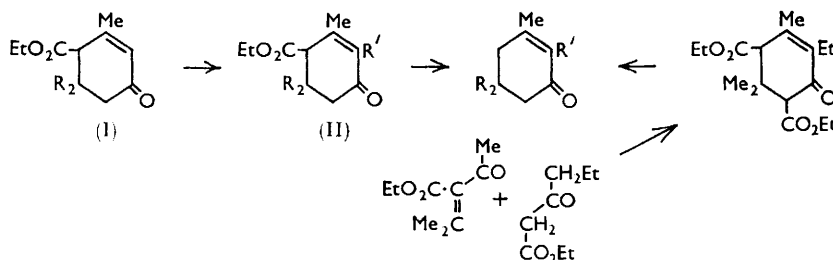


288. Alkylation of Ethyl 2,6,6-Trimethyl-4-oxocyclohex-2-ene-carboxylate.

By M. A. KAZI, ISHRAT HUSSAIN KHAN, and MOHAMMED YOUSUF KHAN.

ALKYLATION of ethyl 2-methyl-4-oxocyclohex-2-enecarboxylate (Hagemann's ester) (I; R = H) was shown by Edgar, Harper, and Kazi¹ to occur exclusively at position 3. We find that a *gem*-dimethyl group at position 6 does not change this result. The orientation of the products has been proved by an independent synthesis in one case. Michael condensation of ethyl α -isopropylideneacetoacetate² and ethyl 3-oxohexanoate³ in presence of potassium *t*-butoxide led to a ketone identical with that prepared from the ester (I; R = Me) by use of ethyl bromide and sodium ethoxide.



Alkylation of the ester (I; R = Me) was accomplished by preparing the sodio-derivative in sodium ethoxide solution and treating this with the alkyl halide. The esters (II; R = Me, R' = alkyl) produced were characterised as 2,4-dinitrophenylhydrazones. The corresponding 2-alkyl-3,5,5-trimethylcyclohex-2-enones were obtained by refluxing these esters with ethanolic potassium hydroxide and subsequent acidification into keto-acids which readily afforded the ketones.

Isopropylideneacetoacetate has been prepared in a better yield by using conditions similar to those for the preparation of isopropylidenemalonate.⁴

Experimental.—Ethyl 2,6,6-trimethyl-4-oxocyclohex-2-enecarboxylate was prepared by Jeger and Buchi's procedure⁵ in 72% yield. It had b. p. 135—138°/5 mm., n_D^{20} 1.4820—1.4824, λ_{\max} 243 m μ (ϵ 9200).

Ethyl 3-alkyl-2,6,6-trimethyl-4-oxocyclohex-2-enecarboxylates. A typical preparation was as follows. The preceding ester (I; R = Me) (10.5 g.) was added during 30 min. to a stirred solution of sodium (1.15 g.) in absolute ethanol (50 ml.) at room temperature. After a further 45 min. (to complete formation of the sodio-derivative) methyl iodide (7.1 g., 0.05 mol.) was added during 45 min. and the mixture was stirred for another 2 hr. and refluxed for 3 hr. Most of the solvent was removed in a vacuum, water was added, and the oil extracted with ether. The dried extract (MgSO₄) was evaporated and distilled, to give ethyl 2,3,6,6-tetramethyl-4-oxocyclohex-2-enecarboxylate (8.4 g., 75%) b. p. 105—107°/0.6 mm., n_D^{20} 1.4816, λ_{\max} 250 m μ (ϵ 8000) (Found: C, 69.6; H, 8.7. C₁₃H₂₀O₃ requires C, 69.6; H, 8.9%). The 2,4-dinitrophenylhydrazone (from ethanol) had m. p. 152—153° (Found: N, 13.5. C₁₉H₂₄N₄O₆ requires N, 13.8%).

The following were prepared similarly:

Ethyl 3-ethyl-2,6,6-trimethyl-4-oxocyclohex-2-enecarboxylate (from ethyl bromide) (74%), b. p. 119—121°/0.2 mm., n_D^{20} 1.4822, λ_{\max} 250 m μ (ϵ 8800) (Found: C, 70.5; H, 9.3. C₁₄H₂₂O₃ requires C, 70.6; H, 9.3%) [2,4-dinitrophenylhydrazone (from ethanol), m. p. 121—122° (Found: N, 13.3. C₂₀H₂₆N₄O₆ requires N, 13.4%)].

Ethyl 2,6,6-trimethyl-4-oxo-3-propylcyclohex-2-enecarboxylate (from propyl iodide) (60%),

¹ Edgar, Harper, and Kazi, *J.*, 1957, 1083.

² Merling and Welde, *Ber.*, 1909, 71, 2090.

³ Wahl and Doll, *Bull. Soc. chim. France*, 1913, 13, 265.

⁴ Cope and Hancock, *J. Amer. Chem. Soc.*, 1938, 60, 2644.

⁵ Jeger and Buchi, *Helv. Chim. Acta*, 1948, 31, 134.

b. p. 117—120°/0.9 mm., n_D^{20} 1.4846, λ_{\max} . 251 m μ (ϵ 10,000) (Found: C, 72.0; H, 9.2. $C_{15}H_{24}O_3$ requires C, 71.5; H, 9.6%). [2,4-Dinitrophenylhydrazone (from ethanol), m. p. 125—126° (Found: N, 13.0. $C_{21}H_{23}N_4O_6$ requires N, 12.9%)]. Ethyl 3-allyl-2,6,6-trimethyl-4-oxocyclohex-2-enecarboxylate (from allyl chloride) (65%), b. p. 128—130°/2.5 mm., n_D^{20} 1.4896, λ_{\max} . 252 m μ (ϵ 8700) (Found: C, 72.0; H, 8.7. $C_{15}H_{22}O_3$ requires C, 71.9; H, 8.8%) [2,4-dinitrophenylhydrazone (from ethanol), m. p. 113—114° (Found: N, 10.4. $C_{21}H_{23}N_4O_6$ requires N, 10.3%)].

Ethyl 3-acetyl-2,6,6-trimethyl-4-oxocyclohex-2-enecarboxylate (from acetyl chloride) (48%), b. p. 104—108°/1 mm., n_D^{20} 1.4816, λ_{\max} . 259 (ϵ 9000) (Found: C, 66.4; H, 8.0. $C_{14}H_{20}O_4$ requires C, 66.6; H, 7.9%) [2,4-dinitrophenylhydrazone (from ethanol), m. p. 117—118° (Found: N, 12.8. $C_{20}H_{24}N_4O_7$ requires N, 12.9%)].

2-Alkyl-3,5,5-trimethylcyclohex-2-enones. A typical preparation was as follows: Ethyl 2,3,6,6-tetramethyl-4-oxocyclohex-2-enecarboxylate (5.6 g.) was heated under reflux with 15% ethanolic potassium hydroxide (12.5 ml.) during 8 hr. Next day most of the ethanol was distilled off and the residue diluted with ice-water (15 ml.). After acidification with dilute hydrochloric acid the mixture was heated at 50° during 1 hr. (to bring about decarboxylation), then cooled, and the product was isolated with ether. Distillation gave 2,3,5,5-tetramethylcyclohex-2-enone (2.3 g., 65%), b. p. 60—62°/0.5 mm., n_D^{20} 1.4836, λ_{\max} . 251 m μ (ϵ 7000) (Found: C, 78.3; H, 10.7. $C_{10}H_{16}O$ requires C, 78.8; H, 10.6%) [2,4-dinitrophenylhydrazone (from ethanol), m. p. 169—170° (Found: N, 16.4. $C_{16}H_{20}N_4O_4$ requires N, 16.8%)].

2-Ethyl-3,5,5-trimethylcyclohex-2-enone (60%), b. p. 62—65°/1.0 mm., n_D^{20} 1.4791, λ_{\max} . 246 m μ (ϵ 9400) (Found: C, 79.0; H, 10.5. $C_{11}H_{18}O$ requires C, 79.0; H, 10.9%) [2,4-dinitrophenylhydrazone (from ethanol), m. p. 131—132° (Found: N, 16.3. $C_{17}H_{22}N_4O_4$ requires N, 16.1%), was similarly prepared.

A mixture of α -isopropylideneacetoacetate (8.5 g.) and ethyl 2-oxohexanoate (7.9 g.) was added to a stirred solution of potassium t-butoxide [from potassium (3 g.) and n-butyl alcohol (50 ml.)] during 1 hr. in an atmosphere of nitrogen and the whole was refluxed for 4 hr. The solvent was distilled off and the residue diluted with water. After acidification with dilute hydrochloric acid the keto-ester was extracted with ether, and the ethereal layer washed, dried (MgSO₄), and evaporated. Distillation gave the last-mentioned ester (5.0 g.), n_D^{20} 1.4780 [2,4-dinitrophenylhydrazone (from ethanol), m. p. and mixed m. p. 131—132°].

Hydrolysis of the keto-esters also gave the following ketones:

3,5,5-Trimethyl-2-propylcyclohex-2-enone (75%), b. p. 76—80°/2 mm., n_D^{20} 1.4736, λ_{\max} . 244 m μ (ϵ 9400) (Found: C, 79.5; H, 10.8. $C_{12}H_{20}O$ requires C, 79.9; H, 11.1%) [2,4-dinitrophenylhydrazone (from ethanol), m. p. 137—138° (Found: N, 15.4. $C_{18}H_{24}N_4O_4$ requires N, 15.5%)].

2-Allyl-3,5,5-trimethylcyclohex-2-enone (68.5%), b. p. 69—72°/0.6 mm., n_D^{20} 1.4856, λ_{\max} . 249 m μ (ϵ 9800) (Found: C, 80.5; H, 10.6. $C_{12}H_{18}O$ requires C, 80.8; H, 10.2%) [2,4-dinitrophenylhydrazone (from ethanol), m. p. 100° (Found: N, 15.4. $C_{18}H_{22}N_4O_4$ requires N, 15.6%)].

2-Acetyl-3,5,5-trimethylcyclohex-2-enone (68%), b. p. 64—66°/0.1 mm., n_D^{20} 1.4786, λ_{\max} . 248 m μ (ϵ 9100) (Found: C, 73.2; H, 8.8. $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.9%) [2,4-dinitrophenylhydrazone (from ethanol), m. p. 129—130° (Found: N, 15.6. $C_{17}H_{20}N_4O_5$ requires N, 15.5%)].

