48. *Degradation of α-Amino-acids by Interaction with Aldehydes.*

By Radwan Moubasher.

In his interpretation of the relative speed of the Strecker degradation of α-amino-acids by monocarbonyl compounds, Baddar (*J.*, 1949, S 163; 1950, 136) ignores steric considerations. The first step proposed, exemplified by $NH_2\cdot CHPh\cdot CO_2H + Ar\cdot CHO \longrightarrow Ar\cdot CH{:}N\cdot CHPh\cdot CO_2H$, is, however, strongly subject to steric hindrance (cf. Schonberg *et al.*, *J.*, 1950, 1422). Moreover, he defines as " active " substances which under severe conditions produce only traces of the degradation product. Again, contrary to Baddar's findings, piperonaldehyde degrades α-phenylglycine at approximately the same speed as does *m*-nitrobenzaldehyde. Baddar's explanation of the comparatively good yield of acetaldehyde obtained from *o*-nitrobenzaldehyde and alanine is questionable as according to him indigo, which is an active agent in the Strecker degradation, is formed in the process. His explanation of the relatively strong degrading power (in hot aqueous glycerol) of *s*-dichloroacetone, when compared with *o*-chlorobenzaldehyde, is also questionable since hydrochloric acid is formed on hydrolysis only in the former case, so that the experimental conditions are not equal in the two cases. His explanation of the mechanism of this degradation seems to be based on insufficient experimental evidence.

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49. *The Heat of Formation of Iodine Pentafluoride.*

By A. A. Woolf.

The determination of the heats of formation of certain halogen fluorides by utilizing their quantitative reactions with oxides has been suggested (Emeléus and Woolf, *J.*, 1950, 164). The heat evolved in the simplest of these reactions, the hydrolysis of iodine pentafluoride, has now been measured and leads to a value of 204·7 kcals. for the reaction $\frac{1}{2}I_2(s.) + 2\frac{1}{2}F_2(g.) = IF_5(l.)$ at 18°, and 194·6 kcals. for the reaction to yield the gaseous pentafluoride. The latent heat of vaporization, 10·1 kcals., was calculated from Ruff and Braida's vapour-pressure equation (*Z. anorg. allgem. Chem.*, 1933, **214**, 91).

A knowledge of the free energy of iodine pentafluoride will be useful in predicting whether certain fluorination reactions are possible with the liquid, but this must await the determination of its entropy. The heat of formation of bromine trifluoride, which cannot be determined by simple hydrolysis since the products of this reaction (bromine, oxygen, hydrobromic, and bromic acids) are formed in variable amounts, may be determined from the heat of the reaction $10BrF_3 + 3I_2 = 6IF_5 + 5Br_2$ now that the heat of formation of the pentafluoride is known.

Experimental.—Iodine pentafluoride, prepared from the elements at room temperature in a nickel apparatus, was decolorized immediately before use by fluorine, and purified by distillation at 20°/5 mm., a middle fraction (10 c.c. out of 40 c.c.) being collected.

The calorimeter, maintained at 20·0° in a thermostat, consisted of a 1·5-l. Dewar flask fitted with an insulated cover through which passed a calibration heater, ampoule holder and breaking rod, stirrer, and a Beckmann thermometer readable to 1/1000°. Sufficient iodine pentafluoride to produce a 1—2°-temperature rise was sealed in a Pyrex-glass ampoule, which was broken under 750 c.c. of water in the calorimeter. After the temperature rise due to the stirring had again become steady, a further one-degree rise was effected by applying a potential difference of 12 v. to the heater for 3 minutes.

The results are given below :—

IF_5/H_2O (mol. ratio)	1/1570	1/1190	1/888
Heat evolved per mol. of IF_5 (kcal.)	22·00	22·09	22·05
Mid-point of temperature rise	18·4°	18·7°	19·2°

The hydrolysis reaction, $IF_5 + 3H_2O = 5HF + HIO_3$, was first shown to occur quantitatively by Prideaux (*J.*, 1906, 316), and by using the following heats of formation (Bichowsky and Rossini, " Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, 1936) : H_2O 68·3(7), HF 75·5(6), and HIO_3 54·6 kcals., the heat of formation of iodine pentafluoride was calculated as 205·3 kcals.

