463. *Esters containing Phosphorus. Part XV.* Preparation and Reactions of Diphenylphosphine Oxide.*

By B. B. HUNT and B. C. SAUNDERS.

WILLIAMS and HAMILTON prepared di-*n*-alkylphosphine oxides, but were unable to isolate any diarylphosphine oxides (*e.g.*, diphenylphosphine oxide).[1] We have succeeded in preparing diphenylphosphine oxide (I) by the action of phenylmagnesium bromide on diethyl hydrogen phosphite:

$$(EtO)_2PH(:O) \longrightarrow Ph_2P(:O)\cdot MgBr \longrightarrow Ph_2PH(:O) \quad (I)$$

We have shown that diphenylphosphine oxide is in equilibrium with diphenylphosphinous acid (II). Infrared measurements indicate that under normal conditions the phosphine oxide form (I) preponderates. However the aqueous solution reacts quantitatively with silver nitrate solution to give silver diphenylphosphinite: this reaction is not instantaneous. Diphenylphosphine oxide was oxidised quantitatively in aqueous solution by bromine yielding diphenylphosphinic acid (III), also produced by dilute hydrogen peroxide solution or acidified potassium permanganate solution.

$$\underset{(I)}{Ph_2PH(:O)} \longrightarrow \underset{(IV)}{Ph_2PCl(:O)} \longrightarrow \underset{(V)}{Ph_2P(:O)\cdot NHPh} \qquad \underset{(III)}{Ph_2P(:O)\cdot OH} \longleftarrow \underset{(II)}{Ph_2P\cdot OH} \longrightarrow Ph_2P\cdot OAg$$

Thionyl chloride converted diphenylphosphine oxide into diphenylphosphinic chloride (IV), the constitution of which was confirmed by an alternative synthesis from the phosphine oxide and *N*-chlorosuccinimide. In these reactions the phosphine oxide almost certainly reacts in the tautomeric form (I). Diphenylphosphinic chloride was readily characterised by its conversion with aniline into the crystalline *NPP*-triphenylphosphinamide (V).

Experimental.—Diphenylphosphine oxide. Bromobenzene (68·4 g.) in ether (100 ml.) was added slowly with stirring to magnesium turnings (12 g.) and ether (100 ml.), and heated under reflux for 15 min. To the cooled reagent, diethyl hydrogen phosphite (20 g.) in ether (80 ml.) was added slowly, with stirring, and the whole heated under reflux for 15 min. (An atmosphere of nitrogen did not increase the yield appreciably.) The mixture was cooled to 0°, 10% hydrochloric acid (200 ml.) was run in slowly and then water (200 ml.). The ether layer was extracted with 2% hydrochloric acid (100 ml. portions) to remove diphenylphosphine oxide. This was ascertained by adding bromine water to a test-sample of the aqueous layer, any diphenylphosphine oxide being converted into insoluble diphenylphosphinic acid. The combined aqueous layers (2·4 l.) were extracted with benzene (50 ml. portions) until the aqueous layer no longer contained diphenylphosphine oxide (bromine-water test). The benzene extracts (650 ml.) were dried (Na_2SO_4) and evaporated, giving *diphenylphosphine oxide* (19·2 g., 66%). The crude product was dissolved in dry ether at 18° and cooled to −60°, yielding colourless hygroscopic needles of the oxide, m. p. 53—56° (14 g., 48%) [Found: C, 71·35; H, 5·4; P, 15·5%; *M* (Rast), 213. $C_{12}H_{11}OP$ requires C, 71·25; H, 5·5; P, 15·3%; *M*, 202].

Principal infrared absorption peaks: 3450, 3050, 2320, 1587, 1484, 1439, 1185, 1162, 1120, 1072, 1027, 1000, 955, 922, 757, 740, 720, 693 cm.$^{-1}$.

Oxidation of diphenylphosphine oxide. (*a*) Quantitatively by bromine. Bromine water (20 ml.; 0·1376N) was added to an aqueous solution of diphenylphosphine oxide (20 ml. containing 0·1457 g.). A precipitate of diphenylphosphinic acid, m. p. 193—195°, appeared immediately (Kosolapoff [2] gave m. p. 190—192°). The excess of bromine was determined by addition of potassium iodide solution and titration with sodium thiosulphate solution [Found: 0·1457 g. of diphenylphosphine oxide required 0·1130 g. of bromine. So 202·2 g. (1 mole) of diphenylphosphine oxide required 15·70 g. of oxygen for oxidation to diphenylphosphinic acid].

* Part XIV, preceding paper.

[1] Williams and Hamilton, *J. Amer. Chem. Soc.*, 1952, **74**, 5418.
[2] Kosolapoff, *ibid.*, 1942, **64**, 2982.

(*b*) By hydrogen peroxide. Hydrogen peroxide (50 ml.; 20-vol.) was added to diphenylphosphine oxide (2 g.) in water (100 ml.). Diphenylphosphinic acid (m. p. **193—194°**) was precipitated within 10 min. at room temperature.

Silver diphenylphosphinite. Diphenylphosphine oxide (0·1406 g.) in water (20 ml.) was added to a known excess of silver nitrate solution (20 ml.; 0·1009N). A precipitate appeared after 5—10 min. at 17° and the reaction required 3—4 hr. for completion. At 100° the reaction time was of the order of 15 min. The silver salt was filtered off (as its solubility product was unknown) and the excess of silver nitrate was determined by Volhard's method [Found: 0·1406 g. of diphenylphosphine oxide required 0·1184 g. of silver nitrate. So 202·2 g. (1 mole) of diphenylphosphine oxide required 170·3 g. of silver nitrate (*M*, 170·0)].

Reaction between diphenylphosphine oxide and thionyl chloride. To diphenylphosphine oxide (9·3 g.) in dry chloroform (50 ml.) was added thionyl chloride (30 g.) in dry chloroform (90 ml.) with stirring in an atmosphere of nitrogen. The mixture was heated for 22 hr. After removal of the chloroform the residue was twice distilled, to give diphenylphosphinic chloride, b. p. 190—194/1 mm. (3·4 g., 32%) (Found: C, 60·8; H, 4·7. Calc. for $C_{12}H_{10}OClP$: C, 60·9; H, 4·3%).

NPP-*Triphenylphosphinamide.* Aniline (1·68 g.) was added to diphenylphosphinic chloride (2·11 g.), the mixture was kept for 1 hr., then extracted with boiling benzene. The benzene was evaporated and the NPP-*triphenylphosphinamide* recrystallised from alcohol as colourless needles, m. p. 242—244° (Found: C, 74·0; H, 5·6; N, 4·8. $C_{18}H_{16}ONP$ requires C, 73·7; H, 5·5; N, 4·8%). Morrison [3] gave m. p. 231—233° for (probably very impure) "diphenylphosphinic anilide," prepared by a different method.

Reaction between diphenylphosphine oxide and N-*chlorosuccinimide.* *N*-Chlorosuccinimide (2·7 g.) was added slowly to diphenylphosphine oxide (4 g.) in dry chloroform (50 ml.) at 0° with shaking. The solution was then cooled to −5° and succinimide was filtered off, the chloroform removed, and the residue fractionated, giving diphenylphosphinic chloride, b. p. 186—189°/0·9 mm. (1·3 g., 28%) (Found: C, 60·9; H, 4·5. Calc. for $C_{12}H_{10}OClP$: C, 60·9; H, 4·3%). The phosphinic chloride was characterised as *NPP*-triphenylphosphinamide (see above) which, recrystallised from alcohol, had m. p. 242—244°.

We are indebted to the Salters' Institute of Industrial Chemistry for a scholarship (to B. B. H.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, January 28th*, 1957.]

[3] Morrison, *J. Amer. Chem. Soc.*, 1951, **73**, 5896.

---

464. *Replacement of the Hydrazino-group in Substituted Nitrophenylhydrazines by Bromine or Iodine.*

By SHIAM SUNDER JOSHI and DALEEP SINGH DEORHA.

THE compounds tabulated have been prepared by the action of bromine in acetic acid or iodine in alcohol on substituted nitrophenylhydrazines:

Phenylhydrazine used	Benzene formed	Yield (%)	M. p.	Total halogen found (%)	Total halogen reqd. (%)
2-Chloro-4 : 6-dinitro-	2-Chloro-1-iodo-4 : 6-dinitro-	64	119°	49·1	49·5
2-Bromo-4 : 6-dinitro-	2-Bromo-1-iodo-4 : 6-dinitro-	62	116	55·3	55·5
3-Methyl-4 : 6-dinitro-	1-Iodo-3-methyl-4 : 6-dinitro-	65	110	41·5	41·2
3-Methyl-2 : 4 : 6-trinitro-	1-Iodo-3-methyl-2 : 4 : 6-trinitro-	63	146	36·1	36·0
6-Chloro-3-methyl-2 : 4-dinitro-	6-Chloro-1-iodo-3-methyl-2 : 4-dinitro-	62	136	47·6	47·4
4-Chloro-2 : 6-dinitro-	4-Chloro-1-iodo-2 : 6-dinitro-	55	129	49·8	49·5
4-Bromo-2 : 6-dinitro-	4-Bromo-1-iodo-2 : 6-dinitro-	54	125	55·9	55·5
3-Chloro-4 : 6-dinitro-	3-Chloro-1-iodo-4 : 6-dinitro-	62	102	49·8	49·5
2-Chloro-4 : 6-dinitro-	1-Bromo-2-chloro-4 : 6-dinitro-	68	62	41·2	41·0
4-Chloro-2 : 6-dinitro-	1-Bromo-4-chloro-2 : 6-dinitro-	60	106	40·85	41·0

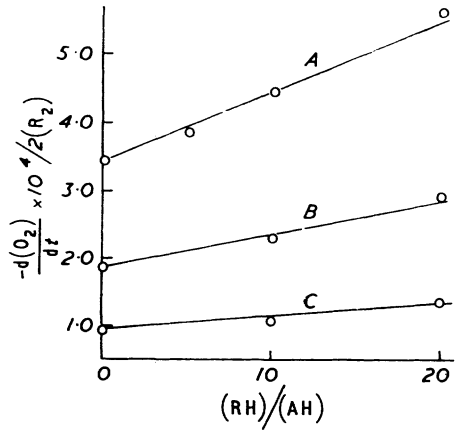
CHEMICAL LABORATORIES, MEERUT COLLEGE, MEERUT, INDIA. [*Received, June 12th*, 1956.]