Ethyl α -isopropylideneacetoacetate (cf. ref. 4). Ethyl acetoacetate (130 g., 1 mol.), acetone (87 g., 1.5 mol.), acetic anhydride (128 ml.), and fused zinc chloride (19 g.) were heated under reflux for 72 hr., then cooled. Benzene (100 ml.) was added and the resulting solution washed with water (6 \times 25 ml.). The combined water washings were extracted with benzene which was then added to the main benzene solution. After drying (MgSO₄) and evaporation, the product was distilled to give fractions (i), b. p. 75—95°/4 mm., n_D^{20} 1.4520—1.4560, and (ii) b. p. 115—135°/1 mm., n_D^{20} 1.4980—1.5050. Fraction (i), on redistillation, gave ethyl isopropylideneacetoacetate (38%), b. p. 82—87°/4 mm., n_D^{20} 1.4545. The semicarbazone (from ethanol) had m. p. 245° alone or mixed with an authentic sample. Fraction (ii), on redistillation, gave a keto-ester, b. p. 130—135°/1 mm., n_D^{20} 1.5085, λ_{\max} . 226 and 247 m μ [semicarbazone (from ethanol), m. p. 230—232°].

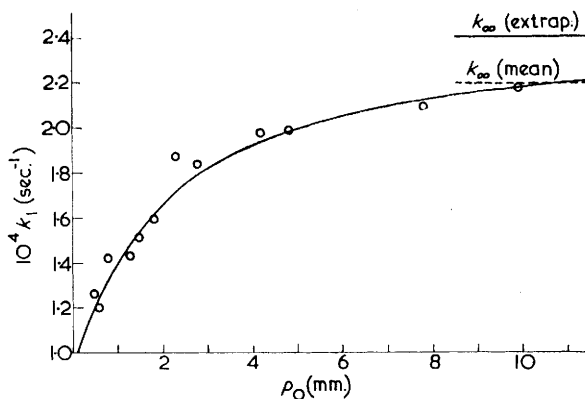
289. The Low-pressure Pyrolysis of Isopropyl Bromide.

By M. N. KALE and ALLAN MACCOLL.

THE thermal decomposition of isopropyl bromide into propene and hydrogen bromide has been studied by a number of workers,¹⁻³ all of whom agree that the reaction follows a unimolecular course. The Arrhenius parameters, all of which are in essential agreement, are ($\log A$): 13.60;¹ 13.62;² 12.74.³ The values of E (kcal. mole⁻¹) are 47.7, 47.8, and 47.0, respectively. The Lindemann theory of unimolecular reactions requires that, as the pressure is decreased, the rate of reaction should depend on a power between one and two of the pressure of reactant, *i.e.*, that the first-order rate coefficients should fall with decreasing initial pressure. The present work was undertaken to verify this.

Isopropyl bromide was purified as described previously² and had b. p. 59.4°/767 mm., n_D^{25} 1.4226 (lit.,⁴ 59.35°/760 mm., n_D^{15} 1.4228). The reaction was investigated in an all-glass apparatus, as previously described,⁵ seasoned with the products of decomposition of allyl bromide. The diaphragm gauge was replaced by a spoon gauge which enabled

Variation of rate constant with pressure in the pyrolysis of isopropyl bromide.



readings to be taken down to 0.05 mm., and a silicone oil manometer was substituted for the mercury manometer.

The reaction was studied at 331.7°, over the pressure range 0.5–48 mm. The variation of rate constant with pressure is shown in the Figure. At high pressures the mean velocity constant, 2.16×10^{-4} sec.⁻¹ compares well with that reported earlier,² namely 2.14×10^{-4} sec.⁻¹. Below about 3 mm. the first-order coefficient begins to fall, reaching about 50% of its high-pressure value at 0.58 mm. The experimental points have been compared with (a) the Lindemann–Hinshelwood theory,⁶ in which no allowance is made for a variation of specific rate constant with the energy in excess of the minimum required for reaction, and (b) the classical Rice–Ramsperger theory.⁷ For the latter, the rate constant is given by:

$$\frac{k}{k_\infty} = \frac{1}{kT\Gamma(n+1)/2} \int \frac{\{\exp[-(E-E_0)/kT]\}[(E-E_0)/kT]^{(n-1)/2}}{1 + (\beta/p)[(E-E_0)^{(n-1)/2}/E^{(n-2)/2}]} d(E-E_0)$$

where $\beta = k_\infty[\Gamma(n/2)/\Gamma(n+1)/2](\sqrt{m/\pi}/4\sigma^2) \exp(E_0/kT)$.

¹ Blades and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 6219.

² Maccoll and Thomas, *J.*, 1955, 979.

³ Semenov, Sergeev, and Kaprilova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **105**, 301.

⁴ Timmermans and Martin, *J. Chim. phys.*, 1929, **25**, 428.

⁵ Maccoll, *J.*, 1955, 965.

⁶ Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, Oxford, 1940.

⁷ Rice and Ramsperger, *J. Amer. Chem. Soc.*, 1927, **49**, 1617.

The results are shown in Table 1, with $\sigma = 5 \text{ \AA}$, k_∞ (obtained from a plot of k^{-1} against p^{-1}) = $2.35 \times 10^{-4} \text{ sec.}^{-1}$, and with $s = 15$ on the Lindemann-Hinshelwood theory and $n = 25$ and 26 on the Rice-Ramsperger theory. It will be seen from Table 1 that rate constants calculated on the basis of the Rice-Ramsperger theory give a better fit to the experimental points.

The experimental data for isopropyl bromide have been examined in the light of the consistency theories of Johnston and White⁸ relating to the general Lindemann theory of unimolecular reactions. In particular the dimensionless quantity L was substantially greater than unity as demanded by the theory. It is interesting to note that isopropyl bromide fits very well into Table 2, due to Johnston and White, showing a strong correlation between molecular complexity and average rate constant, $\langle C \rangle_{AV}^T$.

TABLE 1.

Comparison of observed and calculated rate constants.

p_0 (mm.)	10	8	5	4	2	1.5	1	0.5
Lindemann-Hinshelwood ($s = 15$)	—	2.19	—	2.05	1.82	1.70	1.49	1.09
Rice-Ramsperger ($n = 25$)	1.99	—	1.86	—	1.64	—	1.43	1.24
Rice-Ramsperger ($n = 26$)	2.11	—	1.95	—	1.71	—	1.53	1.29
Observed	2.09	1.47	1.97	1.91	1.62	1.50	1.35	1.17

TABLE 2.

Molecular complexity and average rate constants.

Molecule	Temp. ($^{\circ}\text{K}$)	E_a/RT	$10^8 \langle C \rangle_{AV}^T$ (sec. $^{-1}$)	No. atoms in mol.
Cyclobutane	722	43	0.03 *	12
Isopropyl bromide	605	40	0.16 *	11
Cyclopropane	743	44	0.48	9
	773	42	0.60 *	
Nitrogen pentoxide	300	37	14	7
Nitrous oxide	888	35	200	3

* Calculated by the approximate relationship $\langle C \rangle_{AV}^T = \nu_1^\infty \text{ c.c. mole}^{-1} \text{ sec.}^{-1}$.

It is seen that as the number of atoms decreases, the average rate constant increases rapidly.

The critical pressure (that below which the first-order rate coefficient begins to fall below its high pressure value), namely about 4 mm., is well in line with those observed by Howlett⁹ for the unimolecular decomposition of some alkyl chlorides. The critical pressures, together with the number of internal degrees of freedom required to fit the

TABLE 3.

The critical pressures.

	$\text{Cl}_2\text{HC}\cdot\text{CH}_3$	Bu^tCl	Pr^iCl	Pr^nBr	Bu^nCl	Pr^oCl
No. degrees of freedom	13	20	24 *	25	28	29
Critical pressure (mm.)	17	6	4	4-5	3	1.2

* Calculated for the Lindemann-Hinshelwood theory.

data by the Rice-Ramsperger theory, are shown in Table 3. These results are in accord with Slater's predictions¹⁰ that the critical pressure tends to decrease as the number of internal degrees of freedom increases.

⁸ Johnston and White, *J. Chem. Phys.*, 1954, **22**, 1969.

⁹ Howlett, *J.*, 1952, 3695.

¹⁰ Slater, *Phil. Trans.*, 1953, **246**, 57.

The results presented here may be taken as further evidence that the isopropyl bromide decomposes by a unimolecular mechanism.

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290. *The Pressure-dependence of the Dissociation Constant of the Hydrogen Sulphate Ion.*

By R. A. HORNE, R. A. COURANT, and G. R. FRYINGER.

THE extent of ionization of weak electrolytes increases with increasing pressure; the ionization constant of acetic acid, for example, at 25° and 3000 atmospheres is more than three times as great as that at one atmosphere.¹ The first ionization of sulphuric acid is presumably complete, but the second ionization, at one atmosphere and an ionic strength of unity, is weak:²



The conductivity of the proton is more than four times that of chloride, sulphate, or other common ions. Therefore, as a first approximation, we can attribute the conductivity of aqueous solutions of acids to the contribution of the proton alone. The Table

Effect of pressure on the conductance of aqueous solutions of hydrochloric and of sulphuric acid.

Pressure (lb./in. ²)	Hydrochloric acid		Sulphuric acid	
	Sp. cond. $K_{0.10M-HCl}$ (ohm ⁻¹ cm. ⁻¹)	Molar cond. Λ_{HCl} (ohm ⁻¹ cm. ² mole ⁻¹)	Sp. cond. $K_{1.55M-H_2SO_4}$ (ohm ⁻¹ cm. ⁻¹)	Molar cond. $\Lambda_{H_2SO_4}$ (ohm ⁻¹ cm. ² mole ⁻¹)
15	0.0380	380	0.588	379
10,000	0.0412	412	0.642	414
20,000	0.0432	432	0.680	439
30,000	0.0448	448	0.718	463
40,000	0.0460	460	0.750	484
50,000	0.0473	473	0.775	499

summarizes values of the specific and the molal conductance of 0.10M-hydrochloric acid and 1.55M-sulphuric acid solutions over the pressure range 15—50,000 lb./in.² The experimental methods have been described elsewhere.³ Note that, even though the two acids being compared differ considerably in their concentrations, the molal conductances are nearly the same, thus substantiating the approximation made above that the proton contribution represents nearly all the total conductance.

