

1062. *Alkylplatinum Chlorides*

By S. F. A. KETTLE

It is a remarkable fact that although trimethylplatinum compounds were first reported by Pope and Peachey in 1907,¹ and have now a fairly extensive chemistry, no analogous compound containing a different alkyl group has ever been reported, although several attempts have been made to synthesise such compounds.²

We now report a more general method for the preparation of the trialkylplatinum halides. The method is simple, gives fairly good yields, and leaves the metal as the only platinum by-product, so facilitating recovery.

Experimental. Dimethylmercury (4.0 g.) was added dropwise to a solution of anhydrous platinum tetrachloride (1.3 g.) in acetone (50 ml.) cooled to -78° until reaction ceased. The black solution was then refluxed until the initially colloidal platinum was precipitated, leaving a pale yellow solution. Removal of solvent followed by vacuum sublimation gave 90% of the methylmercuric chloride required by



Trimethylplatinum chloride was obtained from the residue by Soxhlet extraction with benzene in *ca.* 50% yield, based on platinum tetrachloride (Found: C, 13.2; H, 3.1; Cl, 13.1. Calc. for $\text{C}_3\text{H}_9\text{ClPt}$: C, 13.1; H, 3.3; Cl, 12.9%). The compound was further characterised by comparison of its cubic unit cell ($a = 10.53 \text{ \AA}$) with the literature value ($a = 10.55 \text{ \AA}$).³

The corresponding *triethyl* compound was similarly prepared in approximately 30% yield (Found: C, 22.9; H, 4.4; Cl, 11.1. $\text{C}_6\text{H}_{15}\text{ClPt}$ requires C, 22.7; H, 4.7; Cl, 11.2%). The molecule is essentially tetrameric in benzene solution (Found: Osmometric M , 1154. Calc.: M , 1271). The compound crystallises in the monoclinic space group $C2/c$, the unit cell ($a = 23.6$, $b = 12.1$, $c = 12.2 \text{ \AA}$, $\beta = 95^{\circ}$) containing four tetrameric molecules.

The infrared and proton magnetic resonance spectra of these compounds were recorded and are discussed elsewhere.

An attempt was made to prepare triphenylplatinum chloride by this technique. Reaction occurred less readily than for the alkyl compounds and no organoplatinum compound was isolated.

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SHEFFIELD 10.

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¹ W. J. Pope and S. I. Peachey, *Proc.*, 1907, **23**, 86; *J.*, 1909, **95**, 571.

² J. Chatt and B. L. Shaw, *J.*, 1959, 4020.

³ R. E. Rundle and J. H. Sturdivant, *J. Amer. Chem. Soc.*, 1947, **69**, 1561.

1063. *The Infrared Spectra of Trimethyl- and Triethyl-platinum Chlorides*

By S. F. A. KETTLE

ALTHOUGH a variety of compounds in which simple alkyl groups are bonded to a transition metal atom have been prepared, the infrared absorption attributable to these groups has not been studied to any great extent. This has been because other regions of the spectrum are a more useful guide to structure, because other C-H groups are present, or simply because

of the instability of the compound. Adams, Chatt, and Shaw^{1,2} studied a variety of Pt^{II}-alkyl compounds and were able to assign some bands to vibrations located within the alkyl groups. The recently prepared compound, triethylplatinum chloride,³ provides an opportunity to study alkyl group frequencies without the disadvantage mentioned above. The spectrum is fairly complex but by comparison with the spectrum of the trimethyl compound and the use of qualitative intensity considerations it has proved possible to assign a symmetry to almost every band.

The infrared spectrum of [Me₃PtCl]₄ in carbon tetrachloride solution shows two regions of absorption in the range 4000—400 cm.⁻¹. Two strong peaks occur at 2984 and 2908 cm.⁻¹ together with two weak peaks at 2852 and 2810 cm.⁻¹ (there is a possible third at *ca.* 2930, hidden in the foot of the 2908 cm.⁻¹ peak). A strong peak at 1238 cm.⁻¹ is accompanied by a weaker peak at 1276 cm.⁻¹. These two regions of absorption must be ascribed to C-H stretching and deformation modes, respectively. The 1276 cm.⁻¹ peak is assigned to the degenerate antisymmetric C-H-methyl group deformation mode, a mode not previously observed. From the symmetric deformation mode at 1238 cm.⁻¹ a peak at *ca.* 526 cm.⁻¹ is predicted corresponding to a Pt-C stretching vibration.¹ There was no absorption in this latter region.

It is evident that there is negligible interaction between the deformation modes of three methyl groups attached to the same platinum atom since the presence of such interaction would have led to the appearance of up to five peaks. In contrast there is considerable interaction between the C-H stretching vibration of the methyl groups. Five peaks are expected, corresponding to two *A*₁ and three *E* vibrational modes. From a consideration of the form of the normal modes it is evident that only two of the five peaks should be intense, and the peak at 2984 cm.⁻¹ is therefore assigned to the *E* mode in which the C-H stretches are in phase within any one methyl group. Similarly, the 2908 cm.⁻¹ peak is assigned to the totally symmetric *A*₁ stretching vibration.

In a spectrum of a carbon tetrachloride solution of [Et₃PtCl]₄ the methyl deformation frequencies occur at the more normal positions of 1446 cm.⁻¹ (asym) and 1372 cm.⁻¹ (sym). In addition to these strong peaks there is a well resolved shoulder at 1433 cm.⁻¹ and a weak peak at 1250 cm.⁻¹, which could arise as a consequence of a variety of interactions within the molecule (lower symmetry than *C*_{3v}), weak coupling between groups, combination bands with low frequency modes). Strong peaks at 1224 and 1205 cm.⁻¹ must be assigned to CH₂ antisymmetric and symmetric deformations, respectively. C-C stretching vibrations absorb at 1024m and 985s cm.⁻¹, the latter, (?) -antisymmetric, mode having a shoulder at 967 cm.⁻¹. As in the methyl analogue, the C-H stretching region is complex, a total of seven peaks being clearly resolved. If *C*_{3v} symmetry is assumed for the Et₃Pt group the methyl vibrations give rise to two *A*₁ and three *E* infrared-active vibrations, as before, and the methylene groups to an *A*₁ and two *E*. The form of the normal vibrational modes are easily obtained in the limit of zero coupling between methyl and methylene groups and probable intensities assessed. As the coupling between the groups is increased, peak shifts will occur so that absorption occurs over a wider range of wavelengths and the weaker bands will gain in intensity at the expense of the stronger.

The effects of coupling are not particularly noticeable in this system, the four strong peaks expected do occur and two (at 2994 and 2911 cm.⁻¹) are readily assigned to anti-symmetric and symmetric methyl modes by comparison with the spectrum of the trimethyl compound. The corresponding methylene group vibrations absorb at 2967 and 2856 cm.⁻¹, respectively. Weak peaks occur at 2870 and 2828 cm.⁻¹ and there is an unresolved shoulder at *ca.* 2945 cm.⁻¹ which, if it is associated with the weak peak at *ca.* 2930 cm.⁻¹ in the spectrum of the trimethyl compound, is probably of symmetry *A*₁. All other weak peaks must then be of species *E*. A peak of medium-weak intensity at 2720 cm.⁻¹ is

¹ D. M. Adams, J. Chatt, and B. L. Shaw, *J.*, 1960, 2047.

² D. M. Adams, *J.*, 1962, 1220.

³ S. F. A. Kettle, preceding Note.

probably the second methylene-group *E* vibration. It is not an overtone band and cannot be a combination band unless some low-frequency skeletal mode involving the platinum and chlorine atoms is coupled with C-H deformation modes. Its assignment as an *E*-type vibration explains the shifts of the bands (also of *E* symmetry) at 2810 and 2852 cm.⁻¹ in the trimethyl to 2828 and 2870 cm.⁻¹ in the triethyl compound. There were no bands in the range 700—400 cm.⁻¹ where Pt-C vibrations usually absorb.

Spectra were recorded on an S.P. 100 spectrometer; mull spectra were used to show the absence of absorption in the 650—900 cm.⁻¹ region.

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1064. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XXI.¹ Arrhenius Parameters for the Chlorination of Biphenyl and Some Related Compounds*

By P. B. D. DE LA MARE and J. S. LOMAS

VARIOUS investigators have reported that, for the chlorination of aromatic compounds in acetic acid, changes in rate with change of structure are largely measures of changes in enthalpy of activation. Bradfield, Brynmor Jones, and their co-workers² reached this conclusion from extensive studies of the relative reactivities of substituted ethers and anilides. A large difference in enthalpy of activation was associated also with a large rate-difference for the chlorination of benzene and naphthalene in aqueous acetic acid;³ in this case the rather slow rate of reaction of benzene made it difficult to be sure whether there was any significant difference in the non-exponential term of the Arrhenius equation also. More recently, however, Mason⁴ reported that the value of the non-exponential term in the Arrhenius equation for the chlorination of benzene in acetic acid differs significantly from the corresponding values for biphenyl, naphthalene, and phenanthrene.

Our own recent accounts of the relative rates of chlorination of biphenyl and a number of its substituted and bridged derivatives^{5,6} raise the question of whether in systems of this kind, in which rotation about the aryl-aryl bond can be fairly free (as in biphenyl) or quite restricted (as in fluorene), the entropies of activation might show significant differences, and hence the enthalpies of activation might be less important in determining the rate of reaction. Evidence has been adduced that, for biphenyl and positive bromine in aqueous acetic acid, this is not an important issue, since the $\frac{1}{2}o : p$ ratio does not change much with temperature.⁷ It seemed worthwhile, however, to make comparisons of chlorination over a wider range of structure, and accordingly we have studied the rates of chlorination of biphenyl, 2,2'-dimethylbiphenyl, 9,10-dihydrophenanthrene, and fluorene in acetic acid over as wide a range of temperature as possible.

Experimental.—2,2'-Dimethylbiphenyl, m. p. 19°, was prepared by the Ullmann condensation of 2-iodotoluene and was purified by several recrystallisations from light petroleum (b. p.

¹ Part XX, P. B. D. de la Mare and R. Koenigsberger, *J.*, 1964, 5327.

² A. E. Bradfield and B. Jones, *J.*, 1928, 1006, 3073; *Trans. Faraday Soc.*, 1941, **37**, 726.

³ P. B. D. de la Mare and P. W. Robertson, *J.*, 1943, 279.

⁴ S. F. Mason, *J.*, 1959, 1233.

⁵ P. B. D. de la Mare, D. M. Hall, M. M. Harris, M. Hassan, E. A. Johnson, and N. V. Klassen, *J.*, 1962, 3784.

⁶ P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J.*, 1964, 5317.

⁷ P. B. D. de la Mare and J. L. Maxwell, *J.*, 1962, 4829.

40–60°) at *ca.* –80°. Fluorene, m. p. 116°; 9,10-dihydrophenanthrene, m. p. 34°; and biphenyl, m. p. 70°, were commercial specimens purified by recrystallisation from methanol.

The kinetic measurements were made in the usual way; even at the higher temperatures (45°), with care the loss of chlorine from blank comparisons could be reduced to no more than about 2%, eight samples being removed successively from the solution. The following is an example of a typical kinetic run with fluorene (0.01082M) and chlorine (0.00454M) at 35°. Aliquot parts (5 ml.) were added to aqueous potassium iodide and titrated with 0.007N-sodium thiosulphate.

Time (min.)	0	0.72	1.62	2.03	2.53	3.00	3.48	4.03	4.55
Titre (ml.)	6.49	5.75	4.79	4.60	4.13	3.97	3.68	3.42	3.16
k_2 (l. mole ⁻¹ min. ⁻¹)	—	16.0	18.4	16.7	18.1	16.7	16.8	16.5	16.8

The Table summarises the results. Rate-coefficients (standard deviation not more than 3% of the mean) were calculated by the usual formula, or from plots of $\log_{10}[(a-x)/(b-x)]$

TABLE

Rates (k_2 , in l. mole⁻¹ min.⁻¹) and derived quantities for chlorination in acetic acid

Compound	2,2'-Dimethyl- biphenyl	Biphenyl	9,10-Dihydro- phenanthrene	Fluorene
k_2 (17.3°)	0.0146	—	—	—
k_2 (17.5°)	—	0.0190	0.554	5.14
k_2 (25.0°)	0.0281	0.0386	0.990	8.26
k_2 (35.0°)	0.0676	—	2.00	16.5
k_2 (35.1°)	—	0.0836	—	—
k_2 (44.0°)	—	—	—	26.6
k_2 (46.0°)	0.150	0.178	3.68	—
E_A (kcal. mole ⁻¹)	15.3	14.6	12.5	11.5
$\log_{10} B$ (l. mole ⁻¹ sec. ⁻¹)	7.99	7.47	7.36	7.54
ΔH^\ddagger (kcal. mole ⁻¹)	14.9 ± 0.1	14.2 ± 0.3	12.0 ± 0.2	11.0 ± 0.3
ΔS^\ddagger (e.u.)	-15.7 ± 0.5	-17.5 ± 0.9	-18.3 ± 0.7	-17.1 ± 0.8

against time. The Arrhenius parameters, from the equation $k_2 = B \exp(-E_A/RT)$, and enthalpies (ΔH^\ddagger) and entropies (ΔS^\ddagger) of activation, from the equation

$$\ln \left(\frac{h k_2}{k T} \right) = \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}$$

were obtained graphically.

Discussion.—These compounds cover a reactivity range of about 300. The results for biphenyl accord reasonably well with the values⁴ ($\Delta H^\ddagger = 15.0$; $\Delta S^\ddagger = -14.3$) calculated from Mason's data. The entropies of activation are of the same general order as those for most other chlorinations by molecular chlorine; the reaction is "slow," in that it has a negative entropy of activation; and hence the transition state must be regarded as more restricted in its modes of motion than the initial state, as is often the case for bimolecular reactions of neutral molecules.⁸ Our results confirm Bradfield and Brynmor Jones's view, that the energies of activation are by far the most important feature involved in determining the rates of these reactions. The small differences in entropies of activation are probably accounted for by the experimental uncertainties, and in our view must be regarded as very nearly constant over the range of structure under investigation. This range includes fluorene, which is held rigidly planar by the bridge; 9,10-dihydrophenanthrene, which is held by the bridge with the planes of the aryl groups at an angle of 16°, but has some measure of flexibility about this conformation;⁹ biphenyl, which has a broad and probably rather shallow¹⁰ potential-energy curve restricting rotation about the coplanar position; and 2,2'-dimethylbiphenyl, which has a fairly large potential-energy

⁸ E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford, 1947, pp. 72 ff.

⁹ K. E. Howlett, J., 1955, 1249 (appendix to Paper by D. M. Hall and E. E. Turner, *J.*, 1955, 1242).

¹⁰ C. A. Coulson, "Theoretical Organic Chemistry," Kekulé Symposium, Butterworths, London, 1959, p. 57.

barrier which restricts rotation and constrains the rings at an average angle of probably¹¹ about 70°. Despite the fact that the angle between the planes of the aryl groups is important in determining their power of mutual conjugation, and hence strongly affects the rate of chlorination,^{5,6} it seems that entropy factors differ rather little, and that most of the difference in reactivity is determined by factors of enthalpy.

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¹¹ H. Suzuki, *Bull. Chem. Soc., Japan*, 1954, **27**, 597.

1065. Preparation of Phenyl Fluorosulphinate

By H. A. PACINI and A. E. PAVLATH

PHENYL FLUOROSULPHINATE can be conveniently prepared by a chlorine-fluorine exchange reaction between phenylchlorosulphinate and a fluorinating agent. The reaction between thionyl fluorochloride and phenol did not yield phenylfluorosulphinate, although phenyl chlorosulphinate can be prepared from thionyl chloride and phenol.

Phenyl chlorosulphinate (b. p. 73–74°/4.5 mm., n_D^{24} 1.5580) was prepared according to the method of Bissinger and Kung.¹ This material was allowed to react with various fluorinating agents, *e.g.*, potassium fluoride, ammonium fluoride, and arsenic trifluoride, and the most satisfactory system was found to be sodium fluoride in acetonitrile. The fluorination was carried out by standard procedures.² Fractionation of the reaction product gave 85% of the phenyl fluorosulphinate boiling at 55°/7 mm., a colourless liquid (Found: C, 45.4; H, 3.4; S, 19.6. Calc. for C₆H₅FO₂S: C, 45.0; H, 3.1; S, 20.0%). The sample for analysis was stored at –78°, because of its slow, but definite decomposition.

When the fluorination was carried out with excess of arsenic trifluoride, similar results were obtained. The product was, however, impure, because it could not be separated completely from arsenic trichloride. The purity was determined by gas chromatography with a 6 ft. Dow Silicone 11 column (10% on acid-washed Chromosorb) at 130°. Similar attempts by using ammonium fluoride and potassium fluoride gave low yields of phenyl fluorosulphinate.

The ¹H and ¹⁹F nuclear magnetic resonance spectra of the compound were recorded. A proton multiplet at 405 c./sec. below tetramethylsilane (aromatic hydrogens) and a fluorine singlet at –62.5 p.p.m. (using CCl₃F as a standard) was obtained. The latter resonance is assigned to the O·S(·O)F group.

The infrared spectrum of the phenyl fluorosulphinate exhibited S=O stretching bands at 7.92 μ and a C–O–S stretching band at 8.45 μ. Benzenesulphonyl fluoride exhibits the characteristic symmetrical and asymmetrical vibration modes of the –SO₂F group at 7.05 and 8.20 μ. The characteristic absorption bands of phenyl fluorosulphinate are shifted to higher frequency, in agreement with the difference in electronegativity of the halogen atoms. The starting material, phenylchlorosulphinate, exhibited absorption bands at 8.12 and 8.80 μ.

Phenyl fluorosulphinate is hydrolysed by dilute sodium hydroxide solution to phenol. This proves that the product is actually phenylfluorosulphinate, and that no rearrangement to phenylsulphonyl fluoride occurred during the chlorine-fluorine exchange reaction.

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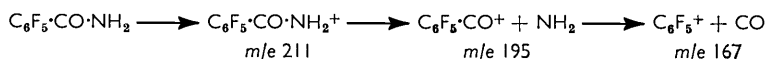
¹ W. E. Bissinger and I. E. Kung, *J. Amer. Chem. Soc.*, 1948, **70**, 2664.

² F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Amer. Chem. Soc.*, 1962, **84**, 4278.

1066. *Electron-impact Fragmentation of Pentafluorobenzamide*

By J. L. COTTER

A PARTIAL mass spectrum of pentafluorobenzamide is presented in Table 1. Fragmentation paths leading to the formation of the ions at m/e 195 ($C_6F_5 \cdot CO^+$) and 167 ($C_6F_5^+$) can be rationalized by Scheme 1.



Scheme 1

Evidence for these fragmentation paths is provided by the presence of two metastable peaks, one at m/e 180.5, $211^+ \longrightarrow 195^+ + 16$, and the other at m/e 143.4, $195^+ \longrightarrow 167^+ + 28$. (The position on the mass scale of metastable ions¹ arising from the transition $m_0^+ \longrightarrow m_1^+ + m_2$ may be calculated from the formula $m = m_1^2/m_0$.)

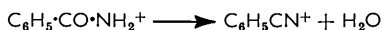
An interesting feature in the mass spectrum is the relatively intense peak at m/e 168 largely corresponding to a rearrangement ion $C_6F_5H^+$.

TABLE 1

Intensities of the principal ions in the mass spectra of pentafluorobenzamide and benzamide

m/e	Relative intensity (%)		m/e	Relative intensity (%)	
	$C_6F_5 \cdot CO \cdot NH_2$	$C_6H_5 \cdot CO \cdot NH_2$		$C_6F_5 \cdot CO \cdot NH_2$	$C_6H_5 \cdot CO \cdot NH_2$
211	74.0		93	7.75	
195	100.0		78		9.16
168	17.3		77		79.2
167	48.1		76		4.05
121		70.4	58		3.52
117	24.2		52		3.55
105		100.0	51		21.6
103		3.82	50		9.04
99	7.16		44	24.0	5.93
98	5.52		31	4.76	

In a previous publication² evidence was presented to show that the fragmentation process,



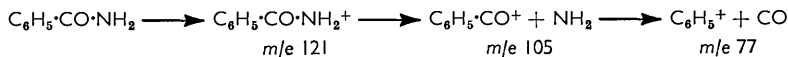
is predominant in the electron-impact breakdown of benzamide. However, further work has revealed that the benzamide samples used in these experiments were undergoing pyrolysis,



before ionisation, and the benzonitrile thus produced was responsible for the intense peak observed at m/e 103 ($C_6H_5 \cdot CN^+$). A partial mass spectrum of benzamide obtained when pyrolysis was not occurring (the reservoir was at 140°) is included in Table 1. As shown by the presence of two metastable peaks, one at m/e 91.4, $121^+ \longrightarrow 105^+ + 16$ and the other at m/e 56.6, $105^+ \longrightarrow 77^+ + 28$, the principal fragmentation paths (Scheme 2) are analogous to the pentafluorobenzamide breakdown pattern.

¹ A full discussion of the origin of metastable ions is given by J. H. Beynon in "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier, London, 1960, p. 251.

² J. L. Cotter, *J.*, 1964, 5477.*



Scheme 2

Ionisation and appearance potential results are presented in Table 2. The inductive effect of substituted fluorine atoms is reflected in the difference (0.6 ev) in the ionisation potentials of pentafluorobenzamide and benzamide.

In the absence of excess energies, the bond-dissociation energy $D(\text{C}_6\text{X}_5\cdot\text{CO}^+-\text{NH}_2)$ involving the breakdown of the molecular-ion $\text{C}_6\text{X}_5\cdot\text{CO}\cdot\text{NH}_2^+ \longrightarrow \text{C}_6\text{X}_5\cdot\text{CO}^+ + \text{NH}_2$ may be expressed by the thermochemical relationship $D(\text{C}_6\text{X}_5\cdot\text{CO}^+-\text{NH}_2) = A(\text{C}_6\text{X}_5\cdot\text{CO}^+) - I(\text{C}_6\text{X}_5\cdot\text{CO}\cdot\text{NH}_2)$, where $A(\text{C}_6\text{X}_5\cdot\text{CO}^+)$ is the appearance potential of the fragment-ion $\text{C}_6\text{X}_5\cdot\text{CO}^+$, and $I(\text{C}_6\text{X}_5\cdot\text{CO}\cdot\text{NH}_2)$ is the ionisation potential of $\text{C}_6\text{X}_5\cdot\text{CO}\cdot\text{NH}_2$. From the results shown in Table 2 $D(\text{C}_6\text{F}_5\cdot\text{CO}^+-\text{NH}_2)$ is estimated to be about 0.8ev greater than $D(\text{C}_6\text{H}_5\cdot\text{CO}^+-\text{NH}_2)$.

TABLE 2

Ionisation and appearance potentials

Ion	Ionisation * or appearance † potential (ev)	No. of determns.	Ion	Ionisation * or appearance † potential (ev)	No. of determns.
$\text{C}_6\text{F}_5\cdot\text{CO}\cdot\text{NH}_2^+$	$10.0 \pm 0.1^*$	4	$\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}_2^+$	$9.4 \pm 0.2^*$	3
$\text{C}_6\text{F}_5\cdot\text{CO}^+$	$11.3 \pm 0.2^\dagger$	3	$\text{C}_6\text{H}_5\cdot\text{CO}^+$	$9.9 \pm 0.1^\dagger$	2
C_6F_5^+	$16.3 \pm 0.3^\dagger$	3	C_6H_5^+	$13.5 \pm 0.1^\dagger$	2

The ionisation potential of the benzoyl radical has been estimated to be 7.4 ev,³ thus from the relationship

$$D(\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}_2) = A(\text{C}_6\text{H}_5\cdot\text{CO}^+) - I(\text{C}_6\text{H}_5\cdot\text{CO})$$

an upper limit of 2.5 ev is obtained for the carbon-nitrogen bond-dissociation energy in benzamide.