465. *Alkylperoxy-radicals. Part IV.* The First Step in the Reaction with Alkylphenols.*

By A. F. Bickel and E. C. Kooyman.

In previous papers of this series, arguments were given supporting the view that the primary step in the interaction of hindered phenols and alkylperoxy-radicals consists in the removal of hydrogen from the hydroxyl group. Thus, nearly identical antioxidant efficiencies were recorded for 2 : 6-di-*tert.*-butyl-4-methylphenol and 2 : 4 : 6-tri-*tert.*-butylphenol,[1] both yielding analogous reaction products, *viz.*, *cyclo*hexadienones carrying a RO·O group in the 4-position.

On the other hand Hammond *et al.*[2] advocated the reversible addition of RO·O· radicals to the phenolic or amine type of antioxidant, to yield a complex which is then destroyed in an irreversible reaction with a second alkylperoxy-radical. Their principal argument is the finding of almost identical rates of oxidation when *N*-methylaniline (or diphenylamine)



Autoxidation of 9 : 10-*dihydroanthracene retarded by* 2 : 6-*di*-tert.-*butyl*-4-*methylphenol.*

A, 64·84°; *B*, 59·94°; *C*, 54·96°.

and the *N*-deuteroamine are compared as retarders for the autoxidation of tetralin initiated by αα″-azo*iso*butyronitrile. In their opinion, the absence of an isotope effect precludes the primary abstraction of hydrogen from the amino-group.

Generally, a low value for the activation energy of a reaction results in a small isotope effect.[3]

Hence it is obvious that the general argument employed by Hammond *et al.* is inconclusive as long as the activation energy involved is unknown, since it may well be very low. To settle this point for the case of a phenolic antioxidant, we have investigated the autoxidation of 9 : 10-dihydroanthracene (RH) initiated by 2 : 2 : 3 : 3-tetraphenylbutane (R_2) and retarded by various amounts of 2 : 6-di-*tert.*-butyl-4-methylphenol (AH) at three temperatures. The rate of oxidation can be represented (Part II) by :

$$-d(O_2)/dt - 2k_D(R_2) = 2k_D(R_2)k_r(RH)/2k_a(AH)$$

where k_D is the rate constant for dissociation of R_2, k_r is the rate constant for RO·O· + RH ⟶ RO·OH + R· (E_r), and k_a is the rate constant for RO·O· + AH ⟶ RO·OH + A· (E_a). The results are presented in the Figure [$d(O_2)/dt$ is in moles/sec. and the other reactants are in moles]. The activation energy (E_D) for the dissociation of R_2 was

* Part III, *J.*, 1957, 2217.

[1] Bickel and Kooyman, *J.*, 1956, 2215.
[2] Hammond, Boozer, Hamilton, and Sen, *J. Amer. Chem. Soc.*, 1955, **77**, 3238.
[3] Wiberg, *Chem. Rev.*, 1955, **55**, 713.

calculated from the points on the vertical axis [(RH) = 0; AH in excess]. It was found to be 28·4 ± 0·5 kcal./mole; the value recorded by Ziegler [4] is 30·0 kcal./mole.

The overall temperature coefficient $E = E_D + E_r - E_a$ was calculated from the slopes of the lines in the Figure to be 36·2 ± 0·5 kcal./mole. Hence $E_r - E_a = 7{\cdot}8 \pm 1{\cdot}0$ kcal./mole. From the work of Bolland and collaborators [5] it is known that E_r for various alkenylaromatic compounds varies from 5 to 9 kcal./mole ($Ph{\cdot}CH_2{\cdot}CH{:}CH_2$ 9·2; $Ph{\cdot}CH_2{\cdot}CH{:}CMe_2$ 5·3); for 9 : 10-dihydroanthracene we may assume this value to be about 7 kcal./mole. It follows that E_a will be close to zero, which, in turn, will lead to a very small isotope effect. In our opinion, therefore, the absence of isotope effects cannot be taken as evidence against removal of hydrogen from the hydroxyl group of phenols as the primary step.

The above reasoning implies that the reaction of a phenol with a less active attacking radical might provide an opportunity of detecting isotope effects, since the activation energy would be higher. In order to investigate this possibility, diphenylpicrylhydrazyl radicals have been allowed to react with a large excess of 2 : 6-di-*tert.*-butyl-4-methylphenol in toluene at 20° and 30° and also with the deuterated analogue. The rate of removal of the hydrazyl is strictly of first order with respect to hydrazyl up to high conversions. The activation energy, calculated from the bimolecular rate constants (k_{bi}) at 20° and 30°, was 5·3 ± 0·5 kcal./mole, whilst the isotope effect at 20° showed a value of 1·95. This provides strong evidence that in this case the rate-determining step consists in an attack at the hydroxyl group. Admittedly, in view of the difference between diphenylpicrylhydrazyl radicals and alkylperoxy-radicals, the above result does not definitely prove that the latter radicals also react at the hydroxyl group.

Experimental (with W. Roest).—*Starting materials.* Deuteration of 2 : 6-di-*tert.*-butyl-4-methylphenol was carried out by refluxing a solution in benzene with changes of 99·9% D_2O until 85—86% of the OD-compound was present, as determined by infrared spectroscopy.

Diphenylpicrylhydrazyl was prepared according to Goldschmidt and Reun's directions.[6]

The other starting materials were prepared as described in Parts I and II.

Initial rates of oxidation. These were determined as recorded in Part II.

Rates of removal of diphenylpicrylhydrazyl. These were measured spectrophotometrically at 6000 Å. In a typical experiment a two-compartment flask was supplied with 3 ml. of a solution of 21 mg. of 2 : 6-di-*tert.*-butyl-4-methylphenol in toluene and with 10 ml. of a solution containing 1·96 mg. of diphenylpicrylhydrazyl in toluene. The flask was placed in a thermostat at 20° and at zero time the solutions were mixed and the recording Cary spectrophotometer set in motion. Immediately afterwards the solution was transferred to the cell of the instrument and the extinction at 6000 Å was measured continuously.

Temp.	20·0°	20·0°	30·0°
Phenol (10^{-3} mole/l.)	7·37 *	7·35	7·35
Hydrazyl (10^{-3} mole/l.)	0·392	0·385	0·385
k_{bi} (l. mole^{-1} sec.$^{-1}$)	0·046 †	0·078	0·105

* 85% deuterated. † Recalc. for pure D compound = 0·040.

The authors thank the Management of the Koninklijke/Shell-Laboratorium, Amsterdam, for their permission to publish this Note.

Koninklijke/Shell-Laboratorium, Amsterdam. [*Received, September 19th,* 1956.]

[4] Ziegler, *Annalen*, 1942, **551**, 150.
[5] Bolland, *Quart. Rev.*, 1949, **3**, 1.
[6] Goldschmidt and Reun, *Ber.*, 1922, **55**, 628.

466. *A Determination of the Heat of Formation of Potassium Manganate.*

By R. A. W. Hill and (the late) J. F. Williamson.

During recent investigations of combustion in solid mixtures of potassium permanganate and metals [1] it was necessary to calculate heats of plausible reactions for comparison with observed heats. For this the heat of formation of potassium manganate, a possible reduction product of potassium permanganate, was needed.

Potassium manganate cannot conveniently be prepared as a pure crystalline substance because of its instability,[2] but the ice-cold, alkaline, aqueous solution is stable for long periods. Thus the heat of formation in solution can be determined by measuring the heat of reduction of potassium permanganate under these conditions. Reduction with hydrogen peroxide may be represented by the three equations :

$$(1)\quad 2KMnO_4 + H_2O_2 + 2KOH \longrightarrow 2K_2MnO_4 + 2H_2O + O_2 + Q_1$$

$$(2)\quad K_2MnO_4 + H_2O_2 \longrightarrow \tfrac{1}{2}K_2O,2MnO_2\downarrow + \tfrac{1}{2}H_2O + KOH + O_2 + Q_2$$

$$(3)\quad H_2O_2 \xrightarrow{K_2O,2MnO_2} H_2O + \tfrac{1}{2}O_2 + Q_3$$

Knowledge of Q_1 allows $\Delta H_f K_2MnO_4$(aq.) to be calculated from tabulated heats of formation [3] of potassium permanganate, potassium hydroxide, hydrogen peroxide, and water. Direct measurement of Q_1 is not easy because even with good stirring reactions (1) and (2) are not quite consecutive. This difficulty has been overcome by use of a special method, in which hydrogen peroxide solution is added at a constant rate to potassium permanganate solution. The rate of rise in temperature at any time is then proportional to a weighted mean of the heats of the reactions then occurring.

Experimental.—Potassium permanganate solution (3·5 g. in 500 ml.), approx. 5N in potassium hydroxide, was contained in a Dewar flask surrounded by ice and water; a pipette containing 20-vol. hydrogen peroxide [about 20% more than that required for reactions (1) and (2)] was completely immersed in this solution. The peroxide was blown into the permanganate solution by means of a steady stream of nitrogen, precooled to 0°, and the temperature was recorded. A typical temperature–time curve is shown in the Figure. It is simpler than was expected in that there is no change in slope during reactions (1) and (2). On the other hand the change from reaction (2) to reaction (3) is sharply indicated. We therefore conclude that Q_1 and Q_2 have nearly the same value and that this may be calculated from the temperature rise A—B and the electrical equivalent of the system, giving :

$$Q_1 = \tfrac{1}{3}(Q_1 + 2Q_2) = 35{\cdot}5 \text{ kcal./mole.}$$

Another way is to compare the slopes corresponding to Q_1 and Q_3; then

$$\frac{Q_3}{Q_1} = \frac{(dT/dt)_3}{(dT/dt)_1}$$

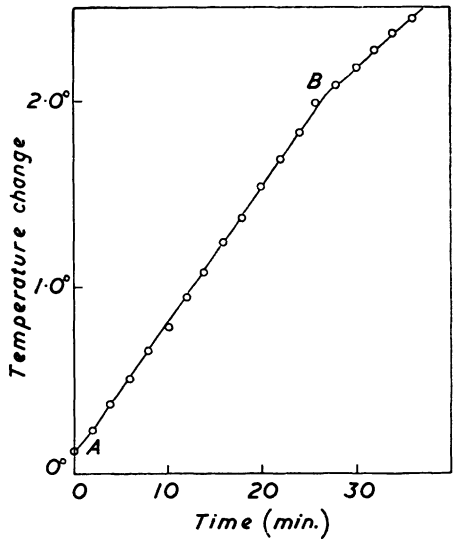
where Q_3 is to be calculated from the tabulated heats of formation [3] of hydrogen peroxide and water. This procedure gives $Q_1 = 35{\cdot}7$ kcal./mole, which is in good agreement.