At 1 atmosphere, the value of [H⁺] in the sulphuric acid solution is 1.64 molal/l; at any pressure this solution can be considered to be equivalent to a hydrochloric acid solution of concentration 1.64($\Lambda_{H_2SO_4}/\Lambda_{HCl}$) moles/l., and the value of K corresponding to this concentration can be calculated from the expression

$$K_P = \frac{[1.64(\Lambda_{H_2SO_4}/\Lambda_{HCl})][1.64(\Lambda_{H_2SO_4}/\Lambda_{HCl}) - 1.55]}{[3.10 - 1.64(\Lambda_{H_2SO_4}/\Lambda_{HCl})]} \quad (2)$$

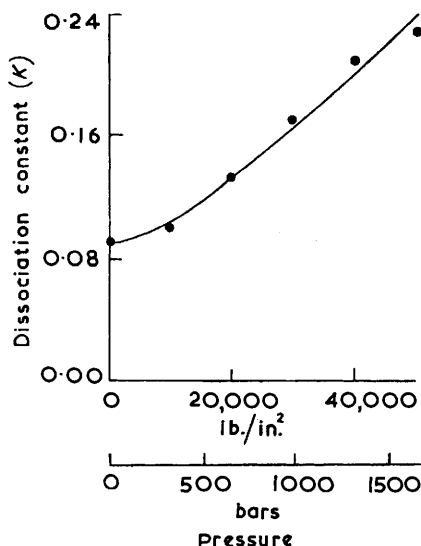
Values of K calculated from equation (2) are shown in the Figure. The hydrogen sulphate ion is two to three times more dissociated at 50,000 lb./in.² than at one atmosphere.

¹ Hamann, "Physico-Chemical Effects of Pressure," Butterworths, London, 1957, Ch. 8.

² Eichler and Rabideau, *J. Amer. Chem. Soc.*, 1955, **77**, 5501.

³ Horne and Frysinger, *J. Geophys. Res.*, 1963, **68**, 1967.

In calculating the molal conductance of 1.55M-sulphuric acid at one atmosphere, the hydrogen ions from the second ionization have been ignored for the sake of simplicity, thereby introducing a 5–6% error. Two further errors, which may be as large as 10%, are introduced by the assumption that hydrochloric and sulphuric acid solutions of the same hydrogen-ion concentration are conductively equivalent, and by the comparison of



Variation of the dissociation constant, K (in mole l^{-1}), of the hydrogen sulphate ion with hydrostatic pressure at 25°.

acids of different concentration. Thus the values in the Figure may be in error by as much as 10–15%, although the probable error is much smaller (the error at one atmosphere is 6.3%).

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291. Hydrazine. Part XII.* Dimethylketazine (NN'-Di-isopropylidenehydrazine) in the Hydrazine-Acetone Phase Diagram.

By M. C. B. HOTZ.

KLOCHKO AND MIKHAILOVA¹ interpreted a peak in their phase diagram at a 1:2 molar ratio of hydrazine to acetone as indicating a compound $N_2H_4 \cdot 2Me_2CO$, m. p. -37.8° . They claimed that no data existed for the solubility in, or reaction of, hydrazine with acetone. Although this addition compound has not been previously reported, the reaction between hydrazine and acetone to form dimethylketazine (NN'-di-isopropylidenehydrazine) is well known.² Gilbert³ who studied the equilibrium, showed that the reaction passes through a hydrazone intermediate, and calculated equilibrium constants

* Part XI, Lamchen and Stephen, *J.*, 1955, 2044.

¹ Klochko and Mikhailova, *Zhur. neorg. Khim.*, 1960, **5**, 2319.

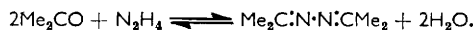
² Curtius and Thun, *J. prakt. Chem.*, 1891, **44**, 161.

³ Gilbert, *J. Amer. Chem. Soc.*, 1929, **51**, 3394.

and enthalpy and free energy data. The analytical evidence of Pugh and his co-workers,⁴ together with conductometric and potentiometric experiments to obtain evidence of its basic character,⁵ have demonstrated the existence of dimethylketazine in acetone solution.

Barrick, Drake, and Lochte⁶ determined the melting point of dimethylketazine (-12.5°), and measured its density, surface tension, and refractive index. Their measured parachor of 302.2 compares well with the value (305.4) calculated from Sugden's parachor equivalents,⁷ whereas that calculated for the compound $N_2H_4 \cdot 2Me_2CO$ is 413.8. Hence there appears to be little doubt that Klochko and Mikhailova's system contained dimethylketazine and not the addition product.

Substitution of Gilbert's results at 15° ($-\Delta H = 9.1$ kcal., $K = 37.0$) in the van't Hoff isochore permits the calculation of the equilibrium constant at -37.8° for the overall reaction



This is found to be ~ 1.0 , whence it can be shown that the system investigated by Klochko and Mikhailova¹ was a mixture of hydrazine, water, dimethylketazine, and acetone in roughly stoichiometric proportions. It is not possible to calculate an approximate melting point for this composition of the system from cryoscopic constants, because all the constituents are volatile, but it seems likely that it would be below Barrick, Drake, and Lochte's melting point for pure dimethylketazine (-12.5°). Klochko and Mikhailova's value (-37.8°) is not unreasonable for such a mixture.

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⁴ Pugh and Stephen, *J.*, 1952, 4138; 1953, 354; Pugh, *J.*, 1953, 3445; Sohn, Marks, and Pugh, *J.*, 1955, 1753.

⁵ Hotz and Spong, *Chem. and Ind.*, 1960, 392; *J.*, 1962, 4283.

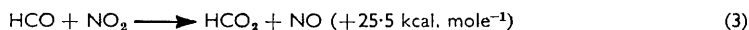
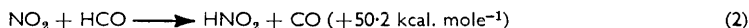
⁶ Barrick, Drake, and Lochte, *J. Amer. Chem. Soc.*, 1936, 58, 160.

⁷ Sugden, *J.*, 1924, 125, 1177.

292. The Disproportionation Reactions between NO_2 and HCO .

By ROBERT SHAW.

THE relative rate constants and rate factors are given for the disproportionation reactions (2) and (3) between NO_2 and HCO , which have been suggested by Thomas¹ to occur in the oxidation of formaldehyde by nitrogen dioxide.²



A steady-state treatment for HCO_2 gives $k_2/k_3 = [CO]/[CO_2]$. Pollard and Wyatt² showed that the ratio $[CO]/([CO] + [CO_2])$ is constant throughout the reaction; the ratio $[CO]/[CO_2]$ is therefore constant. From their results, $[CO]/[CO_2]$, *i.e.*, k_2/k_3 can be calculated

Temp. ($^\circ K$)	373	427	493
$[CO]/([CO] + [CO_2])$	0.58	0.60	0.63
$[CO]/[CO_2]$, <i>i.e.</i> , k_2/k_3	1.38	1.50	1.70

giving $E_2 - E_3 = 650$ cal. mole⁻¹, $\log A_1/A_2 = 0.51$, and $\log k_1/k_2 = 0.17$ at $427^\circ K$.

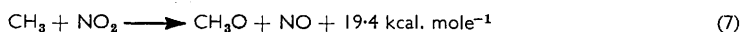
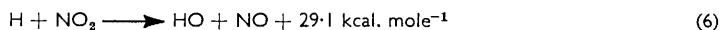
¹ Thomas, *Trans. Faraday Soc.*, 1953, 49, 630.

² Pollard and Wyatt, *Trans. Faraday Soc.*, 1949, 45, 760.

The absolute rates of reactions (2) and (3) are unknown, but (3) is an example of the general oxygen-transfer reaction (5), where R is a radical,



The rate constants of two other examples of reaction (5), namely, reactions (6) and (7), have been measured recently. For reaction (6), $\log k$ has been given as 13.5,^{3,4} and 13.7



or 14.3 $\log \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$; ⁵ for reaction (7) the values are 13.3 ⁶ and 12.8.⁷ Reactions (6) and (7) are very fast, and must occur on almost every collision. It would not be surprising if reaction (3) were also very fast, with $\log k_3$ of the order of 13 $\log \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$. At 400°K, $\log k_2$ would therefore also be around 13 $\log \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$. If this were so, the absolute activation energies would not be greater than, say, 2 kcal. mole⁻¹, and the absolute values of the $\log A$ factors would be about 13–14 $\log \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$.

The following heats of formation, in kcal. mole⁻¹, of gas at 298°K and 1 atmosphere, were used to calculate the heats of reaction: NO₂ 8.1, HCO -2.9, CO -26.4, H 52.1, NO 21.7, HO 9.3, CH₃ 31.9 (all from ref. 8), HNO₂ -18.6,⁹ HCO₂H -90,¹⁰ CH₃O -0.5,¹¹ and HCO₂ -42, assuming $D(\text{HCO}_2\text{-H}) = 100 \text{ kcal. mole}^{-1}$.

MINISTRY OF AVIATION, EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT,
WALTHAM ABBEY, ESSEX. [Received, July 9th, 1963.]

³ Rosser and Wise, *J. Phys. Chem.*, 1961, **65**, 532.

⁴ Phillips and Schiff, *J. Chem. Phys.*, 1962, **37**, 1233.

⁵ Ashmore and Tyler, *Trans. Faraday Soc.*, 1962, **58**, 1108.

⁶ Preston, Thesis, Cambridge, 1963.

⁷ Phillips and Shaw, unpublished result.

⁸ JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan, U.S.A., 1960—1961.

⁹ Ashmore and Tyler, *J.*, 1961, 1017.

¹⁰ Waring, *Chem. Rev.*, 1952, **51**, 171.

¹¹ Gray, *Trans. Faraday Soc.*, 1956, **52**, 344.

293. *An Improved Synthesis of Lilolidine.*

By G. HALLAS and D. C. TAYLOR.

LILOLIDINE¹ (III) has been prepared² in *ca.* 40% yield by reaction of indoline with 1-bromo-3-chloropropane. We obtained varying yields of this base (max. 41%) by adaptation of a preparation³ of julolidine, 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine, but separation of the required amine by fractionation was difficult. Several other routes have been used to synthesise the lilolidine ring system. Barger and Dyer⁴ obtained lilolidine in poor yield from 1-amino-1,2,3,4-tetrahydroquinoline and pyruvic acid by using the Fischer indolisation, followed by decarboxylation and hydrogenation of the product. A related preparative sequence⁵ from 1-aminoindoline also gave the amine. Sugimoto⁶ used the Stollé oxindole synthesis⁷ to obtain 2-oxolilolidine from 1,2,3,4-tetrahydroquinoline, and other workers^{8,9} prepared 6-oxolilolidine by cyanoethylation of

¹ Bamberger and Sternitzki, *Ber.*, 1893, **26**, 1298.

² von Braun, Heider, and Wyczkowska, *Ber.*, 1918, **51**, 1219.

³ Glass and Weissberger, *Org. Synth.*, 1946, **26**, 40.

⁴ Barger and Dyer, *J. Amer. Chem. Soc.*, 1938, **60**, 2414.

⁵ Rapoport and Tretter, *J. Amer. Chem. Soc.*, 1958, **80**, 5574.

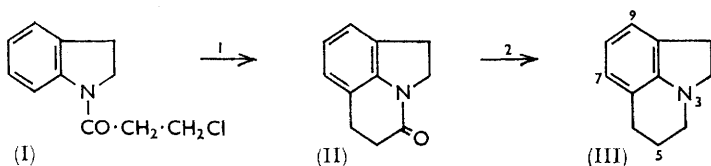
⁶ Sugimoto, *J. Pharm. Soc. Japan*, 1944, **64**, No. 7A, 4.