The heat of mixing of iodic and hydrofluoric acids in the quantities resulting from the above hydrolysates was found by direct experiment to be negligible, and hence formation of difluoroiodic acid, if it occurred at all, had no thermal effect. The possibility of heat being evolved by attack on the Pyrex glass by the dilute hydrofluoric acid formed was also ruled out for the following reasons: (*a*) doubling the concentration of this acid did not alter the heat of hydrolysis within the estimated experimental error (1 in 250), (*b*) the temperature rise on hydrolysis reached its maximum value within 30 seconds (attack by hydrofluoric acid would not be instantaneous and a further rise in temperature would be expected), and (*c*) the attack on Pyrex glass by the hydrolysate in a period three times that of the above experiments was found by direct weighing to be negligible.

The heat of hydrolysis of the pentafluoride with N/4-potassium hydroxide was determined as a final check. The values found in duplicate experiments were 118·8 and 119·0 kcals., the increase in heat evolved as compared with aqueous hydrolysis being due to the heats of neutralization of the acids formed. From the equation $6KOH + IF_5 = 5KF + KIO_3 + 3H_2O$ by using the following heats of formation: KOH 114·8(0), KIO_3 114·7(7), and KF 138·3(9), the heat of formation of iodine pentafluoride was found to be 204·2 kcals. The difference between this figure and the one obtained in the aqueous hydrolysis is greater than experimental error and is probably due to errors in the heats of formation used. The heat of formation of iodic acid, 54·6 kcals., for example, is one chosen from a series which vary from 53·8 to 55·8 kcals. (Bichowsky and Rossini, *loc. cit.*).

The author is indebted to Professor H. J. Emeléus, F.R.S., for his encouragement, and to the Department of Scientific and Industrial Research for a maintenance grant.

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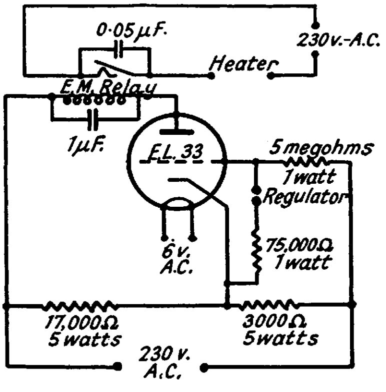
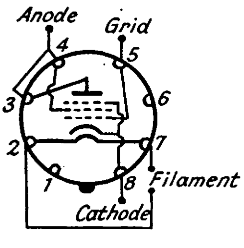
50. *An Inexpensive Thermostat Relay.*

By DUNCAN TAYLOR.

IT has become popular in recent years to employ some type of thyratron relay to afford accurate thermostatic control and to reduce the current at the mercury contact of the mercury–toluene regulator to not more than a few microamps. The regulator, therefore, provided that clean mercury is used for the initial filling, has a practically indefinite life, but not by any means can this be claimed for the thyratron valve. During recent studies in this Department on heterogeneous equilibria, accurate, continuous, and reliable thermostatic control was necessary for six months, and it was found that a thyratron relay could not be relied on to give more than, at most, three months' continuous service. To overcome this trouble, an inexpensive relay (see figure) was developed, and experience has shown that it combines all the desirable features of the thyratron type of relay with a useful life of six months' continuous running. Another good feature is that the thermostat heaters are cut off or switched on at the same instant as the regulator contacts close or open, respectively. The general principle involved in this relay is well established (cf. Cooke and Swallow, *J. Sci. Instr.*, 1929, **6**, 287), but the circuit illustrated has the advantage of operating from A.C. mains, uses inexpensive modern components and requires no rectifier. The principle is simply that of an electromagnetic relay of the Post Office type in the anode circuit of a valve, the grid potential of which is varied by the opening and closing of the regulator contacts.





The electromagnetic relay should have a coil resistance of 1000 Ω and be fitted with heavy-duty normally-closed contacts (supplied for example by Londex Ltd., London, S.E.20). The relay will function satisfactorily in this circuit if the contacts open smartly on the application of 10 v. D.C. to the coil. A 1-μF. condenser (750 v. D.C. test) must be connected across the relay coil to prevent continuous chatter, and a 0·05-μF. condenser (500 v. D.C. test) connected across the contacts is desirable though not essential as a spark suppressor when the contacts are interrupting a current of about 1 amp., *i.e.*, when using 250-w. heaters. There are no doubt several types of valve which could be used in this circuit, but the one preferred is a Mullard EL33, an ordinary radio output valve; this is rated to give a maximum anode current of about 33 ma., and in the circuit above the valve delivers only 13 ma. to the relay coil when the regulator closes. Under-running the valve in this way contributes to its long life on continuous usage. The connections to the valve are indicated in the figure. There is no difficulty in obtaining the necessary resistors, but it was convenient and less expensive to wind the 5-w. resistors from 41-S.W.G. enamelled resistance wire. The 230 v. A.C. to the network and the 6 v. A.C. to the valve can best be supplied from a small mains transformer.

