methyl-, and 2,4,6-tribromo-iodosobenzene with nitric acid. Only in the case of the *m*-nitro-compound was a reasonably stable nitrate-derivative obtained, and its composition, acidimetric equivalent, and infrared spectrum are in accord with an oxygen-bridged structure of the type established for the unsubstituted compound. The *p*-methyl-compound gave a nitrate-derivative which, although too unstable for detailed examination, probably has a similar structure. The 2,4,6-tribromo-compound did not give a nitrate-derivative.

¹ Dasant and Waddington, *Proc. Chem. Soc.*, 1960, 71; *J.*, 1960, 3350.

² Willgerodt, *Ber.*, 1892, 25, 3498; 1893, 26, 1308.

Experimental.—*Nitrato-derivative of m-nitroiodosobenzene.* *m*-Nitroiodosobenzene diacetate, prepared by the method of Masson and Hanby,³ had m. p. 150—151° (decomp.) (lit.,³ 147°; lit.,² 148—155°). To the diacetate (1.0 g.), nitric acid (*d* 1.4; 20 ml.) was added and the resulting solution allowed to stand in air overnight. The yellow crystals of μ -*oxo-dinitratodi*-(*m*-nitrophenyl)*di-iodine* were filtered off and dried *in vacuo*, m. p. 149° (decomp.) (Found: C, 22.3; H, 1.6; N, 8.7. $C_{12}H_8I_2N_4O_{11}$ requires C, 22.6; H, 1.25; N, 8.8%) [Equiv. (by titration with potassium hydroxide in methanol), 330. Calc., 319. The equivalent of *m*-nitroiodosobenzene diacetate was determined as a check on the method. Found, 183. Calc., 184]. No solvent suitable for a molecular-weight determination could be found, as the nitrato-derivative decomposed partially or completely in all solvents in which it dissolved.

The infrared spectrum was measured on mulls in Nujol and hexachlorobutadiene, using a Perkin-Elmer 21 double-beam recording spectrophotometer with sodium chloride and potassium bromide optics. Precautions as previously described¹ were taken to prevent exchange of the nitrato-groups with the halide in the salt plates. The assignments of the observed maxima (other than those attributable to absorption by the *m*-substituted benzene rings) are as follows. *m*-Nitro-substituent: 1530, 1350 (lit.,⁴ 1518, 1349); nitrato-group: ν_1 1259, ν_2 993, ν_3 720, ν_4 1490, ν_5 730, ν_6 811 (lit.,^{5,6} ν_1 1253—1290, ν_2 970—1034, ν_3 706—721, ν_4 1427—1531, ν_5 717—749, ν_6 781—802); C-I stretch: 480 (lit.,¹ 447—489); I-O-I asymm. stretch 585, sym. stretch 430 (lit.,¹ 585, 427 cm^{-1}).

Nitrato-derivative of p-methyliodosobenzene. *p*-Methyliodosobenzene diacetate, prepared according to the method of Pausacker,⁷ had m. p. 103—105° (lit.,⁷ 104°). Nitric acid (2M; 3 ml.) was added to the diacetate (0.3 g.) dissolved in glacial acetic acid (1 ml.). The very pale yellow crystals of μ -*oxo-dinitratodi*-(*p*-methylphenyl)*di-iodine* were filtered off at the pump and dried in air, m. p. 80° (decomp.). The crystals were very unstable and decomposed slowly on standing in dry air. Decomposition, which was accelerated by light and by the application of a vacuum, was very rapid if the crystals were allowed to remain in contact with the mother-liquor [Equiv. (by titration with potassium hydroxide in aqueous methanol; three separate preparations): 293, 292, 294. Calc. for $C_{14}H_{14}I_2N_2O_7$: 288. *M* (cryoscopic in nitrobenzene), 532, 562. Calc., 576].

Attempted preparation of a nitrato-derivative of 2,4,6-tribromoiodosobenzene. The procedure of McCrae⁸ was followed for the preparation of 2,4,6-tribromoiodosobenzene diacetate. Microscopic examination of the white crystalline product showed that it was heterogeneous, but after repeated washings with ether, and recrystallisation from benzene, the crystals had m. p. 162—163°, unchanged by further recrystallisation. [Equiv. (by titration with potassium hydroxide in methanol), 274. Calc., 279. Iodometric equivalent (by titration in acetic acid solution with sodium thiosulphate, after addition of potassium iodide), 276. Calc., 279]. McCrae, who apparently did not recognize the heterogeneity of the initial product, reported⁸ m. p. 137° (with sintering at 98°) for his diacetate. Treatment of the diacetate with nitric acid, under a wide range of concentration and solvent conditions, did not give any nitrato-derivative.

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³ Masson and Hanby, *J.*, 1938, 1699.

⁴ Randle and Whiffen, *J.*, 1952, 4153.

⁵ Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

⁶ Gatehouse and Comyns, *J.*, 1958, 3965.

⁷ Pausacker, *J.*, 1953, 107.

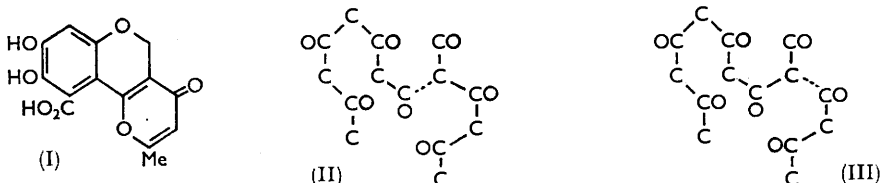
⁸ McCrae, *J.*, 1898, 73, 691.

666. *Studies in Relation to Biosynthesis. Part XXXIV.* The Branched-chain Origin of Citromycetin.*

By A. J. BIRCH, S. F. HUSSAIN, and R. W. RICKARDS.

WHEREAS most polyketides could arise biogenetically from an unbranched carbon chain, some must arise either from a branched chain or by fission of a ring system produced from an unbranched chain. We pointed out¹ that citromycetin (I) is a good example in this latter group, in which a decision between pathways involving one or two chains might be reached as a result of the expected lower incorporation of [¹⁴C]malonic acid into the "methyl-terminal" unit of a precursor chain (*cf.* ref. 2). In the meantime, Gatenbeck and Mosbach³ have provided minimal experimental evidence that two chains are, in fact, involved in this case. We report briefly our own results in support of this conclusion.

Experimental.—The mycelium from 6-days' old surface cultures of *Penicillium frequentans* Westling (I.M.I. No. 91914) was re-flooded with phosphate buffer (pH *ca.* 5) and incubated in the presence of diethyl [2-¹⁴C]malonate for 16 hr., giving [¹⁴C]citromycetin with 1.4% tracer incorporation. The metabolite (relative molar activity⁴ 8.30×10^4) gave, to Kuhn-Roth oxidation, acetic acid, which was degraded by Schmidt degradation into methylamine (r.m.a. as *N*-methyl-2,4-dinitroaniline, 1.03×10^4) and barium carbonate (r.m.a. 0.017×10^4). The total activity of these acetic acid fragments (r.m.a. 1.05×10^4) represents that of one methyl-terminal unit. Decarboxylation of citromycetin (I) gave barium carbonate (r.m.a. 1.00×10^4) derived from the aromatic carboxyl group. Assuming that the small degree of randomisation of isotope within the various C₂ units is approximately constant, the remaining five C₂ units must, from all previous results, carry equal activity, with r.m.a. 1.25×10^4 . Since the experimental error is considered to be $\pm 3\%$, these results show that two end-units of lower radioactivity are present in the molecule, and two precursor chains are initiated at positions which ultimately become the methyl group of the pyrone ring and the aromatic carboxyl group.



To obtain, if possible, information as to the exact point of junction of the two chains, *e.g.*, as in (II) or (III), the organism after 3 days' growth was incubated for 95 hr. with sodium [1-¹⁴C]butyrate, in the hope that the [1-¹⁴C]acetoacetyl coenzyme-A derived by β -oxidation would not equilibrate entirely with acetyl coenzyme-A but would be incorporated to some extent as a unit. This hope was not realised, and the tracer merely behaved as a source of carboxyl-labelled "acetate" units. However, unlike the earlier experiments⁵ with sodium [1-¹⁴C]-acetate itself, which gave uniform labelling throughout the molecule, it was possible in this case to detect preferential labelling in the pyrone C-methyl group, corresponding to a methyl-terminal chain unit. Unfortunately it has not been possible to devise a degradation to examine directly the labelled benzenoid carbon corresponding to the terminal unit of the other chain. The result is important in supporting the malonate conclusions, however, since it provides further evidence that there is incomplete equilibration of acetyl and malonyl coenzyme-A under the incubation conditions used.

* Part XXXIII, Birch and Farrar, *J.*, 1963, 4277.

¹ Birch, *Proc. Chem. Soc.*, 1962, 3.

² Bu'Lock and Smalley, *Proc. Chem. Soc.*, 1961, 209; Birch, Cassera, and Rickards, *Chem. and Ind.*, 1961, 792; Bu'Lock, Smalley, and Smith, *J. Biol. Chem.*, 1962, 237, 1778.

³ Gatenbeck and Mosbach, *Biochem. Biophys. Res. Comm.*, 1963, 11, 166.

⁴ Birch, Massy-Westropp, Rickards, and Smith, *J.*, 1958, 360.

⁵ Birch, Fitton, Pride, Ryan, Smith, and Whalley, *J.*, 1958, 4576.