⁷ Stollé, Bergdoll, Luther, Auerhahn, and Wacker, *J. prakt. Chem.*, 1930, **128**, 1.

⁸ Rapoport and Tretter, *J. Org. Chem.*, 1958, **23**, 248.

⁹ Astill and Boekelheide, *J. Org. Chem.*, 1958, **23**, 316.

indoline followed by hydrolysis and cyclisation of the product (a technique first used by Almond and Mann¹⁰). Reduction of these ketones led to only moderate overall yields of lilolidine.



Reagents: 1, AlCl_3 , 2, $\text{LiAlH}_4\text{-Et}_2\text{O}$.

We now describe a new route to lilolidine, based on a synthesis¹¹ of julolidine, which results in a good overall yield of the base (60%). The route involves the initial formation of 1- β -chloropropionylindoline (I) which is cyclised to form 4-oxolilolidine (II), reduction of which gives lilolidine.

Experimental.—1- β -Chloropropionylindoline. To a solution of indoline (17.9 g.) in dry acetone (80 ml.), β -chloropropionyl chloride¹² (20 g.) was added dropwise with stirring. The mixture was then boiled for 1 hr. After cooling, the solution was poured into stirred dilute hydrochloric acid (200 ml.). The crude product was crystallised from aqueous ethanol (charcoal) to give 1- β -chloropropionylindoline (26.2 g., 83%) as needles, m. p. 90–91° (Found: C, 63.3; H, 5.7; Cl, 17.0; N, 6.5. $\text{C}_{11}\text{H}_{12}\text{ClNO}$ requires C, 63.0; H, 5.8; Cl, 16.9; N, 6.7%).

4-Oxolilolidine. An intimate mixture of 1- β -chloropropionylindoline (14.0 g.) and aluminium trichloride (20 g.) was heated over a small flame until evolution of hydrogen chloride ceased (about 15 min.). The melt was cooled and the excess of aluminium trichloride decomposed by cautious addition of a chilled mixture of concentrated hydrochloric acid (20 ml.) and water (500 ml.). The resulting slurry was thoroughly extracted with ether. Removal of the solvent from the dried (Na_2SO_4) organic layer gave a solid which was sublimed at 100° (bath)/5 mm. to give 4-oxolilolidine (9.8 g., 85%) as needles, m. p. 112–113° (lit.,⁵ m. p. 112–113°). Crystallisation from ethanol–light petroleum did not raise the m. p.

Lilolidine. A slurry of 4-oxolilolidine (30.5 g.) in dry ether (800 ml.) was added to a stirred suspension of lithium aluminium hydride (13.2 g.) in ether (200 ml.). The mixture was then refluxed for 10 hr. After cooling, the excess of reagent was destroyed with ethyl acetate (30 g.), and the resulting suspension was added to stirred dilute sulphuric acid (1800 ml.) at 0°. An excess of 40% sodium hydroxide was added and the ethereal layer was then separated, dried (NaOH pellets), filtered, and evaporated, leaving a residue which was distilled under reduced pressure to give lilolidine (24.2 g., 86%) as an almost colourless oil, b. p. 112–113°/5 mm. (lit.,⁴ b. p. 140°/12 mm.), m. p. 17–18°, n_D^{25} 1.5841. The picrate crystallised from ether in yellow needles, m. p. 170–171° (decomp.) (lit.,⁹ m. p. 167.5–168.5°).

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¹⁰ Almond and Mann, *J.*, 1952, 1870.

¹¹ Smith and Tung-yin Yu, *J. Amer. Chem. Soc.*, 1952, **74**, 1096.

¹² Fieser and Seligman, *J. Amer. Chem. Soc.*, 1936, **58**, 2482.

294. Solubility of Hydrogen Chloride in Sulphones, Sulphonates, and Sulphonyl Chlorides.

By J. CHARALAMBOUS, M. J. FRAZER, and W. GERRARD.

THERE is a close correlation between the electron density on oxygen and the solubility of hydrogen chloride in an organic compound containing oxygen,¹ the electron density being predictable from a consideration of electronegativity effects and π -bonding. Further examples of this correlation for compounds XYSO_2 are now shown in the Table, and the transmission of electronic effects through the sulphur atom are clearly discernible. The sum of the Taft σ^* polar factors of the groups X and Y are given to illustrate correlations with the solubility data.

	XYSO_2		$\text{HCl}/\text{XYSO}_2 \dagger$		HCl/XYSO_2 per oxygen atom †		$\Sigma\sigma^*$ (a)	νSO_2 (cm. ⁻¹)	
	X	Y	25°	0°	25°	0°		Asym.	Sym.
1	Pr ⁱ	Pr ⁱ	0.712	1.174	0.356	0.587	-0.380	1250	1119
2	Bu ⁿ	Bu ⁿ	0.627	—	0.314	—	-0.260	1258	1130
3	Pr ⁿ	Pr ⁿ	0.622	1.010	0.311	0.505	-0.230	1281	1130
4	$-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-$		0.402	0.763	0.201	0.382	—	1297	1144
5	Et	OBu ⁿ	0.316	0.630	0.105	0.210	$\sim +1.3$	1345	1168
6	Me	OBu ⁿ	0.255	0.510	0.085	0.170	$\sim +1.4$	1351	1176
7	<i>p</i> -CH ₃ ·C ₆ H ₄	OBu ⁿ	0.249	0.445	0.083	0.148	—	1351	1174
8	Ph	OBu ⁿ	0.213	0.419	0.071	0.140	$\sim +2.0$	1359	1187
9	<i>p</i> -Cl·C ₆ H ₄	OBu ⁿ	0.083	0.210	0.028	0.070	—	1361	1182
10	Pr ⁱ	Cl	—	0.126	—	0.063	+2.75	1370	1161
11	Et	Cl	0.056	0.098	0.028	0.049	+2.84	1376	1166
12	Me	Cl	0.044	—	0.022	—	+2.94	1382	1179
13	Ph	Cl	0.042	—	0.021	—	+3.54	1385	1187
14	Cl	OBu ⁿ	0.057	0.117	0.019	0.039	$\sim +4.3$	1410	1193
15	Cl	Cl	—	0.032	—	0.016	+5.88	1417	1196
16	OH	OH	—	<0.020	—	<0.005	+3.10	1410 §	1170 §

(a) From Newman; ¹¹ it is assumed that σ^* for OBuⁿ is $\sim +1.4$, from the value $+1.45$ for OMe.
 † Moles HCl per mole of XYSO_2 . § See ref. 12.

The highest solubilities are shown by sulphones in which X and Y have the lowest electronegativities. It is postulated that the solubility is mainly due to a donor-acceptor function, $-\text{O} \cdots \text{H}-\text{Cl}$, and indeed, from conductimetric titrations with boron trichloride in liquid hydrogen chloride, it has been claimed ² that dimethyl and diphenyl sulphones are "moderately strong bases" whereas sulphuryl chloride has "no basis properties." We have prepared adducts of n-propyl, n-butyl, and tetramethylene sulphones with boron trichloride.³ Other complexes have been mentioned ⁴ but the original papers contain little supporting evidence.

The sulphonates, $\text{X}\cdot\text{SO}_2\cdot\text{OBu}^n$, showed solubilities in the order $\text{X} = \text{Et} > \text{Me} > \textit{p}\text{-Me}\cdot\text{C}_6\text{H}_4 > \text{Ph} > \textit{p}\text{-Cl}\cdot\text{C}_6\text{H}_4 > \text{Cl}$ in agreement with inductive effect of X; and there is a similar trend in the sulphonyl chlorides, $\text{X}\cdot\text{SO}_2\cdot\text{Cl}$, with $\text{X} = \text{Pr}^i > \text{Et} > \text{Me} > \text{Ph} > \text{Cl}$. The solubilities are lower in the sulphonyl chlorides than the sulphonates with the same X, probably because the OBuⁿ group has a lower electron-withdrawing effect than Cl, due to a lower electronegativity or to O-S π -bonding. Also the ester oxygen probably makes a greater contribution to solubility than the sulphonyl oxygens because the lone pairs of electrons on the ester oxygen will be in orbitals with approximately sp^3 character,

¹ Gerrard, Madden, and Tolcher, *J. Appl. Chem.*, 1955, **5**, 28; Gerrard and Macklen, *ibid.*, 1956, **6**, 241; 1959, **9**, 85; 1960, **10**, 57; *Chem. Rev.*, 1959, 1105; *Chem. and Ind.*, 1959, 1521, 1549; *Proc. Chem. Soc.*, 1958, 200; Gerrard, Mincer, and Wyvill, *J. Appl. Chem.*, 1959, **9**, 89; 1960, **10**, 115; *Chem. and Ind.*, 1958, 894.

² Peach and Waddington, *J.*, 1962, 2880.

³ Charalambous, Frazer, Gerrard, and Ghaffar, unpublished.

⁴ Lindqvist, "Inorganic Adduct Molecules of Oxo Compounds," Springer-Verlag, Berlin, 1963.

which will have lower electronegativity than the orbitals with approximately sp^2 character holding the lone pairs of the sulphonyl oxygen atoms.

It has been suggested that the values of the MO stretching frequencies in compounds of the type MO·XYZ depend on the sum of electronegativities of X, Y, and Z.⁵ A linear relation between the asymmetric SO_2 stretching frequencies in sulphonyl fluoride and chloride and the sum of electronegativities of fluorine and chlorine was assumed in order to estimate the electronegativity of CF_3 in $F_3C\cdot SO_2F$ and $F_3C\cdot SO_2Cl$.⁶ We now find that the solubilities of hydrogen chloride in moles of hydrogen chloride per mole of solvent *per oxygen atom* decreases in the same order as the increase in ν_{SO_2} (asymmetric). For molecules containing carbonyl groups, Cook⁷ has shown that ν_{CO} is related to donor ability as measured by ionisation potentials, and the H-Cl and H-C stretching frequencies, in hydrogen chloride and phenylacetylene solutions.

Di-n-butyl sulphate and some butyl sulphinates appeared to react further with hydrogen chloride, probably in a similar manner, to sulphites.⁸

Experimental.—The sulphonates were prepared by the Tipson's method.⁹ *n-Butyl p-chlorobenzenesulphonate*, b. p. $138^\circ/0.4$ mm., n_D^{20} 1.5165, d_4^{20} 1.247 (Found: C, 48.2; H, 5.7; Cl, 14.3; S, 12.7. $C_{10}H_{13}ClO_3S$ requires C, 48.1; H, 5.7; Cl, 14.2; S, 12.8%) was obtained in 50% yield. Propane-2-sulphonyl chloride was prepared by the chlorination of the disulphide.¹⁰ The sulphones and other sulphonyl chlorides were purified commercial samples.