The composition of the precipitated manganite was investigated to check the correctness of equation (2), particular attention being given to the oxygen : manganese ratio, which affects

[1] Hill, *Proc. Roy. Soc.*, 1954, *A*, **226**, 455; Hill and Wallace, *Nature*, 1956, **178**, 692.
[2] Duke, *J. Phys. Chem.*, 1952, **56**, 882.
[3] "Selected Values of Chemical Thermodynamic Properties," Circular 500, Nat. Bur. Stand., U.S.A., 1952.

the calculation of Q_1 from $Q_1 + 2Q_2$. The procedure followed was that described by Maxwell, Butler, and Thirsk [4] with the difference that the potassium was estimated by precipitation as cobaltinitrite instead of photometrically. The composition was found to correspond to $1{\cdot}04K_2O,2MnO_{1{\cdot}97}(xH_2O)$, or within the limits of error $K_2O,2MnO_2(xH_2O)$, as required by equation (2). The water content could not be determined because washing and drying the precipitate altered the Mn : O and the K : O ratio, but this does not affect the calculation of Q_1.

Two complete runs were carried out, giving four values of Q_1 : by temperature rise *A*—*B*, 35·4, 35·7; by ratio of slopes, 35·4, 36·0 kcal./mole; average 35·6 ± 1·5 kcal./mole. The error was calculated from estimates of the accuracy of measurement of temperature rise *A*—*B* (±2%), of slope (1) (±2%), slope (3) (±4%), of electric power (±1%), and of stoicheiometry, as indicated by the oxygen : manganese ratio of the precipitate. Three successive determinations of an electrical equivalent with different voltages and times of heating gave **668, 671, 669** cal. °c^{-1}, indicating that the random error in this part of the experiment is less than the systematic error (±1%).



The heats of formation of hydrogen peroxide, potassium hydroxide, and water are very well established and do not contribute to the error in the calculated heat of formation of potassium manganate. That of potassium permanganate rests on Thomsen's early work and is less certain; tentatively we allow an extra ½ kcal. for this. Then :

$$Q_1 = 35{\cdot}5 \pm 1{\cdot}5;\ \Delta H_f K_2MnO_4(\text{aq.}) = -273 \pm 2 \text{ kcal./mole.}$$

It will be seen that a bigger uncertainty than 2 kcal. is involved below in allowing for the heat of solution.

Discussion.—For the purpose of calculating heats of solid–solid reactions a heat of solution assumed to be the same as that of $KMnO_4$ (10 kcal./mole) was added to the above value to give :

$$\Delta H_f K_2MnO_4(\text{cryst.}) = -283 \text{ kcal./mole}$$

The difference between this and Mixter's value for crystalline sodium manganate,[3] −274 kcal./mole, obtained by a dry-way method, is typical of corresponding sodium and

[4] Maxwell, Butler, and Thirsk, *J.*, 1952, 4210.

potassium salts, the heats of formation of which usually differ by about 6 kcal./g.-atom of alkali metal. Both values, therefore, are probably correct to within 4 kcal., which is a useful accuracy for present requirements.

The authors thank Dr. A. P. Zeelenberg for analysing the precipitated potassium manganite.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, NOBEL DIVISION,
RESEARCH DEPARTMENT, STEVENSTON, AYRSHIRE. [*Received, November 23rd*, 1956.]

---

467. *The Vapour Pressures of Some Solid Organic Compounds.*

By R. LITTLEWOOD.

DURING recent work on the evaporation coefficient,[1] effusion rates through small orifices of the saturated vapours of various solid organic compounds were determined. From these results, the saturation vapour pressures have been calculated according to Knudsen's method.[2]

Experimental.—The apparatus was essentially similar to the second described by Bradley, Evans, and Whytlaw-Gray (ref. 3, p. 387), but the differential method was not employed. The ends of the two small glass effusion tubes were closed by sheet platinum caps fused to the glass and pierced by holes, through which effusion took place. Hole diameters ranged from 1 to 3 mm. The holes were drilled by clamping the platinum sheet between two sheets of $\frac{1}{4}$ in. brass and using a pillar drill; they were perfectly circular and free from " burrs ". The area of each hole was found, with good agreement in several determinations, by photographing the silhouette with a photomicrographic apparatus and weighing the image of the hole cut from a print on photographic paper. The method was calibrated by use of a $\frac{1}{4}$ mm. graticule. The hole diameters were checked by means of a travelling microscope, after fusion of the discs into the tubes. Small corrections (about 3%) were applied to the areas to allow for the thickness of the platinum foil.

Crystals of the material to be studied were finely powdered, introduced into the effusion tubes, and then fused and allowed to run over the glass surface so that a solid film of large surface area was formed in the vessel. Several tubes with different hole sizes were used for each substance.

The filled tubes, in pairs, were subjected to high vacuum in the apparatus for about an hour, after which dry air was admitted and the tubes weighed in turn on an analytical microbalance against an empty tube which had been similarly treated. The two tubes were replaced in the apparatus and allowed to come to equilibrium with the thermostat. The apparatus was then evacuated, a technique which ensured that the pressure fell below 10^{-3} mm. within 30 sec. being used. A half-minute was subtracted from the duration of all runs to allow for this. At the end of the run, dry air was admitted to the apparatus and the effusion tubes were removed and weighed as before.

Solid carbon dioxide–acetone was used in the cold traps. Materials were purified by recrystallisation twice from a suitable solvent and the setting points of the purified materials were checked against data from standard references.

Vapour pressures were calculated from $p = qT^{\frac{1}{2}}/(3{\cdot}50AM^{\frac{1}{2}})$, where p = vapour pressure (mm.), q = rate of effusion (g. per min.), T = absolute temperature, M = molecular weight of effusing vapour, and A = area of orifice (cm.^{2}).

Results.—Calibration with benzophenone, recrystallised twice from light petroleum (b. p. 60—80°), gave a vapour pressure of $3{\cdot}14 \times 10^{-4}$ mm. at 20·0° (mean of 4 determinations, mean deviation 7%) (cf. $3{\cdot}24 \times 10^{-4}$ mm. calculated from the data of Neumann and

[1] Littlewood and Rideal, *Trans. Faraday Soc.*, 1956, **52**, 1598.
[2] Knudsen, *Ann. Physik*, 1909, **29**, 179.
[3] Bradley, Evans, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1946, **186**, *A*, 368.

Völker [4]). The results for each material studied showed a similar scatter (see Table), but there was no apparent dependence on orifice diameter or on the duration of the run. It was inferred that no errors were arising due to self-cooling or to uncertainties in the exact time at which effusion commenced, and that the apparatus was operating satisfactorily.

An Arrhenius plot of the results for lauric acid gave a latent heat of sublimation of 28,000 ± 700 cal./mole.

Material	Temp.	No. of determinations	Mean deviation (%)	Vapour pressure (mm. Hg)	Material	Temp.	No. of determinations	Mean deviation (%)	Vapour pressure (mm. Hg)
Stearic acid	60°	1	—	$1{\cdot}42 \times 10^{-6}$	Myristic acid	40°	2	4	$1{\cdot}10 \times 10^{-5}$
Lauric acid	20	8	4	$4{\cdot}91 \times 10^{-6}$	Hexadecanol	30	2	8	$3{\cdot}06 \times 10^{-6}$
,,	25	2	5	$8{\cdot}80 \times 10^{-6}$	Tetradecanol	20	4	9	$1{\cdot}03 \times 10^{-5}$
,,	30	8	7	$2{\cdot}34 \times 10^{-5}$	Phenanthrene	20	4	3	$5{\cdot}67 \times 10^{-5}$
,,	35	2	8	$4{\cdot}36 \times 10^{-5}$	Diphenylmethanol	20	6	6	$2{\cdot}73 \times 10^{-5}$
,,	40	8	9	$1{\cdot}09 \times 10^{-4}$	Erythritol ...	20	1	—	$<10^{-8}$

KING'S COLLEGE, LONDON, W.C.2. [*Received, November 28th*, 1956.]

[4] Neumann and Völker, *Z. phys. Chem.*, 1932, **161**, 33.

---

468. *Some Potentially Cytotoxic Alkyl Sulphonates.*

By W. C. J. Ross and (in part) W. DAVIS.

2-CHLOROETHYL METHANESULPHONATE is known to be effective in preventing the growth of a transplanted rat tumour [1] and to have unusual mutagenic properties.[2] Some related sulphonic esters have now been prepared for biological testing.

The 2-chloroethyl ester may be prepared by heating a mixture of ethylene chlorohydrin and methanesulphonyl chloride until no more hydrogen chloride is evolved [3] but a more general method is to treat the alcohol with the acid chloride in the presence of pyridine at low temperature. Methyl and ethyl butane-1 : 4-disulphonate, however, were more conveniently prepared from the diacid chloride and sodium alkoxide in the corresponding alcohol.

To increase their aqueous solubility, toluene-*p*-sulphonic esters were oxidised to the corresponding *p*-carboxy-derivatives which were administered as sodium salts.

Kiprijanow [4] reported that esters of 2 : 4-dinitrobenzenesulphonic acid are highly reactive as alkylating agents and this has prompted the preparation of the 2-chloroethyl ester. In this instance owing to the greater reactivity of the ester it was necessary to use 2 : 6-lutidine in place of pyridine and to carry out the reaction at −40°.