The [$1\text{-}^{14}\text{C}$]butyrate-labelled citromycetin (r.m.a. 9.67×10^4 , 1.3% tracer incorporation) gave, on Kuhn-Roth oxidation and Schmidt degradation of the resulting acetic acid, methylamine (r.m.a. as *N*-methyl-2,4-dinitroaniline, 0.06×10^4) and barium carbonate (r.m.a. 1.44×10^4). This represents a total activity for one terminal C_2 unit of 1.50×10^4 , compared with the value of 1.38×10^4 required if all seven units present are equally labelled. Conversion of citromycetin (I) into its dimethyl ether methyl ester⁶ (r.m.a. 9.69×10^4) and hydrolysis with 2*N*-aqueous sodium hydroxide^{5,6} afforded acetic acid, which was decarboxylated under Schmidt conditions to give finally barium carbonate (r.m.a. 1.34×10^4). Since this acetic acid is probably derived mainly from the first two C_2 units of the pyrone ring, and would thus encompass the acetoacetyl chain in (III), the absence of high activity here shows that the butyric acid skeleton is not incorporated intact. This conclusion is reinforced by the activity of the carbon dioxide (r.m.a. 1.32×10^4) simultaneously produced during the alkaline hydrolysis, which probably came mainly from the pyrone carbonyl group and would thus carry the labelled 1-position of any butyrate incorporated as a unit as in (III). This latter carbon dioxide is not derived from decarboxylation of the aromatic carboxyl group, since similar hydrolysis of citromycetin dimethyl ether methyl ester labelled by [$2\text{-}^{14}\text{C}$]malonate tracer gave inactive carbon dioxide.

We are grateful to the Pakistan C.S.I.R. for a maintenance grant (to S. F. H.).

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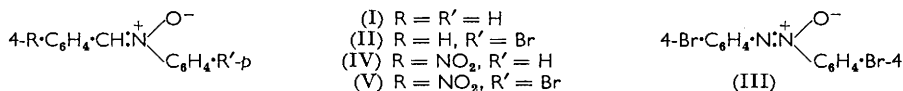
[Received, November 8th, 1963.]

⁶ Robertson and Whalley, *J.*, 1949, 848.

667. *The Bromination of Aromatic Nitrones.*

By J. K. SUTHERLAND and D. A. WIDDOWSON.

IN an attempt to prepare α -bromo-nitrones we have studied the bromination of benzylideneaniline *N*-oxide (I) in the hope that α -bromination would occur by analogy with the chlorination of oximes to hydroxyimino-chlorides.¹ Reaction of (I) with one mole of bromine in chloroform gave a 17% yield of a monobromo-compound, whose structure (II) followed from its hydrolysis by base to benzaldehyde (identified as its dimedone derivative) and 4,4'-dibromoazoxybenzene² (III), which is derived from *p*-bromophenylhydroxylamine by base-catalysed autoxidation.³ The nitrone (II) was synthesised by condensation of benzaldehyde with *p*-bromophenylhydroxylamine. Bromination of 4-nitrobenzylideneaniline *N*-oxide gave the analogous bromo-nitron (V); again the position of substitution was confirmed by degradation to (III). Reaction of (I) under more forcing conditions with an excess of bromine yielded, as the only crystalline product, 2,4,6-tribromoaniline, whilst reaction of (I) with *N*-bromosuccinimide gave only the azoxybenzene (III).



The position of bromination of these compounds was unexpected. In view of the ready dissociation of some nitrones in solution to the carbonyl compound and hydroxylamine⁴ we investigated the bromination of phenylhydroxylamine under the same conditions. In this case 82% of the one mole of bromine used was recovered as 2,4,6-tribromoaniline hydrobromide; presumably, two of the nuclear bromines were introduced by electrophilic attack and the other by acid-catalysed nucleophilic displacement of the

¹ Werner and Buss, *Ber.*, 1894, **27**, 2193.

² Gore and Wheeler, *J. Amer. Chem. Soc.*, 1956, **78**, 2160.

³ Bamberger, *Ber.*, 1894, **27**, 1552.

⁴ Boyland and Nerry, *J.*, 1963, 3141.

hydroxyl group of the hydroxylamine.⁵ This result suggests that no dissociation takes place before bromination. The similarity of our results to the nitration of benzylidene-aniline in sulphuric acid to give benzylidene-*p*-nitroaniline⁶ suggests the occurrence of the same type of directing effect in the two molecules.

The bromination of *N*-4-nitrobenzylidenemethylamine *N*-oxide was also examined. In this case *p*-nitrobenzoic acid and *p*-nitrobenzaloxime were isolated. The first product could have arisen from hydrolysis of an α -bromo-nitrone and the second by demethylation of the starting material by hydrogen bromide.

Experimental.—*Bromination of benzylideneaniline N-oxide*⁷ (I). Bromine (600 mg.) in chloroform (15 ml.) was added dropwise to a stirred solution of the nitrone (I) (500 mg.) in chloroform (20 ml.) at room temperature. The solution was refluxed for 15 min., washed with water, dried, and concentrated, to give the *nitrone* (II) (140 mg.), m. p. 180–181° (from ethanol) (Found: C, 56.4; H, 3.8; N, 5.2. C₁₃H₁₀BrNO requires C, 56.5; H, 3.6; N, 5.05%).

Hydrolysis of benzylidene-p-bromoaniline N-oxide (II). The nitrone (II) (156 mg.) in acetonitrile (5 ml.) was stirred with 0.1*N*-sodium hydroxide (10 ml.) at room temperature for 16 hr. The precipitate was filtered off and recrystallised from acetonitrile, to give 4,4'-dibromoazoxybenzene (85 mg.), identified by m. p., mixed m. p., and comparison of i.r. spectra.

*Bromination of 4-nitrobenzylideneaniline N-oxide*⁸ (IV). Bromine (670 mg.) in chloroform (15 ml.) was added dropwise to a stirred solution of the nitrone (IV) (1.0 g.) in chloroform (40 ml.) at room temperature. The bromine was absorbed immediately, and triethylamine (0.7 ml.) in chloroform (10 ml.) was added, the precipitate filtered off, and the solution evaporated. The residue was extracted with benzene, the extract evaporated, and the red solid remaining recrystallised from acetonitrile–nitromethane, to give yellow needles (340 mg.) of the *nitrone* (V), m. p. 209° (Found: C, 48.3; H, 3.1; N, 8.7; Br, 24.85. C₁₃H₁₃BrN₂O₃ requires C, 48.6; H, 2.8; N, 8.7; Br, 24.9%).

Alkaline hydrolysis of (V), as above for (II), gave 4,4'-dibromoazoxybenzene, identical with an authentic specimen.

Dibromination of (I). Bromine (1.65 g.) and the nitrone (I) (1.0 g.) were refluxed in chloroform (40 ml.) for 1 hr. The solution was reduced in volume and a precipitate separated. After recrystallisation from ethanol, the solid (1.0 g.) was shown to be 2,4,6-tribromoaniline by m. p., mixed m. p., and comparison of i.r. spectra.

Bromination of (I) with N-bromosuccinimide. The nitrone (I) (500 mg.) and *N*-bromosuccinimide (455 mg.) were refluxed in carbon tetrachloride (30 ml.) for 1 hr. After filtration and evaporation, the residue was recrystallised from ethanol, to give 4,4'-dibromoazoxybenzene, identical with an authentic specimen.

Bromination of N-4-nitrobenzylidenemethylamine N-oxide.⁹ The nitrone (1 g.) was refluxed with bromine (0.89 ml.) in chloroform (40 ml.) for 4 hr. The solution was filtered, evaporated, and the residual oil chromatographed over silica gel (B.D.H. for chromatography). Elution with benzene yielded *p*-nitrobenzaloxime (97 mg.), identical with an authentic sample. From the 5% ethanol–chloroform fraction *p*-nitrobenzoic acid (56 mg.) was isolated.

Bromination of N-phenylhydroxylamine.¹⁰ Bromine (2 g.) in chloroform (10 ml.) was added dropwise to a stirred solution of the hydroxylamine (1.2 g.) in chloroform (10 ml.), below 20°. After evaporation to dryness and washing of the residue with anhydrous ether, 2,4,6-tribromoaniline hydrobromide (2.1 g.) was obtained. On stirring with water 2,4,6-tribromoaniline was isolated, identical with an authentic sample.

Analyses were by Miss Cuckney and staff of the Microanalytical Laboratory. We thank the D.S.I.R. for financial assistance (D. A. W.).

CHEMISTRY DEPARTMENT, IMPERIAL COLLEGE, LONDON S.W.7. [Received, November 8th, 1963.]

⁵ Bamberger, *Annalen*, 1921, **424**, 233; 1925, **441**, 207.

⁶ Arnall and Lewis, *J. Soc. Chem. Ind.*, 1929, **48**, 159.

⁷ Wiemann and Glacet, *Bull. Soc. chim. France*, 1950, 176.

⁸ Grammatikakis, *Bull. Soc. chim. France*, 1951, 965.

⁹ Brady, Dunn, and Goldstein, *J.*, 1926, **2386**.

¹⁰ Kamm, *Org. Synth.*, 1925, **4**, 57.

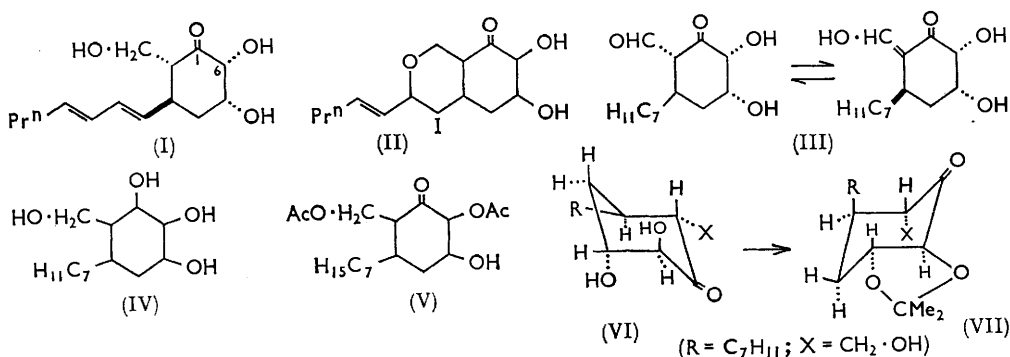
668. *The Absolute Configuration of Palitantin.*

By JOHN FREDERICK GROVE and B. K. TIDD.