When this circuit was being developed, it seemed at first sight preferable that the relay should work in the opposite way from that given in the figure, namely, that the relay coil should carry normally-open contacts which would close on energising of the coil by opening the regulator contacts. The circuit can in fact be arranged to operate in this manner, but then some instability is introduced, such that when current is flowing in the relay coil merely touching the regulator contacts with the fingers causes a large drop in current which may be sufficient to de-energise the coil. No such unpleasant features have been encountered in the circuit as given above.

Acknowledgments are due to Dr. R. Scott for some helpful discussions.

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51. *The Dissociation Constant of Calcium Hydroxide.*

By C. W. DAVIES and BERNARD E. HOYLE.

CALCIUM HYDROXIDE was shown to be incompletely dissociated in water by Kilde (*Z. anorg. Chem.*, 1934, **218**, 113), who obtained the value $K = 0{\cdot}04$ for the process $CaOH^{\cdot} \rightleftharpoons Ca^{\cdot\cdot} + OH'$ at 25°. This value was derived from measurements of the solubility of calcium iodate in alkaline solutions, and was subject to small corrections for the presence of $NaIO_3$ and $CaIO_3^{\cdot}$ ion pairs in the solutions studied; the revised value is $K = 0{\cdot}031$ (Davies, *J.*, 1938, 278). Recently, Bell and Prue (*J.*, 1949, 362) have obtained $K = 0{\cdot}051$ from measurements of the rate of decomposition of diacetone alcohol in calcium hydroxide solutions. The difference between the two values is of considerable interest, since the higher value is based on the assumption that only the free OH ion (and not the $CaOH^{\cdot}$ ion) catalyses the decomposition, and the discrepancy might be interpreted as indicating that this assumption is inaccurate. On the other hand, as Bell and Prue point out, Kilde's measurements were at relatively high ionic strengths so that part, at least, of the difference could be due to extrapolation errors.

The present note reports new measurements on the solubility of calcium iodate in calcium hydroxide solutions. These lead to $K = 0{\cdot}050$ for the second dissociation constant of calcium hydroxide, in agreement with Bell and Prue's value.

Calcium iodate hexahydrate was prepared, and its solubility measured, according to the methods described previously (*J.*, 1938, 273, 277). The calcium hydroxide was prepared from calcium carbonate "AnalaR," which was heated in a platinum crucible. The product, after cooling, was added to a suitable amount of carbon dioxide-free water, and the resulting solution was introduced into the saturator after the latter had been swept out with carbon dioxide-free air. When saturation had been attained, still in the absence of carbon dioxide, samples were withdrawn and rapidly titrated with 0·05N-hydrochloric acid, after which the iodate was estimated in the usual way. The experimental results are given in the first two columns of the table, which give the calcium hydroxide and iodate contents of the samples, both in millimols. per litre.

$Ca(OH)_2$.	$Ca(IO_3)_2$.	$CaIO_3^{\cdot}$.	$CaOH^{\cdot}$.	*I*.	*K*.
0	7·84	0·48	—	0·02256	—
3·63	7·27	0·54	0·67	0·03028	0·050
4·29	7·19	0·55	0·82	0·03170	0·049
10·28	6·65	0·63	2·38	0·04477	0·050
12·86	6·48	0·66	3·11	0·05048	0·051
14·26	6·42	0·68	3·67	0·05334	0·049
15·13	6·37	0·69	3·90	0·05532	0·050
18·60	6·23	0·72	5·25	0·06255	0·048
20·93	6·15	0·74	6·20	0·06736	0·048

In addition to $Ca^{\cdot\cdot}$, IO_3', and OH' the solutions will contain $CaOH^{\cdot}$ and $CaIO_3^{\cdot}$. The dissociation constant of the latter is known ($K = 0{\cdot}13$), as is the solubility product of calcium iodate ($7{\cdot}119 \times 10^{-7}$). Activity coefficients were estimated from the equation :

$$-\log_{10} f_z = 0{\cdot}5z^2\{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}20I\} = 0{\cdot}5z^2 . F(I)$$

(Davies, *J.*, 1938, 2093), and by successive approximations the equations :

$$\log\,[Ca^{\cdot\cdot}][IO_3']/[CaIO_3^{\cdot}] = \log 0{\cdot}13 + 2F(I)$$

and $$\log [\mathrm{Ca}^{\cdot\cdot}][\mathrm{IO}_3{}']^2 = \log S_0 + 3\mathrm{F}(I)$$

were solved to give [$\mathrm{CaIO}_3{}'$], [$\mathrm{Ca}^{\cdot\cdot}$], and, by difference, [$\mathrm{CaOH}^{\cdot}$]. The calculations are summarised in Cols. 3, 4, and 5 of the table, and the dissociation constants given in the last column are obtained from

$$\log K_{\mathrm{CaOH}} = \log [\mathrm{Ca}^{\cdot\cdot}][\mathrm{OH}']/[\mathrm{CaOH}^{\cdot}] - 2\mathrm{F}(I)$$