The effectiveness of the compounds as inhibitors of the transplanted Walker rat carcinoma is shown in the Table. None of the compounds is more effective than the original chloroethyl ester but methyl, ethyl, and fluoroethyl methanesulphonate are of the same order of activity when given at somewhat higher dose levels.

Experimental.—Preparation of alkyl sulphonates : general method. The alcohol (1 mole) in dry pyridine (150 ml.) and ether (150 ml.) at −10° to 0° was stirred whilst methanesulphonyl chloride (1 mole) was added during 1 hr. After being at 0° overnight the mixture was poured on ice–water containing concentrated sulphuric acid (75 ml.). An ether extract was dried (K_2CO_3–Na_2SO_4) and distilled under reduced pressure in the presence of a few pieces of potassium

[1] Haddow and Ross, *Nature*, 1956, **177**, 995.
[2] Fahmy and Fahmy, *ibid.*, p. 996.
[3] Cf. Clemo and Perkin, *J.*, 1922, **121**, 644.
[4] Kiprijanow, XIVth Internat. Cong. Pure Appl. Chem. Handbook, 1955, p. 320.

Compound	B. p./mm.	n_D (temp.)	Formula	Required (%) C	H	Cl	S	Found (%) C	H	Cl	S	Biolog. activity
Methyl methanesulphonate †	96—98°/19 [a]	1·4150 (20°)	—	—	—	—	—	—	—	—	—	+
Ethyl ,, †	90°/10 [b]	1·4194 (15°)	—	—	—	—	—	—	—	—	—	+
n-Propyl ,,	115°/21	1·4209 (20°)	$C_4H_{10}O_3S$	34·8	7·3	—	23·2	34·2	7·2	—	23·2	— ve
n-Butyl ,, †	118°/14 [c]	1·4249 (20°)	$C_5H_{12}O_3S$	39·4	8·0	—	21·1	38·9	8·1	—	21·0	— ve
Methyl ethanesulphonate *†	100—101°/24 [d]	1·4189 (18°)	$C_3H_8O_3S$	29·0	6·5	—	25·8	29·1	6·4	—	25·8	Low
Ethyl ,, *†	108—112°/24 [e]	1·4232 (18°)	$C_4H_{10}O_3S$	34·8	7·3	—	23·2	35·5	7·5	—	23·8	— ve
2-Fluoroethyl methanesulphonate	130°/19	1·4150 (21°)	$C_3H_7O_3FS$	25·3	5·0	—	22·5	25·1	4·8	—	22·7	+
2-Chloroethyl ,,	130°/11 (M. p. 5—6°)	1·4570 (19°)	$C_3H_7O_3ClS$	22·7	4·5	22·4	20·3	23·0	4·6	22·0	20·3	+
2-Bromoethyl ,,	126—128°/5	1·4835 (19°)	$C_3H_7O_3BrS$	17·7	3·5	(Br, 39·3)	—	17·9	3·5	(Br, 38·5)	—	— ve
2-Iodoethyl ,,	140°/6	1·5300 (21°)	$C_3H_7O_3IS$	14·4	2·8	(I, 52·0)	—	14·3	2·9	(I, 51·0)	—	— ve
2-Cyanoethyl ,,	(M. p. 34—36°) [1]	—	$C_4H_7O_3NS$	32·2	4·7	(N, 9·4)	21·5	32·0	4·5	(N, 9·4)	20·7	— ve
2-Chloroethyl toluene-*p*-sulphonate [f]	205—208°/20	1·5303 (18°)	—	—	—	—	—	—	—	—	—	— ve
,, carboxybenzenesulphonate	(M. p. 186—188°) [2]	—	$C_9H_9O_5ClS$	40·8	3·7	13·4	12·1	40·9	3·5	13·4	12·1	— ve
,, ethanesulphonate *	128—130°/13	1·4559 (18°)	$C_4H_9O_3ClS$	27·8	5·3	—	—	28·1	5·2	—	—	+
,, propane-1-sulphonate	146°/16	1·4565 (19°)	$C_5H_{11}O_3ClS$	32·4	6·0	19·1	17·2	32·3	5·9	19·1	16·5	— ve
,, toluene-ω-sulphonate *	(M. p. 47°) [3]	—	$C_9H_{11}O_3ClS$	46·0	4·7	15·1	13·6	45·7	4·6	15·2	13·0	— ve
Ethylene 1 : 2-di-(*p*-carboxybenzenesulphonate)	(M. p. 262—264°) [4]	—	$C_{16}H_{14}O_{10}S_2$	44·7	3·3	—	14·9	44·6	3·5	—	14·4	— ve
1-Chloro-2-methanesulphonyloxypropane [g]	132—133°/15	1·4530 (20°)	$C_4H_9O_3ClS$	27·8	5·3	20·6	18·6	27·7	5·1	20·8	18·2	— ve
3-Chloropropyl methanesulphonate	144—146°/13	1·4588 (16°)	$C_4H_9O_3ClS$	27·8	5·3	20·6	18·6	27·7	4·9	20·6	18·7	Low
1 : 3-Dichloro-2-methanesulphonyloxypropane	160—162°/13	1·4825 (20°)	$C_4H_8O_3Cl_2S$	23·2	3·9	34·3	15·5	23·9	4·1	34·5	14·5	— ve
1 : 3-Dichloro-2-toluene-*p*-sulphonyloxypropane†	229—230°/20 [h]	1·5350 (20°)	$C_{10}H_{12}O_3Cl_2S$	42·4	4·3	25·1	—	42·6	4·2	25·1	—	— ve
1 : 3-Dichloro-2-*p*-carboxybenzenesulphonyloxypropane	(M. p. 206—209°) [5]	—	$C_{10}H_{10}O_5Cl_2S$	38·4	3·2	22·7	—	38·5	3·4	22·9	—	Low
1-Bromo-3-chloro-2-methanesulphonyloxypropane	164—166°/14	1·5002 (19°)	$C_4H_8O_3BrClS$	19·1	3·2	(Total halogen 45·8)	12·8	19·8	3·3	(Total halogen 45·2)	13·0	+
1 : 2-Dibromopropyl methanesulphonate	190—192°/16	1·5292 (16°)	$C_4H_8O_3Br_2S$	16·2	2·7	—	10·8	16·9	2·9	—	11·0	Low
Propylene 1 : 2-dimethanesulphonate	(M. p. 54—56°) [6]	—	$C_5H_{12}O_6S_2$	25·9	5·2	—	27·6	26·0	5·2	—	27·0	— ve
4-Chlorobutyl methanesulphonate	166—170°/15	1·4602 (18°)	$C_5H_{11}O_3ClS$	32·4	6·0	—	—	32·6	6·2	—	—	Low
2-Chloroethyl 2 : 4-dinitrobenzenesulphonate *	(M. p. 106·5°) [7]	—	$C_8H_7O_7NClS$	30·9	2·3	(N, 9·0)	—	31·1	2·4	(N, 8·6)	—	— ve
Dimethyl butane-1 : 4-disulphonate	(M. p. 93—94°) [8]	—	$C_6H_{14}O_6S_2$	29·7	5·7	—	26·3	29·8	5·9	—	26·1	— ve
Diethyl butane-1 : 4-disulphonate	(M. p. 64—65°) [8]	—	$C_8H_{18}O_6S_2$	35·1	6·6	—	23·4	35·2	6·7	—	23·9	— ve

[a] Voss and Blanke (*Annalen*, 1931, **485**, 258) give b. p. 101—102°/25 mm., n_D^{17} 1·4157. [b] Billeter (*Ber.*, 1905, **38**, 2018) gives b. p. 85—86°/10 mm. [c] Sekera and Marvel (*J. Amer. Chem. Soc.*, 1933, **55**, 345) give b. p. 105—106°/6 mm., n_D^{25} 1·4319. [d] Carius (*J. prakt. Chem.*, 1870, **2**, 270) gives b. p. 197·5—200·5°. [e] Meuwsen and Gebhardt (*Ber.*, 1937, **70**, 792) give b. p. 88·5—89°/8—9 mm. [f] Prepared by Clemo and Perkin's method (*J.*, 1922, **121**, 642); they give b. p. 210°/21 mm. and Tipson and Cretcher (*J. Amer. Chem. Soc.*, 1942, **64**, 1162) give n_D^{20} 1·5280. [g] Prepared by the method of Sletzinger, Chamberlin, and Tishler (*ibid.*, 1952, **74**, 5619) who give b. p. 76—77°/0·4 mm. [h] Blanchard (*Bull. Soc. chim. France*, 1927, **41**, 824) gives b. p. 180—210°/13 mm., n_D 1·5357.

* These compounds were prepared by Dr. W. Davis. † These known compounds were prepared by our general method.

[1] Prisms from methanol. [2] Needles from benzene. [3] Prisms from *cyclo*hexane. [4] Prisms from acetone. [5] Plates from benzene. [6] Prisms from acetone–ether. [7] Needles from benzene–*cyclo*hexane. [8] Plates from chloroform–pentane.

carbonate to prevent autocatalytic decomposition.[5] For the more reactive methanesulphonates, *e.g.*, those from methanol and ethanol, it was advisable to keep the temperature below −30° continuously before pouring on ice.

2-Chloroethyl p-*carboxybenzenesulphonate.* 2-Chloroethyl toluene-*p*-sulphonate (3 g.) in concentrated sulphuric acid (30 ml.) and water (30 ml.) was treated slowly on a steam-bath with chromic acid (8 g.) in water (20 ml.). After ½ hr. solid began to separate and after addition of water the mixture was extracted with ether (500 ml.). The acid, which was extracted from the ether layer with 2N-sodium carbonate and recovered by acidification, formed prismatic needles, m. p. 186—188°, from benzene. The oxidation could also be carried out in glacial acetic acid without the addition of sulphuric acid. 1 : 2-Di-*p*-carboxybenzenesulphonyloxyethane and 1 : 3-dichloro-2-*p*-carboxybenzenesulphonyloxypropane were similarly prepared.