THE absolute configuration (I), with a conjugated *trans*-heptadienyl side-chain, was tentatively assigned to the mould product palitantin by Bowden *et al.*¹ The nuclear magnetic resonance (n.m.r.) spectra of palitantin^{2,3} and its derivatives lead to some additional arguments which, without resort to discussion of the probable steric course of the palitantin-palitantic acid rearrangement, support this assignment.

The ready interconversion of palitantin and iodopalitantin (II) requires the participation of a *trans*-double bond. The n.m.r. spectrum of iodopalitantin shows the olefinic protons as a multiplet in which lines centred at τ 4.6 and 4.1 are clearly recognisable as the AB part of a PABX₂ system with $J_{AB} = 16$ c./sec., in agreement with the *trans*-configuration assigned to this double bond in palitantin.¹

The cyclohexanone ring will adopt the conformation in which the bulky β -heptadienyl substituent is equatorial. Since reduction of both frequentin (III) and palitantin with sodium borohydride gave the same tetraol, palitantal (IV), the hydroxymethyl substituent in palitantin must also be equatorial and therefore α -oriented. The equilibrium (III)^{2,3} ensures that the formyl group in frequentin has the equatorial configuration.



Although the multiplet in the palitantin spectrum arising from the hydrogens at positions 5 and 6 is unresolved, the overall width at half-height (11 c./sec.) excludes the possibility that a large (16 c./sec.)⁴ coupling constant associated with *trans*-diaxial protons is involved. The width at half-height compares with reported⁵ widths of *ca.* 21 c./sec. and *ca.* 7 c./sec. for a single proton with and without such a coupling, respectively. This conclusion is strongly reinforced by the spectrum of diacetyltetrahydropalitantin (V) where, in the presence of a trace of trifluoroacetic acid to promote the hydroxyl proton exchange and sharpen up the spectrum, the resonance peaks are separated into a two-proton doublet ($CH_2 \cdot OAc$) at τ 5.57, a one-proton doublet ($CH \cdot OAc$) at τ 4.55 ($J_{5,6} = 3$ c./sec.), and a one-proton unresolved multiplet ($CH \cdot OH$) at τ 5.3 (width at half-height, 9 c./sec.). An identical argument, excluding the presence of *trans*-diaxial protons, applies to 5,6-isopropylidenepalitantin ($CH_2 \cdot OH$ doublet at τ 6.3) which is not therefore formed from a palitantin structure (VI) with *trans*-diaxial hydroxyl groups by a forced ring-conformational change [(VI) \rightarrow (VII)]. The hydrogens at positions 5 and 6 in palitantin are therefore *cis*: of

¹ Bowden, Lythgoe, and Marsden, *J.*, 1959, 1662, and references therein.

² Grove and Tidd, *Chem. and Ind.*, 1963, 412.

³ Sigg, *Helv. Chim. Acta*, 1963, 46, 1061.

⁴ Williamson and Johnson, *J. Amer. Chem. Soc.*, 1961, 83, 4623.

⁵ Lemieux, Kullnig, Bernstein, and Schneider, *J. Amer. Chem. Soc.*, 1958, 80, 6098; Musher, *ibid.*, 1961, 83, 1146.

the two possible arrangements, that represented by (I) is correct since the large coupling constant, $J_{4\beta, 5\alpha}$, expected for an axial 5-hydrogen is not observed.

Nuclear magnetic resonance spectra were obtained for deuteriochloroform solutions (tetramethylsilane as internal reference) with a Varian Associates A.60 spectrometer (60 Mc.). Palitantin derivatives were prepared by literature methods¹ by Mr A. E. Field.

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THE FRYTHE, WELWYN, HERTS.

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669. Purification of Tetralin.

By K. C. BASS.

NAPHTHALENE is one of the principal impurities in commercial tetralin, and its removal is necessary when pure tetralin is required for use in reactions which give naphthalene as a product, *e.g.*, in hydrogen-transfer reactions where tetralin may be used as the hydrogen donor. Mair and Streiff¹ purified tetralin by repeated fractional crystallisation from solutions containing *ca.* 50% by volume of dichlorodifluoromethane. Morton and de Gouveia^{2,3} converted tetralin into purified barium tetralin-6-sulphonate,⁴ from which the sodium salt was prepared and decomposed in 60% sulphuric acid solution with superheated steam at 160—180°. A method is described here for the removal of naphthalene from commercial tetralin through formation of ammonium tetralin-6-sulphonate⁵ and its decomposition by steam-distillation from acid solution.^{6,7} The purity of the tetralin was checked by ultraviolet spectroscopy and the results compared with those of Morton and de Gouveia.²

Experimental.—*Preparation of ammonium tetralin-6-sulphonate.* Commercial tetralin (272 ml., 2.0 moles) was extracted with concentrated sulphuric acid (3 × 30 ml.), washed with water (250 ml.), 10% sodium carbonate solution (250 ml.), and water (250 ml.), dried (Na₂SO₄), and distilled from clean sodium through a lagged 5-in. Vigreux column, to give a colourless liquid (230 ml.), b. p. 206—207° (±1°). Concentrated sulphuric acid (150 ml.) was added slowly to this material and the mixture was stirred vigorously; it became hot and most of the tetralin dissolved. The mixture was heated on a water-bath, with constant stirring, for *ca.* 2 hr., after which all the tetralin had dissolved. The warm mixture was poured into a solution of ammonium chloride (120 g.) in water (400 ml.), and the white solid which crystallised immediately from the solution was filtered off and recrystallised from the minimum amount of boiling water, to give rectangular plates of ammonium tetralin-6-sulphonate which were washed with small quantities of 50% aqueous ethanol and dried at 100°. Further quantities were obtained by evaporation of both mother-liquors.

The combined crops were dissolved in an excess of boiling water and the solution was evaporated on a water-bath, to remove traces of naphthalene, which were steam-volatile. Finally, the naphthalene-free ammonium tetralin-6-sulphonate was crystallised from boiling water until it was pure, as judged from its appearance in colourless rectangular plates. Further quantities were obtained from the mother-liquors. The total yield of pure salt was 240 g. (62%).

Decomposition of ammonium tetralin-6-sulphonate. Pure ammonium tetralin-6-sulphonate (229 g., 1 mole) was mixed with concentrated sulphuric acid (266 ml., 5.0 moles; *d* 1.84), and the mixture was steam-distilled from an oil-bath at 165—170°. The distillate was extracted with ether, and the ether layer was washed with 10% sodium carbonate solution and water,

¹ Mair and Streiff, *J. Res. Nat. Bur. Stand.*, 1941, **27**, 343.

² Morton and de Gouveia, *J.*, 1934, 919.

³ "Elsevier's Encyclopaedia of Organic Chemistry," ed. Radt, Elsevier, Amsterdam, 1948, vol. 12B, p. 65.

⁴ Willstätter and Seitz, *Ber.*, 1923, **56**, 1392.

⁵ Schroeter, *Annalen*, 1922, **426**, 111.

⁶ Armstrong and Miller, *J.*, 1884, **45**, 148.

⁷ Friedel and Crafts, *Bull. Soc. chim. France*, 1884, **42**, 66.

dried (Na_2SO_4), and the ether removed by distillation. The remaining tetralin was refluxed over clean sodium for 1 hr. and distilled from sodium through a lagged 5-in. Vigreux column, to give the pure compound (89 ml., 65%), b. p. 207—208° ($\pm 1^\circ$), n_D^{20} 1.5413.

The ultraviolet absorption spectrum in spectroscopically pure cyclohexane, measured on a Beckman Ratio Recording Spectrophotometer DK2 over the range 2500—3300 Å, showed λ_{max} 2750 and 2670 Å (lit.,² 2740 and 2670 Å), and the characteristic naphthalene bands at 3010, 3040, 3050, 3110, and 3200 Å (in cyclohexane), which were present in the spectrum of the original tetralin, were absent. The final naphthalene content of the tetralin was thus less than 0.4%, which is the limit of detection by the spectroscopic method used.

DEPARTMENT OF APPLIED CHEMISTRY, NORTHAMPTON COLLEGE OF ADVANCED TECHNOLOGY,
ST. JOHN STREET, LONDON E.C.1. [Received, November 18th, 1963.]

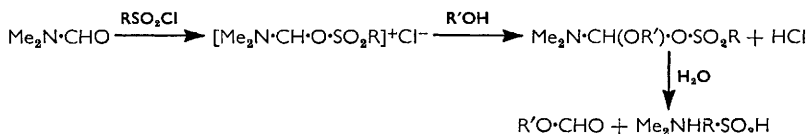
670. Side Reactions during Tosylation of Bis-2-hydroxyethyl Terephthalate.

By R. A. EDINGTON.

IN continuation of the work of Zahn and his co-workers on oligoesters of terephthalic acid and ethylene glycol,¹ certain tosyl esters were required as intermediates. Anomalous behaviour, however, was observed during the tosylation and investigation of the anomalies revealed several interesting reactions, which have been briefly studied. Apart from normal tosylation, reactions were observed leading to (a) formate esters, (b) alkyl chlorides, and (c) carboxylic esters. Yields may be very good (94%) in (a) and (b) but poor (not above 50%) in (c).

(a) *Formation of Formate Ester.*—When bis-2-hydroxyethyl terephthalate is treated, at low temperatures for short periods, with tosyl (toluene-*p*-sulphonyl) chloride using a solvent containing dimethyl- or diethyl-formamide, the product is the formate ester. The reaction is fast and nearly quantitative at low temperatures (*e.g.*, 94% after 15 minutes at -5°): at higher temperatures, or during prolonged reaction periods, the chlorination reaction (b) begins to compete. The order of addition of reactants is important: highest yields of formate ester are obtained by mixing the formamide and tosyl chloride (and diluent if used) and then adding the alcohol. If the dimethylformamide is added last the product is the tosyl ester.