The most trustworthy K is probably given by the consistent results obtained in the more dilute solutions, since the slight falling off at the two highest ionic strengths might reflect increasing inaccuracy in the empirical activity equation used. This value, $K = 0{\cdot}050$, is in very good agreement with the value derived by Bell and Prue (*loc. cit.*; see also Bell and Waind, *J.*, 1950, 1979).

The solubility of calcium hydroxide in water at 25° is 0·020 mol./l. (Bassett, *J.*, 1934, 1270). Successive approximations based on the dissociation constant $K = 0{\cdot}050$ show that the saturated solution contains 5·00 millimols. per litre of the species $\mathrm{CaOH}^{\cdot}$; that is, one quarter of the calcium in a saturated lime solution is in this form.

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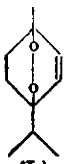
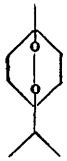
52. *The Thermal Decomposition of Dihydroascaridole.*

By C. G. MOORE.

PAGET (*J.*, 1938, 829) has shown that when ascaridole (I) is partially hydrogenated in the presence of platinic oxide as catalyst the double bond is preferentially reduced giving dihydroascaridole (II) as the only product. This has now been confirmed by both quantitative microhydrogenation and partial macro-hydrogenation of the pure peroxide.


(I.)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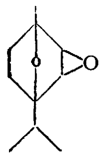
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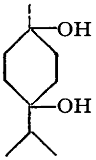
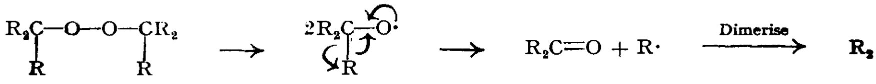
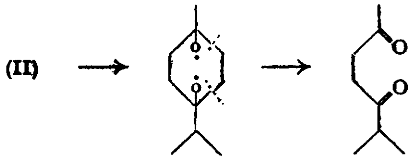

(IV.)

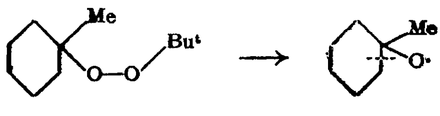
Dihydroascaridole, unlike ascaridole and the other known transannular peroxides, shows thermal stability. Thus ascaridole when heated alone at 130—150° decomposes violently with the evolution of combustible gases, chiefly propane (*Chem. Centr.*, 1908, I, 1839). It undergoes controlled decomposition to the isomeric dioxide (III) when heated at 130—150° in cymene (Nelson, *J. Amer. Chem. Soc.*, 1911, **33**, 1404; 1913, **35**, 84) and xylene (Henry and Paget, *J.*, 1921, 1714). In contrast to this it has now been found that dihydroascaridole is quantitatively recovered after being heated with *cyclo*hexene at 140° for 18 hours. Further, when heated in the liquid phase at 240°, dihydroascaridole decomposes non-explosively with the evolution of unidentified gaseous products and the formation of 6-methylheptane-2 : 5-dione (VI), together with a large amount of unidentified polymeric material.

These findings are relevent to the mode of thermal decomposition of di-*tert.*-alkyl peroxides (George and Walsh, *Trans. Faraday Soc.*, 1946, **42**, 94; Milas and Surgenor, *J. Amer. Chem. Soc.*, 1946, **68**, 205, 643; Milas and Perry, *ibid.*, 1938; Raley, Rust, and Vaughan, *ibid.*, 1948, **70**, 88), which when heated in the vapour phase undergo a homogeneous, first-order, non-chain, radical decomposition according to the following generalised scheme :


$$\underset{\mathrm{R}}{\mathrm{R_2C}}\!-\!\mathrm{O}\!-\!\mathrm{O}\!-\!\underset{\mathrm{R}}{\mathrm{CR_2}} \longrightarrow 2\underset{\mathrm{R}}{\mathrm{R_2C}}\!-\!\mathrm{O}\cdot \longrightarrow \mathrm{R_2C{=}O} + \mathrm{R}\cdot \xrightarrow{\text{Dimerise}} \mathrm{R_2}$$

The formation of the diketone (VI) from dihydroascaridole, which may be regarded as a *cyclic* di-*tert.*-alkyl peroxide, can be accounted for in a similar way :


(V.) (VI.)