Solubilities were determined as described previously,¹ except with a U-tube as absorption vessel. The sulphones were solids at room temperature; hydrogen chloride was passed into the melt for $\frac{1}{2}$ hr., and the melt then cooled to the recorded temperature. Compounds 2, 12, and 13 were solids at 0° even after hydrogen chloride had been dissolved in them at a higher temperature. Compounds 10 and 15 were too volatile for a measurement to be made at 25° .

The infrared spectra were measured as Nujol mulls (1, 2, 3, 4) or in carbon tetrachloride (6, 7, 8, 9, 14) or as a capillary film (5, 10, 11, 12, 13, 15); and the collaboration of Dr. E. F. Mooney and Mr. F. Butcher is gratefully acknowledged.

NORTHERN POLYTECHNIC,
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⁵ Bell, Heisler, Tannenbaum, and Goldenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5185; Kagarise, *ibid.*, 1955, **77**, 1377; Daasch, *Spectrochim. Acta.*, 1958, **13**, 257.

⁶ Lagowski, *Quart. Rev.*, 1959, **13**, 233.

⁷ Cook, *J. Amer. Chem. Soc.*, 1958, **80**, 49.

⁸ Gerrard, Machell, and Tolcher, *Research*, 1955, **8**, S7.

⁹ Tipson, *J. Org. Chem.*, 1944, **9**, 235.

¹⁰ Douglass and Johnson, *J. Amer. Chem. Soc.*, 1938, **60**, 1486.

¹¹ Newman, "Steric Effects in Organic Chemistry," J. Wiley & Sons Inc., New York, 1956.

¹² Giguere and Savoie, *J. Amer. Chem. Soc.*, 1963, **85**, 287.

295. Dissociation Constants of the Gibberellins.

By B. K. TIDD.

THE fundamental importance of ionisation in determining biological activity in the plant growth regulators has frequently been emphasised (see for example ref. 1). In view of the wide range in order of biological activity shown by the different gibberellins when they are tested against various plant species,² and to assist in the rational selection of buffer solutions for the extraction of the natural gibberellins from plant material (cf. ref. 3), the

¹ Brian and Rideal, *Biochim. Biophys. Acta*, 1952, **9**, 1.

² Brian, Hemming, and Lowe, *Nature*, 1962, **193**, 946.

³ Hayashi and Rappaport, *Nature*, 1962, **195**, 617.

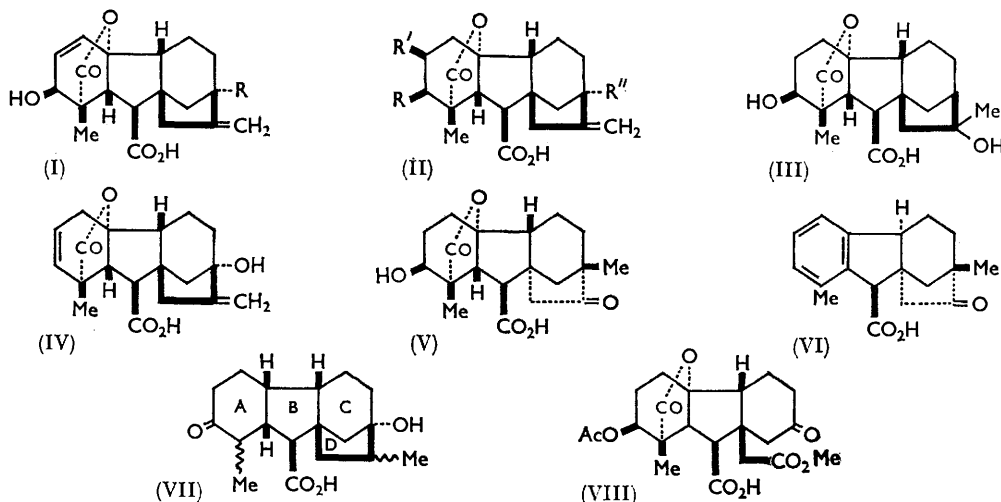
dissociation constants of the gibberellins have been measured in aqueous solution. Only small differences in pK values were found (see Table).

pK 's of the gibberellins and related compounds.

Compound	Concn. (10^4M)	pK
Gibberellic acid (I; R = OH)	5.0	3.97
Gibberellin A_1 (II; R = R'' = OH, R' = H)	3.0	4.09
A_2 (III)	4.9	4.21
A_4 (II; R = OH, R' = R'' = H)	4.4	4.21
A_5 (IV)	1.6	4.09
A_6 (II; RR' = O<, R'' = OH)	1.4	4.03
A_7 (I; R = H)	5.6	4.11
A_8 (II; R = R' = R'' = OH)	2.1	4.04
A_9 (II; R = R' = R'' = H)	1.2	4.26
Keto-acid ^a (V)	2.4	4.05
Gibberic acid (VI)	3.2	4.24
Keto-acid (VII) ^b	2.5	4.73
Keto-acid (VIII) ^c	2.1	4.29

^a Cross, *J.*, 1960, 3022. ^b Mulholland, *J.*, 1963, 2606. ^c Bourn, Grove, Mulholland, Tidd, and Klyne, *J.*, 1963, 154.

Cyclopentanecarboxylic acid ⁴ has pK 4.97, and the gibberellins are, therefore, stronger acids, as might have been expected. Inversion of ring D as in the keto-acid (V), introduction of an unsaturated linkage in ring A (compare gibberellic acid and



gibberellin A_5 with gibberellin A_1), and variation in the number of hydroxyl substituents on rings A and D, have only a very small effect on the acid strength. When, however, the (1→4a)-lactone bridge is absent as in the keto-acid (VII), the pK is 4.73, only 0.24 pK units less than cyclopentanecarboxylic acid. Similarly, gibberic acid (VI) is a slightly stronger acid than phenylacetic acid,⁵ pK 4.31. It seems possible that this is an "anomalous" acid-strengthening effect such as has previously been reported for *n*-butyric acid,⁶ diethylacetic acid,⁶ and *trans*-2-methylcyclohexanecarboxylic acid.⁷

⁴ M. Kilpatrick and J. G. Morse, *J. Amer. Chem. Soc.*, 1953, **75**, 1854.

⁵ Dippy and Williams, *J.*, 1934, 166.

⁶ Dippy, *Chem. Rev.*, 1939, **25**, 151.

⁷ Dippy, *J.*, 1954, 4102.

The 9-methylene group of the gibbane structure is released from the strained ring D in the seco-acid (VIII), and becomes closer to the carboxyl group. However, the expected enhancement of the acid-strengthening effect in this compound would appear to be masked by the acid-weakening effect due, perhaps, to increased steric hindrance to solvation of the carboxyl group.

Experimental.—Solutions (40 ml.; 10^{-3} – 10^{-4} M) of the compounds were transferred to the titration cell, which was maintained at 25° in a thermostat bath. Standard 0.1N-sodium hydroxide was delivered into the cell by means of an Agla micrometer syringe and a length of polythene cannula whilst a slow stream of nitrogen was maintained through the solution. The pH was followed by means of a Vibron electrometer in conjunction with the C33B pH-measuring attachment which was calibrated before each run by using phthalate and phosphate buffers of which the pH values (4.01 and 6.96) are international standards.⁸ Readings were corrected for the slight instrumental drift by recalibration after each run.

The treatment of the results followed Gage⁹ using the Henderson equation in its exact linear form

$$xh = Kc - Kx$$

where $x = m + h - K_w/h$ and h is the hydrogen-ion concentration, c is the initial concentration of the compound, m is the concentration of base, and K_w is the dissociation constant of water at 25°. The value of pK_{class} -derived graphically from the above equation was then corrected to give the thermodynamic pK value by means of the Debye-Huckel expression

$$-\log f \simeq 0.51\sqrt{I}$$

where f is the activity of the ion produced and I is the ionic strength taken to be equal to the value of x at half neutralisation.

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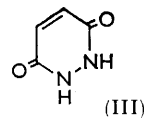
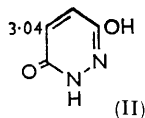
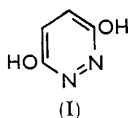
⁸ Bates and Guggenheim, *Pure and Appl. Chem.*, 1960, **1**, 163.

⁹ Gage, *Analyst*, 1957, **82**, 219.

296. Application of Proton Resonance Spectroscopy to Structural Problems. Part XI.¹ The Structure of Maleic Hydrazide.

By A. R. KATRITZKY and A. J. WARING.

MALEIC HYDRAZIDE could exist in any of the forms (I)–(III). Much evidence has been adduced for the predominance of the second of these (for a summary see ref. 2), but Gompper and Altreuther³ recently concluded that the formulation (III) was correct, as



only one ring-proton signal was found in the nuclear magnetic resonance spectrum. We have already pointed out⁴ that structure (II) would also give only one signal if proton

¹ Part X, Bedford, Dorn, Hilgetag, and Katritzky, *Rec. Trav. Chim.*, in the press.

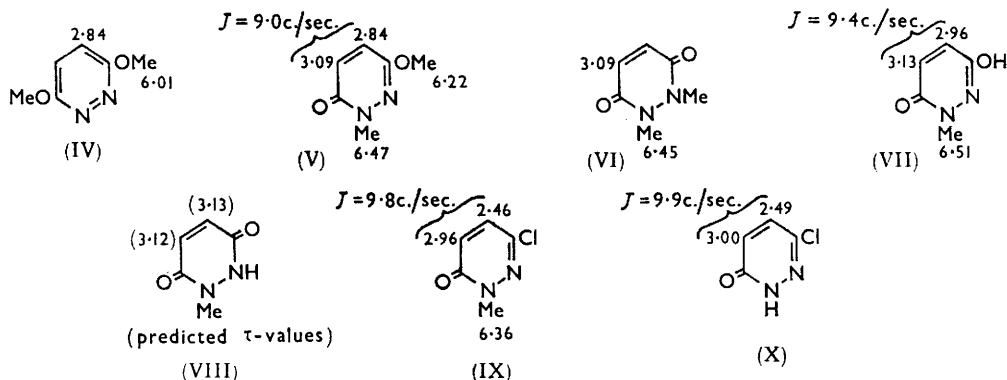
² Katritzky and Lagowski, *Adv. Heterocyclic Chem.*, 1963, **1**, 367.

³ Gompper and Altreuther, *Z. analyt. Chem.*, 1959, **170**, 205.

⁴ Katritzky and Waring, *Chem. and Ind.*, 1962, 695.

exchange were rapid; we now report work designed to adduce chemical-shift evidence for this structure.