The use of the addition compounds of formamides with oxyhalides, particularly phosphorus oxychloride, for *C*-formylation, *i.e.*, the formation of aldehydes, is well-known as the Vilsmeier–Haack reaction.² The only example in the literature of *O*-formylation, *i.e.*, the preparation of formic esters, by such methods is that reported by Stevens,³ using iodine pentafluoride. The present reaction is also notable for the mildness of the conditions under which it proceeds in comparison with the Vilsmeier–Haack reaction. The mechanism of this *O*-formylation may, however, be analogous to that of the Vilsmeier–Haack reaction:⁴



¹ Zahn, Borstlap, and Valk, *Makromol. Chem.*, 1963, **64**, 18.

² Vilsmeier and Haack, *Chem. Ber.*, 1927, **60**, 119.

³ Stevens, *Chem. and Ind.*, 1958, 1090.

⁴ Kuhle, *Angew. Chem.*, 1962, **74**, 861.

(b) *Formation of Alkyl Chloride*.—When bis-2-hydroxyethyl terephthalate is treated with tosyl chloride and pyridine, with or without dimethylformamide, for longer periods or at higher temperatures than would lead to good yields of the formate ester or of the tosyl ester, respectively, a reaction leading to the formation of alkyl chloride begins to compete and under suitable conditions may predominate (*e.g.*, over 90% may be isolated after 4 hours at 65° or 15 minutes at 100°). Preformed tosyl ester may be converted into the alkyl chloride by treatment with pyridine, tosyl chloride, and toluene-*p*-sulphonic acid under similar conditions of time and temperature, but preformed formate ester is recovered unchanged.

There have been previous observations of the formation of chlorides during tosylations, particularly of alcohols of enhanced reactivity, but there is no record of nearly quantitative yields of the chloride from alcohols of apparently normal reactivity as in the present instance. The mechanism of the reaction is more obscure than that of the formylation reaction: in particular it is remarkable that the reaction should proceed equally well in the presence or absence of dimethylformamide although the reaction complexes in the two cases would be expected to be quite different.

During this work it was found that the chlorination reaction could be retarded by addition of toluene-*p*-sulphonic acid to the reaction mixture; such addition, together with the use of low temperatures and short reaction times, is therefore advantageous for a maximum yield of tosyl ester.

(c) *Formation of Carboxylic Esters*.—Treatment of a diol (*e.g.*, ethylene glycol or bis-2-hydroxyethyl terephthalate) with one equivalent of a carboxylic acid and with tosyl chloride and pyridine, under conditions which in the absence of the carboxylic acid would lead to high yields of the tosyl ester or of the chloride, gives instead a product which contains no tosyl ester or chloride, but is a mixture of the diol and the carboxylic acid with the carboxylic diester of the diol. The yield of carboxylic ester varies between 25 and 50%. Treatment of preformed tosyl ester under these conditions leads to quantitative recovery of the tosyl ester.

The chief interest of this reaction is that it apparently does not proceed by the obvious route, *i.e.*, interaction of sulphonyl chloride and acid to give carboxylic acid chloride, which would then react with the alcohol. The evidence against this simple mechanism is that, although this esterification reaction is slow and incomplete and although excess of tosyl chloride is present under conditions which in the absence of carboxylic acid would lead to rapid and complete tosylation or chlorination, in fact no tosyl ester or chloride is formed.

Experimental.—*Formylation. Preparation of Bis-2-formyloxyethyl Terephthalate*. Bis-2-hydroxyethyl terephthalate (2 g.) and tosyl chloride (6 g.) were placed in a lightly stoppered boiling-tube. A mixture of dry pyridine (10 ml.) was added, the mixture shaken vigorously until solution was complete, and then placed in a bath at -5° (bath temperature) for 15 min. While the tube was still in the cold bath, water (1 ml.) was added and the mixture shaken vigorously for 30 sec. and then poured into water (100 ml.). The precipitated *bis-2-formyloxyethyl terephthalate* was filtered off, washed well with water, and dried (2.29 g., 94%, m. p. 78—81°). Recrystallisation from 50% aqueous methanol raised the m. p. to 80—82°. [Found: C, 54.3; H, 4.5%; *M*, 309 (vapour pressure osmometry). C₁₄H₁₄O₈ requires C, 54.3; H, 4.5%; *M*, 310.]

Chlorination. Preparation of bis-2-chloroethyl terephthalate. Bis-2-hydroxyethyl terephthalate (2 g.) and tosyl chloride (3 g.) were dissolved in dimethylformamide (20 ml.) and heated at 100° for 30 min. Water (1 ml.) was added and the mixture shaken for 30 sec. and poured into water (100 ml.). The precipitated *bis-2-chloroethyl terephthalate* was filtered off, washed well with water, and dried (2.15 g., 94%, m. p. 85—89°). Recrystallisation from 50% aqueous methanol raised the m. p. to 92—94° (Found: C, 49.5; H, 4.1; Cl, 24.0. C₁₂H₁₂Cl₂O₄ requires C, 49.5; H, 4.2; Cl, 24.4%). The use of a mixture of pyridine (10 ml.) and dimethylformamide (10 ml.) as solvent gives the same product, in lower yield (70%).

*Partial esterification. Preparation of ethylene di-(*p*-methoxycarbonylbenzoate)*. Pyridine (16

ml.), ethylene glycol (0.60 g.), toluene-*p*-sulphonic acid monohydrate (2 g.), methyl hydrogen terephthalate (3.6 g.), and tosyl chloride (8 g.) were mixed at 60°, shaken to dissolve, and kept at 60° for 15 min. Water (1 ml.) was added at the same temperature and the mixture shaken vigorously for 30 sec. and then poured into cold water (100 ml.). The precipitated solid (1.90 g., 49%) had m. p. 155—160°, raised on recrystallisation from ethanol to 164—166°. The m. p. was not depressed on admixture with an authentic specimen of ethylene di-(*p*-methoxycarbonylbenzoate).⁵ Ethylene glycol and methyl hydrogen terephthalate were identified in the aqueous mother-liquors.

Tosylation. Preparation of bis-2-toluene-p-sulphonyloxyethyl terephthalate. Bis-2-hydroxyethyl terephthalate (2 g.), toluene-*p*-sulphonic acid monohydrate (2 g.), tosyl chloride (8 g.), and pyridine (10 ml.) were shaken vigorously to dissolve the solids and the solution then placed in a bath at -5° for 15 min. Water (1 ml.) was added to the tube at this temperature and the mixture shaken for 30 sec. and poured into water (100 ml.). The precipitated *bis-2-toluene-p-sulphonyloxyethyl terephthalate* was filtered off, washed well with water, and dried (m. p. 113°, 3.91 g., 88%). Recrystallisation from methanol raised the m. p. to 119° (Found: C, 55.5; H, 4.7; S, 11.3. C₂₆H₂₆O₁₀S₂ requires C, 55.5; H, 4.7; S, 11.4%).

This work was carried out at the German Wool Research Institute, Aachen, West Germany, and the author thanks Professor Dr. Ing.-H. Zahn (Director) and Dr. G. Heidemann for hospitality and co-operation.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
FIBRES DIVISION, HOOKSTONE ROAD, HARROGATE.

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⁵ Zahn and Krzikalla, *Makromol. Chem.*, 1957, **23**, 31.

671. *The Reductive Cyclisation of 2-Nitro-p-terphenyl. 2-Phenylcarbazole.*

By G. W. GRAY and D. LEWIS.

DURING a preparation of 2-nitro-*p*-terphenyl¹ from 2-nitro-4'-*N*-nitrosoacetamidobiphenyl, when the last traces of benzene were being removed from the reaction mixture by distillation (using a free flame), the residue suddenly decomposed. In addition to 2-nitro-*p*-terphenyl, the black ash yielded a small amount (4%) of a compound which was identified as 2-phenylcarbazole. Since carbazole is obtained in good yield by reductive cyclisation of 2-nitrobiphenyl, either by heating to high temperatures with ferrous oxalate² or by boiling with triethyl phosphite,³ it seemed of interest to study the mode of formation of the 2-phenylcarbazole obtained apparently by a direct pyrolysis of 2-nitro-*p*-terphenyl.

The preparation of 2-nitro-*p*-terphenyl¹ was repeated, ensuring that the products did not undergo thermal decomposition. The residue was chromatogrammed on alumina, and a 63% yield of 2-nitro-*p*-terphenyl was obtained. No 2-phenylcarbazole was isolated from the chromatogram, or from pyrolysates of all other fractions obtained from the column. 2-Phenylcarbazole must, therefore, be formed by the pyrolysis of 2-nitro-*p*-terphenyl, and not by the direct cyclisation or the pyrolysis of any small amounts of reduction products formed during the *N*-nitrosoacetamide reaction. Moreover, no likely intermediates of this kind were isolated or detected; *e.g.*, 2-amino-*p*-terphenyl and its *N*-acetyl derivative, 2-hydroxyamino-*p*-terphenyl and its *ON*-diacetyl derivative, diazoamino-compounds,

¹ Culling, Gray, and Lewis, *J.*, 1960, 1547.

² Waterman and Vivian, *J. Org. Chem.*, 1949, **14**, 289; U.S.P. 2,292,808 (1942).

³ Cadogan and Cameron-Wood, *Proc. Chem. Soc.*, 1962, 361.

and hydroxytriazens. While examining the significance of possible intermediates, it was shown that the pyrolysis of crude 2-hydroxyaminobiphenyl at $>220^\circ$ did yield carbazole (4%), but that the pyrolysis of the *ON*-diacetyl derivative and of 1,3-bis-2-biphenyltriazene yielded no carbazole. Since this work was carried out, pure 2-hydroxyaminobiphenyl, m. p. $69-71^\circ$, has been prepared by Wenkert and Barnett⁴ as part of their study of the cyclisation of α -phenylcyclohexanone oxime. The pure hydroxyamino-compound gave no carbazole when heated to 250° .