Experimental.—A sample of pentafluorobenzamide, m. p. 150°, was kindly provided by Mr. J. Thrower. Benzamide, m. p. 127°, was purified as previously described.²

Mass spectra were obtained with 70v electrons and an accelerating voltage of 1972v using an Associated Electrical Industries Ltd. mass spectrometer M.S.2-H. Ionisation and appearance potentials were obtained by the method of Dibeler and Reese;⁴ krypton was used to calibrate the electron energy scale. The temperature of the inlet reservoir was 140°, the ion-source temperature (270°) was estimated from the 57/58 ratio in isobutane using the data of Fox and Hipple⁵ extrapolated to higher temperatures.

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ROYAL AIRCRAFT ESTABLISHMENT, FARNBOROUGH, HANTS. [Received, February 1st, 1965.]

² J. R. Majer and C. R. Patrick, *Trans. Faraday Soc.*, 1963, **59**, 1266.

⁴ V. H. Dibeler and R. M. Reese, *J. Res. Nat. Bur. Stand.*, Sect. A, 1955, **54**, 127.

⁵ R. E. Fox and J. A. Hipple, *J. Chem. Phys.*, 1947, **15**, 208.

1067. Catalysis by Iodine and Iodine Monochloride, and Co-catalysis by Hydrogen Iodide, in the Friedel-Crafts Acylation of Anthracene

By P. H. GORE and J. A. HOSKINS

TRACE amounts of iodine have been used to effect acylations of several reactive aromatic substrates, mainly aromatic ethers,^{1,2} heterocyclic compounds,^{2,3} naphthalene,¹ biphenyl,² and mesitylene.² Less-reactive benzene derivatives, *viz.*, acetanilide¹ and toluene,⁴ have also been successfully acylated through the agency of iodine, under rather more vigorous conditions. The acylation of mesitylene, in particular, prompted a study, here reported, of the effect of iodine in the benzylation and acetylation of anthracene, the most reactive (*meso*-) position of which is also a hindered position.

The Friedel-Crafts benzylation of anthracene has been shown⁵ to proceed in high yield under mild conditions, especially with ethylene chloride as solvent, with many catalysts. Conditions under which aluminium chloride, for example, affords a quantitative yield of 9-benzoylanthracene, *viz.*, 24 hr. at 20°, fail completely when iodine is used. Low yields (Table 1) of this ketone were obtained, however, after 7 hours' boiling, from reactions

TABLE I
Benzoylation of anthracene

Catalyst	Molar proportion of catalyst *	Acyl component	Solvent	Time (hr.)	Temp.	Yield of 9-benzoylanthracene (%)
I ₂	0.1	Benzoyl chloride	Ethylene chloride	7	ca. 85°	11
ICl	0.1	"	"	7	"	6
ICl	0.1	"	"	24	20	0
I ₂	0.1	Benzoic anhydride	"	7	ca. 85	0
{ I ₂	0.1	"	"	7	"	48
{ HI	ca. 0.01	"	"	"	"	"
ICl	0.1	"	"	7	"	1.5
{ ICl	0.1	"	"	7	"	41
{ HI	ca. 0.01	"	"	"	"	"
HI	ca. 0.01	"	"	7	"	Trace
I ₂	0.008	Benzoyl chloride	Nitrobenzene	3	ca. 212	68
I ₂	0.008	"	—	5	230	55

* *I.e.*, moles of catalyst per mole of anthracene.

using either benzoyl chloride or benzoic anhydride as acyl component, and trace amounts of iodine or iodine monochloride as catalyst. It was not unexpected that iodine monochloride would show some catalytic activity in Friedel-Crafts acylations, especially in conjunction with acyl chlorides, since it had been shown⁶ from free-energy studies of trihalide ions that the Lewis-acid strengths of halogens decrease in the sequence ICl \gg BrCl $>$ IBr \gg I₂ $>$ Br₂ \gg Cl₂. Iodine monochloride also exhibits, in nitrobenzene solution, an acid strength comparable with that of antimony trichloride or picric acid.⁷

¹ S. Chodroff and H. C. Klein, *J. Amer. Chem. Soc.*, 1948, **70**, 1647.

² I. A. Kaye, H. C. Klein, and W. J. Burlant, *J. Amer. Chem. Soc.*, 1953, **75**, 745.

³ (a) H. D. Hartough and A. I. Kosak, *J. Amer. Chem. Soc.*, 1946, **68**, 2639; 1947, **69**, 1012; (b) R. A. Benkeser and R. B. Currie, *ibid.*, 1948, **70**, 1780; W. G. Emerson and T. M. Patrick, jun., *J. Org. Chem.*, 1948, **13**, 722; B. C. McKusick, U.S.P. 2,467,439/1949; F. Challenger and R. Emmott, *J. Inst. Petroleum*, 1951, **37**, 396; R. J. Tuite, A. D. Josey, and H. R. Snyder, *J. Amer. Chem. Soc.*, 1960, **82**, 4360.

⁴ G. A. Olah, M. E. Moffatt, S. J. Kuhn, and B. A. Hardie, *J. Amer. Chem. Soc.*, 1964, **86**, 2198.

⁵ P. H. Gore and J. A. Hoskins, *J.*, 1964, 5666.

⁶ R. L. Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 1550.

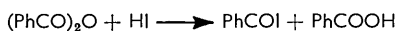
⁷ I. M. Kolthoff, D. Stocesca, and T. S. Lee, *J. Amer. Chem. Soc.*, 1953, **75**, 1834.

Furthermore, studies⁸ of the equilibrium $\text{ICl} + \text{Cl}^- \rightleftharpoons \text{ICl}_2^-$ suggested that iodine monochloride should be capable of promoting the polarisation of an acyl chloride:

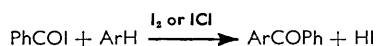


thereby promoting acylation. In the event, the catalytic activity of iodine monochloride in Friedel-Crafts acylations was shown to be weak, and comparable with that of iodine. It is apparent that nuclear iodination by iodine monochloride, which can take place with reactive substances such as pentamethylbenzene,⁹ does not occur here.

Trace amounts of hydrogen iodide have been found^{3b,10} to be effective catalytically in the acylation of furan using acid anhydrides. When here examined hydrogen iodide was found to be inactive. However, when added in traces (as I_2 -free 55% hydriodic acid, which would cause 5% of the anhydride to hydrolyse to the acid) to acylations catalysed by iodine or iodine monochloride, hydrogen iodide increased the yield of 9-benzoylanthracene from 0 or 1.5%, to 48 or 41%, respectively. This dramatic improvement in yield can be explained in terms of a co-catalysis by hydrogen iodide, which permits the intermediate formation of benzoyl iodide. Thus, activation



will be followed by the acylation stage



which regenerates the hydrogen iodide. This acylation stage would be promoted by the well-established¹¹ ability of molecular iodine to take up an iodide in the equilibrium, $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$, which would promote polarisation of the acyl-iodine bond. For the acylation of mesitylene, a maximum catalytic activity of the acyl halides was observed to occur with the iodide,¹² albeit only in acetylations. Certainly all the acylations examined (Table I) which cannot involve a benzoyl iodide intermediate give low yields of 9-benzoylanthracene.

A report¹³ of a quantitative yield of 9-benzoylanthracene by the action on anthracene of benzoyl chloride in boiling nitrobenzene in the absence of a catalyst was refuted by later workers.¹⁴ More recently the earlier claim has been vindicated, a 58% yield of the ketone being reported.¹⁵ Under conditions identical with those used in this latter experiment, but with the addition of traces of iodine, we obtained a somewhat improved yield (68%) of 9-benzoylanthracene, in the higher-melting modification.⁵ Again, a comparable yield of ketone was obtained in the presence of iodine, but in the absence of a solvent. In all these benzoylations, the 9-isomer was the only one formed, in agreement with the pattern of other catalysts tried.⁵

It was of interest to see what the effect of iodine catalysis would be on the acetylation

⁸ E. Pungor, K. Burger, and E. Schulek, *J. Inorg. Nuclear Chem.*, 1959, **11**, 56; H. M. Neumann, Paper presented at 133rd Meeting of Amer. Chem. Soc., San Francisco, April 1958, Division of Inorg. Chem., Abstr. No. 84; H. Appelman, *J. Inorg. Nuclear Chem.*, 1960, **14**, 308; cf. J. H. Faull, *J. Amer. Chem. Soc.*, 1934, **56**, 522; G. S. Forbes, S. W. Glass, and R. M. Fuoss, *ibid.*, 1925, **47**, 2892; Y. Y. Fialkov, *Zhur. neorg. Khim.*, 1960, **5**, 1567.

⁹ L. J. Lambourne and P. W. Robertson, *J.*, 1947, 1167.

¹⁰ H. D. Hartough and A. I. Kosak, *J. Amer. Chem. Soc.*, 1948, **70**, 867; U.S.P. 2,460,822/1949.

¹¹ H. W. Dodgen and W. F. Libby, *J. Chem. Phys.*, 1949, **17**, 951; O. E. Myers, *ibid.*, 1958, **28**, 1027; J. Cantacuzene, *J. Chim. phys.*, 1961, **58**, 475; J. H. Stern and A. A. Passchiev, *J. phys. Chem.*, 1962, **66**, 752; E. N. Rengevich and E. A. Shilov, *Ukrain. khim. Zhur.*, 1962, **28**, 1080.

¹² N. O. Calloway, *J. Amer. Chem. Soc.*, 1937, **59**, 1474; Y. Yamase, *Bull. Chem. Soc. Japan*, 1961, **34**, 480, 484; Y. Yamase and R. Goto, *J. Chem. Soc. Japan*, 1960, **81**, 1906.

¹³ C. D. Nenitzescu, D. A. Isacescu, and C. N. Ionescu, *Annalen*, 1931, **491**, 210.

¹⁴ N. P. Buu-Hoi and P. Cagniant, *Rec. Trav. chim.*, 1943, **62**, 713.

¹⁵ P. Rona and U. Feldman, *J.*, 1958, 1737.

of anthracene, a reaction known¹⁶ to give different amounts of isomers under different conditions. A maximum yield (62%) of acetylanthracenes was obtained by the use of iodine monochloride (Table 2). Addition of hydrogen iodide does not materially alter the

TABLE 2

Acetylation of anthracene with acetic anhydride in ethylene chloride at 85° for 7 hr.

Catalyst	Molar proportion of catalyst *	Yield of products (%)			
		Total	9-Acetyl-anthracene	1-Acetyl-anthracene	1,5-Diacetyl-anthracene
I ₂	0.1	43	39	3.7	—
ICl	0.1	62	61	1.0	Trace
I ₂ ,HI	0.1, ca. 0.01	40	28	12	—

* *I.e.*, moles of catalyst per mole of anthracene.

overall yield of ketones obtainable with iodine as catalyst. Whereas the ketone formed with iodine or iodine monochloride was almost pure 9-acetylanthracene, with only a small proportion of the 1-isomer, the addition of hydrogen iodide to the iodine reaction caused an increase in the proportion of 1-acetylanthracene to 30%, at the expense of the 9-isomer. In one experiment a trace of 1,5-diacetylanthracene was observed, but 2-acetylanthracene was not found. The formation of a high proportion of 9-acetylanthracene in these reactions can be considered to be analogous to the observation⁴ that acetylation in the presence of iodine leads to high proportions of methyl *o*-tolyl ketone in the reactions between toluene and acetyl chloride (35%), acetyl bromide (48%), or acetic anhydride (29%). It would follow¹⁷ that, under these conditions, the effective acylating reagent has low steric requirements, and may be (or approach) the free acyl cation.

Experimental.—Infrared spectra were measured on a Grubb-Parsons model GS3 spectrometer, and ultraviolet spectra on an Optika CF4NI recording spectrophotometer. Thin-layer chromatography was carried out as described earlier,⁵ using silica gel G and a one-dimensional single- or double-development technique. Separations in the acetylation experiments were effected using 9:1 carbon tetrachloride-diisobutyl ketone, which gave the following typical R_F values, relative to 9-acetylanthracene: 1,5-diacetylanthracene 0.2, 2-acetylanthracene 0.6, 1-acetylanthracene 0.8, 9-acetylanthracene 1.0.

9-Benzoylanthracene. (a) *General method with ethylene chloride.* A mixture of anthracene (4.5 g., 0.05 mole), the catalyst (I₂ or ICl) (0.005 mole), benzoyl chloride (or benzoic anhydride) (0.055 mole), and ethylene chloride (60 ml.) was boiled under reflux for 7 hr. The mixture was cooled, 6*N*-hydrochloric acid (100 ml.) added with stirring, any undissolved solid (*i.e.*, anthracene) filtered off, the organic layer (to which a chloroform washing of the precipitated solid had been added) separated, washed with aqueous sodium hydrogen sulphite, *N*-sodium hydroxide, and water, and evaporated to dryness. The yield of 9-benzoylanthracene in the residue was determined (generally in duplicate) using the C=O band at 1670 cm.⁻¹ (CCl₄), as described earlier.⁵ The purity of the ketone was checked by thin-layer chromatography.

In two experiments 55% hydriodic acid (0.1 ml.), purified by shaking with mercury, was added together with the catalyst, in one experiment substituted for it.

(b) *In nitrobenzene.* A mixture of anthracene (8 g., 0.045 mole), iodine (0.045 g., 0.00035 mole), benzoyl chloride (12.5 g., 0.09 mole), and nitrobenzene (16 g.) was boiled under reflux for 3 hr., then set aside for 4 hr. An excess of 6*N*-hydrochloric acid was then added with stirring, and the mixture set aside overnight. The solvent was removed by steam-distillation, the residue taken up in chloroform, and the extract washed with *N*-sodium hydroxide then with

¹⁶ P. H. Gore, *Chem. Rev.*, 1955, **55**, 229; H. F. Bassilios, M. Shawky, and A. Y. Salem, *Rec. Trav. chim.*, 1962, **81**, 679; 1963, **82**, 298.

¹⁷ P. H. Gore, *Chem. and Ind.*, 1954, 1385; *J. Org. Chem.*, 1957, **22**, 135; *Bull. Chem. Soc. Japan*, 1962, **35**, 1627; P. H. Gore in "Friedel-Crafts and Related Reactions," ed. G. A. Olah, John Wiley (Interscience), New York and London, 1964, vol. III, p. 65.

water, dried (Na_2SO_4), and evaporated to dryness. The residue was chromatographed on alumina (Spence, Type H) in benzene giving, after an initial band containing anthracene, a yellow main band, which afforded the high-melting modification of 9-benzoylanthracene (8.6 g., 68%), from benzene-light petroleum, m. p. 161–162°, undepressed by admixture with an authentic specimen.⁵

(c) *Without solvent.* A mixture of anthracene (8 g., 0.045 mole), iodine (0.045 g., 0.00035 mole), and benzoyl chloride (7.5 g., 0.054 mole) was heated under reflux to 230° for 5 hr. The mixture was allowed to cool, the product dissolved in chloroform, excess of 3*N*-hydrochloric acid added with stirring, and the product separated and purified by chromatography, in the usual manner, to give high-melting 9-benzoylanthracene (7.0 g., 55%) from benzene-light petroleum, m. p. 163–164°, undepressed by admixture with the above specimen. Thin-layer chromatography showed the absence of 1- and 2-benzoylanthracenes and of 9,10-dibenzoylanthracene.

Acetylation of anthracene. (a) A mixture of anthracene (8.9 g., 0.05 moles), iodine (0.64 g., 0.005 mole), acetic anhydride (6.0 g., 0.06 mole), and ethylene chloride (50 ml.) was boiled under reflux for 7 hr. After cooling, the mixture was treated with an excess of 6*N*-hydrochloric acid, and the product isolated in the usual way. Chromatography on alumina from benzene gave several fractions containing ketonic components (thin-layer chromatography); these were combined, and separated quantitatively by preparative thin-layer chromatography, and estimated by ultraviolet spectroscopy. Total yield of ketone was 4.8 g. (43%); estimated proportions: 1-acetylanthracene (99%), λ_{max} (EtOH): 2410, 2550, 3640, and 3850 Å, λ_{inf} 3490 Å (ϵ 61,600, 68,900, 5500, 6050, and 4300) and 9-acetylanthracene (91%), λ_{max} (EtOH): 2530, 3300, 3480, 3630, and 3800 Å (ϵ 128,000, 2650, 5950, 7900, and 6800).

(b) Reaction carried out as for (a), but on half-scale, and using iodine monochloride (0.12 ml., 0.0025 mole). Total yield of ketones was 3.4 g. (62%); estimated proportions: 1-acetylanthracene (1.7%), 9-acetylanthracene (98%), and 1,5-diacetylanthracene (trace).

(c) Reaction carried out as for (a), on half-scale, with addition of 55% hydriodic acid (0.1 ml., *ca.* 0.0005 mole), which had been purified by shaking with mercury. Total yield of ketones was 2.2 g. (40%); estimated proportions: 1-acetylanthracene (30%) and 9-acetylanthracene (70%).

The gift by Dr. H. F. Bassilios of a specimen of 1,5-diacetylanthracene is gratefully acknowledged.

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1068. α -Ethoxy-4-nitrophenylacetic Acid and a New Mixed Acetal of 4-Nitrobenzaldehyde

By B. WLADISLAW and A. GIORA

It has been recorded¹ that the anodic methoxylation of α -alkoxyphenylacetic acids leads to the benzaldehyde and benzophenone simple and mixed acetals. There is good reason to believe that the reaction proceeds through the intermediate carbonium ion which is stabilised by alkoxy-groups.²⁻⁵

An exploratory investigation of the electrolysis of the ring-substituted phenylacetic acids has shown that the 4-methoxyphenylacetic acid gave *ca.* 90% of the methoxylation

¹ B. Wladislaw and A. M. J. Ayres, *J. Org. Chem.*, 1962, **27**, 281.

² E. J. Corey, N. L. Bauld, R. T. La Londe, J. Casanova, and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1960, **82**, 2645.

³ B. Wladislaw, *Chem. and Ind.*, 1962, 1868.

⁴ L. Ebersson, *Acta Chem. Scand.*, 1963, **17**, 1196.

⁵ W. A. Bonner and F. D. Mango, *J. Org. Chem.*, 1964, **29**, 430.

products,⁶ whilst the 4-nitrophenylacetic acid afforded mainly 4,4'-dinitrobiphenyl and only 16% of the methoxylation product.⁷

It was of interest to study the effect of the α -alkoxy-groups on the electrolysis of the ring-substituted phenylacetic acids, especially by carbonium-ion destabilising groups, in order to find out to what extent this electrolytic method could be applied to the synthesis of ring-substituted acetals.

α -Ethoxy-4-nitrophenylacetic acid has been chosen as a suitable compound for the preliminary study. The synthesis of this hitherto unreported acid was attempted by several routes, but the only successful method was the nitration of α -ethoxyphenylacetic acid.

The electrolysis of α -ethoxy-4-nitrophenylacetic acid in methanol afforded, as the only identified product, 4-nitrobenzaldehyde methyl ethyl acetal in 50% yield.

This result indicates that the introduction of an α -methoxy-group into the 4-nitrophenylacetic acid increases the yield of the methoxylation product and suppresses the normal Kolbe coupling.

Anodic syntheses of other ring-substituted simple and mixed acetals are being carried out.

Experimental.—*Reaction of 4-nitromandelic acid with ethyl iodide and silver oxide.* A mixture of 4-nitromandelic acid⁸ (2 g.), ethyl iodide (12.5 g.), and silver oxide (6.2 g.) was allowed to react at room temperature, and then heated under reflux for 1 hr. To the residual oil (2 g.), which was isolated by means of ether, glacial acetic acid (12.4 ml.) and 28% of sulphuric acid (1.24 ml.) were added. The mixture was refluxed for 4 hr. and poured into water to give 4-nitrobenzoic acid (1.6 g., 88%), m. p. and mixed m. p. 240—243°.

Reaction of ethyl α -bromo-4-nitrophenylacetate with sodium ethoxide. α -Bromo-4-nitrophenylacetic acid, m. p. 111—112°, was obtained in 71% yield by reaction of 4-nitrophenylacetic acid with bromine and phosphorus trichloride. (The method of Heyns and Schultze⁹ gives only 50% yield.)

Esterification of this acid (3 g.) by boiling with dry ethanol (100 ml.) containing 3% of sulphuric acid gave *ethyl α -bromo-4-nitrophenylacetate* (3 g., 90%), b. p. 172°/1 mm. (Found: C, 41.9; H, 3.5; Br, 27.9. $C_{10}H_{10}BrNO_4$ requires C, 41.7; H, 3.5; Br, 27.7%).

To a solution of sodium (2.89 g.) in absolute ethanol (110 ml.), cooled in an ice-bath, ethyl 4-nitrophenylacetate (30 g.) was added, dropwise, with stirring. The mixture was allowed to come slowly to the room temperature, refluxed for 3 hr., poured into crushed ice, and then extracted with ether. Evaporation of the ether left a yellow oil, free from bromine. After three crystallisations from ethanol it gave *ethyl 4,4'-azoxymandelate* as a yellow solid (9 g.), m. p. 118—119° (Found: C, 59.9; H, 4.9. $C_{20}H_{22}N_2O_7$ requires C, 59.7; H, 5.4%).

α -Ethoxy-4-nitrophenylacetic acid. α -Ethoxyphenylacetic acid¹⁰ (13 g.) was added gradually with stirring, to fuming nitric acid (85 ml.) at -18 to -20° and then poured on to crushed ice. The oily product was extracted with ether, from which the acid was removed by a saturated solution of potassium hydrogen carbonate. Acidification with 10% hydrochloric acid gave an oil which was extracted with ether. The ethereal solution was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to give an oil which could not be crystallised.

From this product (5 g.) the *S*-benzylisothiuronium salt (8.5 g., 96%), m. p. 142—143° (from water) was prepared in the usual way

This salt (9 g.) was hydrolysed with 10% hydrochloric acid (20 ml.) to give *α -ethoxy-4-nitrophenylacetic acid* (3 g., 55%), which did not crystallise (Found: C, 53.8; H, 5.3%; neut. Equiv., 217. $C_{10}H_{11}O_5$ requires C, 53.3; H, 4.9%; neut. Equiv., 225). The infrared spectrum showed a strong band at 1100 cm^{-1} (C—O—C antisym str.) in addition to two typical nitro-group bands at 1517 and 1347 cm^{-1} .

Oxidation of ethyl α -ethoxy-4-nitrophenylacetate. α -Ethoxy-4-nitrophenylacetic acid (1.2 g.) was esterified by means of absolute ethanol, saturated with dry hydrochloric acid. The

⁶ B. Wladislaw and H. Viertler, *Chem. and Ind.*, 1965, 39.

⁷ B. Wladislaw and A. Giora, *J.*, 1964, 1037.

⁸ G. Heller, *Ber.*, 1913, **46**, 285.

⁹ H. Heyns and H. Schultze, *Annalen*, 1958, **611**, 55.

¹⁰ A. McKenzie, *J.*, 1899, 753.

solution, worked up in the usual way, gave *ethyl α -ethoxy-4-nitrophenylacetate* (1.2 g., 88%), b. p. 160°/1 mm. (Found: C, 56.7; H, 5.8. $C_{12}H_{15}O_5N$ requires C, 56.9; H, 5.9%).

To this ester (0.24 g.), acetic acid (3 ml.) and hydrogen peroxide (6 ml.) were added, and the mixture was refluxed for 6 hr. The solid which deposited after cooling was removed and washed with ice-water. Crystallisation from benzene gave 4-nitrobenzoic acid (0.16 g., 100%), m. p. and mixed m. p. 242—243°.