Measured chemical shifts for the "fixed" methylated derivation are indicated on structures (IV)—(VI); assignment is unambiguous, all peaks being singlets except that the ring protons in (V) are coupled, with $J = 9.0$ c./sec. If the mono-*N*-methyl derivative exists as (VII), the chemical shifts should be the same as those in (V), except for the effect of changing methoxyl to hydroxyl. The work of Diehl,⁵ as extended by Smith,⁶ on the effect of substituents on aromatic systems, shows that replacement of methoxyl by hydroxyl shifts an *ortho*-proton 0.11 ± 0.04 p.p.m. and a *meta*-proton 0.07 ± 0.04 p.p.m. to higher field. Hence, the aromatic protons for structure (VII) are predicted to occur at τ 2.95 and 3.16, in excellent agreement with experiment. By contrast, the predicted



values for the alternative form (VIII) are not in agreement. These predicted values were obtained from the di-*N*-methyl derivatives (VI) by using compounds (IX) and (X) to estimate the effect on the ring-protons of changing an *N*-methyl group to hydrogen.

Hence the chemical-shift evidence is strongly in favour of the hydroxy-form (VII) for the mono-*N*-methyl derivative. For maleic hydrazide itself, calculations as above give predicted values of 3.02, 3.06, and 3.16, for forms (I), (II), and (III), respectively. The experimental value is 3.04, and this, together with the existence of the mono-*N*-methyl derivative in the hydroxy-form, is a good indication that maleic hydrazide does not exist in the dioxo-form (III).

Experimental.—Compounds were prepared by previously used methods⁷ and had m. p.'s in agreement with published values. Spectra were obtained on a Perkin-Elmer 40 Mc./sec. permanent-magnet spectrometer with sample-spinning. All values are quoted for m-solutions in dimethyl sulphoxide with tetramethylsilane as internal standard.

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⁵ Diehl, *Helv. Chim. Acta*, 1961, **44**, 829.

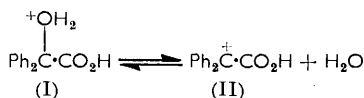
⁶ G. W. Smith, personal communication.

⁷ Druey, Meier, and Eichenberger, *Helv. Chim. Acta*, 1954, **37**, 121; Eichenberger, Staehelin, and Druey, *ibid.*, 1954, **37**, 837; Itai and Igeta, *J. Pharm. Soc. Japan*, 1954, **74**, 1195.

297. Reactions of 2-Bromoethyl Benzilate and 2-Bromoethyl Mandelate with Secondary Amines; a Correction and Extension.

By G. P. ELLIS, J. KING, and T. B. LEE.

THE crystalline product, m. p. 148—149°, obtained by the interaction of benzoic acid and 2-bromoethanol, was assumed by us¹ to be the ester; we now agree with the finding² that the compound is the isomeric (2-bromoethoxy)diphenylacetic acid, and it is therefore this ether which, on treatment with piperidine in benzene, gives a good yield of 3-oxo-2,2-diphenyl-1,4-dioxan. Esterification of other α -hydroxy-acids, for example, mandelic¹ and 1-hydroxycycloalkanecarboxylic acids,³ with halogenoalkanols under identical conditions, that is, heating under reflux with concentrated sulphuric acid and removal of the water formed as an azeotrope by means of a water-entrainment device, produces only the ester. Benzoic acid therefore behaves differently from many other α -hydroxy-acids under these esterifying conditions, as it also does in amide formation.⁴ However, on heating benzoic acid and ethanol under reflux in a Dean and Stark apparatus with benzene and concentrated sulphuric acid, ethyl benzoate was the only product. Cyclohexyl-



phenylglycollic acid has now been treated similarly, and the only product was 2-bromoethyl cyclohexylphenylglycollate. We have now confirmed that benzoic acid can be esterified by heating it with 2-bromoethanol in the presence of concentrated sulphuric acid, without using a device for removal of the water.⁵ If a large amount of sulphuric acid (35% of the weight of benzoic acid) and an excess of the alcohol is present, then, on prolonged heating, the product is 2-bromoethyl (2-bromoethoxy)diphenylacetate.⁵ The facile formation of the ether acid may be due to the formation, under the conditions mentioned above, of the carbonium ion (II), formed by the dehydration of the protonated hydroxy-acid (I), and also to the increased acidity of the hydroxyl group of 2-bromoethanol compared with that of ethanol. The carbonium ion (II) would be expected to be more stable than the corresponding ion derived from mandelic acid or an alicyclic hydroxy-acid.

2-Bromoethyl benzoate has been prepared by heating equimolar quantities of the acid and alcohol under reflux with a small amount of concentrated sulphuric acid. On reaction with a two-fold excess of piperidine it gave 2-piperidinoethyl benzoate hydrochloride in 63% yield; this was identical with a sample prepared by the Horenstein-Pählicke method.⁶ From this reaction, a very small amount (4%) of 3-oxo-2,2-diphenyl-1,4-dioxan was also isolated.

Experimental.—2-Bromoethyl benzoate. The following preparation is a modification of that of Yoshida and Iwashige⁵ in that a 1 : 1 and not a 4 : 1 molar ratio of alcohol to acid was used in an attempt to ensure preferential ester formation. Benzoic acid (24.0 g., 0.106 mole), 2-bromoethanol (13.4 g., 0.106 mole), carbon tetrachloride (160 ml.), and concentrated sulphuric

¹ Ellis, King, and Lee, *J.*, 1962, 685.

² Ioffe and Kuznetsov, *Zhur. obshchei Khim.*, 1961, **31**, 3051.

³ Leon, Barthel, and Hall, *J. Org. Chem.*, 1954, **19**, 490; Ellis, Golberg, King, and Sheard, *J. Medicin. Chem.*, 1963, **6**, 111.

⁴ Gray and Heitmeier, *J. Amer. Chem. Soc.*, 1959, **81**, 4347.

⁵ Yoshida and Iwashige, *Chem. and Pharm. Bull. (Japan)*, 1955, **3**, 417.

⁶ Blicke and Maxwell, *J. Amer. Chem. Soc.*, 1942, **64**, 428.

acid (20 drops) were heated together under reflux (no azeotroping device) for 6 hr. The mixture was allowed to cool and was set aside overnight. It was then washed with water, an excess of dilute sodium carbonate solution, and water. After drying the solution (Na_2SO_4) and filtering it, the solvent was removed and the residue distilled, to give 2-bromoethyl benzilate as a colourless oil, b. p. 179—182°/0.4 mm. [only a small central portion (4.72 g.) of the main fraction was taken] (Found: Br, 24.1. Calc. for $\text{C}_{16}\text{H}_{15}\text{BrO}_3$: Br, 23.8%).

2-Piperidinoethyl benzilate hydrochloride. 2-Bromoethyl benzilate (3.2 g., 0.0095 mole), piperidine (1.62 g., 0.019 mole), and benzene (30 ml.) were heated together under reflux for 16 hr. The mixture was cooled and diluted with ether. Piperidine hydrobromide (1.46 g.) (Found: Br, 47.9. Calc. for $\text{C}_5\text{H}_{11}\text{N}, \text{HBr}$: Br, 48.1%) was filtered off, and an excess of ethereal hydrogen chloride was added to the filtrate. The colourless solid (3.1 g., 86%) which was precipitated was filtered off and washed with ether, and the filtrate and washings were retained. The 2-piperidinoethyl benzilate hydrochloride (2.25 g., 63%) (from ethanol-ether), had m. p. 175—177° (Found: C, 66.8; H, 7.1; Cl, 9.5. Calc. for $\text{C}_{21}\text{H}_{25}\text{NO}_3, \text{HCl}$: C, 67.1; H, 7.0; Cl, 9.4%). Further crystallization from ethanol gave material with m. p. and mixed m. p.⁶ 178—181°. Infrared spectroscopy also confirmed its identity.

The retained filtrates (above) were washed with water several times, dried (Na_2SO_4), and filtered, and the solvent was removed, leaving a small amount of oil which crystallized from light petroleum (b. p. 60—80°) to give 3-oxo-2,2-diphenyl-1,4-dioxan (0.1 g., 4%), m. p. 96—97° (Found: C, 75.5; H, 5.7. Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_3$: C, 75.6; H, 5.6%). Recrystallization led to m. p. and mixed m. p.¹ 97—98°. The infrared spectra of the two samples were identical.

2-Bromoethyl cyclohexylphenylglycolate. A mixture of cyclohexylphenylglycollic acid (4.6 g., 0.02 mole), 2-bromoethanol (2.5 g., 0.02 mole), carbon tetrachloride (70 ml.), and concentrated sulphuric acid (5 drops) was heated under reflux for 20 hr. (with separation of the water formed). After cooling, the solution was washed with water, aqueous sodium carbonate solution, and water, and dried (Na_2SO_4). The drying agent and solvent were removed, and the residue was distilled, to yield the *ester* (4.25 g., 62%), b. p. 175—179°/2 mm. (Found: Br, 23.0. $\text{C}_{16}\text{H}_{21}\text{BrO}_3$ requires Br, 23.4%). Acidification of the sodium carbonate solution yielded a negligible amount of the original acid.

Reaction of benzilic acid with ethanol. Benzilic acid (22.8 g., 0.1 mole), ethanol (6 ml., 0.1 mole), concentrated sulphuric acid (4 drops), and benzene (75 ml.) were heated under reflux for 15 hr. in a Dean and Stark apparatus. The cooled mixture was washed with water, saturated sodium hydrogen carbonate solution, and water; it was then dried (Na_2SO_4) and filtered, and the solvent removed. Distillation of the resulting oil gave the ethyl ester (15.8 g.), b. p. 160—163°/7 mm. (lit.,⁷ 188—190°/15 mm.). The sodium hydrogen carbonate extracts were acidified, and the precipitate (3.4 g.) of benzilic acid (3.0 g.) had m. p. and mixed m. p. 148—150° (from water).

The authors thank the directors of Benger Laboratories Limited for permission to publish these results, and the Analytical Department for the analyses.

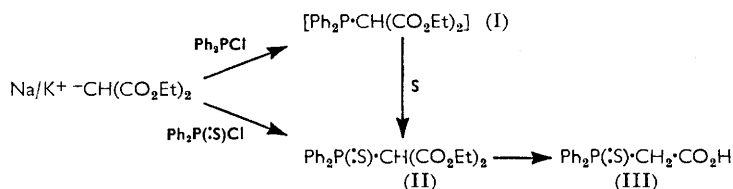
RESEARCH DEPARTMENT, BENGER LABORATORIES LTD., HOLMES CHAPEL, CHESHIRE.
(G. P. E.) DEPARTMENT OF CHEMISTRY AND BIOLOGY,
WELSH COLLEGE OF ADVANCED TECHNOLOGY, CARDIFF. [Received, September 10th, 1963.]