2-Chloroethyl 2 : 4-dinitrobenzenesulphonate. 2 : 4-Dinitrobenzenesulphonyl chloride (14 g.) was added during ½ hr. to a stirred solution of ethylene chlorohydrin (50 ml.) in dry 2 : 6-lutidine (50 ml.) and ether (25 ml.) at −40°. After 4 hr. the temperature was allowed to rise to 0° and the mixture was poured on ice–water containing concentrated sulphuric acid (20 ml.). The *ester* which was extracted with chloroform formed yellow needles (9·6 g.), m. p. 104·5—106·5°, from benzene–*cyclo*hexane (1 : 3).

Esters of butane-1 : 4-disulphonic acid. To a cooled solution of sodium (0·91 g.) in methanol (100 ml.) was added a solution of butane-1 : 4-disulphonyl chloride (5 g.) in methanol (25 ml.). After 1 hour's shaking at room temperature the solvent was removed under reduced pressure. The residue was extracted with chloroform (3 × 25 ml.) and on the addition an excess of pentane the *dimethyl ester* separated as plates. The diethyl ester was similarly prepared.

This investigation was supported by grants to this Institute from the British Empire Cancer Campaign, the Jane Coffin Childs Memorial Fund for Medical Research, the Anna Fuller Fund, and the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service. The authors thank Professor A. Haddow for permission to quote the results of tumour-growth inhibition studies.

CHESTER BEATTY RESEARCH INSTITUTE,
INSTITUTE OF CANCER RESEARCH: ROYAL CANCER HOSPITAL,
FULHAM ROAD, LONDON, S.W.3. [*Received, December 12th,* 1956.]

[5] Cf. Scott and Lutz, *J. Org. Chem*, 1954, **19**, 830.

---

469. *Synthesis of 2 : 3 : 9-Trimethyl- and 2 : 3 : 8 : 9-Tetramethylphenanthrene.*

By W. CARRUTHERS and J. D. GRAY.

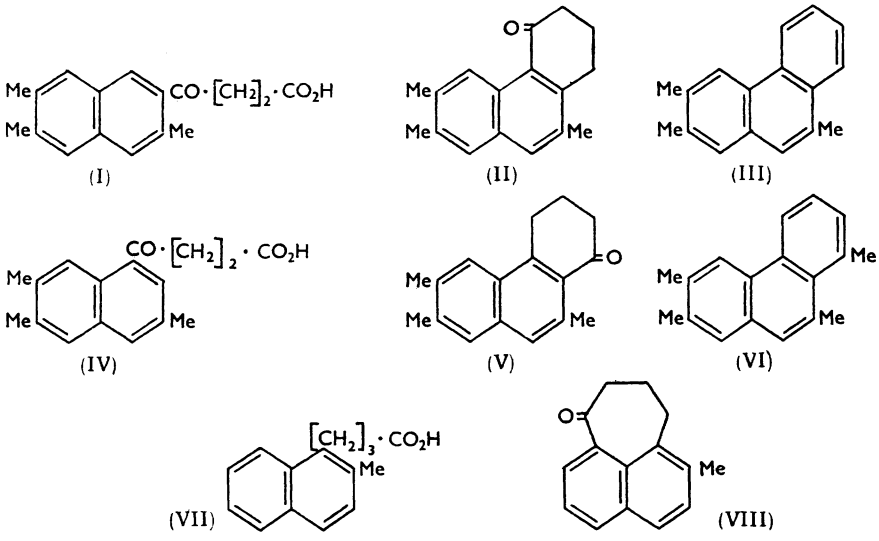
THE two compounds named in the title have been synthesised, for comparative purposes, from 2 : 3 : 6-trimethylnaphthalene. Reaction with succinic anhydride in presence of aluminium chloride afforded two homogeneous acids in small yield. One of these exhibited three regions of ultraviolet absorption typical of 2-acylnaphthalenes,[1] and is clearly the 2-substitution product (I). Huang-Minlon reduction of the carbonyl group and cyclisation of the butyryl chloride with stannic chloride gave the tetrahydro-oxophenanthrene (II), and hence, by standard methods, 2 : 3 : 9-trimethylphenanthrene (III). In agreement with its assigned structure the ketone (II), like other 1-acylnaphthalenes,[1] showed only two regions of absorption (max. at 222 and 330—340 mμ).

An attempt to prepare 2 : 3 : 5 : 9-tetramethylphenanthrene from the ketone (II) and methylmagnesium iodide was unsuccessful. Dehydration and dehydrogenation of the crude alcohol by palladium gave only a mixture of phenanthrene derivatives. A similar

[1] Dannenberg and Dannenberg-von Dressler, *Annalen*, 1955, **593**, 246.

difficulty was encountered by Bendas and Djerassi [2] in an attempt to prepare 4-ethylphenanthrene, and is presumably due to migration and elimination of the alkyl group from the sterically hindered 4-position during dehydrogenation.[3]

The second acid isolated from the Friedel–Crafts reaction must be a 1-naphthoylpropionic acid, and, in agreement, the ultraviolet absorption spectrum was similar to that of other 1-acylnaphthalenes.[1] Reduction and cyclisation (at 0°), as above, gave the



ketone (V) in high yield, having a typical 2-acylnaphthalene spectrum. Reaction of the ketone with methylmagnesium iodide, dehydration, and dehydrogenation gave 2 : 3 : 8 : 9-tetramethylphenanthrene (VI) with characteristic phenanthrene absorption. Production of a phenanthrene derivative by this series of reactions confirms the structure assigned to the ketone (V). The structure of the keto-acid produced is thus established as (IV) : cyclisation of the butyric acids derived from the three other possible keto-acids would not have produced a tetrahydro-oxophenanthrene unless accompanied by methyl migration and this seems unlikely under the conditions used. This is supported by the fact that cyclisation of γ-(2-methyl-1-naphthyl)butyryl chloride (VII) with stannic chloride at 45° is reported [4] to yield the ketone (VIII).

Experimental.—Ultraviolet absorption spectra were determined in 95% ethanol with a Unicam spectrophotometer.

Reaction of 2 : 3 : 6-trimethylnaphthalene with succinic anhydride. 2 : 3 : 6-Trimethylnaphthalene (10 g.) and succinic anhydride (5·9 g.) were added to an ice-cold solution of aluminium chloride (15·3 g.) in nitrobenzene (60 c.c.), then kept at room temperature for 3 hr. Ice and hydrochloric acid were added, and nitrobenzene was removed with steam. The residue was extracted with ether, and the extract shaken with aqueous sodium carbonate. Acidification and crystallisation from methanol gave *β-(3 : 6 : 7-trimethyl-1-naphthoyl)propionic acid* (IV) (1·3 g.), m. p. 183—188° (Found : C, 75·8; H, 6·8. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%). Light absorption : max. 220—225 (infl. 250—255), 300—330 mμ [log ε 5·0 (4·42), 3·96]. The *methyl ester* had m. p. 86° (Found : C, 75·8; H, 7·3. $C_{18}H_{20}O_3$ requires C, 76·05; H, 7·1%).

The crude residual mixture of acids was esterified with diazomethane, and the esters crystallised from methanol. *Methyl β-(3 : 6 : 7-trimethyl-2-naphthoyl)propionate* (1·3 g.) had m. p.

[2] Bendas and Djerassi, *J. Amer. Chem. Soc.*, 1956, **78**, 2474.
[3] Haworth, Mavin, and Sheldrick, *J.*, 1934, 454.
[4] Cagnaint and Cagnaint, *Bull. Soc. chim. France*, 1952, 970.

93—94° (Found: C, 75·7; H, 7·0%) and gave, on hydrolysis, the *acid*, needles (from methanol), m. p. 165—172° (Found: C, 75·4; H, 6·6%). Light absorption: max. 255, 290, 340 mμ (log ε 4·75, 4·04, 3·17).

γ-(3 : 6 : 7-*Trimethyl*-2-*naphthyl*)*butyric acid*. Methyl β-(3 : 6 : 7-trimethyl-2-naphthoyl)propionate (1 g.), sodium hydroxide (0·5 g.), and 90% hydrazine hydrate (0·5 c.c.) in diethylene glycol (8 c.c.) were boiled for 1 hr. The temperature was raised to 195—200° by distilling off water, and refluxing continued for 3 hr. The solution was diluted with water and acidified, and the product extracted with ethyl acetate. The *acid*, crystallised from benzene–light petroleum (b. p. 40—60°), had m. p. 164° (Found: C, 79·5; H, 7·5. $C_{17}H_{20}O_2$ requires C, 79·65; H, 7·9%).

1 : 2 : 3 : 4-*Tetrahydro*-6 : 7 : 10-*trimethyl*-4-*oxophenanthrene*. Phosphorus pentachloride (0·4 g.) and the above butyric acid (0·4 g.) in benzene (15 c.c.) were kept at room temperature for 1 hr., then for 5 min. on the water-bath. Stannic chloride (0·4 c.c.) in benzene (0·4 c.c.) was added to the solution at 0° and the mixture left for 15 min. The complex was decomposed with ice and hydrochloric acid, and the benzene solution separated. The *ketone* (0·33 g.), recovered in the usual manner and crystallised from *cyclo*hexane, had m. p. 163—164° (Found: C, 85·8; H, 7·9. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%). Light absorption: max. 222 (infl. 255—260), 330—340 mμ [log ε 4·70 (4·17), 3·83].

2 : 3 : 9-*Trimethylphenanthrene*. The foregoing ketone (0·15 g.) was reduced with lithium aluminium hydride (0·24 g.) in boiling ether for 3 hr. The *alcohol*, isolated in the usual manner and crystallised from benzene, had m. p. 175—177° (Found: C, 85·2; H, 8·5. $C_{17}H_{20}O$ requires C, 84·95; H, 8·4%).

The alcohol (0·15 g.) was dehydrated with fused potassium hydrogen sulphate (0·015 g.) at 180° for 10 min. and the distilled product was dehydrogenated in carbon dioxide with 30% palladium–charcoal (0·1 g.) at 240°. 2 : 3 : 9-*Trimethylphenanthrene* was sublimed from the mixture and crystallised from methanol as plates, m. p. 107—108° (Found: C, 92·9; H, 7·2. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%). Light absorption: max. 255, 272, 280, 300, 320, 328, 334, 352 mμ (log ε 4·84, 4·32, 4·23, 4·02, 2·61, 2·53, 2·64, 2·67). The *picrate* formed orange-red needles (from ethanol), m. p. 179—181° (Found: C, 61·2; H, 4·3. $C_{17}H_{16},C_6H_3O_7N_3$ requires C, 61·5; H, 4·3%).