(VII.) **(VIII.)**

It is noteworthy that in the diradical (V) the ring C–C bonds adjacent to the C–O bonds are broken in preference to the C–Me and C–Pr^i bonds. This accords with the fact that the peroxide (VII) yields the radical (VIII) which then breaks at a ring C–C bond in preference to the C–Me bond [Milas and Perry (*loc. cit.*); see also Walsh (*J.*, 1948, 331, 398) for a general discussion of this subject].

The unreactivity of dihydroascaridole towards *cyclo*hexene at 140° contrasts with the considerable reaction of di-*tert.*-butyl peroxide with this olefin under similar conditions (Farmer and Moore, *J.*, 1951, 131, 142). In the latter case the *tert.*-butoxy-radicals, by virtue of their dehydrogenative capacity, effect a high degree of "dehydropolymerisation" of the olefin ($Bu^tO\cdot + RH \longrightarrow Bu^tOH + R\cdot$; $2R \longrightarrow R_2$, etc.). The *tert.*-butoxy-radicals undergo, in minor degree, decomposition to acetone and methyl radicals, and the latter may compete, to a small extent, with the *tert.*-butoxy-radicals in the dehydro-polymerisation reaction of the olefin.

The inertness of dihydroascaridole compared with di-*tert.*-butyl peroxide may be due to the greater dissociation energy of the cyclic-peroxide bond. Alternatively, homolytic fission of the O–O bonds may occur at comparable rates in both compounds, but the resulting radical units produced in (V), being held in close proximity by the *cyclo*hexane bridge, may have a marked tendency to recombine. Adverse steric factors may also operate to hinder effective collision between the *tert.*-alkoxy-radicals in (V) and olefin molecules.

The presence of the double bond in ascaridole probably acts in two ways as an important modifying influence in its thermal stability, compared with dihydroascaridole. Firstly, it presents a highly reactive site very close to the peroxide group. Secondly, as revealed by an examination of molecular models, it introduces additional strain in the C_6 ring and thence in the peroxide bond, thus making the steric factors considered above likely to be far less potent in influencing the reactivity of the radical units.

Experimental.—(Analyses by Dr. W. T. Chambers, Miss E. Farquhar, and Mrs. H. Hughes.) Ascaridole was freshly distilled before use, the fraction, b. p. 66—67°/1 mm., n_D^{15} 1·4752, being used (Found: C, 71·7; H, 9·6. Calc. for $C_{10}H_{16}O_2$: C, 71·4; H, 9·6%).

Quantitative hydrogenation of ascaridole. The peroxide (30·38 mg.) was hydrogenated in absolute ethanol (10·0 ml.), platinic oxide (10 mg.) being used as catalyst. 8·01 Ml. (N.T.P.) of hydrogen were absorbed, representing 98·8% of theory for complete reduction to *cis*-1 : 4-terpin (IV). The rate of hydrogenation shows that 1 mole of hydrogen per mole of peroxide is absorbed rapidly (*ca.* 5 minutes) and a second mole is absorbed more slowly taking a total of 18 hours for completion.

Dihydroascaridole. This was prepared essentially as described by Paget (*J.*, 1938, 829). It crystallised from cooled light petroleum (b. p. 40—60°) in large prisms, m. p. 19—20°, n_D^{15} 1·4690 (Found: C, 70·3; H, 10·65%; I.V., 0. Calc. for $C_{10}H_{18}O_2$: C, 70·6; H, 10·7%; I.V., 0).

Thermal decomposition of dihydroascaridole. (*a*) The peroxide (10·0 g.) was heated under an efficient reflux at an oil-bath temperature of 240° for 6 hours; a gaseous product (1·5 g.) was evolved. The liquid product (8·50 g.) on fractional distillation gave the fractions: (i) (3·1 g.), b. p. 79—82°/9 mm.; (ii) unchanged peroxide (1·4 g.), b. p. 104—106°/10 mm.; and (iii) a dark-brown viscous polymeric residue (*ca.* 4·0 g.) which was not further investigated. Fraction (i) was identified as 6-methylheptane-2 : 5-dione (VI), n_D^{20} 1·4322 (Found: C, 67·7; H, 9·85. Calc. for $C_8H_{14}O_2$: C, 67·55; H, 9·9%). Semmler (*Ber.*, 1909, **42**, 522) gives b. p. 82—86°/10 mm.; n_D 1·433; von Auwers and Hinterseber (*Ber.*, 1915, **48**, 1357) give b. p. 90—91°/16 mm., n_D^{20} 1·4330. The diketone gave a dioxime which crystallised from acetone in rectangular prisms, m. p. 137° (Found: C, 55·95; H, 9·5; N, 16·25. Calc. for $C_8H_{16}O_2N_2$: C, 55·8; H, 9·35; N, 16·3%). Wallach and Meister (*Annalen*, **362**, 264) and Ciamician and Silber (*Ber.*, 1913, **46**, 3077) record m. p. 137°. The semicarbazide derivative (2-methyl-5-*iso*propyl-1-ureido-pyrrole) separated from absolute ethanol in micro-crystals, m. p. 199—200°. Ciamician and Silber (*loc. cit.*) record m. p. 201°.