Electrolysis of α -ethoxy-4-nitrophenylacetic acid. The acid (2.85 g.), in methanol (60 ml.) containing sodium (0.01 g.) was electrolysed, as previously described,¹ by passage of a current of 1 A for 55 min. The methanolic solution, filtered from an insoluble dark material, was evaporated under reduced pressure. The residue was dissolved in ether, the mixture filtered from a dark polymeric material, and the solution evaporated. Distillation *in vacuo* of the residue yielded 4-nitrobenzaldehyde methyl ethyl acetal (1.3 g., ca. 50%), b. p. 134°/0.4 mm. (Found: C, 56.8; H, 6.0; N, 6.4. $C_{10}H_{13}NO_4$ requires C, 56.9; H, 6.2; N, 6.6%).

The infrared spectrum showed a typical acetal series of four bands in the region 1060—1210 cm^{-1} ,¹¹ which was identical with that of an authentic specimen of the 4-nitrobenzaldehyde diethyl acetal.

A small sample of the mixed acetal was refluxed with 5% hydrochloric acid and cooled to give 4-nitrobenzaldehyde, m. p. and mixed m. p. 105°.

The authors are indebted to "Conselho Nacional de Pesquisas" and "Fundação de Amparo à Pesquisa do Estado de São Paulo" for financial assistance.

The infrared spectra were measured on a Perkin-Elmer 221 spectrophotometer by Dr. G. Vicentini.

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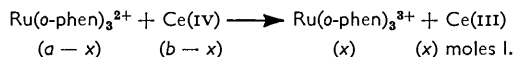
¹¹ E. D. Bergman and S. Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161.

1069. *The Kinetics of Oxidation of the Ruthenium(II)-Tris-o-Phenanthroline Complex by Cerium(IV)*

By J. D. MILLER and R. H. PRINCE

THE oxidation of ferroin and some substituted ferroins by cerium(IV) in 0.50*F*-sulphuric acid has been studied by Dulz and Sutin,¹ who found that the second-order rate constants and the activation energies for the oxidation of the various ferrous complexes decreased as the formal oxidation potential of the complex increased. We have found that the kinetic data for the oxidation of the ruthenium(II)-tris-o-phenanthroline complex by cerium(IV) in 0.50*M*-sulphuric acid show an extension of these dependences.

The reaction was followed optically at 452 $m\mu$ by means of a rapid-mixing device, injecting reactant solution into a Unicam S.P. 600 spectrophotometer adapted to enable a pen recorder to be used, as previously described.² Since the ruthenium(III) complex can be prepared³ by the oxidation of the ruthenium(II) complex by cerium(IV), and the experimental results fit the equation given below, the oxidation studied has the stoicheiometry



for which the rate expression is:

$$kt(b-a) = \ln \left\{ \frac{a}{b} \left[\frac{\varepsilon(b-a) + \Delta}{\Delta} \right] \right\}$$

¹ G. Dulz and N. Sutin, *Inorg. Chem.*, 1963, **2**, 917.

² D. N. Hague, Ph.D. Thesis, Cambridge, 1963.

³ F. P. Dwyer and E. C. Gyarfás, *J. Proc. Roy. Soc. New South Wales*, 1949, **83**, 184.

where ϵ is the extinction coefficient at 452 m μ of the Ru(II) complex,⁴ taken to be $(1.85 \pm 0.02) \times 10^4$ l. mole⁻¹ cm.⁻¹; Δ is the optical density at time t minus that at infinite time. This equation is derived from the standard second-order rate equation,⁵ on the assumptions that the extinction coefficient of the ruthenium(II) complex is very much greater than that of any other species present, and that the oxidation goes essentially to completion. These assumptions are supported by the observation that the optical density, at 542 m μ , of the reaction solution drops almost to zero at times sufficiently long after initiation.

From studies over a temperature range from 15.5° to 40.0° and a range of initial cerium(IV) concentrations from 6.12×10^{-5} to 2.04×10^{-5} moles/l., with an initial complex concentration of 9.3×10^{-6} moles/l., we find that $k = (5.8 \pm 0.5) \times 10^3$ l. mole⁻¹ sec.⁻¹ at 25.0° and that the activation energy of the reaction is 4.9 ± 0.3 kcal./mole. These results are strictly comparable with those for the ferrous complexes previously studied.¹ For example, the activation energy appears to vary linearly with the formal oxidation potential of the complex as shown in the Table.

Reductant	Oxidation potential of complex (volts)	Activation energy (kcal./mole)
Aquo ferrous ion	0.68 (ref. 6)	9.5 (ref. 1)
Fe(<i>o</i> -phen) ₃ ²⁺	1.08 (ref. 7)	6.5 (ref. 1)
Ru(<i>o</i> -phen) ₃ ²⁺	1.27 (ref. 8)	4.9 \pm 0.3

Such a relationship is consistent with the theory of Marcus,^{9,10} if the reactions proceed through similar outer-sphere mechanisms and the heat of activation is the dominant term in the activation free energy.

The ruthenium complex was prepared by the reported procedure,¹¹ and analysed by the micro-analytical department of the Department of Organic, Inorganic and Theoretical Chemistry of Cambridge University (Found: C, 49.9; H, 3.2; Cl, 9 ± 1 . Calc. for Ru(*o*-phen)₃(ClO₄)₂.H₂O: C, 49.8; H, 3.0; Cl, 8.3%)

Solutions of oxidant were prepared by dissolving AnalaR ammonium ceric sulphate in AnalaR molar sulphuric acid.

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⁴ C. V. Banks and J. W. O'Laughlan, *Analyt. Chem.*, 1957, **29**, 1412.

⁵ See, e.g., D. R. Stranks, "Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience, New York, 1960, p. 96.

⁶ G. F. Smith, *Analyt. Chem.*, 1951, **23**, 925.

⁷ W. W. Brandt and G. F. Smith, *Analyt. Chem.*, 1949, **21**, 1313.

⁸ F. P. Dwyer, *J. Proc. Roy. Soc. New South Wales*, 1949, **83**, 134.

⁹ R. A. Marcus, *Discuss. Faraday Soc.*, 1960, **29**, 21.

¹⁰ R. A. Marcus, *Canad. J. Chem.*, 1959, **37**, 155.

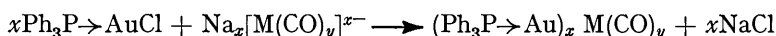
¹¹ F. P. Dwyer, J. E. Humpoletz, and R. S. Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1947, **80**, 212.

1070. *Metathetical Reactions of (Tertiary phosphine)monohalogenogold(I): Synthesis and Properties of (Triphenylphosphine sulphide)monochlorogold(I)*

By I. M. KEEN

Some metathetical reactions of trialkyl- and triaryl-phosphine-monohalogenogold(I) complexes, $R_3P \rightarrow AuCl$, are examined and compared with those of $R_3PS \rightarrow AuCl$. Thus, the complexes $R_3P \rightarrow Au[S_2P(OC_3H_7)_2]$ ($R = Ph$) and $R_3P \rightarrow AuSCH_2Ph$ ($R = Bu^u$ or Ph) have been synthesised.

TRIETHYLPHOSPHINEMONOCHLOROGOLD(I), $Et_3P \rightarrow AuCl$, reacts with the disodium salt of toluene-3,4-dithiol in warm ethanol to give the stable derivative, $C_6H_3(CH_3)(SAuPEt_3)_2$.¹ $Et_3P \rightarrow AuBr$, however, is ultimately reduced to gold on prolonged heating with sodium nitrite. The colourless organic compounds of gold(I) of the form $RAuPR'_3$ ($R = Me, Et, Ph$, or $C \equiv CPh$; $R' = Et$ or Ph) have been synthesised from the tertiary phosphine-monohalogenogold(I) complexes and the appropriate organolithium reagent in ether.² Recently Nyholm and his collaborators³ have shown that triphenylphosphinemonochlorogold(I), $Ph_3P \rightarrow AuCl$, reacts smoothly with various carbonyl anions at room temperature in tetrahydrofuran, according to the general equation:



where $M = Mn$ ($x = 1, y = 5$), Fe ($x = 2, y = 4$), and Co ($x = 1, y = 4$).

The present work extends the scope of the metathetical reaction. Thus, $R_3P \rightarrow AuCl$ ($R = Bu^u$ or Ph) reacts readily with alkali-metal salts of *OO*-di-isopropyl hydrogen phosphorodithioate and toluene- ω -thiol in dry ethanol to give the stable $R_3P \rightarrow AuS_2P(OPr^i)_2$ and $R_3P \rightarrow AuSCH_2Ph$. Further, $Ph_3P \rightarrow AuCl$ reacts slowly with silver thiocyanate in both boiling acetone and benzene to give $Ph_3P \rightarrow AuSCN$. Attempted metatheses of $Ph_3P \rightarrow AuCl$ with hot, ethanolic sodium acetate and ethoxide brought about rapid decomposition to a gold mirror; the complex is normally stable in boiling ethanol. The isolation of sodium chloride from these mixtures indicated metatheses.

Triphenylphosphine sulphide reacts with methanolic ammonium chloroaurate at room temperature to give orange $Ph_3PS \rightarrow AuCl_3$. Similarly, its reaction with sulphite-reduced ammonium chloroaurate in cold aqueous ethanol yields colourless (triphenylphosphine sulphide)monochlorogold(I), $Ph_3PS \rightarrow AuCl$. This quantitatively decomposes in ethanol at room temperature in the presence of *S*-potassium *OO*-di-isopropylphosphorodithioate, giving triphenylphosphine sulphide and gold.

The easy replacement of the chlorine in monomeric $R_3P \rightarrow AuCl$ ($R = alkyl$) depends on electron-withdrawal from the gold-chlorine bond. This is assured by π -bonding between the filled metal and vacant phosphorus *d*-orbitals, and nucleophilic attack at the gold is made easier. It is tentatively suggested that repulsion between non-bonded sulphur electrons and the gold *d*-orbitals minimises the synergic σ - π -bonding in $R_3PS \rightarrow AuCl$. Hence, preferential decomposition to R_3PS and failure to undergo metatheses might be expected. This effect may be compared with the instability and displacement reactions of (diethyl sulphide)monochlorogold(I), $Et_2S \rightarrow AuCl$. Stronger donors, *e.g.*, pyridine, readily displace the diethyl sulphide to form more stable complexes.⁴

¹ F. G. Mann and D. Purdie, *J.*, 1940, 1235.

² G. E. Coates and C. Parkin, *J.*, 1962, 3220.

³ C. E. Coffey, J. Lewis, and R. S. Nyholm, *J.*, 1964, 1741.

⁴ P. C. Ray and D. C. Sen, *J. Indian Chem. Soc.*, 1930, **7**, 67.

EXPERIMENTAL

All complexes, $R_3P \rightarrow AuX$, show bands in the 400—5000 cm^{-1} region characteristic of the R_3P and X groups.

Tributyl- and triphenyl-phosphinemonochlorogold(I) were synthesised by standard methods.⁵ (*Triphenylphosphine sulphide*)monochlorogold(I).—Triphenylphosphine sulphide was prepared by the action of dibenzoyl disulphide on triphenylphosphine in boiling toluene.⁶ Ammonium chloroaurate (0.025 mole) in methanol (600 ml.) and water (400 ml.) was stirred at $<10^\circ$ and the solution saturated with ammonium chloride before carefully reducing to gold(I) with aqueous sulphite. Ethanolic triphenylphosphine sulphide (0.025 mole) was promptly added to this at *ca.* 5° giving a grey (gold-contaminated) solid. This was recrystallised from ethanol giving colourless plates (4.9 g., 37%) decomposing above 130° on heating. [Found: C, 40.9; H, 3.0; Cl, 6.9; P, 5.7; S, 5.9%; *M* (benzene), 530. $C_{18}H_{15}AuClPS$ requires C, 41.0; H, 2.8; Cl, 6.7; P, 5.9; S, 6.1%; *M*, 527], far-infrared bands at 369w, 350w, 339s, 334sh, 327w cm^{-1} .

(*Triphenylphosphine sulphide*)trichlorogold(III).—Ethanolic triphenylphosphine sulphide was added to well-stirred ethanolic ammonium chloroaurate at room temperature. The orange precipitate was recrystallised from benzene–chloroform as needles, m. p. *ca.* 140° , in poor yield [Found: C, 35.9; H, 2.8; Cl, 17.7; P, 5.1; S, 5.8%; *M* (benzene), 603. $C_{18}H_{15}AuCl_3PS$ requires C, 36.1; H, 2.5; Cl, 17.8; P, 5.2; S, 5.4%; *M*, 598] far-infrared triplet band at 362s, 343s, 328s cm^{-1} . The product is decomposed to gold by most boiling solvents.

Triphenylphosphine-(*OO-di-isopropylphosphorodithio*)gold(I).—Ethanolic potassium *OO*-di-isopropylphosphorodithioate (14.4 mmoles) was slowly added to a refluxing solution of $Ph_3P \rightarrow AuCl$ (7.2 mmoles) in chloroform (80 ml.)–dry ethanol (240 ml.). After 1–5 hr. the mixture was filtered from potassium chloride and evaporated to *ca.* 50 ml. On cooling, the product separated as colourless plates (4.4 g., 91%). Recrystallisation from ethanol gave plates, m. p. 139 – 140° [Found: C, 43.1; H, 4.4; P, 9.1; S, 9.5%; *M* (chloroform), 671. $C_{24}H_{20}AuO_2P_2S_2$ requires C, 42.5; H, 4.4; P, 9.2; S, 9.5%; *M*, 673] far-infrared bands at 369w, 355m, 281w, 260w, 253w, and 225w cm^{-1} .

A similar preparation, using $Ph_3P \rightarrow AuCl$ (9.3 mmoles) and sodium benzylthioate (18.4 mmoles), gave colourless crystals (4.2 g., 74%) of *triphenylphosphine*(benzylthio)gold(I). Recrystallisation from ethanol gave fine, prismatic needles, m. p. 132 – 133° [Found: C, 51.6; H, 3.9; P, 5.3; S, 5.5%; *M* (benzene), 683. $C_{25}H_{22}AuPS$ requires C, 51.5; H, 3.8; P, 5.3; S, 5.3%; *M*, 582], far-infrared bands at 340s, 286w, 233w $br\ cm^{-1}$.

Tri-n-butylphosphine(benzylthio)gold(I).—Ethanolic $Bu^*_3P \rightarrow AuCl$ and a slight excess of sodium benzylthioate gave, on boiling off all solvent, a viscous orange oil, purified by washing its chloroform solution with water [Found: C, 40.4; H, 5.7; Au, 36.9, 38.4. $C_{19}H_{34}AuPS$ requires C, 43.6; H, 6.6; Au, 37.7%], far-infrared band at *ca.* 340vw cm^{-1} . The product decomposes near its boiling point at *ca.* 0.01 mm.

The author thanks Professor G. Wilkinson and Dr. W. R. McWhinnie (Queen Elizabeth College, London) for measurement of molecular weights and far-infrared spectra, respectively.

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⁵ F. G. Mann, A. F. Wells, and D. Purdie, *J.*, 1937, 1828.

⁶ A. Schonberg, *Ber.*, 1935, 68, 163.

1071. An Anionic Chloroperoxy-complex of Chromium(VI)

By D. G. TUCK and (in part) B. D. FAITHFUL

THE compound known as perchromic acid, and usually formulated as CrO_5 , in fact exists as an adduct with some donor molecule^{1,2} in all the systems investigated. In some cases, these addition compounds are solid at room temperature, and X-ray-crystallographic examination of the pyridine adduct^{3,4} has shown that the structure is essentially that predicted on the basis that the two peroxy-groups are bonding to the metal through their π - and π^* -orbitals.² The co-ordination of the metal is completed by the pyridine nitrogen, and an oxygen atom, which from the bond length (Cr-O distance^{3,4} $1.72 \pm 0.05 \text{ \AA}$, 1.64 \AA) must be bonded essentially as in the chromate anion (Cr-O distance⁵ $1.60\text{--}1.64 \text{ \AA}$).

An apparently related anionic chromium(VI) peroxy-species has been reported by Dwyer and Gibson⁶ as $\text{Ph}_3\text{MeAsCrO}_6$, a stable blue solid. These authors noted, however, the difficulties implicit in this formulation, in that, although the compound contained two peroxy-groups and was monomeric in chloroform, it showed only a weak temperature-independent paramagnetism, and therefore contained Cr^{VI} and not Cr^{V} , despite the impossibility of balancing the charges in these circumstances. These problems are resolved if the anion is in fact $[\text{CrO}(\text{O}_2)_2\text{Cl}]^-$, as the preparative route suggests, and the preparation of $\text{Ph}_4\text{As}[\text{CrO}(\text{O}_2)_2\text{Cl}]$ by a method similar to that used by Dwyer and Gibson is now reported.

Addition of a solution of tetraphenylarsonium hydrogen dichloride to potassium dichromate in dilute sulphuric acid produced a voluminous yellow precipitate. This was found to be tetraphenylarsonium chlorochromate, which is insoluble in aqueous acid, dissolves in alkali to give chromate, and is readily soluble in chloroform, acetone, ethyl acetate, and similar solvents. The infrared spectrum showed, in addition to the many bands of the cation, absorptions at 910m, 950vs and 434s cm^{-1} . Following Stammreich, Sala, and Kawai,⁷ the first two of these we assign to the symmetric and antisymmetric stretches of the Cr-O bonds, and the band at 434 cm^{-1} to the Cr-Cl stretching mode. Although Dwyer and Gibson⁶ did not isolate the corresponding product in their preparation, it is clear from the known solvent-extraction properties of such systems⁸ that chloroform would have extracted $\text{Ph}_3\text{MeAsCrO}_3\text{Cl}$ under the aqueous-phase conditions used by them.

In accordance with the method of Dwyer and Gibson, $\text{Ph}_4\text{AsCrO}_3\text{Cl}$ in chloroform-ethyl acetate solution was treated with ice-cold 30% hydrogen peroxide. The resulting blue organic solution yielded royal-blue crystals, which were soluble in the common organic solvents, insoluble in acid, and which decomposed in aqueous alkali with the evolution of oxygen to give chromate. Analysis showed that the solid was the tetraphenylarsonium salt of the $[\text{CrO}(\text{O}_2)_2\text{Cl}]^-$ anion. The conductivity in nitromethane shows that the substance is a 1:1 electrolyte in this solvent. The retention of the Cr-Cl bond during the $\text{CrO}_3\text{Cl}^- \rightarrow [\text{CrO}(\text{O}_2)_2\text{Cl}]^-$ substitution reaction is worth noting; in previous work, a similar stability of this bond in a process involving reduction and change of co-ordination number $\{\text{CrO}_3\text{Cl}^- \rightarrow [\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}\}$ was reported.⁹

Absorptions due to the anion in the infrared spectrum of $\text{Ph}_4\text{AsCrO}(\text{O}_2)_2\text{Cl}$ were detected at 940s, 950s, and 430m cm^{-1} , of which the latter is clearly the Cr-Cl stretch. One of the two higher-frequency bands must be the Cr=O stretch (cf. the chlorochromate spectrum

¹ D. F. Evans, *J.*, 1957, 4013.

² D. G. Tuck and R. M. Walters, *Inorg. Chem.*, 1963, 2, 428; D. G. Tuck, *J. Inorg. Nuclear Chem.*, 1964, 26, 1525.

³ R. Stomberg, *Nature*, 1962, 196, 570.

⁴ B. F. Pedersen and B. Pedersen, *Acta Chem. Scand.*, 1963, 17, 557.

⁵ A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, 3rd edn., 1962, p. 443.

⁶ F. P. Dwyer and N. A. Gibson, *Chem. and Ind.*, 1953, 153.

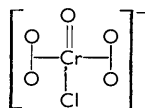
⁷ H. Stammreich, O. Sala, and K. Kawai, *Spectrochem. Acta*, 1961, 17, 226.

⁸ R. M. Diamond and D. G. Tuck, *Prog. Inorg. Chem.*, 1960, 2, 109.

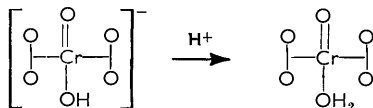
⁹ D. G. Tuck and R. M. Walters, *J.*, 1963, 4712.

above). The other band has not been assigned; it may be the O—O stretch of the peroxy-group, or a stretching vibration of Cr—peroxy-oxygen.

By analogy with the $[\text{CrO}_5\text{py}]$ compound, the structure suggested for the chloro-peroxy anion is



and the preparation of other such $[\text{CrO}(\text{O}_2)_2\text{X}]^-$ anions should be possible. Griffith¹⁰ has already reported that the "violet perchromate" salts contain the anion $[\text{CrO}(\text{O}_2)_2\text{OH}]^-$, which is clearly the analogue with $\text{X} = \text{OH}$. In aqueous solution, acid was shown¹⁰ to convert the anion into perchromic acid, which was identified by extraction into ether; from the above and earlier² arguments, the reaction in the aqueous phase occurring here can be represented as



Experimental.—Spectra. Infrared spectra of the solids (Nujol mulls) in sodium chloride and caesium iodide cells were recorded with a Perkin-Elmer 521 spectrophotometer over the range 4000—250 cm^{-1} .

Tetraphenylarsonium chlorochromate (vi). Tetraphenylarsonium hydrogen dichloride (2 g.) (Messrs. Light Ltd.) in concentrated (10% w/v) aqueous solution was added slowly to AnalaR potassium dichromate (1 g.) dissolved in 0.05M-sulphuric acid (50 ml.). The precipitate was filtered off, washed with dilute sulphuric acid, sucked dry, and recrystallised from chloroform-acetone.

The determination of chromium in this, and in the chloroperoxy-compound, is complicated by their insolubility in aqueous acid. In the method finally adopted, dissolution in alkaline solution was followed by reduction of chromium(vi) with sulphur dioxide; after removal of the excess of reducing agent by acidification and boiling, chromium(III) hydroxide was precipitated with warm aqueous sodium hydroxide and filtered off. Chloride ion in the filtrate was determined by titration with silver nitrate; the chromium(III) hydroxide was subsequently oxidised with potassium persulphate and the chromium determined titrimetrically with ferrous iron [Found C (micro-analysis), 54.6; H, 3.9; Cl, 6.8; Cr, 9.8. $\text{C}_{24}\text{H}_{20}\text{AsClCrO}_3$ requires C, 55.5; H, 3.9; Cl, 6.85; Cr, 10.0%].

Tetraphenylarsonium chlorodiperoxychromate(vi). Ice-cold 30% hydrogen peroxide (50 ml.) was added dropwise to tetraphenylarsonium chlorochromate (1 g.) in chloroform-ethyl acetate solution. The resultant blue solution was separated and dried over anhydrous sodium sulphate; addition of cold light petroleum gave crystals, which were washed with more light petroleum and dried *in vacuo* over sulphuric acid.

Peroxide analysis involved (slow) decomposition in contact with potassium permanganate solution, followed by back-titration with ferrous ion [Found C, 52.4; H, 3.8; Cl, 6.3; Cr, 9.5%; 2.3 ± 0.5 peroxide groups per Cr. $\text{C}_{24}\text{H}_{20}\text{AsClCrO}_5$ requires C, 52.3; H, 3.6; Cl, 6.45; Cr, 9.45%; 2.0 peroxide groups].

The molar conductivity of a 0.0008M-solution in nitromethane was 97 $\text{ohm}^{-1} \text{cm}^2$; values of 70—90 and 120—130 $\text{ohm}^{-1} \text{cm}^2$ have been reported¹¹ for 1 : 1 electrolytes in this solvent.

The analytical method for chromium was suggested to us by Dr. W. E. Addison. We thank the D.S.I.R. for the award of a Research Studentship (to B. D. F.), and Mr. A. J. Carty and Dr. E. J. Woodhouse for experimental assistance.