γ-(3 : 6 : 7-*Trimethyl*-1-*naphthyl*)*butyric acid*. This *acid* was obtained in 90% yield from β-(3 : 6 : 7-trimethyl-1-naphthoyl)propionic acid as described above for the 2-naphthylbutyric acid. It had m. p. 155—159° (from benzene) (Found: C, 80·0; H, 8·0%).

1 : 2 : 3 : 4-*Tetrahydro*-6 : 7 : 10-*trimethyl*-1-*oxophenanthrene*. The above butyric acid (0·9 g.) was converted into its acid chloride with phosphorus pentachloride (1 g.) in benzene, and this was cyclised with stannic chloride (1 c.c.) as described above. The *ketone* (0·9 g.) crystallised from benzene–light petroleum as prisms, m. p. 129—130° (Found: C, 85·6; H, 7·9%). Light absorption: max. 260, 294, 304, 356 mμ (log ε 4·96, 4·22, 4·17, 3·48).

2 : 3 : 8 : 9-*Tetramethylphenanthrene*. The foregoing ketone (0·9 g.) in benzene was added to ethereal methylmagnesium iodide [from methyl iodide (6 g.) and magnesium turnings (1 g.)]. Most of the ether was distilled off and the mixture refluxed in benzene solution for 3 hr. The crude product was isolated in the usual way, and was dehydrated and dehydrogenated simultaneously by 30% palladium–charcoal (0·1 g.) at 280—290° in carbon dioxide. After chromatography on alumina with light petroleum (b. p. 60—80°), 2 : 3 : 8 : 9-*tetramethyl*-*phenanthrene* was obtained as colourless plates m. p. 106—107° (from methanol) (Found: C, 92·6; H, 7·7. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). Light absorptions: max. 260, 282, 293, 305, 324, 339·5, 356 mμ (log ε 4·81, 4·15, 4·03, 4·09, 2·89, 3·07, 3·08). The *picrate* formed orange-red needles (from ethanol), m. p. 167—169° (Found: C, 62·5; H, 4·8. $C_{18}H_{18},C_6H_3O_7N_3$ requires C, 62·2; H, 4·6%), and the *s*-trinitrobenzene *complex* yellow needles, m. p. 181—183° (Found: C, 64·7; H, 4·7. $C_{18}H_{18},C_6H_3O_6N_3$ requires C, 64·4; H, 4·8%).

One of us (W. C.) was supported by the Medical Research Council. We are indebted to the Department of Scientific and Industrial Research for a maintenance allowance (to J. D. G.). Microanalyses were by Mr. J. M. L. Cameron and Miss M. Christie.

UNIVERSITY OF GLASGOW. [*Received, December 14th*, 1956.]

470. *The Configuration of the So-called "Diphenylmaleinitrile."*

By A. J. Williams and R. J. W. Le Fèvre.

Cook and Linstead [1] found "diphenylmaleinitrile" a suitable starting material for the preparation of porphyrazines. A *cis*-configuration was accepted because of the ease of conversion into a cyclic imide or, through the acid, into the corresponding anhydride. Linstead and Timmons [2] raised the possibility that the dinitrile was the *trans*-, and not the *cis*-form, as had previously been supposed. Very recently Timmons and Wallwork [3] reported that *X*-ray analysis indicates a *trans*-structure of the molecules in the crystal.

The problem seemed one in which polarity measurements should be helpful. Specimens of "diphenylmaleinitrile" were prepared as described by Cook and Linstead [1] and purified chromatographically in benzene over alumina; after crystallisation from benzene–light petroleum the material appeared as white needles, m. p. 161° (lit.,[4] various between 156° and 160°).

Dielectric-constant and density observations were made on solutions in carbon tetrachloride by means of the apparatus noted in ref. 5. Symbols and procedures have been explained before.[6] At first considerable irregularities were found when ε_{12} values were plotted against concentration; later these were traced to the fact that daylight rapidly caused the dielectric constant of a solution to increase. The Table lists the results obtained before and after about 4 hours' exposure, in ordinary glass flasks, to bright sunlight.

Dielectric polarisation measurements of "diphenylmaleinitrile," m. p. 161°.

Before illumination

$10^5 w_2$	168·5	193·7	250·3	255·0	281·4	313·8	336·8	344·8	364·8
ε^{25}	2·2290	2·2295	2·2298	2·2321	2·2339	2·2291	2·2336	2·2362	2·2346
d_4^{25}	—	1·5833	—	1·5830	1·5828	1·5828	1·5825	1·5824	1·5823

After illumination

$10^5 w_2$	241·3	255·0 *	281·4	344·8	364·8
ε^{25}	2·3006	2·3055	2·2891	2·3277	2·3303
d_4^{25}	—	1·5830	—	$1·5825_5$	$1·5824_5$

* This solution was illuminated for 6 hr., *i.e.*, 1·5 times as long as were the other three.

	$(\alpha\varepsilon_1)_{mean}$	$(\beta d_1)_{mean}$	${}_{\infty}P_2$ c.c.	${}_{D}P$ (c.c.)	μ (D)
Before illumination	1·79	$-0·606_6$	102·0	78·5	$1·0_7$
After illumination	28·1	$-0·377_8$	737·8		$5·6_8$

In order to compute the apparent dipole moments an estimate of the distortion polarisations has been made from the ${}_{T}P$ (29·7 c.c.) reported by Bloom and Sutton [7] for fumaronitrile in benzene, together with the group refractions for H (1·03 c.c.) and C_6H_5 (25·36 c.c.)

(I) R′·C·CN ⟶ R′·C·CN (II)
‖ ‖
NC·C·R″ R″·C·CN

given by Vogel.[8] Relevant data are at the foot of the Table. The moments emerge as 1·1 D and 5·7 D. Such a marked difference can be most obviously explained by light effecting the change (I) ⟶ (II). The preparation having m. p. 161° is therefore recognised as

[1] Cook and Linstead, *J.*, 1937, 929.
[2] Linstead and Timmons, quoted by Linstead, *J.*, 1953, 2873.
[3] Timmons and Wallwork, *Chem. and Ind.*, 1955, 62.
[4] Beilstein's *Handbuch*, 4th edn., 1926, IX, 945, also second supplement, IX, 675.
[5] Buckingham, Chau, Freeman, Le Fèvre, Narayana Rao, and Tardif, *J.*, 1956, 1405.
[6] Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. 2.
[7] Bloom and Sutton, *J.*, 1941, 727.
[8] Vogel, *J.*, 1948, 1833.

predominately of *trans*-content. That the observed moment is not nearer to zero may be due to at least two causes : an underestimation of $_{D}P$, and the sensitivities of the solutions to light. We note that, during our work, the isomerides (I) and (II) with R″ = H have been reported to have moments of 1·9 and 6·1 D (" preliminary values ") by Beech and Piggott,[9] or 2·71 and 7·98 D by Schneider.[10] The polarity differences are roughly of the same order as those shown in the Table for $(CN{\cdot}CPh{:})_2$; however, in neither case is photoisomerisation mentioned.

The material of m. p. 161° has also been examined, with exclusion of daylight, as 10^{-4}M- and 5×10^{-4}M-solutions in ethanol, in a Hilger " Uvispek " spectrophotometer. Three maxima of ultraviolet absorption were noted : at 237·5 mμ (log ε 4·22), at 263 mμ (log ε 3·98), and *ca.* 339 mμ (broad ; log ε 4·37). Exposure to bright sunlight for 15 min. caused marked alterations : the intensity of the first band was slightly weakened (to log ε 4·08), that of the second band was raised (to log ε 4·33), and that of the third band diminished (to log ε *ca.* 3·6). Only at 237·5 mμ was no wavelength shift noted ; illumination moved the 263·0 mμ maximum to 267·2 mμ, and destroyed the broad smooth peak centred around 339 mμ, producing in its place signs of maxima of lower intensity between 320 and 350 mμ together with two peaks at 374·2 mμ (log ε 2·98) and 399·5 mμ (log ε 2·94). Both in the dielectric constant and in the photometric measurements no reversion to the pre-illumination state was observed after prolonged storage in the dark. The diminution of intensity of the band at *ca.* 339 mμ, produced by irradiation, is reminiscent of the behaviour of the *K*-bands of many azo-derivatives, when similarly treated (cf. refs quoted by Le Fèvre and Sousa [11]), and is in harmony with the spectra of *trans*- and *cis*-stilbene,[12] *syn*- and *anti*-oximes,[13,14] etc.

Present observations therefore support the conclusions of refs. 2 and 3. Presumably the isomeride with m. p. 243° (quoted in ref. 4) is in fact diphenylmaleinitrile(*cis*), and the configurations hitherto written for the two isomers of $(CN{\cdot}CPh{:})_2$ should be interchanged. This pair, and the αβ-dicyanostyrenes already mentioned, thus seem to be uncommon cases among geometrical isomerides in that the higher-melting form is the *cis*- and not the *trans*-form.

Grateful acknowledgments are made to Beetle-Elliott Ltd. for a scholarship to A. J. Williams.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA. [*Received, December 27th,* 1956.]

[9] Beech and Piggott, *J.*, 1955, 423.
[10] Schneider, *J. Amer. Chem. Soc.*, 1955, **77**, 2796.
[11] Le Fèvre and Sousa, *J.*, 1955, 3154; 1957, 745.
[12] Smakula and Wassermann, *Z. phys. Chem.*, 1931, *A*, **155**, 353.
[13] Brady, *J.*, 1914, **105**, 2104; Brady and Grayson, *J.*, 1933, 1037.
[14] Raffouf, *J. Amer. Chem. Soc.*, 1946, **68**, 1765.

471. *The Effect of Potassium Iodide Concentration on the Oxidation of Glucose by Alkaline Iodine Solutions.*

By R. L. Colbran and T. P. Nevell.