⁷ Curtius, *J. prakt. Chem.*, 1917, [2], 95, 195.

298. Reactions of Organophosphorus Chlorides with Diethyl Malonate.

By P. C. CROFTS and K. GOSLING.

MANY examples are known of the formation of carbon-phosphorus bonds by reactions of both simple and substituted phosphorus halides with Grignard reagents and similar organometallic compounds. There are, however, few records¹ of the formation of such bonds by use of metal derivatives of enolisable compounds, although reactions of this type are potentially valuable as providing routes to organophosphorus compounds containing carbon-functional groups. We now report reactions of alkali-metal derivatives of diethyl malonate with diphenylphosphinous chloride and diphenylphosphinothioic chloride. Both reactions were carried out in tetrahydrofuran after formation of the metal derivatives by use of a sodium-potassium alloy which was liquid at room temperature. This reacted with diethyl malonate much more rapidly than either sodium or potassium separately, and gave a white gelatinous suspension which reacted readily with the acid chlorides. The substituted phosphine (I) was not isolated but was treated with sulphur



to give the same phosphine sulphide (II) as was formed directly in the reaction involving the phosphinothioic chloride. Alkaline hydrolysis of the ester (II), and decarboxylation by heating in acid solution, gave the known monocarboxylic acid (III).

Experimental.—*Reaction of diethyl potassio/sodiomalonate with diphenylphosphinous chloride.* Sodium (0.44 g.) and potassium (1.59 g.) were alloyed by stirring vigorously in refluxing tetrahydrofuran (20 ml.) under nitrogen. After cooling, diethyl malonate (9.6 g.) and tetrahydrofuran (100 ml.) were added, and the mixture was stirred at room temperature for 4 hr. Diphenylphosphinous chloride (13.2 g.) in tetrahydrofuran (15 ml.) was added with stirring during 2 hr., and followed, after a further 3 hr., by sulphur (1.92 g.). After being stirred overnight, the mixture was poured into water, the resulting solution was extracted with chloroform, and the extract was dried (MgSO₄) and evaporated under reduced pressure. The resulting solid (21.5 g.) was recrystallised from a mixture of light petroleum (b. p. 30–40°), ether, and chloroform, to give *diethyl diphenylphosphinothioylmalonate* (14.0 g., 62%) as white prisms, m. p. 76.5–77° (Found: C, 60.3; H, 5.3%; Saponification equiv., 182. C₁₉H₂₁O₄PS requires C, 60.6; H, 5.6%; Saponification equiv., 188). In another experiment, the crude product was heated under reflux with 2*N*-sodium hydroxide for 2½ hr., and the solution was filtered, acidified, and boiled to effect decarboxylation. The oil which separated was extracted with chloroform, and the extract was dried (Na₂SO₄) and evaporated, giving, after recrystallisation of the residue from chloroform and then from light petroleum (b. p. 60–80°)–ethanol, diphenylphosphinothioylacetic acid, m. p. 196.5–197.5° (decomp.) (lit.² 190°) (Found: C, 60.8; H, 4.5; S, 11.7%; Equiv., 284. Calc. for C₁₄H₁₃O₂PS: C, 60.9; H, 4.7; S, 11.6%; Equiv., 276).

Reaction of diethyl potassio/sodiomalonate with diphenylphosphinothioic chloride. A suspension of the mixed metal derivatives was prepared, as described above, from sodium (0.32 g.), potassium (1.17 g.), and diethyl malonate (7.1 g.), in tetrahydrofuran (100 ml.). Diphenylphosphinothioic chloride (11.1 g.) in tetrahydrofuran (20 ml.) was added during 1 hr., and the

¹ Kreutzkamp, *Chem. Ber.*, 1955, **88**, 195; Pudovik and Moshkina, *Zhur. obshchei Khim.*, 1957, **27**, 1611.

² Issleib and Thomas, *Chem. Ber.*, 1960, **93**, 803.

mixture was stirred overnight and worked up as in the previous experiment, to give a solid (14.0 g.) which, on recrystallisation from light petroleum (b. p. 30–40°)-chloroform, yielded diethyl diphenylphosphinothioylmalonate, m. p. and mixed m. p. 76.5–77°.

We are grateful to Mr. V. Manohin for microanalyses.

THE MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY,
MANCHESTER 1.

[Received, September 21st, 1963.]

299. "Generalisation of Robins-Walker Aromatisation"; an Addendum.

By R. W. ALDER and M. C. WHITING.

WE recently described,¹ under the above title, examples of the conversion of cyclohexane-1,4-diones into aromatic ethers. In one respect we overstated the extent to which these went beyond the original work of Robins and Walker; we wrote of this, "Methanol was unique as the alcoholic component," whereas in fact the formation of an ethyl and a benzyl ether by this process was already described.² Our sentence continued "and a necessary role was allotted to the ethylenic linkage which indeed often migrated during the reaction"; we illustrated a simple case, proceeding in low yield, in which migration did *not* occur. This could be reworded more precisely "a necessary role was allotted² to the ethylenic linkage, and its importance emphasised,³ a halochromic cation being an assumed intermediate. Later, examples of the reaction were observed⁴ in cases where, although an ethylenic linkage was present in the same relative position, halochromic cations could not be formed; in these cases, *e.g.*, the example illustrated,¹ the reaction proceeded in low yield and without the migration of the ethylenic bond." Our own examples proceeded in good yield under conditions different from those used by Robins and Walker in cases in which no ethylenic bond was present at all. We were anxious not to appear to contradict Robins and Walker's view that an ethylenic linkage placed so that it could migrate, giving a conjugated halochromic cation, facilitated the reaction, especially as we had been unable to effect such reactions with cyclohexane-1,4-dione itself.

THE DYSON PERRINS LABORATORY, OXFORD.

[Received, November 18th, 1963.]

¹ Alder and Whiting, *J.*, 1963, 4598.

² Robins and Walker, *J.*, 1956, 3260.

³ Robins and Walker, *J.*, 1957, 177.

⁴ Robins and Walker, *J.*, 1958, 409.

300. Some New Alkylaminosilanes.

By E. W. ABEL and G. R. WILLEY.

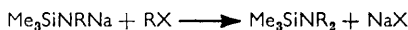
WE have synthesised a wide variety of aminosilanes and silazanes, including four new compounds.

N-Isobutylamino-, *N*-*s*-butylamino-, *NN*-di-isopropylamino-, and *NN*-di-*s*-butylamino-trimethylsilane have been prepared from the direct interaction of trimethylchlorosilane and the appropriate amine. *N*-Isobutylaminotrimethylsilane was also prepared by the ammonium sulphate-catalysed reaction between hexamethyldisilazane and isobutylamine. Like Fessenden and Crowe,¹ we also failed to obtain *NN*-di-isopropylamino- and *NN*-di-*s*-butylamino-trimethylsilane by this method.

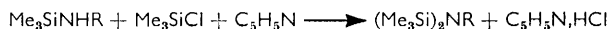
We believe that some of our reactions are novel for the types of compound concerned.

¹ Fessenden and Crowe, *J. Org. Chem.*, 1961, **26**, 4638.

In the presence of styrene, sodium reacts with *N*-alkylaminotrimethylsilanes to give compounds of the type Me_3SiNRNa , their reaction with alkyl halides constituting a new preparation for the *NN*-dialkylaminotrimethylsilanes.



The *N*-alkylaminotrimethylsilanes react with trimethylchlorosilane in the presence of pyridine to give *N*-alkylhexamethyldisilazanes.

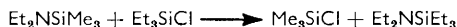


The bromomagnesium derivative of aniline, $\text{PhN}(\text{MgBr})_2$, formed by the action of aniline upon ethylmagnesium bromide, reacted with trimethylchlorosilane to produce *N*-phenylhexamethyldisilazane.

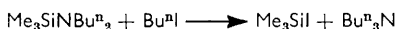


Efforts to produce the compounds $(\text{Me}_3\text{Si})_2\text{NR}$, where R is isopropyl, *s*-butyl, or *t*-butyl, by any of these methods and others already known, were not successful.

Triethylchlorosilane reacts very slowly with *NN*-diethylaminotrimethylsilane, to displace trimethylchlorosilane and produce *NN*-diethylaminotriethylsilane.



This displacement of trimethylhalogenosilane has also been noted in the reaction of alkyl halides with dialkylaminotrimethylsilanes. The products are often complex mixtures of amines and alkylammonium halides. However, from the reaction of di-*n*-butylaminotrimethylsilane with iodobutane it was possible to isolate 21% of tri-*n*-butylamine.



Experimental.—*Preparation of alkylaminotrimethylsilanes from trimethylchlorosilane and primary amine.* The reactions were carried out on an approximately 0.25 molar scale. To the amine (2 mol.) maintained at 0° was added dropwise with stirring the chlorosilane (1 mol.). The semi-solid mixture was heated at *ca.* 100° with constant stirring for 2 hr., suction-filtered, and the residue extracted with dry ether. Ether was removed from the combined extracts and filtrate, and the product fractionally distilled. *N*-Isobutylaminotrimethylsilane (32%) had b. p. 128°, d_4^{20} 0.758, n_D^{20} 1.4073 (Found: C, 57.4; H, 14.0; N, 9.3. $\text{C}_7\text{H}_{19}\text{NSi}$ requires C, 57.9; H, 13.2; N, 9.6%). *N*-*s*-Butylaminotrimethylsilane (30%) had b. p. 124°, d_4^{20} 0.756, n_D^{20} 1.4060 (Found: C, 58.1; H, 14.2; N, 9.4%).

N-*s*-Butylaminotrimethylsilane (31%), b. p. 124°, n_D^{20} 1.4069 (Found: N, 9.4%), was also obtained from the action of *s*-butylamine upon hexamethyldisilazane in the presence of a small quantity of ammonium sulphate.

Preparation of dialkylaminotrimethylsilanes from trimethylchlorosilane and secondary amine. The reactions were carried out on an approximately 0.5 molar scale. The amine (2 mol.) was allowed to solidify in a heavy-walled glass bomb immersed in a Dewar flask containing liquid air, and trimethylchlorosilane (1 mol.) was added. The bomb was allowed to warm to room temperature, and the contents were then well mixed with a thin steel rod. After being cooled in liquid air, the bomb was sealed, and then heated (160° for 24 hr.). Upon cooling and opening the bomb, the contents were extracted with ether (3 × 50 c.c.). Removal of solvent and subsequent distillation gave the product. *NN*-Di-isopropylaminotrimethylsilane (26%) had b. p. 157°, d_4^{20} 0.786, n_D^{20} 1.4241 (Found: C, 62.7; H, 13.0; N, 8.0. $\text{C}_9\text{H}_{23}\text{NSi}$ requires C, 62.3; H, 13.4; N, 8.1%). *NN*-Di-*s*-butylaminotrimethylsilane (21%) had b. p. 195°, d_4^{20} 0.817, n_D^{20} 1.4385 (Found: C, 66.1; H, 13.2; N, 6.9. $\text{C}_{11}\text{H}_{27}\text{NSi}$ requires C, 65.6; H, 13.5; N, 7.0%).