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¹⁰ W. P. Griffith, *J.*, 1962, 3948.

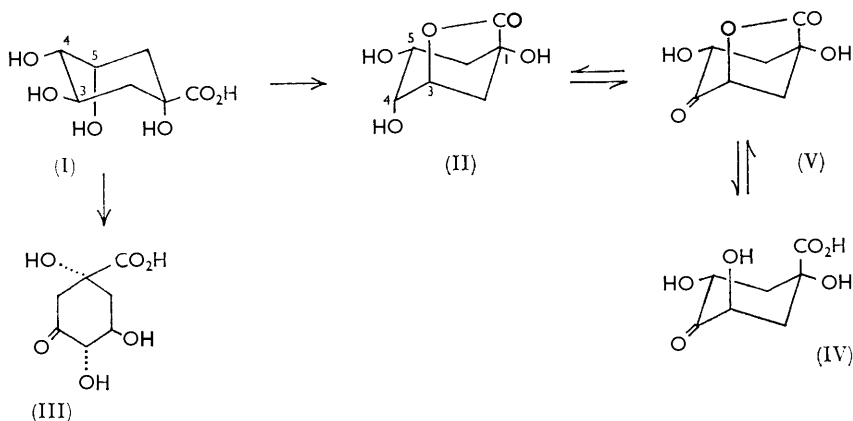
¹¹ R. S. Nyholm and R. V. Parish, *Chem. and Ind.*, 1956, 470; J. E. Fergusson and R. S. Nyholm, *Nature*, 1959, 183, 1039.

1072. 4-Dehydroquinic acid

By E. HASLAM and J. E. MARRIOTT

QUINIC acid (I), although not commonly found in bacteria, is widely distributed in the plant community¹ but its role there in carbohydrate metabolism has not been examined in great detail.² The acid is utilised in microbial aromatic metabolism³ when quinic dehydrogenase is present to catalyse its oxidation to 5-dehydroquinic acid (III) and if in plants it is assimilated by alternative pathways then these may involve different modes of oxidation. The preparation and properties of 4-dehydroquinic acid (IV) which is of interest in this respect are described here.

The platinum-catalysed dehydrogenation of secondary hydroxyl groups in the cyclitols⁴ is similar to bacterial oxidation⁵ in its stereospecificity since only axial groups are affected and it has been suggested that this selectivity is derived in both cases from a preferential mode of adsorption of the substrate on the "catalytic" surface. Catalytic dehydrogenation of quinic acid (I) thus gives 5-dehydroquinic acid (III) exclusively.^{6,7} Conversion of quinic acid into quinide (II) must involve an inversion of the preferred conformation of quinic acid⁸ such that in quinide (II) the 4-hydroxyl group is now axially disposed. Catalytic dehydrogenation of quinide (II) gave a solution reducing both



Fehling's and sodium hypiodite solutions and from which the crystalline 4-dehydroquinic acid (IV) was isolated after treatment with base and ion-exchange chromatography. Formulation of the product as compound (IV) followed from its mode of preparation, its reduction in neutral solution to give quinic acid (I) and its infrared spectrum which showed no evidence of lactol formation. Reduction in acid media gave a mixture of acids in which 4-deoxyquinic acid was tentatively identified (thin-layer chromatography); normally this reaction proceeds with reduction of the carbonyl to a methylene group⁴ but presumably, as in the case⁹ of 1-D-myoinosose the presence of an axial hydroxyl group adjacent to the

¹ M. Hasegawa, "Wood Extractives," Academic Press, London, 1962, p. 263.

² L. H. Weinstein, C. A. Porter, and H. J. Laurencot, *Contributions Boyce Thompson Inst.*, 1959, **20**, 121.

³ B. D. Davis and I. I. Salamon, *J. Amer. Chem. Soc.*, 1953, **175**, 5567.

⁴ K. Heyns and H. Paulsen, *Adv. Carbohydrate Chem.*, 1962, **17**, 169.

⁵ B. Magasanik and E. Chargaff, *J. Biol. Chem.*, 1948, **174**, 173.

⁶ K. Heyns and H. Gottschalck, *Chem. Ber.*, 1961, **94**, 343.

⁷ E. Haslam, R. D. Haworth, and P. F. Knowles, *J.*, 1961, 1854.

⁸ H. Orloff, *Chem. Rev.*, 1954, **54**, 84.

⁹ L. Anderson and C. G. Post, *Abs. Amer. Chem. Soc. Meeting*, 1958, **134**, 12D.

carbonyl group leads in these circumstances to loss of this group also. Heating 4-dehydroquinic acid (IV) with acetic acid converted it into the lactone (V) which on reduction gave quinide (II) thus contrasting with the behaviour of the isomeric dehydroquinic acids which under similar acidic conditions aromatised. This relative stability did not extend to aqueous acidic and alkaline media where in common with its isomers (and other inososes)¹⁰ the acid was readily dehydrated to give protocatechuic acid. This lability to strong acids and bases has prevented the use of the isomeric dehydroquinic acids as intermediates in the synthesis of specifically substituted derivatives of quinic acid; thus acetylation and exchange dioxolanation both resulted in aromatisation.

Preliminary experiments showed that the acid (IV) was not readily assimilated by several micro-organisms under normal conditions of growth.

Experimental.—Paper chromatography⁷ was carried out in the system benzyl alcohol-propan-2-ol-2-methylpropan-2-ol-water-formic acid (75:25:25:25:3) at $20^\circ \pm 3^\circ$. Spray reagents used consisted of (a) sodium metaperiodate, piperazine, and sodium nitroprusside,¹¹ (b) sodium metaperiodate and an ethanolic solution of aniline,¹² and (c) Fehling's solution.

4-Dehydroquinic acid. Freshly prepared platinum (2 g.) was added to a solution of quinide (2 g.) in water (15 c.c.) at 40° and a vigorous stream of oxygen passed through the solution for 8 hr. The catalyst was then filtered off and used to oxidise more quinide (2 g.) as above. The combined solutions were treated with aqueous sodium hydroxide (0.05N; 24 c.c.), passed through a column of Zeo-Karb 215 (30 × 3 cm.; H⁺ form), concentrated to smaller bulk (15 c.c.), and adsorbed on Amberlite C.G. 400 (40 × 3 cm.; acetate form) and the acids eluted by gradient elution using a reservoir containing 6N-acetic acid (2000 c.c.) and a mixing chamber containing water (500 c.c.). Fractions (10 c.c.) were collected at the rate of 4 per hour and analysed by paper chromatography. Fractions (15—30) gave quinic acid, (55—85) gave 4-dehydroquinic acid as a gum which crystallised from acetone, as small needles (0.5 g.), m. p. 138—140° (Found: C, 43.8; H, 5.5. C₇H₁₀O₆ requires C, 44.2; H, 5.3%); ν_{\max} 3400 and 1710 cm.⁻¹; R_F 0.19.

4-Dehydroquinide. A solution of the above acid (0.2 g.) in acetic acid (10 c.c.) was heated at 100° for $\frac{1}{2}$ hr., cooled, and passed down a column of Amberlite C.G. 400 (20 × 2 cm.; acetate form). The eluate was concentrated by rotary evaporation at 30° and the lactone crystallised from acetone as needles (0.10 g.), m. p. 167—168° (Found: C, 49.2; H, 5.0. C₇H₈O₅ requires C, 48.9; H, 4.7%); ν_{\max} 3400, 1790, and 1650 cm.⁻¹; R_F 0.46. Reduction of 4-dehydroquinide over platinum and crystallisation from ethanol gave quinide, m. p. and mixed m. p. 198°.

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¹⁰ S. J. Angyal, *Quart. Rev.*, 1957, **11**, 212.

¹¹ R. A. Cartwright and E. A. H. Roberts, *Chem. and Ind.*, 1955, 231.

¹² S. Yoshida and M. Hasegawa, *Arch. Biochem.*, 1957, **70**, 377.

1073. The Reaction of Benzoyl Peroxide with Nitrogen Dioxide

By G. B. GILL and GARETH H. WILLIAMS

THE use of nitrogen dioxide as a scavenger for organic free radicals has been little investigated, although its reaction with aryl radicals might provide a useful synthetic route to specific nitro-compounds. Tilney-Bassett and Waters¹ have found that nitrogen dioxide reacts with 2-cyano-2-propyl and similar radicals to give the corresponding nitro-compounds. An analogous process with carbon monoxide, which, although not a free radical, reacts

¹ J. F. Tilney-Bassett and W. A. Waters, *J.*, 1957, 3129.

readily with organic free radicals, has been studied by Walling and Savas,² who obtained the expected products.

The results of experiments in which benzene and carbon tetrachloride were used as solvents are summarised in Tables 1 and 2, respectively. The formation of nitrobenzene

TABLE 1

Decomposition of benzoyl peroxide in benzene in the presence of nitrogen dioxide

Benzoyl peroxide (moles)	0	0.0214	0.0062	0.0124	0.0124
Nitrogen dioxide (moles)	0.0500	0	0.0531	0.0573	0.0538
Benzoic acid ^a	0	0.403	1.475	1.670	1.441
Biphenyl ^a	0	0.30	0.30	0.29	—
Phenyl benzoate ^a	0	0.05	0.03	0.06	—
Benzoic anhydride ^a	0	0.012	0.106	0.051	—
Nitrobenzene ^a	0.003	0	0.409	0.296	0.320
Residue (g./g. Bz ₂ O ₂) ^c	—	0.389 ^d	0.069	0.042	0.051

^a Moles/mole benzoyl peroxide, except where otherwise stated. ^b Moles/mole nitrogen dioxide. ^c Containing a trace of the isomeric nitrobiphenyls. ^d *p*-Quaterphenyl (0.013 mole/mole peroxide, m. p. 319°) was also isolated.

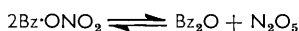
TABLE 2

Decomposition of benzoyl peroxide in carbon tetrachloride in the presence of nitrogen dioxide

Benzoyl peroxide (moles)	0.0124	0.0062	0.0124	0.0124
Nitrogen dioxide (moles)	0	0.0486	0.0609	0.0511
Chlorobenzene ^a	1.50	0.20	0.25	0.20
Terephthalic acid ^{a,b}	0.14	—	—	—
Benzoic acid ^{a,c}	0	1.356	1.205	1.391
Benzoic anhydride ^a	0	0.05	0.05	0.02
Nitrobenzene ^a	0	0.14	0.17	0.19
Hexachloroethane ^a	0.30	—	—	0.01
Residue (g./g. Bz ₂ O ₂)	0.083	0.008	0.040	0.002

^a Moles/mole benzoyl peroxide. ^b By hydrolysis of *p*-trichloromethylbenzoic acid. ^c Contaminated with a little *p*-trichloromethylbenzoic acid.

in both solvents indicates that direct combination occurs between phenyl radicals, formed from benzoyl peroxide, and nitrogen dioxide, and this is supported by the observation that *p*-dinitrobenzene is formed in similar reactions with *p*-nitrobenzoyl peroxide. Indeed, this process provides a useful synthetic route to the difficultly accessible *p*-dinitrobenzene. The high yields of benzoic acid probably arise from the reaction of benzoyloxy-radicals with nitrogen dioxide to give, initially, benzoyl nitrate, the hydrolysis of which during the working-up of the products should give benzoic acid. The presence of benzoyl nitrate is also indicated by the formation of a little benzoic anhydride, which is formed from benzoyl nitrate by reversible disproportionation:³



Any hydrolysis of benzoic anhydride which might have occurred during the working-up should, of course, also give benzoic acid. The formation of these products is indicative of the efficiency of nitrogen dioxide as a radical-scavenger, since most of the benzoyloxy-radicals combine with it before decarboxylation to phenyl radicals, although the latter process is known to be rapid, since the yields of benzoyloxylation products formed in reactions of benzoyl peroxide with aromatic solvents are generally small in comparison

² C. Walling and E. S. Savas, *J. Amer. Chem. Soc.*, 1960, **82**, 1738.

³ V. Gold, E. D. Hughes, and C. K. Ingold, *J.*, 1950, 2467.

with the yields of phenylation products.⁴⁻⁶ While it is possible that some of the nitrobenzene isolated from the reactions in benzene (Table 1) might have been formed by nitration of the solvent by dinitrogen pentoxide,³ the occurrence of direct combination of phenyl radicals with nitrogen dioxide is clearly established by the formation of nitrobenzene in reactions in carbon tetrachloride (Table 2). The other products mentioned in the Tables are readily accounted for, since they are known to be formed in the reactions of benzoyl peroxide with benzene and carbon tetrachloride, respectively, in the absence of nitrogen dioxide.⁷

Experimental.—Solvents were purified by standard methods. Benzoyl peroxide (99.98% \pm 0.02%) was purified and estimated as previously described.⁶ *p*-Nitrobenzoyl peroxide [100.05% \pm 0.05%; m. p. 156.5–157° (decomp.)], was prepared by the method of Price and Krebs.⁸

Dinitrogen tetroxide, prepared by heating anhydrous lead nitrate in steel tubes, was condensed in liquid air after passage through phosphoric oxide, redistilled in oxygen through phosphoric oxide, condensed, and sealed in ampoules. The solid product was white, indicating the absence of dinitrogen trioxide, and therefore of water.

Decomposition of diaryl peroxides in the presence of nitrogen dioxide. Benzoyl peroxide (1–3 g.), benzene (20 ml.), and an ampoule containing a known weight of dinitrogen tetroxide (~3 g.) were sealed in a Carius tube under nitrogen or carbon dioxide, or *in vacuo*. The ampoule was broken by shaking the tube, which was maintained at 80° for 72 hr. or 100° for 20 hr. in a thermostat. After being cooled to room temperature the tube was opened and the excess of nitrogen dioxide allowed to evaporate in a stream of nitrogen. Acids were then extracted as previously described.⁶ After addition of methanol (100 ml.) to the dried (CaCl₂) organic portion, the mixture was boiled under reflux for 12 hr. in order to convert any benzoic anhydride which might have been formed into benzoic acid and methyl benzoate.⁹ The excess of solvent was removed by fractional distillation, and benzoic acid was again extracted, giving the yield of the anhydride. Distillation of the dried (CaCl₂) organic portion gave several fractions which were analysed by gas chromatography (silicone elastomer column at 150°), using the method of internal normalisation, and consisted largely of nitrobenzene and biphenyl, together with a little methyl benzoate. The analysis was accurate to \pm 3%. Careful redistillation of the fractions after combination gave specimens of nitrobenzene and biphenyl which were identified by their infrared spectra, and by the refractive index (for nitrobenzene) and m. p. and mixed m. p. (for biphenyl). The mixtures obtained from similar experiments with carbon tetrachloride as solvent were treated similarly.

The reaction of *p*-nitrobenzoyl peroxide (3.00 g.) with nitrogen dioxide (2.79 g.) in carbon tetrachloride (20 ml.) was allowed to proceed *in vacuo* at 80° for 72 hr., and gave 4-nitrobenzoic acid (1.84 g., m. p. 238°), which was extracted as described above. On evaporation, the dried (CaCl₂) organic portion deposited *p*-dinitrobenzene [0.34 g.; m. p. and mixed m. p. 173° (lit., 174°)]. The infrared spectrum was identical with that of an authentic specimen, and reduction with ethanolic sodium sulphide and crystallisation of the product from acetone gave 4,4'-dinitroazobenzene, m. p. 222° (lit., 222–223°).

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⁴ D. I. Davies, D. H. Hey, and G. H. Williams, *J.*, 1961, 562.

⁵ D. H. Hey, M. J. Perkins, and G. H. Williams, *J.*, 1964, 3412.

⁶ G. B. Gill and G. H. Williams, *J.*, 1965, 995.

⁷ D. H. Hey and J. Peters, *J.*, 1960, 79.

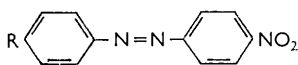
⁸ C. C. Price and E. Krebs, *Org. Synth.*, Coll. Vol. III, 649.

⁹ D. I. Davies, Ph.D. Thesis, London, 1960.

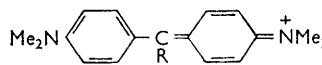
1074. A Ferrocene Analogue of Malachite Green

By C. C. BARKER, G. HALLAS, and M. N. THORNER

THE triferrocenylcarbonium ion,¹ from triferrocenylmethane and triphenylmethyl perchlorate is blue and must therefore absorb at considerably longer wavelength than the triphenylcarbonium ion,² a phenomenon consistent with the greater electron-donating power of the ferrocenyl group compared with the phenyl group. The bathochromic shift produced by the *p*-nitro-group in *p*-ferrocenyl-*p*'-nitroazobenzene (I; R = ferrocenyl) has also been associated with the electron-donating property of the ferrocenyl group.³ A ferrocene analogue of Malachite Green (II; R = ferrocenyl) has now been prepared as the dye-base which is converted into the dye in acetic acid, but the colour rapidly fades (half-life *ca.* 10 min.). Addition of 10% of ethanol to the acetic acid stabilises the dye considerably, and in ethanolic hydrogen chloride it shows little change of intensity during 2 hours.



(I)



(II)

Replacement of the phenyl group of Malachite Green (II; R = Ph) by the ferrocenyl group brings about a hypsochromic shift of the first band and a marked bathochromic shift of the second band. A similar effect is brought about by the introduction of the strongly electron-donating methoxyl group into the *para*-position of Malachite Green,⁴ and it appears that the effect of the ferrocenyl group can be associated with its electron-donating capacity. It is also relevant that the *p*-methoxy-group and the ferrocenyl group each bring about a marked increase in the intensity of the second band relative to that of the first. However, the low intensity of the first band of the ferrocene dye is not readily explained; it is not due to incomplete conversion of the dye-base into dye since the intensity is essentially unchanged on passing from 10⁻⁵M- to 10⁻³M-ethanolic hydrogen chloride as solvent. Moreover, studies⁵ of the solvolysis of α -ferrocenyl esters show that ferrocene stabilises a carbonium ion.

The dye-base was prepared by the action of *p*-dimethylaminophenyl-lithium on methyl ferrocenoate. The corresponding leuco-base was prepared by condensing ferrocenealdehyde with *NN*-dimethylaniline but attempts to oxidise it to the dye by means of lead dioxide or chloranil were unsuccessful.

Spectra of Malachite Green, its *p*-methoxy-derivative, and its ferrocene analogue

Dye	$\lambda_{\max.}$ (m μ) (10 ⁻⁴ ϵ in parentheses)
(II; R = Ph) *	621 (10.4); 427.5 (2.0)
(II; R = <i>p</i> -MeO·C ₆ H ₄) *	608 (10.6); 465 (3.4)
(II; R = ferrocenyl) †	607.5 (5.2); 457.5 (1.8)

* In 98% acetic acid. † In 5 × 10⁻⁵M-ethanolic hydrogen chloride.

Experimental.—*Di*-(*p*-dimethylaminophenyl)ferrocenylmethane. A mixture of ferrocenealdehyde (2.33 g.), *NN*-dimethylaniline (3.9 g.), ethanol (30 ml.), and 36% hydrochloric acid

¹ P. L. Pauson and W. E. Watts, *J.*, 1962, 3881.

² V. Gold and B. W. V. Hawes, *J.*, 1951, 2102.

³ W. F. Little and A. K. Clark, *J. Org. Chem.*, 1960, 25, 1979.

⁴ C. C. Barker, M. H. Bride, G. Hallas, and A. Stamp, *J.*, 1961, 1285.

⁵ E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, 1961, 83, 3840.

⁶ G. D. Broadhead, J. M. Osgerby, and P. L. Pauson, *J.*, 1958, 650.

(2.6 g.) was boiled for 20 hr. The cooled mixture was basified with aqueous-ethanolic ammonia, and the resulting solid was twice crystallised from ethanol (charcoal), giving deep yellow needles of the *leuco-base* (3.1 g.), m. p. 151—152° (Found: C, 74.3; H, 7.0; N, 6.5. $C_{27}H_{30}FeN_2$ requires C, 74.0; H, 6.9; N, 6.4%).

Di-(p-dimethylaminophenyl)ferrocenylmethanol. Etheral *p*-dimethylaminophenyl-lithium, from *p*-bromo-*NN*-dimethylaniline (2.8 g.), was filtered under nitrogen into etheral methyl ferrocenoate⁷ (0.85 g.), and the mixture was boiled for 30 min. Addition of water and removal of solvent from the dried (Na_2SO_4) organic layer yielded a solid which, twice crystallised from ethanol containing a trace of sodium hydroxide, gave orange needles of the *dye-base*, m. p. 155—156° (decomp.) (Found: C, 71.4; H, 6.9; N, 6.0. $C_{27}H_{30}FeN_2O$ requires C, 71.4; H, 6.7; N, 6.2%).

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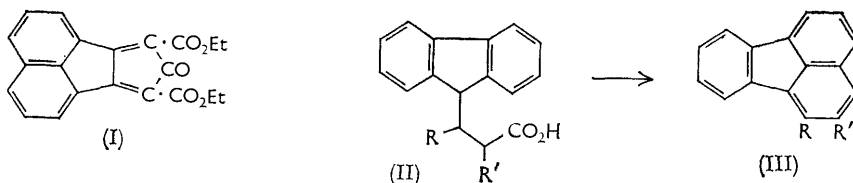
[Received, March 9th, 1965.]

⁷ W. F. Little and R. Eisenthal, *J. Amer. Chem. Soc.*, 1960, **82**, 1577.

1075. *The Monophenylfluoranthenes*

By D. A. CROMBIE and S. SHAW

Of the five possible isomeric monophenylfluoranthenes the 3- and 7-isomers have been reported.^{1,2} Syntheses are now described of the remaining isomers, which were required as reference compounds in some phenylation studies. The cyclenone³ (I) underwent Diels-Alder addition with excess of hot cinnamic acid. Loss of carbon monoxide and dehydrogenation took place during the reaction, and hydrolysis of the resulting diester gave 8-phenylfluoranthene-7,9,10-tricarboxylic acid which was decarboxylated to 8-phenylfluoranthene.



1-Phenylfluoranthene was prepared by the method of Campbell and Wang.⁴ 9-Benzyl-9-hydroxyfluorene with excess of boiling maleic anhydride gave 1-phenylfluoranthene-2,3-dicarboxylic anhydride directly. Decarboxylation, which could only be achieved by soda-lime, gave 1-phenylfluoranthene (III; R = Ph, R' = H) accompanied by a good deal of tar. 1-Phenylfluoranthene was prepared in better yield by a Michael condensation⁵ between methyl fluorene-9-carboxylate and ethyl cinnamate, followed by hydrolysis and decarboxylation of the product to β -phenyl- β -(9-fluorenyl)propionic acid (II; R = Ph, R' = H). Ring closure, Clemmensen reduction, and dehydrogenation with chloranil gave 1-phenylfluoranthene. The analogous series (R = H, R' = Ph) using ethyl atropate gave 2-phenylfluoranthene.

¹ J. Von Braun and G. Manz, *Ber.*, 1937, **70**, 1610; H. W. D. Stubbs and S. H. Tucker, *J.*, 1950, 3288.

² P. G. Copeland, R. E. Dean, and D. McNeil, *J.*, 1960, 1687.

³ S. H. Tucker, *J.*, 1958, 1462.

⁴ N. Campbell and H. Wang, *J.*, 1949, 1513.

⁵ S. H. Tucker, *J.*, 1952, 803.