(*b*) A mixture of the peroxide (8·2 g.) and *cyclo*hexene (45·0 g.) was heated in a nitrogen-filled sealed tube at 140° for 18 hours. Fractionation of the product (53·2 g.) gave *cyclo*hexene, b. p. 83—84°, and unchanged dihydroascaridole (8·2 g., 100%), b. p. 58—60°/1 mm., n_D^{15} 1·4690, m. p. 18—19° (Found: C, 70·85; H, 10·6%). Its identity as the unchanged peroxide was further confirmed by catalytic hydrogenation (in ethanol over palladium–charcoal) whereupon *cis*-1 : 4-terpin (96%), m. p. 117° (Found: C, 70·2; H, 11·9. Calc. for $C_{10}H_{20}O_2$: C, 69·7; H, 11·7%), was obtained.

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53. *The Reaction of Di*-tert.*-butyl Peroxide with Butan-2-one and* cyclo*Hexanone.*

By C. G. Moore.

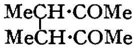
It has been shown previously (Farmer and Moore, *J.*, **1951**, 131, 142; Raley, Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88, 95, 1336) that *tert.*-butoxy-radicals formed by the liquid-phase thermal decomposition at 140° of di-*tert.*-butyl peroxide are highly effective agents for the "dehydro-polymerisation" of olefins, paraffins, and alkylbenzenes. The *tert.*-butoxy-radicals display a highly selective action, being utilised almost entirely in abstracting α-methylenic hydrogen atoms of the hydrocarbon to form *tert.*-butanol and a hydrocarbon radical which is stabilised by dimerisation :

$$\text{RH} + \text{Bu}^t\text{O}\cdot \longrightarrow \text{R}\cdot + \text{Bu}^t\text{OH};\ 2\text{R}\cdot \longrightarrow \text{R}_2$$

The *tert.*-butoxy-radicals decompose in small degree under these conditions to give acetone and methyl radicals and the latter compete, to a small extent, with the former in the dehydro-polymerisation of the hydrocarbon solvent :

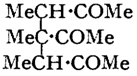
$$\text{Bu}^t\text{O}\cdot \longrightarrow (\text{CH}_3)_2\text{C:O} + \text{CH}_3\cdot;\ \text{CH}_3\cdot + \text{RH} \longrightarrow \text{CH}_4 + \text{R}\cdot;\ 2\text{R}\cdot \longrightarrow \text{R}_2$$

Di-*tert.*-butyl peroxide has now been shown to be a highly effective reagent for the cross-linking of cyclic and acyclic monoketones at the α-methylenic position giving 1 : 4-diketones and, by subsequent reaction of the peroxide with the primary reaction product, higher "dehydro-polymeric" ketones. Thus, heating the peroxide with a large excess of butan-2-one at 140° gave a mixture of ketonic "polymers," which on distillation gave : (i) pure 3 : 4-dimethylhexane-2 : 5-dione (I) (50·7% of the "polymer"), (ii) a slightly impure triketone, presumably (II) (10·7%), and (iii) a residue (38·6%), consisting of higher ketonic "dehydro-polymers."



$$\begin{array}{l}\text{MeCH·COMe}\\ \text{MeCH·COMe}\end{array}$$

(I.)

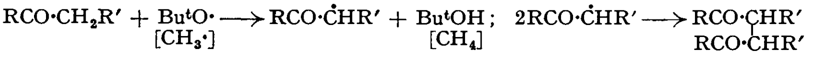


$$\begin{array}{l}\text{MeCH·COMe}\\ \text{MeC·COMe}\\ \text{MeCH·COMe}\end{array}$$

(II.)

Similarly, *cyclo*hexanone when heated with the peroxide at 140—150° gave, in addition to a mixture of approximately tetrameric ketone "polymers," a mixture of the two stereoisomeric 2 : 2′-diketodi*cyclo*hexyls from which the higher-melting form (m. p. 73—74°) was separated. This ketone has been synthesised by unambiguous means by Plant (*J.*, 1930, 1595).