During an investigation of the oxidation of the reducing end-groups in hydrocelluloses by alkaline solutions of iodine, it was found that the reaction was considerably affected by the concentration of potassium iodide in the reagent. It is well known that the hypoiodite in these solutions disproportionates to iodate and iodide, and it has several times been reported [1] that, in solutions of moderate alkalinity, this reaction is retarded by increasing the total iodide concentration. We have found no mention of the effect of this on the oxidation of aldoses, however, and some experiments were therefore made to show the effect of iodide concentration on the oxidation of glucose.

The work was done at 20° with 0·01N-iodine in a carbonate–bicarbonate buffer of pH 10·8. Fig. 1 shows the effect of potassium iodide concentration on the rate at which the concentration of available iodine (*i.e.*, free hypoiodous acid, hypoiodite ion, tri-iodide ion, and free iodine) falls under these conditions as a result of disproportionation. The results were obtained by adding an excess of 0·02N-sodium arsenite to aliquot portions of the solution, and back-titration with 0·01N-iodine, the arsenite being buffered so that the pH of the mixture was 6·7. Whereas with 8 g. of potassium iodide per l. nearly all the iodine has been converted into iodate and iodide within 5 hr., with 80 g. per l. a substantial proportion of the iodine remains available for oxidation purposes even after two days. According to Ingles and Israel,[2] the oxidising species in alkaline solutions of iodine is hypoiodous acid. In the solutions mentioned above, however, only a small proportion of the available iodine is present as hypoiodous acid; the rest exists largely as tri-iodide ion. If the hydrolysis constant of iodine K_1, the dissociation constant of hypoiodous acid K_2, and the equilibrium constant for the formation of tri-iodide ion K_3, are known, the concentration of undissociated hypoiodous acid present at any time in a given solution can be calculated from the curves in Fig. 1. Specimen results of these calculations are given in the Table. The following values for the constants were used: $K_1 = 1{\cdot}56 \times 10^{-13}$ at 20° (calc. from values [3] at 0° and 25°), $K_2 = 4{\cdot}5 \times 10^{-13}$ (Skrabal [4]), $K_3 = 806$ at 20° (calc. from values [5] at 0° and 25°).

	[HOI] (10^{-7}M)			
Time of decomp. (hr.)	0	4	10	24
KI present : 8 g./l.	312	3·32	2·24	1·02
80 g./l.	2·67	2·48	2·24	1·95

Fig. 1 and the Table show that, in a solution containing 8 g. of potassium iodide per l., the concentrations of hypoiodous acid and of available iodine fall rapidly to low values. In a solution containing 80 g. of potassium iodide per l., however, the hypoiodous acid concentration is always very low, but it remains nearly constant, and the concentration of available iodine remains high.

The rate of oxidation of D-glucose (0·00111M) by 0·01N-iodine at pH 10·8 and 20° was measured by adding acid to aliquot portions of the reaction mixture after various times, and titrating the liberated iodine with thiosulphate. The results for solutions containing

[1] Lonnes, *Z. anal. Chem.*, 1894, **33**, 409; Forster, *J. phys. Chem.*, 1903, **7**, 640; Skrabal, *Monatsh.*, 1911, **32**, 815.
[2] Ingles and Israel, *J.*, 1948, 810.
[3] Jones and Hartmann, *J. Amer. Chem. Soc.*, 1911, **33**, 1485; Bray and Connolly, *ibid.*, 1915, **37**, 241.
[4] Skrabal, *Ber.*, 1942, **75**, 1570.
[5] Jones and Kaplan, *J. Amer. Chem. Soc.*, 1928, **50**, 1845.

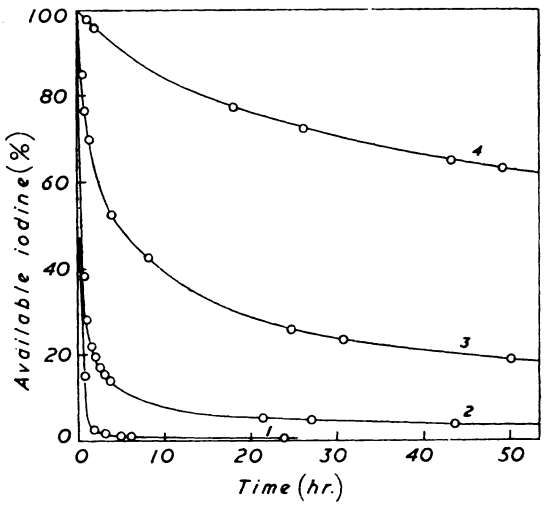


FIG. 1. *Effect of potassium iodide concentration on the stability of* 0·01N-*iodine at* pH 10·8 *and* 20°.

KI per l. : (1) 8 g., (2) 20 g., (3) 40 g., (4) 80 g.

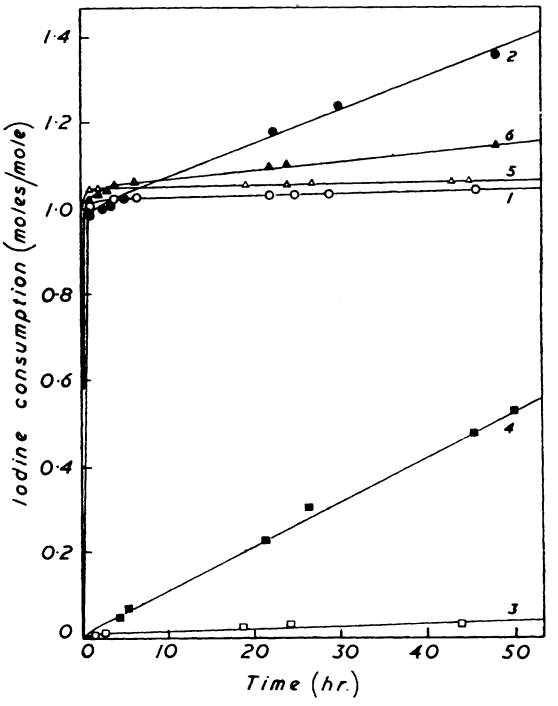


FIG. 2. *Effect of potassium iodide concentration on the rate of oxidation of* 0·00111M-D-*glucose,* -D-*glucono-γ-lactone, and* -D-*glucuronolactone by* 0·01N-*iodine at* pH 10·8 *and* 20°.

(1, 2) Glucose; (3, 4) gluconolactone; (5, 6) glucuronolactone. (1, 3, 5) 8 g. of KI per l. (2, 4, 6) 80 g. of KI per l.

8 g., and 80 g., of potassium iodide per l. (see Fig. 2) show that a consumption of 1 mole of iodine per mole of glucose (corresponding to the formation of gluconic acid) was attained within 2 hr. in both reagents. This consumption was, however, reached more quickly in the presence of 8 g., than of 80 g., of potassium iodide per l., as would be expected from the figures in the Table. It may also be seen from Fig. 2 that, whilst in the first solution oxidation had virtually ceased when the amount of iodine reduced was equivalent to the conversion of the glucose into gluconic acid, in the second solution further oxidation (" over-oxidation ") occurred at a low, but constant, rate. Similarly, D-glucono-γ-lactone (0·00111M) was hardly oxidised at all by the reagent containing 8 g. of potassium iodide per l., but was oxidised at a constant rate by that containing 80 g. per l. (Fig. 2). It thus appears that the oxidation of groups other than semiacetal groups cannot be due to hypoiodous acid, since the concentration of this species is higher in the first solution than in the second at all times up to 10 hr.

The oxidation of D-glucuronolactone (0·00111M) was also examined in the presence of 8 g. and 80 g. of potassium iodide per l.; the results are shown in Fig. 2. The rate curve is almost identical with that for glucose in the first solution, but the rate of over-oxidation is much lower than that of glucose in the second solution. This suggests that the over-oxidation of glucose is mainly a reaction of the primary, rather than the secondary, alcohol groups.

The divergence of opinion on the extent to which over-oxidation interferes with the determination of aldoses by the iodine method may be due to the use of different concentrations of potassium iodide by various workers. The results presented here demonstrate the importance of keeping this concentration as low as possible, consistent with the necessity of maintaining a sufficient excess of available iodine until the oxidation is complete.

BRITISH COTTON INDUSTRY RESEARCH ASSOCIATION, SHIRLEY INSTITUTE,
DIDSBURY, MANCHESTER, 20. [*Received, December 28th,* 1956.]

---

472. *The Heat of Formation of Cyanuric Chloride and the Heat of Trimerisation of Cyanogen Chloride.*

By A. R. HUMPHRIES and G. R. NICHOLSON.

THE only published value for the heat of formation of cyanuric chloride, −107·9 kcal./mole, was calculated by Lemoult [1] from his value of the heat of combustion of the solid compound, 292·9 kcal./mole. Lemoult did not state what the products of combustion were, but if we assume that all of the chlorine went to $Cl_2(g)$ the heat of formation of cyanuric chloride should be +10·7 kcal./mole, and if, alternatively, we assume that sufficient water was present, and fairly dilute hydrochloric acid with no $Cl_2(g)$ was formed, the derived heat of formation should be about −4 kcal./mole. The origin of the value −107·9 kcal./mole is obscure. We therefore redetermined the heat of formation of cyanuric chloride and incidentally obtained a value for the heat of trimerisation of cyanogen chloride.

Experimental.—A suitable calorimetric bomb was not available for determining the heat of combustion of chlorine-containing compounds, so the heat of hydrolysis of cyanuric chloride to cyanuric acid was measured. The calorimeter was a Bunsen-type naphthalene calorimeter described by Beynon and Humphries; [2] this operates isothermally at the m. p. of naphthalene. Hydrolysis was complete in 1½ hr. at 80° in a buffer solution composed of 2·5 moles each of acetic

[1] Lemoult, *Compt. rend.*, 1896, **123**, 1276.
[2] Beynon and Humphries, *Trans. Faraday Soc.*, 1955, **51**, 1065.

acid and sodium acetate made up to 1 l. with distilled water. Completeness of the reaction was checked by titration of the final solution for chloride ion.