That steric interference prevents coplanarity of the phenyl groups with the fluoranthene skeleton in the 1-, 3-, and 7-phenyl derivatives is confirmed by the similarity of their ultraviolet spectra and the resemblance of the spectra to that of fluoranthene.⁶ By contrast, the 2- and 8-isomers, which can adopt the planar configuration with resulting enhanced conjugation, give spectra which differ from those of the unsubstituted parent and the other isomers.^{7,8}

Ultraviolet spectra (wavelength in $m\mu$, $\log \epsilon$ in parentheses beside wavelength) of substituted fluoranthenes in ethanol

Substituent								
1-Phenyl	242 (4.61)	—	279 (4.43)	290 (4.41)	—	—	338 (4.14)	—
3-Phenyl ⁹	240 (4.65)	—	—	294 (4.43)	—	314 (3.65)	358 (4.10)	370 (4.12)
7-Phenyl	234 (4.67)	—	282 (4.26)	289 (4.32)	—	312 (3.60)	327 (3.76)	360 (3.86)
2-Phenyl	227 (4.52)	260 (4.67)	277 (4.69)	—	—	331 (4.10)	350 (4.15)	365 (4.16)
8-Phenyl	227 (4.55)	236 (4.55)	263 (4.23)	—	319 (4.89)	—	356 (3.74)	373 (3.83)

It is noteworthy that the planar 2-phenyl derivative melts at a lower temperature than do the hindered 1- and 3-isomers (cf. ref. 8).

Experimental.—*8-Phenylfluoranthene.* A mixture of the cyclenone (I) (4 g.) and cinnamic acid (12 g.) was heated at about 260° for 2 hr. and poured into ethanol (30 ml.). On cooling, the solution gave 7,10-dithoxycarbonyl-8-phenylfluoranthene-9-carboxylic acid (1.2 g.), straw-coloured needles (from acetic acid), m. p. 316—318° (Found: C, 74.9; H, 4.5. $C_{29}H_{22}O_6$ requires C, 74.7; H, 4.7%). The diester (1 g.) on being refluxed with 20% potassium hydroxide (50 ml.) for 4 hr. gave 8-phenylfluoranthene-7,9,10-tricarboxylic acid (0.7 g.), yellow needles (from acetic acid), m. p. 335—345° (Found: C, 73.0; H, 3.2. $C_{25}H_{14}O_6$ requires C, 73.2; H, 3.4%). The tricarboxylic acid (0.6 g.) was heated with soda-lime (12 g.) to red heat in a Pyrex tube. 8-Phenylfluoranthene which sublimed along the tube was isolated by chromatography (0.1 g.) as green fluorescent plates (from xylene and acetic acid), m. p. 237—238° (Found: C, 95.2; H, 5.0. $C_{22}H_{14}$ requires C, 95.0; H, 5.0%). The 1,3,5-trinitrobenzene adduct crystallised as orange needles (from benzene), m. p. 197° (Found: N, 8.3. $C_{28}H_{17}N_3O_6$ requires N, 8.5%).

1-Phenylfluoranthene. (a) A mixture of 9-benzyl-9-hydroxyfluorene (5 g.) and maleic anhydride (20 g.) was heated at 200—210° for 10 hr. and poured into acetic acid (30 ml.). On being kept overnight the solution deposited 1-phenylfluoranthene-2,3-dicarboxylic anhydride (0.6 g.) as bronze crystals (from acetic acid), m. p. 334—335° (Found: C, 82.6; H, 3.5. $C_{24}H_{12}O_3$ requires C, 82.8; H, 3.5%). The anhydride (0.3 g.) was heated with soda-lime (4 g.). Chromatography of the sublimate gave 1-phenylfluoranthene in poor yield as straw-coloured elongated plates (from acetic acid or light petroleum), m. p. 109—110° (Found: C, 95.0; H, 4.9. $C_{22}H_{14}$ requires C, 95.0; H, 5.0%). The 1,3,5-trinitrobenzene adduct crystallised from ethanol as yellow needles, m. p. 134—135° (Found: N, 8.3. $C_{28}H_{17}N_3O_6$ requires N, 8.5%).

(b) A solution of methyl fluorene-9-carboxylate (11.2 g.), ethyl cinnamate (9 g.), and sodium (0.5 g.) in dry methanol (30 ml.) on being kept overnight deposited ethyl β -phenyl- β -(9-methoxycarbonyl-9-fluorenyl)propionate (16 g.), needles (from methanol), m. p. 99—100° (Found: C, 77.6; H, 6.0. $C_{26}H_{24}O_4$ requires C, 78.0; H, 6.0%). The diester (15 g.) was refluxed with 10N-potassium hydroxide (30 ml.) and methoxyethanol (75 ml.) for 90 min. and water added. Acidification gave β -phenyl- β -(9-fluorenyl)propionic acid (8 g.) needles (from acetic acid), m. p. 180—181° (lit.,¹⁰ 181—182°). The acid was caused to react with thionyl chloride and the resultant acid chloride treated with aluminium chloride (4 g.) in dry benzene (40 ml.) at 40—50° for 1 hr. 1-Phenyl-1,2,3,10b-tetrahydrofluoranthene-3-one (3.6 g.) was isolated in the usual way, m. p. 162° (lit.,¹⁰ 162—163°). Reduction of the ketone (3.5 g.) in sulphur-free toluene (75 ml.) with zinc amalgam (50 g.) and concentrated hydrochloric acid (75 ml.) for 15 hr. gave

⁶ M. Orchin and L. Reggel, *J. Amer. Chem. Soc.*, 1947, **69**, 506; H. W. D. Stubbs and S. H. Tucker *J.*, 1954, 227.

⁷ R. A. Friedel, M. Orchin, and L. Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.

⁸ E. B. McCall, A. J. Neale, and T. J. Rawlings, *J.*, 1962, 4902.

⁹ H. W. D. Stubbs and S. H. Tucker, *J.*, 1951, 2936.

¹⁰ N. Campbell and A. E. S. Fairfull, *J.*, 1949, 1239.

1-phenyl-1,2,3,10b-tetrahydrofluoranthene (2.8 g.). This compound appeared to dehydrogenate readily and a satisfactory analysis sample could not be obtained. The crude tetrahydro-derivative (2 g.) was dehydrogenated by boiling with chloranil (4 g.) in sulphur-free xylene (50 ml.) for 3 hr. 1-Phenylfluoranthene (1.1 g.), identical with the compound prepared as described in (a) [mixed m. p. and i.r. spectrum] was isolated by chromatography.

2-Phenylfluoranthene. A solution of methyl fluorene-9-carboxylate (11.2 g.), ethyl atropate (8 ml.), and sodium (1 g.) in dry methanol was kept overnight. In some runs a small quantity of ethyl α -phenyl- β -(9-methoxycarbonyl-9-fluorenyl)propionate was deposited as compact prisms (from methanol), m. p. 89—90° (Found: C, 78.3; H, 5.9. $C_{26}H_{24}O_4$ requires C, 78.0; H, 6.0%). Optimum results were obtained by removing the methanol from the mixture and boiling the residual oily diester with 10N-potassium hydroxide (30 ml.) and methoxyethanol (75 ml.). Acidification of the diluted mixture gave α -phenyl- β -(9-fluorenyl)propionic acid (8 g.), needles (from acetic acid), m. p. 185—187° (Found: C, 84.3; H, 5.6. $C_{22}H_{18}O_2$ requires C, 84.1; H, 5.7%). The acid (7.5 g.) on reaction with thionyl chloride and cyclisation with aluminium chloride in dry benzene at 40—50° gave 2-phenyl-1,2,3,10b-tetrahydrofluoranthene-3-one (3.8 g.), needles (from acetic acid), m. p. 172—173° (Found: C, 89.3; H, 5.3. $C_{22}H_{16}O$ requires C, 89.2; H, 5.4%). Clemmensen reduction of the ketone (1.8 g.) gave 2-phenyl-1,2,3,10b-tetrahydrofluoranthene (1 g.) which, like the 1-phenyltetrahydrofluoranthene, could not be purified satisfactorily. Dehydrogenation of the crude material with chloranil gave 2-phenylfluoranthene (0.5 g.) pale-yellow needles, isolated by chromatography (from light petroleum), m. p. 80—81° (Found: C, 94.7; H, 5.0. $C_{22}H_{14}$ requires C, 95.0; H, 5.0%). The 1,3,5-trinitrobenzene adduct crystallised as yellow needles from ethanol, m. p. 178—179° (Found: N, 8.2. $C_{28}H_{17}N_3O_6$ requires N, 8.5%).

We thank the Huddersfield Education Authority for a Research Scholarship (to S. S.) and Dr. R. E. Dean for kindly supplying a specimen of 7-phenylfluoranthene.

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1076. The Reaction of Sodium Phenylacetylde with Phenyl Isocyanate

By C. W. BIRD

THE addition of diphenylketen to phenylacetylene gives 3,4-diphenylnaphthol possibly through rearrangement of an intermediate cyclobutenone (I).¹ In the course of attempts² to effect an analogous reaction between phenyl isocyanate and phenylacetylene, which might proceed through the azetidone (II),³ the reaction between sodium phenylacetylde and phenyl isocyanate was examined. Three products could be isolated when different ratios of reactants were used. Two of these were derived from two molecules of phenyl isocyanate and one molecule of phenylacetylene, and the third from three molecules of phenyl isocyanate and one of phenylacetylene, m. p. 260°. Wartime conditions prevented further work on this reaction but a re-examination has now been undertaken at the suggestion of Dr. Tyabji.

Difficulty was experience in repeating these reactions until it was realised that they were originally carried out at a high relative humidity (90%) and excess of phenylacetylene was added. However, the third product, m. p. 260°, was not encountered. Using a 1 : 2 ratio of sodium phenylacetylde to phenyl isocyanate a pale yellow compound, $C_{22}H_{16}N_2O_2$, m. p. 189—190°, was obtained. The infrared spectrum showed

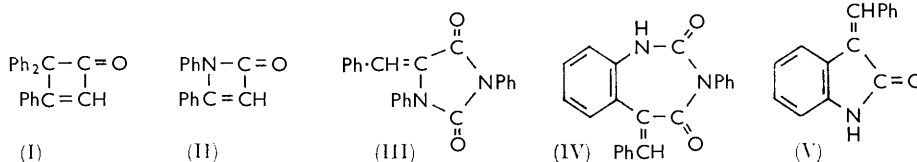
¹ L. I. Smith and H. H. Hoehn, *J. Amer. Chem. Soc.*, 1939, **61**, 2619.

² A. Tyabji, *J. Univ. Bombay*, 1942, **10**, 110.

³ A synthesis of this compound has been described recently: K. R. Henery-Logan and J. V. Rodricks, *J. Amer. Chem. Soc.*, 1963, **85**, 3524.

a pair of bands at 1775 and 1725 cm^{-1} characteristic of a $-\text{CO}\cdot\text{NR}\cdot\text{CO}-$ grouping in a five-membered ring together with a band of comparable intensity at 1650 cm^{-1} ($\text{C}=\text{C}$). In conjunction with the ultraviolet spectrum [λ_{max} 319 $\text{m}\mu$, ϵ 15,100] this suggested that the compound was the hydantoin (III). This was confirmed by comparison with an authentic specimen.⁴

An isomeric yellow compound, m. p. 202—203°, was obtained in very small amounts using a 1 : 1 ratio of reactants. Other ratios produced inseparable mixtures of these two yellow products sometimes accompanied by triphenyl isocyanurate. This second isomer



was shown by its infrared spectrum to have an N-H group (3300 cm^{-1}), a $-\text{CO}\cdot\text{NR}\cdot\text{CO}-$ grouping in unstrained ring (1760 and 1700 cm^{-1}), and a $\text{C}=\text{C}$ (1645 cm^{-1} strong). A detailed analysis of the nuclear magnetic resonance spectrum, measured in deuteriochloroform at 60 Mc./sec., was not possible. All the proton resonances occurred between 390 and 460 c./sec. relative to tetramethylsilane. However, two bands at 427 and 448 c./sec., each corresponding to five protons, probably arise from phenyl groups in different environments. Although the small amounts available preclude a detailed chemical examination, a colourless dihydro-derivative was obtained by hydrogenation in ethanol with a palladium on charcoal catalyst. This dihydro-derivative showed infrared bands at 3400 cm^{-1} (N-H), 1790 and 1700 cm^{-1} ($-\text{CO}\cdot\text{NR}\cdot\text{CO}-$), and 750 cm^{-1} (*o*-disubstituted benzene).

The foregoing evidence, together with consideration of possible modes of formation, suggests the tentative formulation of this second yellow isomer as compound (IV). This structure also appears to accommodate the ultraviolet spectrum which has absorption bands at 250 $\text{m}\mu$ (ϵ 27,300), 286 $\text{m}\mu$ (shoulder, ϵ 7760), and 410 $\text{m}\mu$ (ϵ 5480). 3-Benzylideneoxindole (V) which has a similar extended conjugated system absorbs at 256 $\text{m}\mu$ (ϵ 14,900), 327 $\text{m}\mu$ (ϵ 18,100), and 385 $\text{m}\mu$ (shoulder, ϵ 4100). Such a comparison, of course, assumes that both compounds (IV) and (V) have a similar configuration about the exocyclic double bond and ignores the probable non-planarity of the chromophore in compound (IV).

Experimental.—Infrared spectra were recorded for Nujol mulls and ultraviolet spectra were measured for ethanol solutions.

Reaction of sodium phenylacetylide with phenyl isocyanate. (a) Sodium phenylacetylide was prepared by the reaction of phenylacetylene (1.5 g.) with sodium (0.25 g.) in ether (15 ml.). The stirred suspension was cooled in an ice-bath and phenyl isocyanate (2.4 g.) slowly added. The reaction mixture was subsequently heated to reflux for several minutes and then set aside at room temperature for 3 days. The red solid was dissolved in a little ethanol. The solution was diluted with water and acidified with hydrochloric acid. The semi-solid product was isolated by chloroform extraction and crystallised from ethanol to give 4-benzylidene-1,3-diphenylhydantoin (0.91 g.), m. p. 189—190° (Found: C, 78.0; H, 4.9; N, 8.1%; *M*, 339. Calc. for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2$: C, 77.6; H, 4.7; N, 8.2%; *M*, 340.4). It did not depress the melting point of an authentic sample⁴ and had a superimposable infrared spectrum.

(b) Repetition of the above preparation using phenyl isocyanate (1.5 g.) gave 5-benzylidene-2,3,4,5-tetrahydro-3-phenyl-1H-1-benzodiazepine-2,4-dione (84 mg.), m. p. 202—203° (Found:

⁴ S. E. Hadley and T. B. Johnson, *J. Amer. Chem. Soc.*, 1915, **37**, 171.

C, 77.3; H, 4.9; N, 8.1%; *M*, 341). Hydrogenation in ethanol solution using a 5% palladium on charcoal catalyst gave a *dihydro*-derivative, m. p. 122—124° (aqueous methanol) (Found: C, 77.1; H, 5.2. $C_{22}H_{18}N_2O_2$ requires C, 77.2; H, 5.3%).

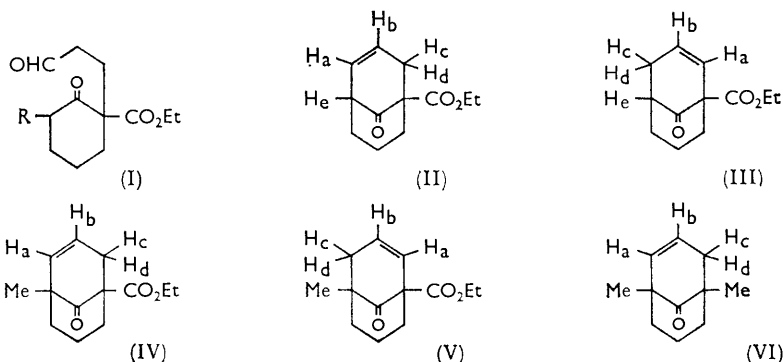
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[Received, March 26th, 1965.]

1077. Bridged Ring Systems. Part VII.* The Acid-catalysed Cyclisation of β -(1-Ethoxycarbonyl-2-oxocyclohexyl)propionaldehyde

By E. W. COLVIN and W. PARKER

It has previously been shown in this Series that the acid-catalysed cyclisation of the oxo-aldehyde (I; R = Me) to the bicyclo[3,3,1]nonane (IV) is accompanied by the formation of two rearrangement products, ethyl 2-acetylbicyclo[3,3,0]oct-1(2)-ene-5-carboxylate and 7-methylindane-4-carboxylic acid.¹ To test the generality of these rearrangements, a re-examination of the similar cyclisation of the lower homologue (I; R = H), previously reported by Cope and Synerholm,² was undertaken. However, sulphuric acid treatment of (I; R = H) furnished no trace of rearrangement products of the above type, and the substance obtained, m. p. 46—47.5° (lit., m. p. 48—49.4°), seemed to be the ketone (II) reported previously. Thin-layer chromatography of this seemingly homogeneous product separated it into two crystalline isomers, m. p. 45—45.5° and 58.5—59.5° (4.7 : 1). Their relationship as the double-bond isomers (II) and (III) was readily established as each gave



the same dihydro-compound on catalytic hydrogenation. Prolonged treatment of each isomer with sulphuric acid gave the same equilibrium mixture of (II) and (III) (1.2 : 1) by the obvious protonation-deprotonation mechanism. Production of these two isomeric species in cyclisations of this type seems general; re-examination of the cyclisation of (I; R = Me) resulted in the isolation of the corresponding two isomers (IV) and (V) (2.8 : 1).

The position of the double bond in each compound was shown by the n.m.r. spectrum. Thus, the isomer of m. p. 45—45.5° exhibited the following olefinic proton signals, showing

* Part VI, P. Doyle, I. R. Maclean, R. D. H. Murray, W. Parker, and R. A. Raphael, *J.*, 1965, 1344.

¹ R. D. H. Murray, W. Parker, R. A. Raphael, and D. B. Jhaveri, *Tetrahedron*, 1962, **18**, 55.

² A. C. Cope and M. E. Synerholm, *J. Amer. Chem. Soc.*, 1950, **72**, 5228.

it to possess structure (II): H_b , two triplets centred at 3.99τ [$J(H_a-H_b) = 9$; $J(H_b-H_{c,d}) = 4$ c./sec.]; H_a , a quartet of triplets centred at 4.39τ [$J(H_a-H_b) = 9$; $J(H_a-H_c) = 6$; $J(H_a-H_{c,d}) = 2$ c./sec.]. The isomer of m. p. $58.5-59.5^\circ$ showed the following olefinic signals, compatible with (III): H_b , two triplets centred at 3.98τ [$J(H_b-H_a) = 9$; $J(H_b-H_{c,d}) = 4$ c./sec.]; H_a , two triplets centred at 4.38τ [$J(H_a-H_b) = 9$; $J(H_a-H_{c,d}) = 2$ c./sec.]. The homologue (IV) showed: H_b , two triplets centred at 4.098τ [$J(H_b-H_a) = 9$; $J(H_b-H_{c,d}) = 4$ c./sec.]; H_a , two quartets centred at 4.76τ [$J(H_a-H_b) = 9$; $J(H_a-H_{b \text{ or } d}) = 2.5$; $J(H_a-H_{c \text{ or } d}) = 2$ c./sec.]. Its isomer (V) showed: H_b , two triplets centred at 4.08τ [$J(H_b-H_a) = 9$; $J(H_b-H_{c,d}) = 4$ c./sec.]; H_a , two triplets centred at 4.45τ [$J(H_a-H_a) = 9$; $J(H_a-H_{c,d}) = 2$ c./sec.].

It is noteworthy that one of the allylic protons in compounds (II) and (IV) is selectively deshielded. Thus, in (II), the allylic protons are seen as: H_c , two multiplets centred at 6.55τ [$J(H_c-H_d) = 20$ c./sec.]; H_d , two quartets centred at 7.55τ [$J(H_d-H_c) = 20$; $J(H_d-H_b) = 4$; $J(H_d-H_a) = 2$ c./sec.]. In (III) they are seen as: $H_{c,d}$, an unresolved multiplet centre at 7.38τ . In (IV), H_c is seen as two multiplets centred at 6.6τ [$J(H_c-H_d) = 18$ c./sec.], and H_d as two quartets centred at 7.61τ [$J(H_d-H_c) = 18$; $J(H_d-H_b) = 4$; $J(H_d-H_a) = 2$ c./sec.], while in (V) the allylic protons are seen as: $H_{c,d}$, two doublets centred at 7.55τ [$J(H_{c,d}-H_b) = 4$; $J(H_{c,d}-H_a) = 2$ c./sec.]. That the 1-ethoxycarbonyl grouping is responsible for this deshielding is shown by the n.m.r. spectrum of the hydrocarbon (VI),³ which exhibits the expected two doublets in the allylic region centred at 7.58τ [$J(H_{c,d}-H_b) = 4$; $J(H_{c,d}-H_a) = 2$ c./sec.].

Experimental.—Melting points were recorded on a Kofler hot-stage apparatus, and are corrected. Thin-layer chromatoplates (1 mm. thick) were prepared from Kieselgel G (Merck). Analytical gas chromatography was performed on a Pye Argon Chromatograph (column, 10% Peg A; 160° ; pressure, 18 p.s.i.; flow rate, 50 c.c./min.). N.m.r. data were obtained, with a Perkin-Elmer 60 Mc. instrument, for carbon tetrachloride solutions, tetramethylsilane being used as internal reference. Infrared spectra were obtained with a Unicam S.P. 200 instrument, for Nujol mulls unless stated otherwise.

β -(1-Ethoxycarbonyl-2-oxocyclohexyl)propionaldehyde (I; R = H). This compound was prepared by the method of Cope and Synerholm.²

Ethyl 9-oxobicyclo[3,3,1]non-3- and -2-ene-1-carboxylate (II) and (III). The oxo-aldehyde (48 g.) was added in fine droplets to concentrated sulphuric acid (96 ml.), cooled in an ice-salt bath. The mixture was left at room temperature for 4 hr., poured on to ice, and the product separated as a non-filterable semi-solid. The total mixture was extracted twice with ether, the extracts were combined, washed with sodium hydrogen carbonate solution and brine, and dried ($MgSO_4$). (Acidification of the hydrogen carbonate washings afforded solely 2-oxocyclohexanecarboxylic acid.) Removal of solvent under reduced pressure furnished a brown solid (27 g.). Chromatography on alumina (Spence H; 150 g.) gave pale yellow crystals (26 g.), m. p. $46-47.5^\circ$. Thin-layer chromatography of these (150 mg.), with 10% ethyl acetate-light petroleum (b. p. $60-80^\circ$) for development, separated the two components; (II) sublimed as *needles* (99.4 gm.), m. p. $45-45.5^\circ$, $\nu_{\max.}$ 3100, 1740, 1715, 1660, 720, 695 cm^{-1} (Found: C, 68.9; H, 7.75). $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.75%, and (III) sublimed as *needles* (21.7 mg.), m. p. $58.5-59.5^\circ$, $\nu_{\max.}$ 3100, 1735, 1715, 1660, 720 cm^{-1} (Found: C, 69.4; H, 7.75%). The ratio of (II) to (III) (4.7: 1) was determined from peak areas on gas chromatography.

A solution of the pure oxo-ester (II) (100 mg.) and hydrazine hydrate (100%; 0.1 ml.) in ethanol (5 ml.) was refluxed for 24 hr., and evaporated to dryness under reduced pressure, to give the crude pyrazolone (75 mg.). This was recrystallised twice from benzene, to afford *needles*, m. p. $217-218^\circ$ (sealed tube) (Found: C 68.15; H, 6.65; N, 16.0. $C_{10}H_{12}N_2O$ requires C, 68.15; H, 6.85; N 15.9%). The pyrazolone of (III) was obtained similarly as *needles*, m. p. $195-196^\circ$ (sealed tube) (Found: C, 67.95; H, 6.9; N, 16.05%).

A suspension of the pure oxo-ester (II) (100 mg.) in aqueous sodium hydroxide (2N; 10 ml.) was stirred until a clear solution was obtained. This was acidified with sulphuric acid (6N) and extracted twice with ether. The extracts were combined, washed with brine, and dried

³ J. Martin, W. Parker, and R. A. Raphael, *J.*, 1964, 289.