After completion of this work, Kharasch, McBay, and Urry (*J. Amer. Chem. Soc.*, 1948, **70**, 1269) published analogous findings of a similar, but more detailed, study of the action of free methyl radicals, derived from diacetyl peroxide, on a large number of aliphatic ketones. A common mechanism is regarded as being operative in both cases :



$$\text{RCO·CH}_2\text{R}' + \underset{[\text{CH}_3\cdot]}{\text{Bu}^t\text{O}\cdot} \longrightarrow \text{RCO·}\dot{\text{C}}\text{HR}' + \underset{[\text{CH}_4]}{\text{Bu}^t\text{OH}};\ 2\text{RCO·}\dot{\text{C}}\text{HR}' \longrightarrow \begin{array}{l}\text{RCO·CHR}'\\ \text{RCO·CHR}'\end{array}$$

(III.)

That the *tert.*-butoxy-radicals are in the present instance the major dehydrogenative agents is shown by the high yield of *tert.*-butanol ($\nless$79% of the peroxide decomposed) obtained in the reaction with *cyclo*hexanone and by the absence of any appreciable gaseous products (methane and ethane) in the reaction with butan-2-one.

Provided the "dehydro-dimer" (III) still possesses α-methylenic hydrogen atoms it will compete with the monomeric ketone for reaction with *tert.*-butoxy-radicals, so giving the observed "dehydro-trimers," etc.

This same parallelism of action of methyl and *tert.*-butoxy-radicals exists in their abilities to produce α-methylenic carbon–carbon cross-linking in alkylbenzenes (Kharasch *et al.*, *J. Org. Chem.*, 1945, **10**, 401; Farmer and Moore, *loc. cit.*) and olefins (Farmer and Moore, *loc. cit.*; Koch, *J.*, 1948, 1111).

The present demonstration that (I) is the sole diketone isolated from the reaction of butan-2-one with di-*tert.*-butyl peroxide, and the formation of substantial amounts of "polymeric" ketones in this reaction, despite the large excess of butan-2-one used, confirm Kharasch, McBay, and Urry's observations (*loc. cit.*) and support the conclusion of many workers that the relative susceptibilities to radical attack of primary, secondary, and tertiary C–H α-methylenic bonds is in the direction C^t—H > C^s—H > C^p—H.

Experimental.—(Analyses by Dr. W. T. Chambers, Miss E. Farquhar, and Mrs. H. Hughes.)

*Reaction of butan-2-one with di-*tert.*-butyl peroxide.* A mixture of the ketone (72 g.) and the peroxide (36·5 g.) was heated in evacuated sealed tubes at 140° for 24 hours. Fractionation of the product gave : (i) b. p. 73—80°/760 mm. (78·65 g.), being a mixture of *tert.*-butanol and unreacted ketone; (ii) a small intermediate fraction, b. p. <74°/8 mm. (0·94 g.); (iii) b. p. 74—76°/8 mm., n_D^{20} 1·4342 (11·55 g.); (iv) a viscous orange liquid, b. p. 76—84°/1 mm., n_D^{20} 1·4651 (2·45 g.), and (v) a dark-orange residue (8·8 g.).

Fraction (iii) was 3 : 4-dimethylhexane-2 : 5-dione [Found : C, 67·6; H, 9·9; *M* (ebullioscopic, in acetone). 138 ± 12. Calc. for $C_8H_{14}O_2$: C, 67·6; H, 9·9%; *M*, 142]. It gave a dioxime monohydrate which crystallised from aqueous ethanol in needles, m. p. 200—201° (Found : C, 50·7; H, 9·7; N, 14·5. Calc. for $C_8H_{16}O_2N_2,H_2O$: C, 50·5; H, 9·55; N, 14·75%. Found, in a sample heated at 100—120° *in vacuo* : C, 55·95; H, 9·45; N, 16·1. Calc. for $C_8H_{16}O_2N_2$: C, 55·8; H, 9·3; N, 16·3%). Ciamician and Silber (*Ber.*, 1912, **45**, 1540) give m. p. 202°. Treatment of the diketone with phenylhydrazine in aqueous acetic acid gave 1 : 2-dihydro-3 : 4 : 5 : 6-tetramethyl-1-phenylpyridazine, which crystallised from aqueous ethanol in needles, m. p. 126—127° (Found : C, 78·5; H, 8·5; N, 12·9. Calc. for $C_{14}H_{18}N_2$: C, 78·5; H, 8·4; N, 13·1%). Ciamician and Silber (*loc. cit.*) give m. p. 130°; Kharasch *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 1269) give m. p. 127—128°.