Pure 2-nitro-*p*-terphenyl was now pyrolysed, but yielded only 1% of crude 2-phenylcarbazole, compared with the 6% (crude) isolated from the pyrolysate of the reaction mixture. This higher yield cannot then result from a simple pyrolysis of 2-nitro-*p*-terphenyl present in the crude product. Bunyan and Cadogan⁵ consider that triethyl phosphite brings about the reductive cyclisation by deoxygenating aromatic *C*-nitroso- and nitro-compounds, and it is possible that the intractable tars (produced in the preparation of 2-nitro-*p*-terphenyl) themselves decompose on pyrolysis, giving products which are oxygen acceptors and on which deoxygenation and cyclisation of the nitro-compound occurs. These ideas are supported by the fact that 2-nitrobiphenyl gives carbazole when heated with oxygen acceptors such as metals and carbon, as well as with ferrous oxalate.² It is possible that our isolation of carbazole from crude 2-hydroxyaminobiphenyl is explained by a similar intervention of breakdown products arising from the impurities present.

Experimental.—2-Phenylcarbazole. The solvent-free residue¹ from the reaction between 2-nitro-4'-*N*-nitrosoacetamidobiphenyl and benzene was heated over a flame. Thermal decomposition gave a crisp, black mass which was extracted with benzene. Chromatography on alumina yielded crude 2-nitro-*p*-terphenyl (7%) (readily eluted from the column) and crude 2-phenylcarbazole (6%) obtained on further elution with benzene or by extraction of the blue fluorescent band from the extruded column. Crystallisation from benzene or ethanol gave pure 2-phenylcarbazole (4%), m. p. $280-281^\circ$ [Found: C, 88.6; H, 5.6; N, 5.6%; *M*(Rast), 216, 254. $C_{18}H_{13}N$ requires C, 88.9; H, 5.3; N, 5.8%. *M*, 243]. The infrared spectrum was closely similar to that of carbazole, with additional strong bands at $690-770\text{ cm.}^{-1}$ corresponding to a monosubstituted benzene ring. The compound gave colour reactions typical of carbazole. Acetylation gave *N*-acetyl-2-phenylcarbazole, m. p. $127.5-128^\circ$ (Found: C, 84.0; H, 5.3. $C_{20}H_{15}NO$ requires C, 84.2; H, 5.3%). The m. p. was undepressed on admixture with 2-phenylcarbazole prepared as described below.

*Pyrolysis of 2-nitro-*p*-terphenyl.* Pure 2-nitro-*p*-terphenyl (2.07 g.) was heated in a glass tube in the hottest part of a Bunsen flame ($1\frac{1}{2}$ min.). The cooled mass was powdered, and digested with boiling benzene (50 ml.). The cold filtrate was passed through a column of alumina (80 g.); 2-nitro-*p*-terphenyl (0.4 g.) was readily eluted. After elution with more benzene (800 ml.), the extruded column, which displayed a blue fluorescence in ultraviolet light, was cut into three equal portions. Only the middle portion yielded crude 2-phenylcarbazole (0.02 g., 1%). The upper range of the m. p. was 269 , raised to 271° on admixture with pure 2-phenylcarbazole, m. p. $280-281^\circ$.

2-Phenylcarbazole. Following the procedure of Cadogan and Cameron-Wood,³ 2-nitro-*p*-terphenyl (0.75 g.) yielded 2-phenylcarbazole (76%), m. p. 281° (from benzene).

2-Hydroxyaminobiphenyl. A method essentially similar to that used by Wenkert and Barnett⁴ was employed. The product was a red oil which rapidly deposited 2-azoxybiphenyl, m. p. $152-153^\circ$, even when stored under nitrogen. Purification of the crude product was not, therefore, attempted, and on pyrolysis at $210-220^\circ$ the only product isolated was 2-azoxybiphenyl⁴ (31% based on 2-nitrobiphenyl), m. p. $155.5-156.5^\circ$ [from benzene-light petroleum (b. p. $40-60^\circ$)] (Found: C, 82.4; H, 5.3; N, 8.2. Calc. for $C_{24}H_{18}N_2O$: C, 82.3; H, 5.2; N, 8.0%). Pyrolysis at $>220^\circ$ yielded 4% of carbazole, m. p. 240° . The crude *ON*-diacetyl derivative of 2-hydroxyaminobiphenyl was a red-brown oil which was not purified (Found: C, 70.2; H, 6.4; N, 5.6. $C_{16}H_{15}NO_3$ requires C, 71.4; H, 5.6; N, 5.2%). Pyrolysis of this material yielded no carbazole.

⁴ Wenkert and Barnett, *J. Amer. Chem. Soc.*, 1960, **82**, 4671.

⁵ Bunyan and Cadogan, *Proc. Chem. Soc.*, 1962, 78.

1,3-Bis-2-biphenyltriazen. This diazoamino-compound was prepared by normal methods and obtained from light petroleum (b. p. 60—80°) as orange crystals, m. p. 158° (lit.,⁶ 165°) (Found: C, 82.1; H, 5.3; N, 12.3. Calc. for C₂₄H₁₉N₃: C, 82.5; H, 5.5; N, 12.0%). Pyrolysis of the diazoamino-compound yielded no carbazole.

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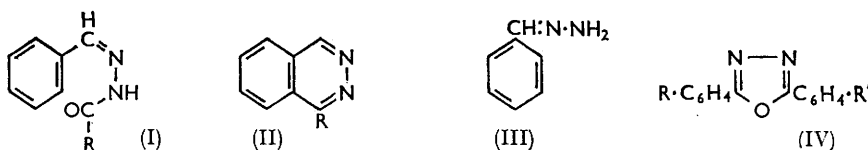
⁶ Richmond, U.S.P. 2,448,155 (1948) (*Chem. Abs.*, 1949, **43**, 898).

672. Polyphosphoric Acid-catalyzed Reactions. Part III.* The Synthesis of 2,5-Disubstituted 1,3,4-Oxadiazoles.

By FRANK D. POPP.

AGGARWAL and his co-workers¹ reported that compounds of type (I) could be converted into 1-substituted phthalazines (II) by treatment with hydrogen chloride in pentyl alcohol. In 1956, it was shown²⁻⁴ that this was incorrect and that 1-benzoyl-2-benzylidenehydrazine (I; R = Ph) gave benzylidenehydrazine (III) and 2,5-diphenyl-1,3,4-oxadiazole (IV; R = R' = H) both under Aggarwal's conditions and with polyphosphoric acid.

After using a wide variety of conditions with a number of compounds of type (I) we never isolated any phthalazines. However, with (I; R = Ph) and polyphosphoric acid at 180—200° for 10 minutes, yields of (IV; R = R' = H) as high as 70% were obtained. A



number of other 1-benzoyl-2-benzylidenehydrazines also gave oxadiazoles in good yield, but 1-benzoyl-2-[4-[di-(2-chloroethyl)amino]benzylidene]hydrazine gave only the azine of *p*-[di-(2-chloroethyl)amino]benzaldehyde.

As 2,5-diphenyl-1,3,4-oxadiazole could be obtained in such good yields from (I; R = Ph) under these conditions, it seemed reasonable to expect that 1,2-dibenzoylhydrazines should give even higher yields of the oxadiazoles through treatment with polyphosphoric acid under these conditions. It has been reported³ that 1,2-dibenzoyl- and 1,2-di-(3-methoxybenzoyl)-hydrazines with polyphosphoric acid at 100° for 3—5 hours gave only 65 and 53% yields of the oxadiazoles. We now find that treatment of 1,2-dibenzoylhydrazines with polyphosphoric acid at 185—205° for 10 minutes gives 80—96% yields of 2,5-disubstituted 1,3,4-oxadiazoles (IV) as indicated in the Table. The conversion of 1,2-dibenzoylhydrazines into 1,3,4-oxadiazoles has been reported by many workers using reagents such as fuming sulphuric acid, chlorosulphonic acid, phosphorus oxychloride, and thionyl chloride, often for very long times. The use of relatively mild polyphosphoric acid for only 10 minutes to give 2,5-disubstituted 1,3,4-oxadiazoles in high yields thus appears to be the method of choice.

* Part II, Popp and Schuyler, *J.*, 1964, 522.

¹ Aggarwal, Darbari, and Ray, *J.*, 1929, 1941.

² Rodda and Rogasch, *J.*, 1956, 3927.

³ Ikeda, Kanahara, and Nishikawa, *Ann. Report Fac. Pharm., Kanazawa Univ.*, 1956, **6**, 1.

⁴ Sagitullin and Kost, *Vestnik Moskov. Univ.*, 1959, **14**, 187 (*Chem. Abs.*, 1960, **54**, 17383).

2,5-Disubstituted-1,3,4-oxadiazoles.