(MgSO₄). Removal of solvent under reduced pressure afforded the crude product (78 mg.) which, after two recrystallisations from methylcyclohexane, gave the pure acid derived from (II) as prisms, m. p. 139.5—140° (lit., 133.8—134.3°), ν_{\max} . 3500—2700, 1720, 1695, 1660, 720, 690 cm.⁻¹ (Found: C, 66.65; H, 6.45. Calc. for C₁₀H₁₂O₃: C, 66.65; H, 6.7%). The isomeric acid from (III) was obtained similarly as prisms, m. p. 143—144°, ν_{\max} . 3500—2700, 1720, 1700, 1660, 720 cm.⁻¹ (Found: C, 66.75; H, 6.8%).

A solution of either pure oxo-ester (II) or (III) (45 mg.) in ethyl acetate (AnalaR; 20 ml.) was separately hydrogenated over 10% palladium-charcoal (5 mg.) until uptake ceased. The catalyst was filtered off through Celite, and the solvent removed under reduced pressure, to give the saturated ester, which was shown to be the same from (II) and (III) by thin-layer and gas chromatography. Sublimation afforded a *solid*, m. p. 26—32° (Found: C, 68.3; H, 8.7. C₁₂H₁₈O₃ requires C, 68.55; H, 8.65%). The *pyrazolone* crystallised from ethanol in prisms, m. p. 221—222° (sealed tube) (Found: C, 67.25; H, 7.75; N, 15.6. C₁₀H₁₄N₂O requires C, 67.4; H, 7.9; N, 15.7%). The corresponding acid crystallised from methylcyclohexane in needles, m. p. 136—137° (lit., 138.6—139.4°) (Found: C, 65.9; H, 7.65. Calc. for C₁₀H₁₄O₃: C, 65.9; H, 7.75%).

Isomerisation of (II) and (III) with sulphuric acid. Separate solutions of the pure oxo-esters (II) and (III) (50 mg.) in concentrated sulphuric acid (5 ml.) were stirred overnight at room temperature, and poured on to ice. The solutions were extracted with ether, and the extracts washed with sodium hydrogen carbonate solution and brine, and dried (MgSO₄). Removal of solvent under reduced pressure gave the product (47 mg.), which in each case was shown by gas chromatography to contain only (II) or (III), in the ratio 1.2 : 1.

Ethyl 5-methyl-9-oxobicyclo[3,3,1]non-2- and -3-ene-1-carboxylate (V) and (IV). This liquid compound was prepared according to the published method¹. Some of the product (100 mg.), on thin-layer chromatography with three portions of 5% ethyl acetate-light petroleum (b. p. 60—80°) for development, was separated into the 3-ene (V) (70 mg.), n_D^{19} 1.4898, ν_{\max} . (liquid film) 3100, 1735, 1720, 1660, 710, 690 cm.⁻¹ (Found: C, 70.05; H, 8.0. C₁₃H₁₈O₃ requires C, 70.25; H, 8.15%), and the 2-ene (VI) (19.5 mg.), n_D^{19} 1.4867, ν_{\max} . (liquid film) 3100, 1740, 1720, 1660, 720 cm.⁻¹ (Found: C, 70.2; H, 8.0%). The ratio of (V) to (VI) (2.8 : 1) was determined from peak areas on gas chromatography.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, GLASGOW W.2. [Received, March 29th, 1965.]

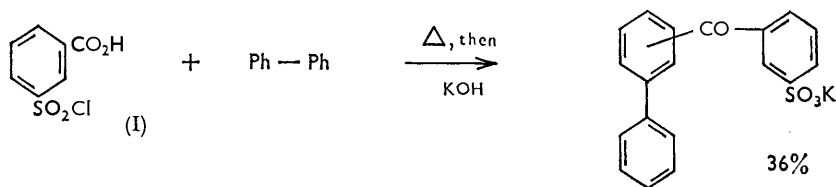
1078. *The Reactions of 3-Carboxyphenylsulphonyl Chloride with Aromatic Compounds*

By ELLIS K. FIELDS

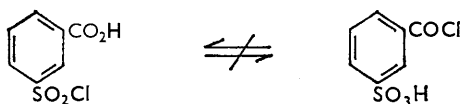
BENZENESULPHONYL CHLORIDE phenylates aromatic compounds, such as biphenyl and naphthalene, at temperatures above 200° through the intermediate formation of free phenyl radicals.¹ A large molar excess (15 : 1) of the high-boiling hydrocarbon is used, making isolation of the reaction products difficult and tedious. It appeared desirable to employ a sulphonyl chloride bearing a functional group to simplify product isolation.

3-Carboxyphenylsulphonyl chloride (I) is readily made by chlorosulphonation of benzoic acid and its reactions with biphenyl and naphthalene have now been investigated. Surprisingly, the products isolated were ketonic sulphonic acids, presumably resulting from electrophilic substitution rather than free-radical attack, *e.g.*,

¹ P. J. Bain, E. J. Blackman, W. Cummings, S. A. Hughes, E. R. Lynch, E. B. McCall, and R. J. Roberts, *Proc. Chem. Soc.*, 1962, 186.



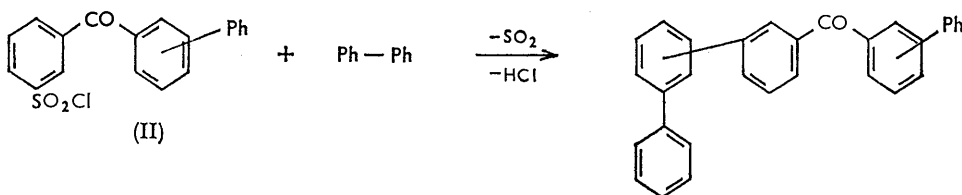
None of the alternative products of electrophilic substitution, the corresponding sulphone-carboxylic acids, were isolated. There was no interchange of carboxyl hydroxyl and sulphonyl chlorine:



This was shown by heating compound (I) at 193° (60° above its melting point) for one hour. Its melting point and mixed melting point were unchanged. Above 200° it decomposed to 3-chlorobenzoic acid.

To shed more light on this reaction, an equimolar mixture of benzoic acid and benzenesulphonyl chloride was allowed to react with 10 moles of biphenyl at 250°. The products, determined by mass spectroscopy, were as follows (the relative abundance assessed from a 70-v spectrum): benzoic acid (115), biphenyl (7164), terphenyls (390), benzoyl-biphenyls (100), phenylsulphonylbiphenyls (7), quaterphenyls (26), and benzoyl-terphenyls (7). Although the predominant reaction was free-radical phenylation, about 20% of the products resulted from acylation.

The yields of ketonic sulphonic acids from compound (I), as well as the above mass spectral data, suggested that products other than those isolated were formed. Total products from the reaction of biphenyl with compound (I) were esterified with methanol and determined by mass spectrometry. In addition to the expected methyl benzoyl-biphenylsulphonate, there were appreciable peaks for Ph·CO·Ar, Ar·SO₂·Ar, Ar·C₆H₄·CO·Ar, Ar·SO₂·C₆H₄·CO·Ar, where Ar = biphenyl [C₆H₅·C₆H₄]. Benzoylbiphenyls could arise from the primary product (II) by transfer of its SO₂Cl group to biphenyl. This reaction is similar to the trans-sulphonation reaction in the formation of aromatic sulphones,² and accounts for the first two products. Biphenyl terphenyl ketone, the third product, could arise from free-radical attack by the primary product (II) on another biphenyl molecule:



The fourth product is evidently the result of electrophilic attack by both functional groups on biphenyl. It is present in much lower concentration than the other three compounds.

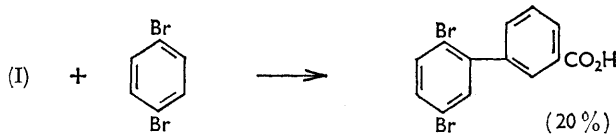
To determine whether free sulphonic acid, formed by hydrolysis by the water liberated, catalysed the acylation, the acid chloride³ of compound (I) was treated separately with

² H. Drews, S. Meyerson, and E. K. Fields, *Angew. Chem.*, 1960, **72**, 493; *J. Amer. Chem. Soc.*, 1961, **83**, 3871.

³ S. Smiles and J. Stewart, *J.*, 1921, **119**, 1792.

biphenyl and naphthalene. In these reactions no water could form, and only hydrogen chloride was eliminated. Both reactions yielded the same products as were obtained from compound (I), and in appreciably higher yields (60 and 57%, respectively).

Products from free-radical reaction of compound (I) were obtained with benzophenone and *p*-dibromobenzene:



Neither benzophenone nor *p*-dibromobenzene undergoes acylation readily, which presumably accounts for the predominance of the free-radical carboxyphenylation reaction.

Experimental.—*Sulphobenzoylation of biphenyl and of naphthalene.* A mixture of compound (I) ² (4.41 g., 0.02 mole) and biphenyl (46.2 g., 0.3 mole) was refluxed for 5 hr., cooled to 85°, and then refluxed for a further hr. after the addition of benzene (200 ml.) and 10% aqueous potassium hydroxide (50 ml.). The hot aqueous solution was separated and cooled to 15°, and the crystals that deposited were recrystallised from water, giving the *potassium salts* of 3-sulphobenzoylbiphenyl isomers (2.7 g., 36%), m. p. 324—333° (Found: C, 60.4, H, 3.7; S, 8.2; K, 10.8. C₁₉H₁₃KO₄S requires C, 60.6; H, 3.5; S, 8.5; K, 10.4%).

Compound (I) (6.62 g., 0.03 mole) and naphthalene (57.7 g., 0.45 mole) after being heated under reflux for 26 hr., gave the crystalline *potassium salts* of 3-sulphobenzoylnaphthalene isomers (2.9 g., 29%), m. p. 276—283° (Found: C, 58.2; H, 3.2; S, 8.9; K, 10.9. C₁₇H₁₁KO₄S requires C, 58.2; H, 3.1; S, 9.1; K, 11.1%).

A mixture of 3-chlorocarbonylbenzenesulphonyl chloride ⁴ (4.7 g., 0.02 mole), and biphenyl (46.2 g., 0.3 mole) after being heated under reflux for 5 hr., gave the potassium salts of 3-sulphobenzoylbiphenyl (4.55 g., 60%), m. p. 339—342° (Found: C, 61.0; H, 3.6; S, 8.4; K, 10.0. C₁₉H₁₃KO₄S requires C, 60.6; H, 3.5; S, 8.5; K, 10.4%).

Similarly, a mixture of the diacid chloride (4.78 g., 0.02 mole) and naphthalene (38.5 g., 0.3 mole), after being heated under reflux for 18 hr., gave the potassium salt of 3-sulphobenzoylnaphthalene (4 g., 57%), m. p. 285—292° (Found: C, 58.0; H, 3.4; S, 8.9; K, 11.4. C₁₇H₁₁KO₄S requires C, 58.2; H, 3.1; S, 9.1; K, 11.1%).

Nujol mulls of the potassium salts from the reaction of the diacid chloride with biphenyl and naphthalene gave infrared spectra indistinguishable from those obtained by use of compound (I). The slightly different melting points may be unimportant, as these are mixtures of isomers in both cases.

Carboxyphenylation reactions. A mixture of compound (I) (6.61 g., 0.03 mole) and benzophenone (72 g., 0.4 mole) was refluxed for 1 hr., cooled to 85°, and refluxed for another 0.5 hr. after addition of 5% aqueous potassium hydroxide (100 ml.) and benzene (100 ml.). The aqueous phase, on being cooled, did not deposit solid. It was acidified to precipitate a mixture of 2', 3', and 4'-benzoylbiphenyl-3-carboxylic acid (7.1 g., 87%). A portion was dissolved in ethanol, decolourised with charcoal, and precipitated by dilution with water. The precipitate, crystallised from dilute alcohol, had m. p. 188—192° (Found: C, 79.1; H, 4.8%; neutral equiv., 297. C₂₀H₁₄O₃ requires C, 79.4; H, 4.6%; neutral equiv., 302).

The methyl ester, prepared by way of the acid chloride, had b. p. 220°/3 mm. Its mass spectrum gave a parent peak at 316 (theoretical *M*, 316).

A mixture of compound (I) (4.42 g., 0.02 mole) and *p*-dibromobenzene (70.8 g.) was refluxed for 168 hr. The same procedure as with benzophenone yielded crude acid (1.4 g., 19%). An identical reaction was run with the addition of cuprous chloride (0.2 g.), as this has been found to catalyse reactions of benzenesulphonyl chloride.¹ The same isolation procedure gave the same yield of acid (1.5 g., 20%), but it seemed easier to crystallise from heptane, to give crystals

⁴ H. Limpricht and L. von UsLAR, *Annalen*, 1857, **102**, 239.

of 2',5'-dibromobiphenyl-3-carboxylic acid, m. p. 213—214° (Found: C, 43·2; H, 2·5; Br, 44·6%; neutral equiv., 368. $C_{13}H_{13}Br_2O_2$ requires C, 43·3; H, 2·3; Br, 44·9%; neutral equiv., 366).

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1079. *The Acid-catalysed Hydrolysis of 1,3-Dioxolan*

By J. LESLIE and D. HAMER

It has been observed in the acid-catalysed hydrolysis of methylal and trioxan in sulphuric acid solutions that the addition of acetic acid caused a change in the rate of reaction.¹ It was concluded that the observed decrease in the rate of hydrolysis of methylal was caused by a "salting-in effect," and that the increase in the trioxan reaction rate was the result of catalysis by undissociated acetic acid. In this Note the rates of hydrolysis of 1,3-dioxolan in aqueous sulphuric acid-acetic acid solutions are presented, and a modification of the interpretation of the results obtained in the hydrolysis of trioxan in similar media is described.

Experimental and Results.—1,3-Dioxolan (from Dr. W. Cule Davies, Associated Chemical Companies, Ltd., Leeds) was purified by distillation from sodium wire. The first-order rate constants, summarised in Table 1, were determined as previously described for methylal.¹

TABLE 1
Acid-catalysed hydrolysis of 1,3-dioxolan at 25°

	<i>Sulphuric acid</i>				
[Acid] (mole/l.)	0·735	1·468	2·185	2·900	
10^4k (sec. ⁻¹)	2·53	9·33	25·7	66·7	
	<i>Sulphuric acid (1·787 m)-acetic acid</i>				
[Acetic acid] (mole/l.)	0	1·046	2·03	2·97	4·10
10^4k (sec. ⁻¹)	15·6	16·4	17·9	18·7	21·5

A plot of $\log k$ against $-H_0$ was linear with a slope of 1·12, but a non-linear one was obtained for solutions containing acetic acid.

Discussion.—Table 1 shows that the rate of the acid-catalysed hydrolysis of 1,3-dioxolan is increased by the addition of acetic acid. This is similar to the behaviour of trioxan in similar media; it was then inferred that the rate increase was due to catalysis by undissociated acetic acid.¹ However, a similar conclusion cannot be reached for the 1,3-dioxolan hydrolysis, since it has been clearly shown that the related compound 2-methyl-1,3-dioxolan is catalysed only by hydrogen ions.² Therefore, the conclusion that trioxan hydrolysis is subject to general acid catalysis must be considered invalid.

A possible explanation of the observed effects of acetic acid in the hydrolyses of trioxan, methylal, and 1,3-dioxolan can be presented by considering the suggestion by Kresge *et*

¹ D. Hamer and J. Leslie, *J.*, 1960, 4198.

² J. N. Bronsted and C. Grove, *J. Amer. Chem. Soc.*, 1930, 52, 1400.

*al.*³ that the kinetic behaviour in concentrated acid solution is not a good criterion of reaction mechanism. They point out that the reaction kinetics should be dependent on the structure of the transition state which will be dependent on the structure of the substrate. The results presented in this Note and in a previous Paper¹ appear to support this hypothesis. Trioxan and 1,3-dioxolan have similar transition states whereas the transition state in the hydrolysis of methylal might be sufficiently different to account for the rate decrease brought about by the acetic acid. It is more reasonable, therefore, to ascribe the differences in kinetic behaviour in the acid hydrolyses to differences in substrate structure, rather than to differences in the reaction mechanism.

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³ A. J. Kresge, R. A. More O'Ferrall, L. E. Hakka, and V. P. Vitullo, *Chem. Comm.*, 1965, 46.

1080. Esterification of Aromatic Acids with Boron Trifluoride-Methanol

By G. HALLAS

DURING the course of our work it became necessary to prepare a number of aromatic methyl esters. Boron trifluoride-methanol appeared to be a suitable reagent for this purpose. Nieuwland and his co-workers¹ showed that boron trifluoride is an effective catalyst for esterification. Aliphatic carboxylic acids are converted essentially quantitatively into their methyl esters on treatment with boron trifluoride-methanol; this technique has been applied in the determination of organic acids.^{2,3} However, incomplete esterifications were recorded^{2,4} for several acids in which the carboxyl group is directly attached to an aromatic nucleus. Thus, although *p*-nitrobenzoic acid was converted quantitatively into the corresponding ester,⁴ the yield of methyl *p*-aminobenzoate was only 53%.

It is now found that high yields of various aromatic esters are obtained by using two equivalents of commercial boron trifluoride-methanol complex in a considerable excess of methanol. The presence of a basic group necessitates the use of a further quantity of reagent.⁴ The simple procedure described below constitutes a convenient method for the preparation of aromatic methyl esters.

The following acids were converted into esters, the times of reflux (in hours) and the percentage yields (parentheses) being indicated: Benzoic, 1 (96); *o*-Toluic, 2 (92); *m*-Toluic, 1.5 (95); *p*-Toluic, 1.5 (89); *o*-Nitrobenzoic, 6 (82); *m*-Nitrobenzoic, 3 (93); *p*-Nitrobenzoic, 1 (98); Salicylic, 3 (91); *m*-Hydroxybenzoic, 1.5 (96); *p*-Hydroxybenzoic, 1.5 (94); Anthranilic, 6 (81); *m*-Aminobenzoic, 4 (75); *p*-Aminobenzoic, 4 (75); *p*-Dimethylaminobenzoic, 4 (94); *o*-Bromobenzoic, 3 (92); *p*-Bromobenzoic, 2 (90); *o*-Chlorobenzoic, 3 (93); *p*-Chlorobenzoic, 2 (88); Anisic, 1.5 (90); Terephthalic, 6 (95); 1-Naphthoic, 3 (94); Ferrocenoic, 2 (88); Furoic, 3 (94); Nicotinic, 6 (91).

¹ H. Bowlus and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1931, **53**, 3835; H. D. Hinton and J. A. Nieuwland, *ibid.*, 1932, **54**, 2017; G. F. Hennion, H. D. Hinton, and J. A. Nieuwland, *ibid.*, 1933, **55**, 2857.

² J. Mitchell, jun., D. M. Smith, and M. W. D. Bryant, *J. Amer. Chem. Soc.*, 1940, **62**, 4; J. Mitchell, jun., and D. M. Smith, "Aquametry, Chemical Analysis," Interscience Publishers Inc., New York, 1948, vol. 5, p. 297.

³ L. D. Metcalfe and A. A. Schmitz, *Analyt. Chem.*, 1961, **33**, 363.

⁴ F. J. Sowa and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1936, **58**, 271.

Experimental.—The acid (0.02 mole) was heated under reflux for 1–6 hr. with boron trifluoride-methanol reagent (B.D.H. product, 51% BF_3 ; 2 equiv., 4.4 ml.) in an excess of dry methanol (5 vol.; 22 ml.). After cooling, the mixture was poured into saturated sodium hydrogen carbonate solution, and the ester was either filtered off and crystallised or extracted with ether and fractionated.

Optimum conditions have not been extensively examined, but each esterification was repeated at least twice; average yields are given. The melting points or boiling points of the esters so obtained agree with reported values.

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1081. Preparation of Unsymmetrical Tertiary Phosphine Oxides from Diethyl Phosphite

By I. M. DOWNIE and G. MORRIS

THE reaction of diethyl phosphite with an excess of Grignard reagent, RMgX , affords a further Grignard reagent,¹ $\text{R}_2\text{P}(\text{O})\text{MgX}$. We have investigated the reactivity of this latter class of Grignard reagent with a series of alkyl chlorides and have realised a straightforward synthesis of tertiary phosphine oxides of the type $\text{R}_2\text{R}'\text{PO}$. The advantage of the method lies in its simplicity; the whole sequence being carried out in a single reaction vessel.

The bromomagnesium salt of diphenylphosphine oxide was treated with a series of alkyl chlorides; the experimental results are tabulated.

Alkyl chloride R' =	Yield (%) $\text{Ph}_2\text{R}'\text{PO}$	M. p.	Found (%)			Formula	Calc. (%)		
			C	H	P		C	H	P
MeOCH_2	24	114–115°	68.3	6.1	12.8	$\text{C}_{14}\text{H}_{15}\text{O}_2\text{P}$	68.3	6.1	12.6
$\text{CH}_2\text{:CH-CH}_2$...	55	108–109	74.0	6.1	12.4	$\text{C}_{15}\text{H}_{15}\text{OP}$	74.4	6.2	12.8
$\text{CH}_2\text{:CMe-CH}_2$...	63 †	137–138	75.1	7.0	12.3	$\text{C}_{16}\text{H}_{17}\text{OP}$	75.0	6.6	12.1
PhCH_2	76	197–198	77.8	6.1	10.2	$\text{C}_{19}\text{H}_{17}\text{OP}$	78.1	5.8	10.6
Ph_2CH	76	300–302	81.7	5.7	8.1	$\text{C}_{25}\text{H}_{21}\text{OP}$	81.5	5.7	8.4

† New compound.

It is of note that only those chlorides which can give rise to resonance-stabilised cations effect alkylation of the Grignard reagent. The three butyl chlorides did not alkylate the reagent, diphenylphosphine oxide being obtained as an oil on work-up. This was characterised as its acetaldehyde adduct.

Experimental.—The following experiment is typical.

Diethyl phosphite (10 g.) in ether (25 ml.) was added to phenylmagnesium bromide [from bromobenzene (39 g.) and magnesium (6 g.)] in ether (150 ml.). The appropriate alkyl chloride (0.09 mole) in ether (25 ml.) was added to the Grignard solution. After completion of addition the mixture was heated under reflux for 4 hr. Hydrochloric acid (300 ml., 1N) was run into the mixture, followed by benzene (100 ml.). The aqueous layer was separated and extracted with benzene (5 × 20 ml.); the extracts were then combined with the organic layer and the whole washed with sodium hydrogen carbonate solution and then water. The ether and benzene were removed under reduced pressure. The resulting solid was recrystallised from benzene-light petroleum (b. p. 80–100°), except in the case of benzhydryldiphenylphosphine oxide which was recrystallised from 2-ethoxyethanol.

We thank Albright and Wilson Ltd. for their support (of G. M.) and Mr. P. Borda for micro-analyses.

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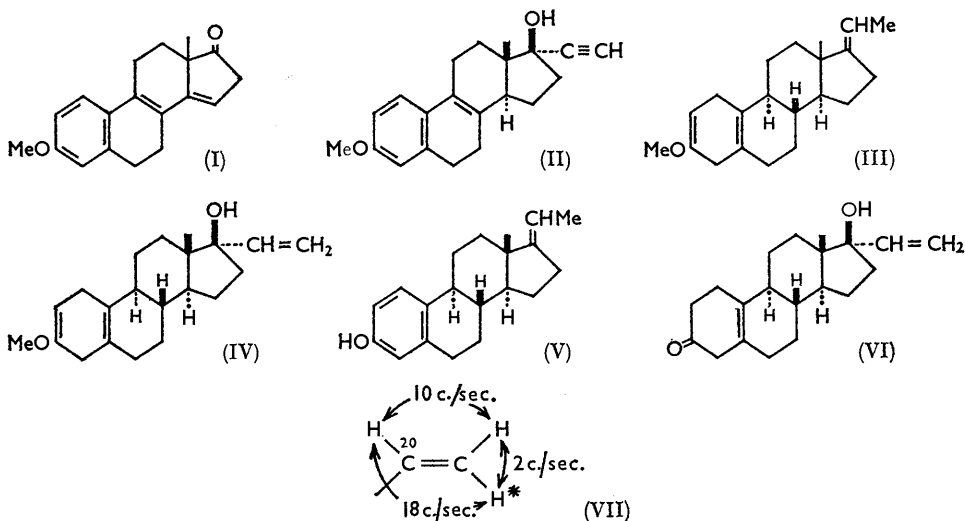
[Received, April 8th, 1965.]