Interaction of sodium N-ethylaminotrimethylsilane and bromoethane. The sodium *N*-ethylaminotrimethylsilane was prepared from sodium (7 g., 0.3 mole), styrene (40 c.c.) and *N*-ethylaminotrimethylsilane (35.2 g., 0.3 mole) in refluxing dry dioxan (120 c.c.), with constant stirring,

under nitrogen. When dissolution of the sodium was complete, bromoethane (32.7 g., 0.3 mole) was added; the mixture was refluxed for 24 hr., cooled, filtered, and distilled, to give *NN*-diethylaminotrimethylsilane² (12.8 g., 29%), b. p. 126°, n_D^{20} 1.4108 (Found: N, 9.5. Calc. for $C_7H_{19}NSi$: N, 9.6%).

Interaction of trimethylchlorosilane, N-ethylaminotrimethylsilane, and pyridine. A mixture of *N*-ethylaminotrimethylsilane (26.9 g., 1 mol.) trimethylchlorosilane (24.8 g., 1 mol.), and pyridine (18.2 g., 1 mol.) was heated for 72 hr. under reflux. After filtration, fractional distillation gave considerable recovery of all three starting materials, but also some *N*-ethylhexamethyldisilazane³ (5.8 g., 13%), b. p. 164°, n_D^{20} 1.4289 (Found: N, 7.2. Calc. for $C_8H_{23}NSi_2$: 7.4%).

N-Phenylhexamethyldisilazane. Ethylmagnesium bromide (2 moles) was prepared from bromoethane (217.9 g., 2 moles) and magnesium (*ca.* 50 g., 2 moles) in ether (400 c.c.), and to this was slowly added aniline (93.1 g., 1 mole). Ethane was evolved, and after heating under reflux for 4 hr., trimethylchlorosilane (218 g., 2 moles) was added. After stirring for 8 hr., the mixture was filtered, and, after removal of solvent, distillation gave *N*-phenylhexamethyldisilazane⁴ (152.6 g., 64%), b. p. 40–41°/0.3 mm., m. p. 16°, n_D^{20} 1.4846, d_4^{20} 0.888 [Found: C, 60.7; H, 9.7; N, 5.8%; *M* (ebullioscopic in benzene), 241. Calc. for $C_{12}H_{23}Si_2N$: C, 60.7; H, 9.8; N, 5.9%; *M*, 238].

Interaction of NN-diethylaminotrimethylsilane and triethylchlorosilane. *NN*-Diethylaminotrimethylsilane (13.4 g., 1 mol.) and triethylchlorosilane (13.9 g., 1 mol.) were heated together under reflux for 1 week; the trimethylchlorosilane, b. p. 57–58°, formed was allowed to distil out of the system. Distillation of the residual liquid gave the unchanged reactants, and also *NN*-diethylaminotriethylsilane (2.9 g., 17%), b. p. 198–199°, n_D^{20} 1.4400 (Found: N, 7.4. Calc. for $C_{10}H_{25}NSi$: N, 7.5%).

With *N*-ethylhexamethyldisilazane and triethylchlorosilane, no trimethylchlorosilane was formed and virtually complete recovery of starting materials was effected.

Interaction of NN-di-n-butylaminotrimethylsilane and iodobutane. The aminosilane (28.2 g., 1 mol.) was added to iodobutane (25.2 g., 1 mol.), and no immediate reaction was observed, but upon heating under reflux for 24 hr. the mixture turned into a brown fuming liquid. Distillation gave trimethyliodosilane, b. p. 108°, and tri-*n*-butylamine, b. p. 209°, n_D^{20} 1.4300, the infrared spectrum of which was identical with that of an authentic sample.

We are grateful to Midland Silicones for a generous supply of alkylchlorosilanes, and to the D.S.I.R. for a research grant (to G. R. W.).

THE UNIVERSITY, BRISTOL 8

[Received, November 22nd, 1963.]

² Sauer and Hasek, *J. Amer. Chem. Soc.*, 1946, **68**, 241.

³ Rühlmann, *Chem. Ber.*, 1961, **94**, 2311.

⁴ Wannagat, Kruger, and Niederprüm, *Z. anorg. Chem.*, 1962, **314**, 80.

301. γ -Biotin.

By A. B. A. JANSEN and P. J. STOKES.

WE recently described¹ the isolation of a by-product, designated γ -biotin, from a sample of commercial biotin, and adduced evidence that it was an *N*-phenylbiotin. Further enquiry, prompted by the similarity between our product and an *N*-benzylbiotin² to which our attention was drawn by Dr. R. L. Switzer, has revealed that the biotin from which it was isolated was not of natural origin as we had supposed, but had been synthesised by a process in which the last stage was debenzilation of *NN'*-dibenzylbiotin. Our structural evidence, except for the microanalysis, was equally compatible with *N*-benzylbiotin, and comparison with authentic material, kindly undertaken by Hoffmann La Roche Inc., New Jersey, U.S.A., proved that the two products were identical, the only

¹ Jansen and Stokes, *J.*, 1962, 4909.

² Goldberg and Sternbach, U.S.P. 2,489,235/1949.

difference, revealed by thin-layer chromatography, being contamination of our material by *ca.* 1% of biotin. The pure material had no vitamin activity.

RESEARCH LABORATORIES, JOHN WYETH & BROTHER LIMITED,
NEW LANE, HAVANT, HANTS.

[Received, December 2nd, 1963.]

302. *The Hydro-desulphurization of Thiophen.*

By R. S. MANN.

FOR the removal of thiophens from crude oils, a mixture of cobalt and molybdic oxide is widely used. The catalytic activity of the cobalt molybdates used for the hydro-desulphurization of thiophen depends on the atomic ratio of Co : Mo and the method of preparation. A method for preparing highly active cobalt molybdate is now described, and its activity compared with other cobalt molybdates.

Experimental.—Catalysts. Catalyst I was prepared by adding 0.1M ammonium paramolybdate (82% MoO₂) solution (600 ml.) to 1M-cobalt nitrate (400 ml.) at room temperature and slowly heating the well-stirred mixture to 70° until a purple-blue precipitate was formed. This precipitate was washed several times with water, dried at 110°, and calcined for 5 hr. at 500°. Catalyst II was prepared by calcining an equimolar mixture of CoO and MoO₃ at 500°. Catalyst III and Catalyst IV were prepared by the methods of Byrns¹ and of Rosenheim.² Catalyst V, commercially available cobalt molybdate, was obtained from City Chemical Corporation, New York. Catalyst VI was prepared by the precipitation of cobalt molybdate from an equimolar solution of cobalt nitrate and sodium molybdate. The Co : Mo ratios of these cobalt molybdates are given in Table I.

Conversion of thiophen at 400°.

Catalyst	I	II	III	IV	V	VI
Atomic ratio Co : Mo	0.985	0.990	1.150	0.167	0.960	0.995
% Conversion	72.0	58.0	39.0	20.7	15.2	13.0

Activity. The catalysts were tested for their activity in the hydrodesulphurization of thiophen in a conventional flow apparatus at atmospheric pressure. The catalysts were pelleted to $\frac{1}{8}$ in. by $\frac{1}{8}$ in. cylinders at 4000 lb. sq. in. pressure, 3–5% polyethylene glycol 6000 being used as binder. Each catalyst was activated first by calcining it at 500° for 4 hr. and then activated in a stream of hydrogen for 5 hr. at 500°.

The catalytic activities were measured by the percentage conversion of thiophen into hydrogen sulphide and hydrocarbons when 1 mole of hydrogen and 5.47×10^{-3} mole of thiophen were passed over 4 ml. of catalyst at 220–450°. The products were collected and analysed by infrared spectroscopy. The conversions obtained at 400° are given in the Table.

It will be seen that catalyst I had outstanding activity. The high catalytic activity is considered to be due to the method of preparation.

DEPARTMENT OF CHEMICAL ENGINEERING,
UNIVERSITY OF OTTAWA, OTTAWA, CANADA.

[Received, November 15th, 1963.]

¹ Byrns, U.S. 2,369,439/1945.

² Rosenheim and Jaenicke, *Z. anorg. Chem.*, 1917, **101**, 235.

303. The Fundamental ν_{12} of Glyoxal.

By A. R. H. COLE and G. A. OSBORNE.*

FOUR of the six infrared-active fundamentals of glyoxal have been known for some time¹ and the two lower frequency vibrations have been assumed to lie beyond the range of previous investigations.² We have recently found the B_u fundamental ν_{12} as a B -type band at 342 cm.^{-1} (envelope maxima $\sim 9\text{ cm.}^{-1}$ on either side of a central minimum) consisting of a series of Q -branches (with a separation of approximately 3.5 cm.^{-1}) similar to those reported previously¹ for the C-H stretching and bending bands, although some of the finer detail was obscured by background water-vapour absorption.

Since all four B_u frequencies of glyoxal and three of those of dideuteroglyoxal² are now known, a product-rule calculation gives 310 cm.^{-1} for ν_{12} of dideuteroglyoxal. The frequencies of 342 and 310 cm.^{-1} are close to that of 320 cm.^{-1} assigned to the corresponding vibration of buta-1,3-diene.³

Experimental.—The measurement was made on a Grubb-Parsons single-beam spectrometer modified for use with a 30 line-per-mm. grating, a sodium chloride crystal chopper, a black Polythene (0.01 mm.) transmission filter, and a calcium fluoride reflection filter. Water-vapour absorption was reduced by flushing the spectrometer with dry nitrogen.

The glyoxal was prepared by heating the monohydrate with phosphorus pentoxide and purified by vacuum distillation. A 10-cm. cell with caesium iodide windows was used with a glyoxal pressure of 70 mm.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WESTERN AUSTRALIA,
NEDLANDS, WESTERN AUSTRALIA. [Received, September 30th, 1963.]

* Reported at the Fourth Australian Spectroscopy Conference, Canberra, August 1963.

¹ Cole and Thompson, *Proc. Roy. Soc.*, 1949, *A*, **200**, 10.

² Brand and Minkoff, *J.*, 1954, 2970.

³ Richards and Nielsen, *J. Opt. Soc. Amer.*, 1950, **40**, 438; Sverdlov and Tarasova, *Optics and Spectroscopy*, 1960, **9**, 159.