R	R'	Yield (%)	M. p.	Lit. m. p.	Ref.	R	R'	Yield (%)	M. p.	Lit. m. p.	Ref.
H	H	92	139—140°	139	2	<i>m</i> -Cl	<i>m</i> -Cl	91	160—161	—	<i>c</i>
H	<i>p</i> -Cl	80	156—157	157·5—158	<i>a</i>	<i>p</i> -Cl	<i>p</i> -Cl	96	248—249	242—243	<i>d</i>
H	<i>p</i> -F	86	152—153	147	<i>b</i>					250—251	<i>e</i>
<i>o</i> -Cl	<i>o</i> -Cl	86	94—95	—	<i>c</i>	<i>p</i> -F	<i>p</i> -F	96	202—203	200—203	<i>d</i>
						<i>p</i> -Me	<i>p</i> -Me	96	174—175	175—176	<i>f</i>

a, Siegrist, Ger. pat. 1,094,755/1960 (*Chem. Abs.*, 1962, **56**, 486). *b*, Grekov and Shvaika, *Zhur. obsheei Khim.*, 1960, **30**, 3802. *c*, Calc. for C₁₄H₈Cl₂N₂O: C, 57·75; H, 2·8; N, 9·6. Found for *o*-Cl isomer: C, 58·0; H, 2·9; N, 9·65. Found for *m*-Cl isomer: C, 57·9; H, 2·8; N, 9·7%. *d*, Hayes, Rogers, and Ott, *J. Amer. Chem. Soc.*, 1955, **77**, 1850. *e*, Schwechten and Neeff, Ger. pat. 1,024,971/1959 (*Chem. Abs.*, 1960, **54**, 9960). *f*, Huisgen, Sauer, Sturm, and Markgraf, *Chem. Ber.*, 1960, **93**, 2106.

Experimental.—2,5-Disubstituted 1,3,4-oxadiazoles. A mixture of a 1,2-diacylhydrazine (1 g.) and commercial polyphosphoric acid (35—45 g.) was heated for 5—10 min. to 185—205° (internal temperature) and held at this temperature for 10 min. with occasional stirring. The hot mixture was poured directly on to ice, and after 1 hr. it was filtered, to give the white solid product (Table) which was recrystallized from 95% ethanol.

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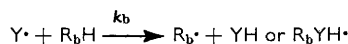
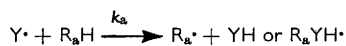
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673. Competitive Oxidations. Part IV.¹ Oxidations of Olefins.

By J. A. KERR, G. LASTRA, and A. F. TROTMAN-DICKENSON.

PREVIOUS Papers in this series¹ described the study of the competitive oxidation of alkanes at high temperatures and at lower temperatures when reaction was initiated by photolysis of a ketone. Similar systems containing olefins are of interest in their own right and because olefins are primary products of the oxidation of alkanes.

The competitive method is based on the assumption that a radical, Y, is first formed which reacts with two hydrocarbons, R_a and R_b, as follows:



Two forms are written because it is not certain, when unsaturated compounds are involved, whether a particular hydrocarbon reacts by loss of a hydrogen atom or by addition to its double bond. The relative rate constants, *k_a* and *k_b*, are given by

$$\frac{k_a}{k_b} = \frac{\log[R_a H]_{\text{initial}} - \log[R_a H]_{\text{final}}}{\log[R_b H]_{\text{initial}} - \log[R_b H]_{\text{final}}}$$

This is accurate only if Y· truly represents a single species (or, if a mixture, species of identical reactivity), if hydrocarbons are consumed by no other reactions, and if the product radicals are efficiently prevented (by reaction with oxygen or by other means) from

¹ Part III, Falconer, Knox, and Trotman-Dickenson, *J.*, 1961, 4285.

reforming the parent hydrocarbons. Results obtained in the earlier studies support these assumptions.

The values of the relative rate constants obtained are listed in Table 1. In one method, the reaction proceeded without assistance from any initiator; it was a normal thermal chain reaction. This general method was used in the earlier studies of alkanes but is not as convenient as the use of initiated reactions. Accordingly, most of the results were obtained at lower temperature with initiation by the photolysis of acetone. In the present, as in the earlier, work the two sets of results were comparable within the limits of experimental error. Formaldehyde was the photochemical initiator for some runs and was also added in large amount to some of the thermal-reaction mixtures. Its presence did not alter the relative rates of disappearance of the hydrocarbons.

Several cross-checks can be made between the values of Table 1; they are all satisfactory. Hence a self-consistent table of reactivities can be drawn up. The reactivities of

TABLE 1.
Competitive oxidations involving olefins.

Mixture R _a H/R _b H	Temp.	k _a /k _b *	E _a - E _b (kcal. mole ⁻¹)	Mixture R _a H/R _b H	Temp.	k _a /k _b *	E _a - E _b (kcal. mole ⁻¹)	
Ethane- ethylene	145°	0.135 ± 0.005 (AP)	2.6	Neopentane- propene	145°	0.10 ± 0.01 (AP)	2.9	
	230	0.23 ± 0.05 (AP)			230	0.17 ± 0.01 (AP)		
Propane- ethylene	145	0.39 ± 0.01 (AP)	2.1	Propene- isobutene	330	0.29 ± 0.02 (T)	5.0	
	230	0.60 ± 0.04 (AP)			145	0.033 ± 0.003 (AP)		
Isobutane- ethylene	145	0.67 ± 0.005 (AP)	1.9	Ethylene- propene	230	0.09 ± 0.02 (AP)	0.8	
	230	0.95 ± 0.03 (AP)			145	0.27 ± 0.02 (AP)		
		0.87 ± 0.03 (FP)			230	0.32 ± 0.03 (AP)		
	320	1.42 ± 0.05 (Y)			230	0.33 ± 0.03 (FP)		
Neopentane- ethylene		1.43 (FT)	2.4	Ethylene- <i>cis</i> -but-2-ene	230	0.10 (AP)	—	
		1.49 (FT)			Propene- isobutene	100		(0.30) (AP)
		1.52 (T)				145		0.27 ± 0.02 (AP)
	145	0.29 (AP)				230		0.38 ± 0.02 (AP)
230	0.48 ± 0.04 (AP)	Propene- <i>cis</i> -but-2-ene	100	(0.31) (AP)		0.8		
	0.51 ± 0.005 (FP)		145	0.27 ± 0.01 (AP)				
	0.48 ± 0.02 (T)		230	0.31 ± 0.01 (AP)				
145	0.040 ± 0.002 (AP)		<i>cis</i> -But-2-ene- 2-methylbut- 2-ene	145	0.25 ± 0.04 (AP)		1.6	
230	0.090 ± 0.002 (AP)	230		0.35 ± 0.04 (AP)				
330	0.19 ± 0.02 (T)							
380	0.24 (T)							

* AP, Acetone present in the photoinitiated reaction; FP, formaldehyde present in the photo-initiated reaction; FT, formaldehyde present in thermal reaction; T, thermal reaction of hydrocarbons and oxygen only.

TABLE 2.
The attack of radicals on olefins.

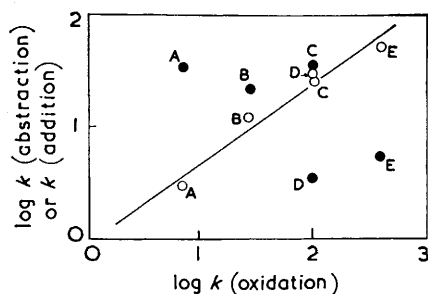
Olefin	Oxidation k/k(ethane) at 145°	E (kcal. mole ⁻¹) *	Methyl-abstraction † 10 ⁻⁶ (mole ⁻¹ c.c. sec. ⁻¹) at 182°	Methyl-addition ‡ k/k(2,2,4-trimethylpentane) at 65°
Ethylene	7	7.8	2.9	34
Propene	27	6.8	12	22
Isobutene	100	5.1	26	36
<i>cis</i> -But-2-ene	100	5.9	30	3.4
2-Methylbut-2-ene ...	400	4.3	53 §	5.6

* Activation energies based on an assumed value for ethane of 10 kcal. mole⁻¹. † Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, p. 200. ‡ Buckley and Szwarc, *Proc. Roy. Soc.*, 1957, *A*, **240**, 396; Szwarc and Binks, "Theoretical Organic Chemistry," Butterworths, London, 1959, p. 262. § Estimated from the value for 3-methylbut-1-ene and other compounds in footnote †.

the olefins relative to that of ethane at 145° are listed in Table 2. The activation energies based on an assumed value of 10 kcal. mole⁻¹ for attack on ethane are also given. Again, these can be derived from Table 1 in several ways; average values have been listed. The values in Table 1 for the higher temperatures are in good agreement with results reported for ethane-ethylene² and for propane-propene.³ The lower activation energy differences found in the present work are to be preferred because they are based on measurements over a considerably greater temperature range.

The relative rates of oxidation of the olefins are compared in Table 2 with the rates for hydrogen-abstraction by methyl radicals at 182° and the relative rates of addition of methyl radicals at 65°. The Figure shows that there is a correlation between the rates of oxidation and of hydrogen-abstraction but none between oxidation and addition. This is good evidence that olefins are primarily consumed in oxidation systems by hydrogen-abstraction reactions.

The slope of the line in the Figure is 0.72. This indicates that the attacking radical is



The logarithms of the rate constants (relative to ethane) for the oxidation of olefins at 145° compared with the rate constants for hydrogen-abstraction by methyl radicals at 182° (open points) and the rate constants for the addition of methyl radicals at 65° (filled points) (relative to the rate of hydrogen abstraction from 2,2,4-trimethylpentane); cf. Table 2.

A, Ethylene; B, propene; C, isobutene; D, *cis*-but-2-ene; E, trimethylethylene.

more selective than methyl; it is presumably also less reactive. The studies of the alkanes did not support this conclusion. The reactivities of the primary, secondary, and tertiary hydrogen atoms in alkanes were found to be in the ratio 1 : 4.5 : 13.2, but the activation energies were almost the same for attack on each class of atom. Since alkanes can presumably only react by loss of a hydrogen atom, no satisfactory explanation can be offered for this fact.

An attempt was made to compare the reactivity of the olefins in oxidations with their reactivity towards hydroxyl in aqueous solution. Hydroxyl radicals were generated⁴ by the photolysis of a 0.3M-solution of hydrogen peroxide in the presence of an equimolecular mixture of ethylene-propene and ethylene-propane. The values adopted for the Bunsen absorption coefficient were: ethylene, 0.1220;⁵ propene, 0.2205;⁵ propane, 0.0543.⁴ Hence, from seven concordant runs, $k(\text{ethylene})/k(\text{propene}) = 1.78$, and, from two runs, $k(\text{propane})/k(\text{ethylene}) = 0.28$. There is some uncertainty about those results because there are considerable discrepancies between absorption coefficients reported by different authors. These experiments do not provide positive evidence for the participation of hydroxyl radicals in oxidations.