The buffer solution (20 c.c.) was placed in the reaction chamber of the calorimeter, a sealed glass capsule containing a weighed amount (about 0·2 g.) of cyanuric chloride was lowered into it and held submerged by the stirrer, and hydrolysis was started by shattering the capsule with the stirrer. The solution was thereafter stirred at regular intervals until reaction was complete. The heat evolved was measured by observing the movement of a mercury thread forced along a calibrated capillary tube by the melting of some of the naphthalene mantle around the reaction chamber. The reaction could be represented as :

$$y(CNCl)_3(s) + 3yH_2O(sol.) \longrightarrow y(CNOH)_3(sol.) + 3yHCl(sol.),$$

in which y was the molar quantity of cyanuric chloride used, the $3y$ moles of water were from the buffer solution, and the y moles of cyanuric acid and $3y$ moles of hydrochloric acid formed were in solution in the buffer from which $3y$ moles of water had been removed. The latter solution was referred to as solution 1. If Δh was the heat of the above reaction, then :

$$\Delta h = \Delta H_f[y(CNOH)_3 \text{ in solution 1}] + \Delta H_f[3yHCl \text{ in solution 1}] - \Delta H_f[y(CNCl)_3(s)] - \Delta H_f[3yH_2O \text{ in buffer}] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In order to determine the heat of formation of cyanuric chloride it was therefore necessary to know the other three heats of formation appearing in equation (1).

$\Delta H_f[y(CNOH)_3$ in solution 1] was obtained by measuring the heat of solution of y moles of cyanuric acid in a solution consisting of 20 c.c. of buffer plus $3y$ moles of hydrochloric acid, and making use of a known value for the heat of formation of solid cyanuric acid. $\Delta H_f[3yHCl$ in solution 1] was obtained by measuring the heat of solution of $3y$ moles of a known aqueous solution of hydrochloric acid in 20 c.c. of buffer in which y moles of cyanuric acid had been dissolved. A correction was then made for the heat of dilution of solution 1 by an amount of water corresponding to that present in the aqueous hydrochloric acid used. $\Delta H_f[3yH_2O$ in buffer] was similarly determined by measuring the heat of dilution by water of the buffer solution. Each of the above three auxiliary quantities was measured in the naphthalene calorimeter.

The results obtained were :

(i) Two measurements of Δh gave $-95·44$ and $-95·33$ kcal./mole; mean $-95·39$ kcal./mole of solid cyanuric chloride.

(ii) Three measurements of the heat of solution of cyanuric acid as above gave $+5·95$, $+5·82$, and $+5·94$ kcal./mole; mean $+5·90$ kcal./mole of solid cyanuric acid. This was taken in conjunction with a value [3] for the heat of combustion of solid cyanuric acid, 219·5 kcal./mole, which is equivalent to a heat of formation of $-165·1$ kcal./mole, to give $\Delta H_f[(CNOH)_3$ in solution 1] $= -159·2$ kcal./mole.

(iii) Measurements of the heat of solution of two widely different concentrations of aqueous hydrochloric acid (HCl,xH_2O with x approx. 23·2 and 3·6) as above, gave, after corrections for the heat of dilution of solution 1 by the corresponding quantities of water, $-39·35$ and $-40·18$ kcal./mole; mean $-39·76$ kcal./mole of hydrochloric acid for $\Delta H_f[HCl$ in solution 1]. Values for the heats of formation of HCl,xH_2O, which were required in the calculation, were obtained from the literature.[4]

(iv) The heat of dilution of the buffer solution by water was very small, and this measurement led to $\Delta H_f[H_2O$ in buffer] $= -68·33$ kcal./mole of water, the value [4] $-68·32$ kcal./mole for the heat of formation of water (liquid) being used.

The results (i)—(iv) were combined by means of equation (1) to give :

$$-95·39 = -159·2 + 3(-39·76) - \Delta H_f[(CNCl)_3(s)] - 3(-68·33)$$

giving $+21·9$ kcal./mole for the heat of formation of solid cyanuric chloride. The measured values used in obtaining this result were all applicable to 80°, whereas the published data used

[3] Thermochemical Bull., March 1955, p. 2. (International Union of Pure and Applied Chemistry. Sub-Commission on Experimental Thermochemistry.)

[4] "Selected Values of Chemical Thermodynamic Properties," U.S. Dept. Commerce, Nat. Bur. Standards, Washington, D.C., 1949.

were applicable to 25°. It was estimated that the net correction to the final result to give its value at 25° would be small compared with the overall experimental error (considered to be ± 1 kcal./mole in view of the indirect nature of the determination).

This result was combined with the heat of formation of cyanogen chloride (gas) given by Lord and Woolf [5] (+31·6 kcal./mole) to obtain the value −72·9 kcal. for the heat of trimerisation at 25°, $3CNCl(g) \longrightarrow (CNCl)_3(s)$. It is interesting that Lemoult [1] gave the value −189·05 kcal. for the heat of the trimerisation, $3CNCl(l) \longrightarrow (CNCl)_3(s)$, based on his erroneous value for the heat of formation of cyanuric chloride and a value by Berthelot (+27·05 kcal./mole) for the heat of formation of cyanogen chloride (liquid).

The authors thank Dr. D. J. Berets of the American Cyanamid Company for permission to use his value of the heat of combustion of cyanuric acid which has not yet been formally published.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, DYESTUFFS DIVISION,
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9. [*Received, January 11th*, 1957.]

[5] Lord and Woolf, *J.*, 1954, 2546.

---

473. *The Heat of Combustion of Acetylacetone.*

By G. R. NICHOLSON.

THE heat of combustion of acetylacetone (liquid) was required in connection with a thermochemical calculation. The only measured value in the literature appeared to be that by Guinchant [1] in 1895 (615·9 kcal./mole). Kharasch,[2] in his well-known compilation of heats of combustion, considered Guinchant's value to be too low and gave an alternative value (638·2 kcal./mole) calculated by his own method involving the structural formula of the compound. In view of this uncertainty it was thought advisable to make a new determination.

Experimental.—An isothermal bomb calorimeter of Dickinson type [3] was used, the calorimeter having previously been calibrated by combustion of benzoic acid (Nat. Bur. Standards sample No. 39 g). Calorimeter temperatures were measured with a platinum resistance thermometer of Meyers's [4] type, which had been constructed and calibrated at fixed points in this laboratory, in conjunction with a Smith's difference bridge. Soda-glass ampoules were completely filled with acetylacetone by means of a hypodermic syringe, and then sealed. Filled ampoules were pressure tested at 30 atm. (equal to the initial oxygen pressure in the bomb), and those surviving were used for combustion. The weight of liquid used, which depended on the size of the individual ampoule, was 1·3—2·0 g. To assist bursting, the ampoules were smeared locally with about 0·01 g. of petroleum jelly which was ignited by means of a platinum wire and cotton-thread fuse. Corrections to the gross heat evolved were made for the heats of combustion of the cotton and petroleum jelly (previously determined), the joule heat in the platinum wire, and the heat produced in the formation of a small quantity of nitric acid in the bomb from residual nitrogen in the oxygen. Corrections were also made for small quantities of residual carbon (0·1—0·8 mg.) found fused in the remains of the ampoule after combustion. Sample weights were corrected for buoyancy by using a density [5] of 0·976 g./c.c. for acetylacetone.

Two fractions of acetylacetone were used, severally of b. p. 71—72°/101—101·5 mm., b. p. 71·5—72°/101·5 mm. Three combustions on fraction 1 gave a mean $-\Delta H_c^\circ/M = 6{\cdot}4944 \pm 0{\cdot}0036$ kcal./g., and five combustions on fraction 2 gave $-\Delta H_c^\circ/M = 6{\cdot}4693 \pm 0{\cdot}0022$ kcal./g. These results referred to the usual standard conditions (isothermal combustion of the liquid at 25°

[1] Guinchant, *Compt. rend.*, 1895, **121**, 354.
[2] Kharasch, *Bur. Stand. J. Res.*, 1929, **2**, 359.
[3] Dickinson, *Bull. Bur. Stand.*, 1915, **11**, 189.
[4] Meyers, *Bur. Stand. J. Res.*, 1932, **9**, 807.
[5] "Handbook of Chemistry and Physics," Chemical Rubber Publ. Co., Cleveland, Ohio, 37th Edn., 1955.

and a constant pressure of 1 atm.), with $CO_2(g)$ and $H_2O(l)$ as products of combustion, and the estimated error was calculated by combining the combustion error (twice the standard error of the mean $-\Delta H_c^\circ/M$) and the benzoic acid calibration error.

In order to see if impurities in these fractions could be identified, both were examined in a mass spectrometer. It was found that the impurity consisted almost entirely of xylene in each case, and it was estimated that fraction 1 contained 2·08% by weight of xylene and fraction 2 1·42%. It was not possible to distinguish amongst the three isomers of xylene, but, fortunately, their heats of combustion are very nearly identical [6] (1088·16 kcal./mole for the *ortho*- and *para*-forms, and 1087·92 kcal./mole for the *meta*-form). It was assumed that the impurity consisted entirely of xylene with $-\Delta H_c^\circ = 1088{\cdot}16$ kcal./mole, or $-\Delta H_c^\circ/M = 10{\cdot}2502$ kcal./g. Calculation then showed that, for acetylacetone alone, fraction 1 gave $-\Delta H_c^\circ/M = 6{\cdot}4146$ kcal./g. and fraction 2 gave 6·4148 kcal./g. These two values were in very satisfactory agreement, and the mean, $-\Delta H_c^\circ/M = 6{\cdot}4147$ kcal./g., is equivalent to $-\Delta H_c^\circ = 642{\cdot}20$ kcal./mole, 100·114 being used as the molecular weight. The estimated error may be taken as $\pm 0{\cdot}36$ kcal./mole.

This result is much higher than Guinchant's value, but is only about 0·6% higher than Kharasch's calculated value

IMPERIAL CHEMICAL INDUSTRIES LIMITED, DYESTUFFS DIVISION,
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9. [*Received, January 11th*, 1957.]

[6] " Selected Values of Properties of Hydrocarbons," U.S. Dept. Commerce, Nat. Bur. Standards, Washington, D.C., 1947.