¹ R. C. Miller, C. D. Miller, W. Rogers, and L. A. Hamilton, *J. Amer. Chem. Soc.*, 1957, **79**, 424.

1082. *Racemic 17 β -Hydroxy-17 α -vinyl α estr-5(10)-en-3-one*

By A. K. HISCOCK and J. S. WHITEHURST

THE present report is an account of the transformation of the totally synthetic compound (I)¹ into racemic 17 β -hydroxy-17 α -vinyl α estr-5(10)-en-3-one (VI).² Partial catalytic reduction¹ of compound (I) followed by treatment of the 14 α ,15-dihydro-product with



acetylene in *t*-butyl alcohol-potassium *t*-butoxide³ gave compound (II). Protection^{2a,4} of the hydroxyl moiety in (II) against hydrogenolysis during the next step of the synthesis was achieved, as far as possible, by formation of the lithium derivative; Birch reduction (Wilds and Nelson's conditions⁵) with ethanol as proton-donor then brought about saturation of the 8,9-bond⁶ and also effected changes in ring A and at C-17. Three compounds were formed, all readily separated from each other by chromatography on alumina; elution gave, successively, compounds (III), (IV), and (V).

The structures allotted to these compounds rest on the following considerations. For compound (V) the presence of only one oxygen atom is attested by elemental analysis, and it is shown to be in a phenolic group at C-3 by infrared absorption at ν_{\max} 3390 cm^{-1} and by the ultraviolet absorption maximum at 280 $\text{m}\mu$ (ϵ 2190) moving to 299 $\text{m}\mu$ (ϵ 3270) in ethanolic 0.01N-potassium hydroxide, a result in complete agreement with the behaviour of α estrone itself.⁷ The infrared spectrum of compound (V) (bands at 1611, 1588, 1498,

¹ G. A. Hughes and H. Smith, *Chem. and Ind.*, 1960, 1022; G. H. Douglas, J. M. H. Graves, D. Hartley, G. A. Hughes, B. J. McLoughlin, J. Siddall, and H. Smith, *J.*, 1963, 5072; D. J. Crispin and J. S. Whitehurst, *Proc. Chem. Soc.*, 1962, 356; 1963, 22; S. N. Ananchenko and I. V. Torgov, *Tetrahedron Letters*, 1963, 1553; T. B. Windholz, J. H. Fried, and A. A. Patchett, *J. Org. Chem.*, 1963, 28, 1092; T. Miki, K. Hiraga, and T. Asako, *Proc. Chem. Soc.*, 1963, 139.

² For the optically active compound see: (a) P. de Ruggieri and C. Ferrari, *Ann. Chim. (Italy)*, 1958, 48, 1042; (b) C. Gandolfi and P. de Ruggieri, *Gazzetta*, 1964, 94, 675.

³ H. E. Stavely, *J. Amer. Chem. Soc.*, 1939, 61, 79.

⁴ N. A. Dobson and R. A. Raphael, *J.*, 1955, 3558.

⁵ A. L. Wilds and N. A. Nelson, *J. Amer. Chem. Soc.*, 1953, 75, 5360.

⁶ W. S. Johnson, E. R. Rogier, J. Szmuskovicz, H. I. Hadler, J. Ackerman, B. K. Bhattacharyya, B. M. Bloom, L. Stalman, R. A. Clement, B. Bannister, and H. Wynberg, *J. Amer. Chem. Soc.*, 1956, 78, 6289.

⁷ K. Pederson-Bjergaard and S. A. Schou, *Quart. J. Pharm.*, 1935, 8, 669; R. K. Callow, *Biochem. J.*, 1936, 30, 906.

1243, and 1217 cm^{-1}) showed a general similarity to those of similarly constituted oestra-trienes.⁸ Though the dealkylation of phenolic ethers by sodium in liquid ammonia is well documented,⁹ we believe the present example to be the first reported in the steroid field.¹⁰ The presence of an ethylidene function in (V) is inferred from the known path^{2a,11} for the metal-ammonia reduction of ethynylcarbinols.

Compound (III) also possessed only one oxygen atom. There was no selective absorption in the 220—300 $\text{m}\mu$ region, and the infrared spectrum showed bands at 1691, 1676, 1222, and 818 cm^{-1} . When its ethanol solution was treated with dilute hydrochloric acid, ultraviolet absorption at 240 $\text{m}\mu$ developed, this evidently arising from the derived conjugated ketone.

The major product of the reaction (IV) was hydroxyl-bearing (ν_{max} 3545 cm^{-1}), and elemental analysis established the presence of two oxygen atoms. Spectroscopic evidence points to the structure given for this compound. Thus, in the ultraviolet region only end-absorption was present, and in the infrared region bands occurred at 1689, 1663, 1220, 1025, 996, and 943 cm^{-1} . The 100 Mc. n.m.r. spectrum showed a quartet of bands centred at τ 3.99 (J_{cis} 10 c./sec.; J_{trans} 18 c./sec.) due to the coupling of the proton attached to C-20 (VII)¹² with the two non-identical protons of C-21. Also present were five bands (τ 4.78—4.96) in the region expected for the C-21 protons. Each of these protons should give rise to a quartet; the spectrum should therefore show eight bands. The τ 4.96 band was more intense than the others, and from its appearance it was obviously complex. The two bands (τ 4.78, 4.80) were evidently half of a quartet centred at τ 5.13 due to the proton H* in (VII). The two bands (τ 4.85, 4.87) are similarly half of the quartet (centre τ 5.09) due to the other proton. When compound (IV) was treated with oxalic acid in aqueous methanol it readily gave the unconjugated ketone 17 β -hydroxy-17 α -vinyl-oestra-5(10)-en-3-one (VI) (ν_{max} 3400, 1704, 992, 931 cm^{-1}). The biological activity of the natural optically active form of this compound has been reported.¹³

Experimental.—3-Methoxyoestra-1,3,5(10),8-tetraen-17-one was prepared by the method of Ananchenko and Torgov.¹

17 α -Ethynyl-3-methoxyoestra-1,3,5(10),8-tetraen-17 β -ol (II). Acetylene, purified by cooling to -70° , was passed into dry ether (250 ml.) for 30 min. (magnetic stirrer). From two separate funnels, solutions of the ketone (5 g.) in ether (250 ml.) and potassium (5 g.) in t-butyl alcohol (100 ml.) containing ether (100 ml.) were added during 30 min. After a further 5 hours' stirring, cold saturated ammonium chloride was added, and the mixture extracted with ether. The extracts were washed with water until neutral, dried (MgSO_4), and evaporated under reduced pressure. The residue (ca. 5 g.) solidified on cooling and scratching. Crystallisation from light petroleum (b. p. 60—80 $^\circ$) containing acetone gave colourless *microprisms*, m. p. 153—154 $^\circ$ (Found: C, 81.5; H, 7.9. $\text{C}_{21}\text{H}_{24}\text{O}_2$ requires C, 81.8; H, 7.85%), ν_{max} (CCl_4) 3632, 3319 cm^{-1} , ν_{max} (KBr) 1606, 1564, 1250, and 1039 cm^{-1} .

Reduction. Liquid ammonia (300 ml., distilled from sodium) was placed under a "dry-ice" condenser, and lithium pieces (total 0.4 g.) were added during 20 min., after which ferric nitrate (one small crystal) was added, the mixture being stirred mechanically. After disappearance of the blue colour, the compound above (3.0 g.), in dry ether (150 ml.), was added during 30 min. After 90 min., lithium (4 g., 20 pieces) was added (20 min.). After another 20 min., absolute ethanol (60 ml.) was added. The blue colour had disappeared after 60 min.; the stirrer was stopped and the ammonia allowed to evaporate overnight. The residue was

⁸ G. Roberts, B. S. Gallagher, and R. N. Jones, "Infrared Absorption Spectra of Steroids," vol. II, Interscience, New York, 1958.

⁹ K. Freudenberg, W. Lautsch, and G. Piazzolo, *Ber.*, 1941, **74**, 1879; A. J. Birch, *J.*, 1947, 102.

¹⁰ Complete removal of a 3-methoxy-group has been reported by J. A. Hartman, A. J. Tomaszewski, and A. S. Dreiding, *J. Amer. Chem. Soc.*, 1956, **78**, 5662.

¹¹ A. J. Birch, *J.*, 1945, 809; F. B. Colton, L. N. Nysted, B. Riegel, and A. L. Raymond, *J. Amer. Chem. Soc.*, 1957, **79**, 1123.

¹² N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, 1964, p. 85, and unpublished results by these authors.

¹³ P. de Ruggieri and R. Matscher, *Boll. Soc. ital. Biol. sper.*, 1959, **35**, 24.

extracted with ether which was then washed with water until neutral, dried (MgSO_4), and evaporated under reduced pressure. The residual oil (*ca.* 3 g.) was chromatographed in light petroleum (b. p. 40–60°) on Camag alumina (neutral, Grade III), and the column developed with light petroleum (b. p. 40–60°), benzene, and finally benzene containing 10% (v/v) of ether.

From the light petroleum fraction (*ca.* 500 ml.) 17-ethylidene-3-methoxyestra-2,5(10)-diene (III) (*ca.* 0.8 g.) was obtained as parallelepipeds, m. p. 124–125°, ν_{max} (Nujol) 1691, 1676, 1222, and 818 cm^{-1} (Found: C, 83.75; H, 10.1. $\text{C}_{21}\text{H}_{30}\text{O}$ requires C, 84.5; H, 10.15%).

From the benzene eluates (*ca.* 1500 ml.) was obtained 3-methoxy-17 α -vinylæstra-2,5(10)-dien-17 β -ol (IV), (*ca.* 1.2 g.) as prisms, m. p. 138.5–140° (from light petroleum–acetone), ν_{max} (Nujol) 3545, 1689, 1663, 1220, 1025, 996, and 943 cm^{-1} (Found: C, 79.6; H, 9.5. $\text{C}_{21}\text{H}_{30}\text{O}_2$ requires C, 80.2; H, 9.6%).

The benzene–ether eluates gave 17-ethylideneæstra-1,3,5(10)-trien-3-ol (V) (*ca.* 0.5 g.) as needles (from acetone–water), m. p. 156–158°, λ_{max} (EtOH) 280 μ (ϵ 2190), ν_{max} (Nujol) 3390, 1611, 1588, 1498, 1243, and 1217 cm^{-1} (Found: C, 84.95; H, 9.25. $\text{C}_{20}\text{H}_{26}\text{O}$ requires C, 85.05; H, 9.3%).

When compound (IV) (1 g.) in methanol (150 ml.) was treated with oxalic acid dihydrate (1.5 g.) dissolved in water (25 ml.) at room temperature and the solution worked up (ether extraction) after 2 hr., 17 β -hydroxy-17 α -vinylæstr-5(10)-en-3-one (VI) was obtained (*ca.* 0.65 g.), prisms from light petroleum, m. p. 138–139°, ν_{max} (Nujol) 3400, 1704, 992, and 931 cm^{-1} (Found: C, 79.4; H, 9.4. $\text{C}_{20}\text{H}_{28}\text{O}_2$ requires C, 79.95; H, 9.4%).

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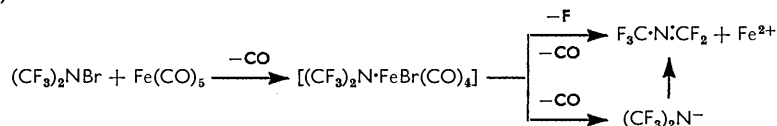
[Received, April 9th, 1965.]

1083. The Reaction of *N*-Halogenobis(trifluoromethyl)amines with Iron Pentacarbonyl

By M. GREEN and A. E. TIPPING

HALOGENS react with iron pentacarbonyl to give iron tetracarbonyl halides. Perfluoroalkyl iodides, which may be regarded as pseudo-interhalogen compounds, react similarly¹ with iron pentacarbonyl to give perfluoroalkyl iron tetracarbonyl iodides. Therefore, it seemed worthwhile to study the reaction between iron pentacarbonyl and *N*-halogenobis(trifluoromethyl)amines as a possible route to compounds containing a nitrogen–iron σ -bond.

N-Bromo- and *N*-chloro-bis(trifluoromethyl)amine both react very rapidly with an excess of iron pentacarbonyl to give an essentially quantitative yield of perfluoro-2-azapropene and ferrous halides. It is possible that a compound containing a nitrogen–iron σ -bond is formed initially, but that rapid fragmentation occurs to give perfluoro-2-azapropene directly or by loss of a fluoride anion from an intermediate bis(trifluoromethyl)amino-anion, *e.g.*,



These reactions are probably related to the recently reported reductive defluorination with

¹ R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3604.

ferrocene or dicumenechromium of compounds containing nitrogen-fluorine² and oxygen-fluorine bonds.³

Experimental.—Volatile products were manipulated in a conventional vacuum system.

The reaction of N-bromobistrifluoromethylamine with iron pentacarbonyl. A mixture of N-bromobistrifluoromethylamine (1.49 g., 6.42 mmoles) and iron pentacarbonyl (3.92 g., 20 mmoles) in a 350-ml. tube, allowed to warm from -196° to room temperature, began to react below 0° and gave unreacted iron pentacarbonyl (2.65 g., 13.5 mmoles) and perfluoro-2-azapropene (0.82 g., 6.19 moles) (96.4%) on trap-to-trap distillation. The perfluoro-2-azapropene was identified by comparison (i.r.) with an authentic sample and by molecular weight measurements. A mixture of ferrous bromide and fluoride remained in the reaction tube.

The reaction of N-chlorobistrifluoromethylamine with iron pentacarbonyl. A mixture of N-chlorobistrifluoromethylamine (0.53 g., 2.28 mmoles) and iron pentacarbonyl (1.96 g., 10 mmoles) reacted as for the bromo-compound, to give iron pentacarbonyl (1.39 g., 7.1 mmoles), perfluoro-2-azapropene (0.37 g., 2.74 mmoles) (97%), and a mixture of ferrous chloride and fluoride.

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[Received, April 12th, 1965.]

² R. A. Mitsch, *J. Amer. Chem. Soc.*, 1965, **87**, 328.

³ J. H. Prager and P. G. Thompson, *J. Amer. Chem. Soc.*, 1965, **87**, 230.

1084. Reductions with Raney Alloy in Acid Solution

By T. VAN ES and B. STASKUN

Two methods^{1,2} were recently reported for the reduction of nitriles to aldehydes using Raney nickel. We have found that this conversion may be conveniently effected, with excellent results in the aromatic series, by refluxing equal weights of the nitrile and Raney alloy in 75% aqueous formic acid. The yields obtained under these optimum conditions are shown in Table I. Use of an increased proportion of alloy (up to 5 g. per 1 g. of nitrile)

TABLE I

The following yields^a (%) were obtained by refluxing 1 g. of the nitrile with 1 g. of alloy in 15 c.c. of 75% aqueous formic acid for 1 hr.

PhCN, 97, 83,^b 15,^c 50^d; *o*-Me-C₆H₄-CN, 8, 39,^e 12,^f 50,^g 25,^h 20,ⁱ 33,^j 60—65,^k 70,^l 70,^m; *m*-Me-C₆H₄-CN, 90; *p*-Me-C₆H₄-CN, 93, 80ⁿ; *o*-HO-C₆H₄-CN, 95; *p*-MeO-C₆H₄-CN, 93; *o*-ClC₆H₄-CN, 73; *p*-ClC₆H₄-CN, 100; *p*-H₂N-O₂S-C₆H₄-CN, 70; 1-C₁₀H₇-CN, 18, 33,^o 55,^p 60—70,^q 65^m; 2-C₁₀H₇-CN, 95; Terephthalonitrile, 70^r; PhCH:CH-CN, 70^r; 3-cyanopyridine, 37^s; CH₃-CN, 3, 12^t; *n*-C₅H₁₁-CN, 40^k; *n*-C₆H₁₃-CN, 28.^u

^a Determined as the 2,4-dinitrophenylhydrazone. ^b 5 g. of alloy, 15 c.c. of 75% aq. HCO₂H for 2 hr. ^c 1 g. of alloy, 15 c.c. of HCO₂H (98—100%) for 1 hr. ^d 1 g. of alloy, 15 c.c. of 90% aq. HCO₂H for 1 hr. ^e 1 g. of alloy, 15 c.c. of 50% aq. HCO₂H for 2½ hr. ^f 1 g. of alloy, 15 c.c. of 66% aq. HCO₂H for 1 hr. ^g 2 g. of alloy, 15 c.c. of 50% aq. HCO₂H for 2 hr. ^h 2 g. of alloy, 30 c.c. of 94% aq. HCO₂H for 1 hr. ⁱ 2 g. of alloy, 30 c.c. of 50% aq. HCO₂H at 75—80° for 1 hr. ^j Same as (i) for 3 hr. ^k 2—4 g. of alloy, 30 c.c. of 50% aq. HCO₂H for 2—3 hr. ^l Reduction as in ref. 2 but using 20 c.c. of 50% aqueous formic acid. ^m As in (l) but using 20 c.c. of 75% aqueous formic acid. ⁿ 2 g. of alloy, 30 c.c. of 50% aq. HCO₂H for 2 hr. ^o 1 g. of alloy, 15 c.c. of 75% aq. HCO₂H for 2½ hr. ^p 2 g. of alloy, 60 c.c. of 50% aq. HCO₂H for 3 hr. ^q Both nitrile groups were reduced. ^r The double bond was not reduced. ^s As the phenylhydrazone; the reaction mixture was filtered and extracted with chloroform, the extracts washed with aqueous sodium hydrogen carbonate, dried, and evaporated. The residue was warmed with phenylhydrazine (1 c.c.) was water-ethanol (1 : 1; 15 c.c.).

¹ O. G. Backeberg and B. Staskun, *J.*, 1962, 3961.

² B. Staskun and O. G. Backeberg, *J.*, 1964, 5880.

did not affect the yield of benzaldehyde appreciably but allowed for a shorter reaction time. Thus, a 97% yield of benzaldehyde resulted in 15 min. on reducing benzonitrile with twice its weight of alloy. The relatively low yields obtained from hindered nitriles such as *o*-tolunitrile and α -naphthonitrile were improved (to 60–65%) by refluxing in 50% aqueous formic acid with an increased weight of alloy for a longer time (Table 1).

TABLE 2

The following yields (%) were obtained by refluxing 1 g. of the nitrile with 1 g. of alloy in 15 c.c. of the appropriate acid.

Nitrile	Yield ^a		
	75% aq. HCO ₂ H	75% aq. CH ₃ ·CO ₂ H	2N-HCl-EtOH (1 : 1)
PhCN	97	50, 70 ^b	65
<i>p</i> -ClC ₆ H ₄ ·CN	100	46	—
<i>p</i> -MeOC ₆ H ₄ ·CN	93	44	72
2-C ₁₀ H ₇ ·CN	95	57	—

^a Determined as the 2,4-dinitrophenylhydrazone. ^b 30 c.c. of 50% of aq. CH₃CO₂H plus 2 g. of alloy for 3½ hr.

During the reduction some carbon dioxide was liberated from the decomposition of formic acid by the nickel.² The alloy was deactivated during refluxing with 75% aqueous formic acid; when the alloy was then used in a normal reduction of benzonitrile a 10% yield only of benzaldehyde was obtained. Optimum yields of aldehyde resulted only when the proportion of water present in the reduction mixture was appreciable (see Table 1, results *c* and *d*). Hydrogen evolution by the action of the formic acid on the alloy becomes more vigorous on addition of water. These results are in contrast with those found when reducing nitriles in formic acid with Raney nickel² when good yields of aldehydes were obtained in formic acid solution containing from 5 to 50% of water (see Table 1, results *l* and *m*, and ref. 2). Other acids may also be used instead of aqueous formic acid but the yields were lowered (Table 2). Other metals and mixtures of metals, *e.g.*, powdered nickel and aluminium (1 : 1), were found to give small yields of the aldehydes. Under the reaction conditions used, carbon-carbon double bonds, ketones, acids, amides, and esters were not affected; oximes and Schiff's bases were hydrolysed. Nitro-compounds were reduced in good yields to the formamides. *m*- and *p*-Nitrobenzonitriles gave 85–90% yields of the formamido-benzonitriles. Nitro-compounds may be reduced to the corresponding amines in 50% aqueous acetic acid but 3 g. of the alloy were required for each gram of nitro-compound.

Experimental.—Reduction of nitriles. The general procedure is illustrated by the preparation of the following aldehydes:

(a) *p*-Chlorobenzaldehyde. Raney alloy (50 : 50; 5.0 g.), *p*-chlorobenzonitrile (5.0 g.), and 75% (v/v) aqueous formic acid (75 c.c.) were refluxed for 1 hr. The mixture was filtered and the residue washed with warm ethanol. For quantitative determination, an aliquot portion of the filtrate was treated with 2,4-dinitrophenylhydrazine reagent (made up by dissolving 10 g. of reagent in 50 c.c. of concentrated sulphuric acid and 400 c.c. of water); it should be noted that after removal of the hydrazone, the somewhat soluble formyl derivative of 2,4-dinitrophenylhydrazine (m. p. 183–184°; yellow needles from ethanol) usually separated from solution. The remainder of the filtrate was diluted with water and extracted with chloroform, and the extracts washed with saturated sodium hydrogen carbonate solution, dried (Na₂SO₄), and evaporated to furnish the crude aldehyde, m. p. 47–48°, in almost theoretical yield; the infrared spectrum of the product indicated the absence of unchanged nitrile.

(b) *p*-Sulphonamidobenzaldehyde. The nitrile (5 g.) was reduced in a similar manner and the reaction filtrate and washings were evaporated to dryness. The residue was shown by its infrared spectrum to be free from nitrile and was crystallised from water to furnish the aldehyde, m. p.

118—120° (3.0 g., 60%); the mother-liquor on treatment with aniline dissolved in glacial acetic acid deposited the sparingly soluble anil (1.4 g., m. p. 205—206°) making the total yield of *p*-sulphonamidobenzaldehyde 80%.

(c) *α*-Naphthaldehyde. The nitrile (5 g.), Raney alloy (10 g.), and 50% (v/v) aqueous formic acid (300 c.c.) were refluxed for 3 hr. (60% yield, as the 2,4-dinitrophenylhydrazone) and the aldehyde isolated as described for *p*-chlorobenzaldehyde; the infrared spectrum of the crude liquid aldehyde (3 g., 60%) confirmed its identity and showed that only a trace of *α*-naphtho-nitrile was present as impurity.

Reduction with other metals. Benzonitrile (1 g.) and the metal or metal mixture (1 g.) in 75% aqueous formic acid (15 c.c.) were refluxed for 1 hr. to give the following yields (%) of aldehyde: zinc dust (nil), zinc dust-copper powder, 1 : 1 (trace), aluminium powder (trace), nickel powder (14), nickel powder-aluminium powder, 1 : 1 (17), Devarda's alloy (14).