Experimental.—The procedures closely followed those employed in the earlier work.^{1,4} For all mixtures, tests showed that one reactant was not the product of the other. The ratios of reactants were varied between 2 : 1 and 1 : 2. When formaldehyde was added the value of $\text{HCHO}/(\text{R}_a\text{H} + \text{R}_b\text{H})$ was varied from 2 to $\frac{1}{3}$, and the value of O_2/HCHO from 10 to $\frac{1}{2}$. It

² Knox and Wells, unpublished results, private communication from Dr. Knox, see also ref. 3.

³ Carabine and Knox, *J.*, 1963, 862.

⁴ Berces and Trotman-Dickenson, *J.*, 1961, 4281.

⁵ Seidell, "Solubilities of Organic Compounds," Van Nostrand, New York, 1941, pp. 94 and 174.

was impossible to use the Janak detector with the involatile 2-methylbut-2-ene, and so a hot-wire detector was used for its mixtures.

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674. *The Infrared Spectra (260—500 cm.⁻¹) of Some Addition Compounds of Titanium, Zirconium, and Molybdenum Tetrahalides.*

By I. R. BEATTIE and M. WEBSTER.

THE potential importance of infrared spectroscopy below 500 cm.⁻¹ (coupled where possible with Raman studies) for studying the stereochemistry of addition compounds of halides of the non-transition elements, has been stressed.¹ Although, in the case of related compounds of the transition elements, other techniques (notably ultraviolet spectroscopy) are frequently available, the additional information supplied by vibrational spectroscopy could be helpful in making stereochemical assignments. The Table summarises our results on certain compounds of titanium, zirconium, and molybdenum tetrahalides. Compared with previous spectra on adducts of non-transition element tetrahalides,¹ the spectra given in the Table are disappointing, as they are not capable of unambiguous interpretation in terms of the stereochemistry of the molecules concerned. The titanium-chlorine stretching modes generally occur in the region 371—395 cm.⁻¹ (as a strong band), followed by a weak band at 278—327 cm.⁻¹. In the case of the other tetrahalides the resolution into two regions is less well defined, but strong bands can be assigned as follows: 284—348 cm.⁻¹ to molybdenum-chlorine stretching modes, 299—354 cm.⁻¹ to zirconium-chlorine stretching modes, 290—328 cm.⁻¹ to titanium-bromine stretching modes, and 260—270 cm.⁻¹ to zirconium-bromine stretching modes.

Solid niobium pentachloride is dimeric,² so that in the caesium bromide region the spectrum of this compound as a solid might be expected to resemble that of a *cis*-adduct. Its spectrum (Table) is characterised by a strong band at 398 followed by a weaker band at 354 cm.⁻¹, in contrast to the group of three bands of approximately equal intensity found for *cis*-[L₂MX₄] (M = Si, Ge, or Sn; X = halogen). On the basis of the spectra of assumed chelate adducts of titanium tetrachloride, it is possible to assign a *cis*-stereochemistry to most of the adducts of titanium tetrachloride. This assignment is only a tentative one and will require Raman data for confirmation.

Experimental.—Spectra were obtained on a Perkin-Elmer 221 spectrophotometer equipped with a caesium bromide prism. Infrared samples of the adducts were prepared in a nitrogen-filled dry-box.

The authors thank Dr. G. W. A. Fowles for the gift of the majority of the compounds, and the D.S.I.R. for financial assistance.

¹ See, e.g., Beattie, *Quart. Rev.*, 1963, **17**, 382; Beattie, Gilson, Webster, and McQuillan, *J.*, 1964, 238.

² Zalkin and Sands, *Acta Cryst.*, 1958, **11**, 615.

The infrared spectra of some addition compounds of titanium, zirconium, and molybdenum tetrahalides; spectra of certain related compounds are also given (range 260—500 cm^{-1}).

Acceptor	Donor	Frequencies (cm^{-1}) *				Previous ref.
TiCl ₄	2,2'-Bipyridyl	447w	416sh	371s, br	306w	7
TiBr ₄	"	444w	414w	362m	328s	
ZrCl ₄	"	290vs, br				
ZrBr ₄	"	434w	351s, br	315w		
		414w	357w	345w		
		~260s, br complex				
MoCl ₄	"	418w	346s	311m		3
TiCl ₄	2(Pyridine)	436m	371s	278m		
ZrCl ₄	"	424m	334s, br			
TiCl ₄	2(Pyrazine)	458m	395s	344w	315w	
TiBr ₄	"	454m	407w, br	315s, br	299sh	4
	Pyrazine	414m				
TiCl ₄	2(2,6-Dimethylpyrazine)	483m	440w	386s	310w	
TiBr ₄	"	485m	359w	303vs, br complex		
	2,6-Dimethylpyrazine †	442s	282w			
TiCl ₄	2(Acetonitrile)	386s, br	318w			
ZrBr ₄	"	411w	402w	~270s, br complex		
MoCl ₄	"	428w	416w	337s	312sh	
TiCl ₄	2(Propionitrile)	379s	325w			
TiCl ₄	2(Propionitrile) ‡	~390	322w			
	Propionitrile	376				
TiCl ₄	Phthalonitrile	485w	465w	433w	395s	
		327w				
	Phthalonitrile	473m	413w	381w		
MoCl ₄	2-(n-Propyl cyanide)	415w	386m	348s, br complex		
TiCl ₄	2(Triphenylphosphine)	496m	487sh	444w	434w	
		381s	325m, br			
MoCl ₄	"	502w	487w	343s	335s	
	Triphenylphosphine)	511m	496s	490s	431w	6, 9, 10
		419w	398vw			
TiCl ₄	Tetraphenyl-PP'-ethylenediphosphine	492w	415w	390m	376m	
		361s				
	Tetraphenyl-PP'-ethylenediphosphine	475s	441m	397w	337m	
TiCl ₄	Triphenylarsine	466s	452sh	384s	323m	
TiBr ₄	"	473w	465m	362sh	357s	
		320w	287s			
	Triphenylarsine	471s	311s			9
MoCl ₄	2(Tetrahydrofuran)	343s	284m			
	Tetrahydrofuran §	No intense absorptions in this region				
TiCl ₄	1,4-Dioxan	392s	341w	328sh	316w	
	1,4-Dioxan §	274				
TiCl ₄	2(1,4-Thioxan)	435w	387s	364sh	311w	
TiBr ₄	"	392w	368w	358w	299vs, br	
	1,4-Thioxan §	389s, br	340w			
TiCl ₄	2(Dimethyl sulphide)	382br				
TiBr ₄	"	373w	~300vs, br			
ZrCl ₄	"	372w	~299s, br			
	Dimethyl sulphide §	281				
TiCl ₄	SS-Diphenylethane-1,2-dithiol	478w	454w	411m	379s	
		315w				
TiBr ₄	"	481w	337m	326s	312s	
	5,5-Diphenylethane-1,2-dithiol	305s				
		473s	338m			5
(NbCl ₅) ₂		398s	354w			

* All spectra of Nujol mulls, unless otherwise stated. † Spectrum of thin film of solid.
‡ Spectrum of solution in propionitrile. § Spectrum of liquid.

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³ Rao, *Z. anorg. Chem.*, 1960, **304**, 176.

⁴ Lord, Marston, and Miller, *Spectrochim. Acta*, 1957, **9**, 113.

⁵ Carlson, *Spectrochim. Acta*, 1963, **19**, 1291.

⁶ Harrab, Ryan, and Tamborski, *Spectrochim. Acta*, 1962, **18**, 21.

⁷ Clark, *J.*, 1963, 1377.

⁸ Siebert, *Z. anorg. Chem.*, 1952, **271**, 65.

⁹ Jensen and Nielsen, *Acta Chem. Scand.*, 1963, **17**, 1875.

¹⁰ Steger and Stopperka, *Chem. Ber.*, 1961, **94**, 3023.

675. Competitive Alkali-metal Flame Reactions. The Reactions of Potassium Atoms with Ethyl, Isopropyl, and *t*-Butyl Chlorides.

By E. U. EMOVON and E. A. LISSI.

A competitive technique for studying alkali-metal flame reactions has recently been developed.¹ Here, we report an extension of the results to include the reactions of potassium atoms with mixtures of ethyl and isopropyl chlorides and of ethyl and *t*-butyl chlorides. Relative rate constants can be obtained for such pairs of reactions by analysing for the total concentration of KCl produced and for the concentration of K³⁶Cl produced from the radioactively labelled chloride in the mixture.

With the ethyl chloride-isopropyl chloride mixtures, the reactions concerned are:

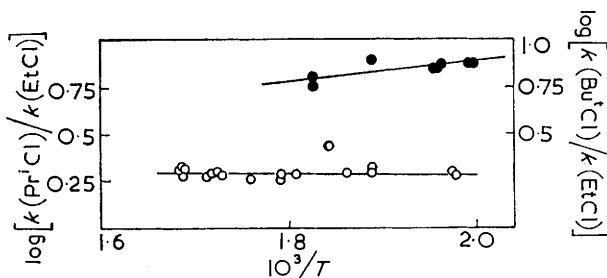


This system was studied over the temperature range 238–325° with chloride ratios, EtCl:PrⁱCl, of 0.55 or 0.76. Relative rate constants (k_2/k_1), calculated as previously described,¹ are shown in the Arrhenius plot in the Figure. The following relative Arrhenius parameters were obtained by a least-mean-squares calculation: $E_2 - E_1 = 125 \pm 136$ cal. mole⁻¹ and $\log(A_2/A_1) = 0.34 \pm 0.05$.

For the other chloride pair, the reactions



were studied between 229 and 275° with chloride ratios, EtCl/Bu^tCl, of 0.28 or 1.06. Relative rate constants (k_3/k_1) were obtained as before, and are also shown in the Figure. The results, $E_1 - E_2 = 2270 \pm 550$ cal. mole⁻¹ and $\log(A_3/A_1) = -0.11 \pm 0.23$, were calculated by a least-mean-squares treatment.



Arrhenius plots for the reactions of potassium atoms.

- $\log [k(\text{isopropyl chloride})/k(\text{ethyl chloride})]$.
- $\log [k(\text{t-butyl chloride})/k(\text{ethyl chloride})]$.

These results extend our information on the reactions of potassium atoms with the series of alkyl chlorides, which is summarised in the Table. The relative rate constants show the same trend as those for the analogous reactions with sodium,² which are in the ratio 1:1.4:2.9:6.5 at 255°. The ΔE values arise partly from changes in the bond dissociation energies and partly from changes in the force constants of the C-Cl bonds in the alkyl

¹ Kerr, Lissi, and Trotman-Dickenson, *J.*, 1964, 1673.

² Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, p. 218.

chloride series. Unfortunately, the limitations of the semi-empirical method of Eyring and Polanyi³ and the lack of accurate data preclude quantitative treatment of these effects.

Reactions of potassium atoms with alkyl halides.

Reactant	<i>E</i> (kcal. mole ⁻¹)	Relative rate constants (at 285°)	Ref.
MeCl.....	6.2 *	1	1
EtCl.....	5.8 *	1.2	1
Pr ⁱ Cl	5.9 *	2.3	This work
Bu ^t Cl	3.5	7.3	This work

* Based on the assumption that the reaction $K + MeCOCl = KCl + MeCO$ has zero activation energy (see ref. 1).

Experimental.—The apparatus, and experimental and analytical procedures were identical with those described by Kerr, Lissi, and Trotman-Dickenson.¹ B.D.H. isopropyl and t-butyl chlorides were distilled, middle-fractions being used in the experiments.

We are grateful to Professor A. F. Trotman-Dickenson and Dr. J. A. Kerr for help, and to the Royal Society for a grant to (E. U. E.).

THE EDWARD DAVIES CHEMICAL LABORATORY, ABERYSTWYTH. [Received, December 23rd, 1963.]

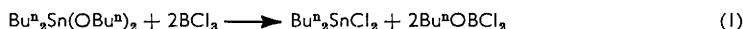
³ Eyring and Polanyi, *Z. phys. Chem.*, 1931, B12, 279.

676. Interaction of Dialkoxydialkyltins and Boron Trichloride.

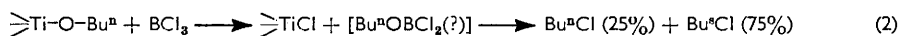
By W. GERRARD and R. G. REES.

RESULTS of the interaction of dialkoxydialkyltins and boron trichloride are relevant to studies in the modes of fission of the R-O-M bonds by reaction with the M'-X bond in inorganic covalent halides (where M = one of P, S, Si, Ti, and B, M' is another of these, and R = alkyl or aryl).¹ In certain systems M-O-M' linkages are formed, in others there is a mutual exchange of halogen and alkoxy(or aryloxy)-group. The mode of fission appears to be correlated with the electronegativity of M, and the electron releasing propensity of the group R.

Di-n-butoxydi-n-butyltin readily reacted according to scheme (1), the mixture of n-butyl chloride and the rearranged isomer s-butyl chloride most likely resulting from thermal decomposition of some dichloroborinate during distillation.²



In the titanium system,³ the $\geq\text{Ti-O-Bu}^n$ group was cleaved to give $\geq\text{Ti-Cl}$, and presumably decomposition products of the dichloroborinate, which could not itself be isolated [reaction (2)]. With the s-butoxy group, both the titanium³ and the tin systems afforded the M-Cl bond and s-butyl chloride, the dichloroborinate not being isolable.



Dimethoxydi-n-octyltin reacted according to scheme (1).

¹ Charalambous, Frazer, and Gerrard, *J.*, 1963, 826, and Papers cited therein.

² Gerrard, Hudson, and Murphy, *J.*, 1962, 1099; 1964, 2314.

³ Cooper and Gerrard, *Chem. and Ind.*, 1961, 320.

Experimental.—Boron trichloride (7.9 g., 2 mol.) was distilled into di-*n*-butoxydi-*n*-butyltin⁴ (12.4 g., 2 mol.) at -80° , and on warming to room temperature an exothermic reaction occurred. On distillation, *n*-butyl dichloroborinate (3.56 g., 35.2%), b. p. $53-55^\circ/18$ mm., n_D^{20} 1.4120 (Found: B, 7.1; Cl, 46.0. Calc. for $C_4H_9BCl_2O$: B, 7.0; Cl, 45.8%), crude di-*n*-butyltin dichloride (8.82 g., 89%), b. p. $96-99^\circ/0.1$ mm., cold trap (-80°) condensates (A and B), and a residue (1.74 g.) (Found: B, 15.2; Cl, 11.2%) were isolated. Condensate (A) (1.13 g.) comprised *n*-butyl chloride (35.0%), *s*-butyl chloride (14.4%), *n*-butyl dichloroborinate (43.5%), and two unidentified compounds [gas chromatography with an argon detector (1250 v) and a 20% silicone (M.S. 710) on 85–100 mesh Celite column at 50° ; 37 ml./min argon flow]. Condensate (B) (2.94 g.), collected during continuation of distillation, comprised *n*-butyl chloride (68.0%), *s*-butyl chloride (10.7%), and *n*-butyl dichloroborinate (21.3%). The di-*n*-butyltin dichloride, m. p. $42-43^\circ$ (Found: Cl, 22.8; Sn, 38.7. Calc. for $C_8H_{18}Cl_2Sn$: Cl, 23.3; Sn, 39.1%), was obtained by recrystallisation from petroleum (b. p. $30-40^\circ$).

Similarly, *di-s-butoxydi-n-butyltin* (13.5 g.) (Found: C, 50.6; H, 9.5; Sn, 30.6. $C_{16}H_{36}O_2Sn$ requires C, 50.7; H, 9.6; Sn, 31.3%), prepared by the general method,⁴ gave a gel-like solid at -80° . Volatile matter (8.24 g.) was removed at $20^\circ/15$ mm. and shown (g.l.c. at 40° ; 10% dinonyl phthalate–Celite; 60 ml./min. argon flow) to be *s*-butyl chloride mixed with a little boron trichloride. The white solid residue (12.57 g.) afforded the di-*n*-butyltin dichloride (8.64 g., 80%), m. p. 42° , and impure boric oxide (1.63 g.).

Dimethoxydi-*n*-octyltin⁴ (14.0 g., 2 mol.) afforded methyl dichloroborinate (7.07 g.) (Found: Cl, 63.6. Calc. for CH_3BCl_2O : Cl, 62.9%), removed at $20^\circ/15$ mm., and di-*n*-octyltin dichloride (10.0 g., 70%), m. p. 46° [from petroleum (b. p. $100-120^\circ$)] (Found: Cl, 16.7; Sn, 27.9. Calc. for $C_{16}H_{34}Cl_2Sn$: Cl, 17.0; Sn, 28.5%).

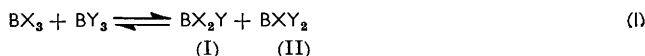
NORTHERN POLYTECHNIC, HOLLOWAY ROAD, LONDON N.7. [Received, December 21st, 1963.]

⁴ Gerrard, Mooney, and Rees, *J.*, 1964, 740.

677. Boron-11 Nuclear Magnetic Resonance Spectra of Mixtures of Boron Trihalides: Evidence for the Formation of the New Mixed Halide BBrClI.

By P. N. GATES, E. F. MOONEY, and D. C. SMITH.

THE formation of mixed boron halides has been studied by infrared and Raman spectroscopy.¹ The use of nuclear magnetic resonance (n.m.r.) spectroscopy has been previously confined² to mixed boron halides containing fluorine. We now report our investigations of the boron-11 resonance (at 12.83 Mc./sec.) of mixtures of boron trihalides. The study of binary systems (I) has permitted the unambiguous assignment of the boron-11 chemical



X = Cl, Y = Br; X = Cl, Y = I or X = Br, Y = I.

shifts of the mixed halides (I and II). In the ternary mixture, of boron trichloride, bromide, and iodide, ten resonance lines are observed (Table) and one, at 14.5 p.p.m. to high field of boron trichloride, is not present in any of the binary mixtures and this line is assigned to the mixed halide BBrClI.

¹ Lindeman and Wilson, *J. Chem. Phys.*, 1956, **24**, 242.

² Coyle and Stone, *J. Chem. Phys.*, 1960, **32**, 1892.

Boron-11 chemical shifts * of mixed boron halides

BCl_2Br	1.2	BCl_2I	10.3	BClI_2	28.3
BClBr_2	3.9	BBrClI	14.5	BBrI_2	34.8
BBr_3	7.4	BBr_2I	19.6	BI_3	53.5

* P.p.m. to high field of boron trichloride as internal standard, or if no trichloride is present the chemical shift of the tribromide was taken as the standard and assumed to be at 7.4 p.p.m. to high field of the trichloride.

The large boron-11 chemical shifts of the mixed halides makes the n.m.r. method of greater use in determining the equilibrium composition of mixtures of boron trihalides and further results will be reported.

We gratefully acknowledge a grant from the D.S.I.R. to purchase the Perkin-Elmer n.m.r. spectrometer, and one of us (D. C. S.) the award of a scholarship from Messrs. F. W. Berk and Co. Ltd. We thank Dr. W. Gerrard for his continued encouragement.

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