Reduction of nitro-compounds with Raney alloy. (a) *In aqueous formic acid.* The following example illustrates the general procedure. Nitrobenzene (1 g.), Raney alloy (1—1.5 g.), and 75% (v/v) aqueous formic acid (15 c.c.) were refluxed for 1 hr. The mixture was filtered, and the filtrate and washings diluted with water and extracted with chloroform. The extracts were washed with saturated sodium hydrogen carbonate, dried (Na₂SO₄), and evaporated to give formanilide, m. p. 48—49° (0.85 g., 86%). The following nitro-compounds were similarly reduced in the indicated yields (%); the method of isolation of the resultant formamide derivative was varied to suit the product, the identity of which was confirmed in each case by a mixture m. p. with authentic sample: *α*-nitronaphthalene (90); *p*-nitrotoluene (80); *o*-bromonitrobenzene (80); *m*-bromonitrobenzene (85); *p*-bromonitrobenzene (85); *o*-nitrobenzoic acid (90); ethyl *p*-nitrobenzoate (95); *p*-nitrobenzamide (90); *o*-nitrophenol (50); *p*-nitroanisole (70); *m*-nitroaniline (quant.); *p*-nitroaniline (quant.); *p*-nitroacetophenone (80); *m*-nitrobenzonitrile (90); *p*-nitrobenzonitrile (90).

(b) *In aqueous acetic acid.* *p*-Nitroacetophenone (1.0 g.) and Raney alloy (3 g.) in 50% (v/v) aqueous acetic acid (15 c.c.) were refluxed for 1 hr. The reaction filtrate and washings were evaporated to dryness to furnish crude *p*-aminoacetophenone (0.8 g., 98%), m. p. 100—106°. The following nitro-compounds were similarly reduced to the corresponding amine in 90—100% yields: nitrobenzene; *p*-nitrotoluene; *o*-nitroaniline; and *p*-bromonitrobenzene.

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1085. *Controlled Oxidations of Organic Compounds with Cerium(IV). The Oxidation of Benzyl Alcohols to Benzaldehydes*

By WALTER S. TRAHANOVSKY and L. BREWSTER YOUNG

ALTHOUGH cerium(IV) is a widely used oxidant in analytical and inorganic chemistry, little attention has been given to its use as an oxidant of organic compounds. The mechanism of the oxidation of alcohols and ketones by cerium(IV) has been studied; however, these reactions were carried out under conditions where an excess of the oxidant converted first-formed products into carbon dioxide, formic acid, or acetic acid,^{1,2} or where an excess of the organic reactant was used so that oxidation of the first-formed product was prevented,³⁻⁵

¹ J. Shorter and C. Hinshelwood, *J.*, 1950, 3276; J. Shorter, *J.*, 1950, 3425; 1962, 1868.

² S. Venkatakrishnan and M. Santappa, *Z. phys. Chem. (Frankfurt)*, 1958, 16, 73.

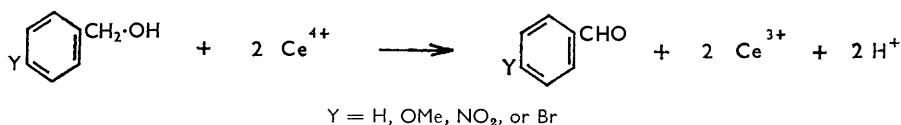
³ M. Ardon, *J.*, 1957, 1811.

⁴ G. Hargreaves and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1955, 51, 1195.

⁵ F. R. Duke and R. F. Bremer, *J. Amer. Chem. Soc.*, 1951, 73, 5179.

or where the reactants were too dilute to be of practical use in synthetic organic chemistry.^{6,7} Also, these oxidations were carried out in relatively strong aqueous acid solutions.

The mechanistic studies indicate that the facile oxidation of carbonyl compounds requires the presence of an α -hydrogen atom.^{1,2,6} Therefore, we felt that conversion of an alcohol into an aldehyde having no α -hydrogen atoms might be carried out as a preparative organic reaction. Moreover, we hoped to find conditions more suitable for the oxidation of organic compounds. Indeed, we have found that benzyl alcohols are converted into



benzaldehydes in >90% yield. The yields (%) of several benzaldehydes are: benzaldehyde, 94 ± 1 ; *p*-methoxybenzaldehyde, 94 ± 2 ; *p*-bromobenzaldehyde, 93 ± 2 ; *p*-nitrobenzaldehyde, 92 ± 9 *; products were identified by infrared and n.m.r. spectra, and the yields are based on gas chromatographic analysis of three separate runs.† Carbonyl compounds that possess α -hydrogens, such as butyraldehyde, cannot be prepared by this method probably because of their facile oxidation by cerium(IV).

The procedure consisted of adding a 50% aqueous acetic acid solution containing 0.5M-ceric ammonium nitrate (reagent grade from Matheson, Coleman, and Bell) to an 0.48 molar ratio of benzyl alcohol. The solution was then warmed on a steam-bath for a few minutes if necessary. After the orange cerium(IV) solution had turned to a pale yellow cerium(III) solution containing a small amount of cerium(IV), the product mixture was extracted with ether. The ether solution was washed with 1.5M-potassium hydroxide and dried. Removal of the ether by distillation left very pure aldehyde, essentially acid- and alcohol-free as determined from infrared and n.m.r. spectra, and gas chromatograms. The convenience of this procedure is obvious and will probably be applicable in the preparation of other types of carbonyl compounds having no α -hydrogens. These mildly acidic conditions complement the mildly basic conditions of lead tetra-acetate in pyridine,⁸ and are, if anything, more convenient.

Currently we are investigating the scope of this reaction and the details of its unusual mechanism. Since our reaction conditions are much less acidic and polar than the strong aqueous acid solutions used previously, we may find completely different kinetic orders, isotope effects, and substituent effects resulting from a gross mechanistic change.

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* A large error in the case of *p*-nitrobenzaldehyde is a result of its low solubility in ether. An 80% yield of the *p*-nitrobenzaldehyde was actually isolated.

† The yields were determined by gas chromatography by adding a measured quantity of ethyl butyrate to the product mixture before extraction. The percentage of aldehyde was calculated from the relative peak areas of the aldehyde and ethyl butyrate, making use of experimentally determined relative thermal conductivities.

⁶ J. S. Littler, *J.*, 1962, 832.

⁷ K. K. Sengupta, *J. Indian Chem. Soc.*, 1964, **41**, 427.

⁸ R. E. Partch, *Tetrahedron Letters*, 1964, 3071.

1086. Comparison of the Acid-catalysed Hydrolyses of Ene-diol Sulphites and Related Compounds

By P. A. BRISTOW, MRS. M. KHOWAJA, and J. G. TILLET

THE mechanism of the acid-catalysed hydrolyses of saturated cyclic and open-chain sulphites has been investigated in some detail.¹ Comparison of the hydrolyses of unsaturated sulphites with their saturated analogues has not hitherto been reported. We now report on the hydrolyses of but-2-ene- and butane-1,4-diol sulphites and dicyclohexyl and diphenyl sulphites as examples of both cyclic and open-chain sulphites.

Hydrolysis of the butenediol sulphite is of particular interest since the reactions of ene-diol sulphites are virtually unknown. All the sulphites studied previously were found to hydrolyse by a bimolecular (*A-2*) mechanism and to involve S-O bond fission, *i.e.*, involving displacement at sulphur. Bunton and Hendy² observed a change in mechanism from bimolecular to predominantly unimolecular when comparing the acid-catalysed hydrolyses of methyl and diphenylmethyl toluene-*p*-sulphinates, implying also a change from S-O to C-O bond fission. Similarly it might be expected that diphenyl sulphite should be structurally favourable for the occurrence of unimolecular C-O bond-fission.

Experimental.—The sulphites were mostly prepared by standard methods. Dicyclohexyl sulphite³ had b. p. 182°/19 mm., n_D^{25} 1.4836; diphenyl sulphite⁴ b. p. 185°/5 mm., n_D^{25} 1.5718; but-2-ene-1,4-diol sulphite⁵ b. p. 73°/3 mm., n_D^{25} 1.4860. Butane-1,4-diol sulphite was prepared by using Reimschneider and Ernst's method for the unsaturated analogue. This gave a sample, b. p. 72°/8 mm., n_D^{25} 1.4651. The yield using this procedure was 90% as compared to the 10% obtained by Szmant and Emerson by using standard methods.⁶

Acid-catalysed hydrolyses. The rates of hydrolysis were determined by a conventional sealed-tube method as described previously (cf. ref. 1). Values of the first-order rate coefficient (k_1), determined from the usual equation, are recorded in the Tables.

TABLE I

The hydrolysis of but-2-ene-1,4-diol sulphite in water *

(a) *Effect of added acids and salts at 25°*

[HClO ₄] (M)	1.00	2.00	3.00	3.50	4.00	4.50	5.00	6.00
10 ³ <i>k</i> ₁ (min. ⁻¹)	0.948	1.99	2.90	3.90	5.58	8.48	12.5	22.6
[HCl] (M)	1.00	3.00	—	—	—	—	—	—
[H ₂ SO ₄] (M)	—	—	1.00	3.00	—	—	—	—
[HClO ₄] (M)	—	—	—	—	2.00	3.00	4.00	—
[NaClO ₄] (M)	—	—	—	—	4.00	3.00	2.00	—
10 ³ <i>k</i> ₁ (min. ⁻¹)	1.22	2.86	10.3	ca. 50	3.52	5.85	12.4	—

(b) *With perchloric acid at different temperatures* (HClO₄ = 1.00 molar)

<i>T</i> (°C)	25.0	45.0	65.0
10 ³ <i>k</i> ₁ (min. ⁻¹)	0.948	6.60	45.8

* Containing 4% dioxan to improve solubility.

¹ C. A. Bunton, P. B. D. de la Mare, and J. G. Tillett, *J.*, 1958, 4754; 1959, 1766; J. G. Tillett, *J.*, 1960, 5138.

² C. A. Bunton and B. N. Hendy, *J.*, 1962, 2562; 1963, 627.

³ W. Voss and E. Blanke, *Annalen*, 1931, 485, 258.

⁴ L. P. Kyrides, *J. Amer. Chem. Soc.*, 1944, 66, 1006.

⁵ R. Reimschneider and W. Ernst, *Z. Naturforsch.*, 1960, 15, 552.

⁶ H. Szmant and W. Emerson, *J. Amer. Chem. Soc.*, 1956, 78, 454.

TABLE 2

Hydrolysis of butane-1,4-diol sulphite in water

(a) Effect of added acids and salts at 25°

[HClO ₄] (M)	0.500	0.750	1.00	1.50	2.00	2.50	0.500	1.00	1.50
[NaClO ₄] (M)	—	—	—	—	—	—	1.50	1.00	0.50
10 ³ k ₁ (min. ⁻¹)	0.147	0.259	0.350	0.559	0.836	1.25	0.254	0.467	0.679
[HClO ₄] (M)	—	—	—	—	0.50	1.00	1.50	2.00	—
[H ₂ SO ₄] (M)	0.500	1.00	—	—	—	—	—	—	—
[HCl] (M)	—	—	0.500	1.00	—	—	—	—	—
10 ² k ₁ (min.)	0.198	0.468	0.441	1.35	0.124*	0.343*	0.520*	0.821*	—

(b) With perchloric acid at different temperatures

[HClO ₄] (M)	0.500	1.00	0.500	1.00	1.00
T (°C)	35.01	35.01	45.01	45.01	0.00
10 ² k ₁ (min. ⁻¹)	0.452	1.25	1.65	4.26	0.134

* In 60% dioxan-water (v/v) as solvent.

TABLE 3

The hydrolysis of dicyclohexyl sulphite in 60% dioxan-water (v/v) at 0°

[HClO ₄] (M)	1.00	2.00	3.00	4.00	—	—	—
[HCl] (M)	—	—	—	—	0.500	1.00	1.50
10 ² k ₁ (min. ⁻¹)	0.102	0.518	0.850	1.340	0.149	0.735	0.962

TABLE 4

The hydrolysis of diphenyl sulphite in 60% dioxan-water (v/v) at 0°

[HClO ₄] (M)	1.00	2.00	3.00	3.50	4.00
10 ³ k ₁ (min. ⁻¹)	0.027	0.248	0.929	1.30	2.73

DISCUSSION

The variation of rate with perchloric acid concentration is qualitatively similar for both the butane and butenediol sulphites. The slopes of the Hammett plots ($\log k$ versus $-H_0$) are 0.72 and 0.60, respectively. Such a pseudo-Hammett correlation could be given by a bimolecular reaction on which was superimposed a large positive salt effect. That this is indeed the case is shown for both compounds by the fact that, in mixtures of perchloric acid and sodium perchlorate at approximately constant perchlorate-ion concentration, the rate is more nearly proportional to the stoichiometric acidity. That the hydrolysis proceeds by an A-2 process is confirmed by the values of the entropy of activation ($\Delta S^* = -8.5$ and -17.5 e.u., respectively), which fall into the range expected for a bimolecular process.⁷

Hydrochloric and sulphuric acids have a pronounced effect on both reactions. This is in accord with their effect on the hydrolyses of other sulphites and is considered to arise from specific anion catalysis by the anion of the acid, the anion competing with water as a nucleophile in the rate-determining step.

Thus unsaturated cyclic aliphatic sulphites seem to hydrolyse by the same mechanism

⁷ F. A. Long, J. G. Pritchard, and F. E. Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2362.

as has already been established for their saturated analogues and they show similar kinetic behaviour. The butenediol sulphite hydrolyses about four times faster than the saturated sulphite. This may arise, in part, from the fact that the double bond somewhat reduces the flexibility of the ring which is virtually strainless in the seven-membered ring saturated sulphites.

Similarly both diphenyl and dicyclohexyl sulphites show almost identical kinetic behaviour in acid solutions. Thus the slopes of the Hammett plots are 0.61 and 0.75, respectively. The effect of added salts and of other acids again confirms that both these compounds hydrolyse by the *A*-2 process. Thus the change in mechanism which occurs on going from methyltoluene- to diphenylmethyltoluene-*p*-sulphinic acid does not occur in dicyclohexyl and diphenyl sulphites. Both sulphites are considered to hydrolyse by the general mechanism of sulphite hydrolysis.

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1087. *Dissociation Constants of 8-Chloro-1-naphthoic Acid and Some Derivatives*

By A. FISCHER, R. E. J. HUTCHINSON, and R. D. TOPSOM

MODERATE steric compression of carboxylic acid groups directly joined to an aromatic ring is known to be acid-strengthening. The effect arises from inhibition of mesomerism between the undissociated acid group and the aromatic nucleus.¹ Once the group is substantially forced out of the plane of the aromatic ring, further steric compression may not increase the acidity much more² and may even result in acid-weakening.^{3,4} Thus, while 2,6-dimethyl-⁵ and 2,6-di-isopropyl-benzoic acid⁴ are considerably stronger than benzoic acid, the corresponding tetra-alkylbenzoic acids are intermediate in strength in spite of the buttressing effect of the additional substituents.^{3,4} This can be explained in terms of the larger effective size of the anion than the undissociated carboxyl group, inhibition of solvation of the anion, and possibly also some loss of mesomerism in the anion as a result of its distortion.⁴

Courtauld models show some steric strain between the substituent groups in 8-chloro-1-naphthoic acid, and suggest that the carboxyl group may be forced so far out-of-plane as to lose all significant conjugation with the ring. The measured *pK* for dissociation in 20% dioxan-water (Table) is only 0.10 *pK* unit lower than that of 1-naphthoic acid, and this indicates that the second (acid-weakening) effect mentioned above may be of significance here. As further evidence of lack of conjugation, only small changes in acidity result on 4,5-substitution by methyl groups or an ethylene bridge (Series C). The changes are

¹ C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, 1953.

² J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, *J.*, 1956, 2995.

³ M. Crawford and J. H. Magill, *Trans. Faraday Soc.*, 1955, 51, 704.

⁴ M. Crawford and M. Woodhead, *Tetrahedron Letters*, 1962, 1189.

⁵ J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, *J.*, 1954, 470.

similar to those found⁶ for the corresponding 2-naphthoic acids (Series B) where conjugation of the substituent with the acid group is not possible. There is no parallel to the marked effect of a 4,5-ethylene bridge found with the 1-naphthoic acids (Series A). This effect was explained⁶ as resulting from hyperconjugative electron release, and necessarily requires conjugation between the substituent and the acid group.

pK Values of substituted naphthoic acids in 20% (w/w) dioxan-water at 25°

	Acid	<i>pK</i>	ΔpK
Series A	1-Naphthoic	4.53	—
	4,5-Dimethyl-1-naphthoic	4.61	0.08
	5-Acenaphthoic	5.30	0.77
Series B	2-Naphthoic	4.89	—
	4,5-Dimethyl-2-naphthoic	5.00	0.11
	4-Acenaphthoic	5.08	0.19
Series C	8-Chloro-1-naphthoic	4.43	—
	8-Chloro-4,5-dimethyl-1-naphthoic	4.57	0.14
	6-Chloro-5-acenaphthoic	4.66	0.23

Experimental.—*Chloro-acids.* 8-Chloro-1-naphthoic acid, recrystallised successively from water, xylene, aqueous acetic acid, and water, had m. p. 168—168.5° (lit.,⁷ 168—169°). 6-Chloro-5-acenaphthoic acid, purified by chromatography on silica gel with benzene-ether (19 : 1) as eluent, had m. p. 227° (from aqueous ethanol) (lit.,⁸ 222—224°).

8-Chloro-4,5-dimethyl-1-naphthoic acid. Small portions of 4,5-dichloro-1,8-dimethylnaphthalene, itself prepared⁹ from 5,6-dichloroacenaphthene⁸ (3.5 g.), and of *n*-butyl chloride (3.3 ml.) were added alternately during 1.5 hr. to refluxing tetrahydrofuran (20 ml.) containing magnesium (1.5 g.) and a trace of iodine. After being stirred for 12 hr., the mixture was poured into tetrahydrofuran (10 ml.) containing "dry-ice" (10 g.). Acidification and evaporation of the tetrahydrofuran allowed collection of the crude *acid*. It was dissolved in aqueous sodium hydroxide (2*N*), the solution filtered, and the compound (2.2 g.) recovered by acidification. Recrystallisation from ethanol and chromatography as for the acenaphthoic acid above gave material with m. p. 227° (Found: C, 66.8; H, 4.9. C₁₃H₁₁ClO₂ requires C, 66.55; H, 4.7%).

Dissociation constants. These were measured in 20% dioxan-water by the spectrophotometric method, using a Beckman DK2A instrument. The method and reagents were as previously described.⁶

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⁶ A. Fischer, W. J. Mitchell, J. Packer, R. D. Topsom, and J. Vaughan, *J.*, 1963, 2892.

⁷ H. G. Rule and A. J. G. Barnett, *J.*, 1932, 175.

⁸ R. L. Letsinger, J. A. Gilpin, and W. J. Vullo, *J. Org. Chem.*, 1962, 27, 672.

⁹ W. J. Mitchell, R. D. Topsom, and J. Vaughan, *J.*, 1962, 2526.

1088. *The Preparation of 4-Methylpyrene*

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4-METHYLPYRENE was required in gram quantities for biological testing. Published methods of synthesis are laborious and unsuitable for preparative scale work, but the hydrocarbon was conveniently obtained in 25% overall yield from 1,2,3,6,7,8-hexahdropyrene by chloromethylation under carefully controlled conditions, followed by reduction with palladium and hydrogen, and dehydrogenation.

Experimental.—Melting points were determined on a Kofler hot-stage apparatus. Light petroleum refers to the fraction of b. p. 60—80°. Ultraviolet spectra refer to solutions in 95% ethanol.

4-Chloromethyl-1,2,3,6,7,8-hexahdropyrene. A solution of 1,2,3,6,7,8-hexahdropyrene (5 g.) and chloromethyl ether (3.25 ml.) in acetic acid (100 ml.) was warmed at 45—50° for 72 hr., poured into water, and extracted with benzene. The extract was washed with sodium carbonate solution and water, and the product (5.7 g.) distilled. The *compound* (2.7 g.) was collected at 180—200°/0.2 mm.; it crystallised from light petroleum as needles, m. p. 116—117° (Found: C, 79.0; H, 6.5; Cl, 13.7. $C_{17}H_{17}Cl$ requires C, 79.4; H, 6.7; Cl, 13.8%). The residue from the distillation was chromatographed on alumina; elution with benzene—light petroleum (1:9) gave the *di(hexahdropyrenyl)methane* (0.35 g.) as fine needles, m. p. 165—166° (Found: C, 92.2; H, 7.7. $C_{33}H_{32}$ requires C, 92.5; H, 7.5%), λ_{max} . 244, 293, 300, 319, 334 $m\mu$ ($\log \epsilon$ 5.23, 4.15, 4.21, 3.93, 3.75). Chloromethylation with chloromethyl ether in carbon disulphide catalysed by stannic chloride, or with paraformaldehyde and hydrogen chloride in acetic acid or phosphoric acid, gave a less pure product.

4-Methylpyrene. The above chloromethyl compound (900 mg.) was reduced with hydrogen and palladised charcoal (10%; 100 mg.) in acetone solution. The recovered 1,2,3,6,7,8-hexahydro-4-methylpyrene (750 mg.) formed needles (from light petroleum), m. p. 114—115° (Found: C, 91.8; H, 8.4. $C_{17}H_{18}$ requires C, 91.8; H, 8.2%). Dehydrogenation of this compound (500 mg.) with palladised charcoal (10%; 500 mg.) in boiling *p*-cymene (10 ml.), and purification of the product by filtration through a column of alumina, afforded 4-methylpyrene (300 mg.) as cubes (from ethanol), m. p. 146—147° alone or mixed with an authentic specimen (lit.,¹ m. p. 147.5—148.5°), λ_{max} . 234, 243, 255, 265, 275, 289, 309, 327, 339, 355, 360, 365, 375 $m\mu$ ($\log \epsilon$ 4.55, 4.85, 3.00, 4.27, 4.56, 3.59, 4.00, 4.38, 4.60, 2.83, 2.60, 2.53, 2.51). Gas-liquid chromatography of the product showed only one peak. Dehydrogenation of the hexahydro-compound with sulphur or with palladised charcoal at 280° without solvent gave a mixture of pyrene and the 4-methyl compound.

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¹ W. E. Bachmann and R. O. Edgerton, *J. Amer. Chem. Soc.*, 1940, **62**, 2970.

1089. *The Nuclear Magnetic Resonance Spectrum of Dihydrosterigmatocystin: A Correction*

By J. A. KNIGHT, JOHN C. ROBERTS, and J. G. UNDERWOOD

SOME of the results recorded¹ for the nuclear magnetic resonance spectrum of dihydrosterigmatocystin are incorrect. We give below new values for the spectrum of this compound. (Figures in parentheses, following the statement of the nature of the signal, indicate intensities.)

The spectrum (deuteriochloroform solution with tetramethylsilane as internal reference, run on a Perkin-Elmer model R 10, 60 Mc./sec., Spectrometer) showed: (i) a singlet (1) at -3.18τ (OH); (ii) a triplet (1) at 2.62τ , $J = 8.2$ c./sec. (H-6); (iii) four doublets (2) at 3.34τ , $J = 8.2$ c./sec. (H-5 and H-7); (iv) a doublet (1) at 3.59τ , $J = 6$ c./sec. (H-c); (v) a singlet (1) at 3.76τ (H-2); (vi) a multiplet (1) at *ca.* 5.8τ , $J = 6$ c./sec. (H-d); (vii) a singlet (3) at 6.09τ (O·CH₃); (viii) a multiplet (2) at *ca.* 6.2τ ($2 \times$ H-b); (ix) a multiplet (2) at 7.74τ ($2 \times$ H-a).

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¹ E. Bullock, J. C. Roberts, and J. G. Underwood, *J.*, 1962, 4180, 4181; E. Bullock, D. Kirkaldy, J. C. Roberts, and J. G. Underwood, *J.*, 1963, 831.