Fraction (iv) was a slightly impure "trimeric" *ketone*, presumably (II) [Found : C, 68·6; H, 9·5; *M* (ebullioscopic, in acetone), 215 ± 24. $C_{12}H_{20}O_3$ requires C, 67·95; H, 9·45; *M*, 212]. Although the liquid gave a positive reaction with aqueous 2 : 4-dinitrophenylhydrazine sulphate no pure derivative could be obtained, nor could a pure oxime be prepared under the usual conditions.

Reaction of cyclo*hexanone with di-*tert.*-butyl peroxide.* The ketone (98 g.; b. p. 56—56·5°/20 mm., n_D^{20} 1·4508) and the peroxide (24·4 g.) were heated under reflux at 140—150° for 48 hours. On distillation, the product, a bright red liquid, gave the fractions : (i) *tert.*-butanol, b. p. 80—83°/763 mm. (17·6 g.); (ii) unreacted peroxide, b. p. 110°/763 mm. (2·5 g.); (iii) unchanged *cyclo*hexanone, b. p. 48—50°/13 mm. (82·4 g.); and a higher-boiling material (13·1 g.), from which were obtained (iv) b. p. 117—120° mm. (5·0 g.), and an undistillable residue (*ca.* 8·0 g.) which set, on cooling, to a bright-orange resin.

Redistillation of (iv) gave a mixture of the two stereoisomeric 2 : 2′-diketodi*cyclo*hexyls as an oil b. p. 110—117° (mainly 116—117°)/1 mm., n_D^{20} 1·4999 (Found : C, 74·2; H, 9·4. Calc. for $C_{12}H_{18}O_2$: C, 74·2; H, 9·35%). On being cooled in solid carbon dioxide the oil partially crystallised. The solid, when separated and crystallised from light petroleum (b. p. 40—60°), gave the higher-melting form as long prismatic needles, m. p. 73—74° (Found : C, 74·2; H, 9·35%). Both Plant (*loc. cit.*) and Kharasch *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 1269) give m. p. 70—71°.

The residue was shown to have the average composition of a *cyclo*hexanone "*dehydro-tetramer*" [Found : C, 76·7, 76·1; H, 8·9, 8·65; *M* (ebullioscopic, in benzene), 360, 370. $C_{24}H_{34}O_4$ requires C, 74·6; H, 8·9%; *M*, 286].

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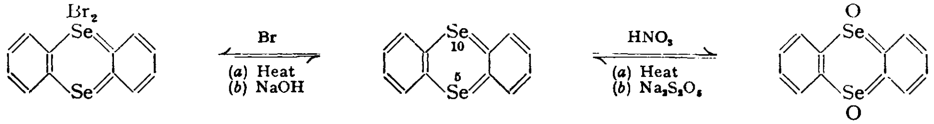
54. *Some Derivatives of Selenanthren.*

By N. M. CULLINANE.

BY treatment of selenanthren (I) with nitric acid Krafft and Kaschau (*Ber.*, 1896, **29**, 443) obtained a dioxide which melted at 270° (decomp.). In the present work a product melting at 265° (decomp.), presumably the same compound, was obtained, but, in addition, a small quantity of material melting at 249° (decomp.); the latter may be a stereoisomeric form of the former.

Selenanthren 5 : 10-dioxide (II), which crystallises from water as a hydrate—a phenomenon also observed in similar compounds, *e.g.*, diphenyl selenoxide (Banks and Hamilton, *J. Amer. Chem. Soc.*, 1939, **61**, 2306) and phenoxselenin (Drew, *J.*, 1928, 511)—is reconverted into the parent substance by heating it to its melting point or treating it with sodium pyrosulphite; thus it is not the 5 : 5-dioxide which would not be reduced by such processes.



(III.) (I.) (II.)

Whereas diphenyl selenoxide (Krafft and Vorster, *Ber.*, 1893, **26**, 2813) and thianthren 5-oxide (Fries and Vogt, *Annalen*, 1911, **381**, 326) both yield dichlorides on treatment with hydrochloric acid, selenanthren 5 : 10-dioxide readily forms a dihydrochloride; there appears to be no other record of selenoxides reacting with hydrochloric acid in this way.

In general selenoxides are not easily oxidised to selenones (Gaythwaite, Kenyon, and Phillips, *J.*, 1928, 2280) and it was not possible to convert selenanthren 5 : 10-dioxide into a selenone.

Bromine converts selenanthren into the dibromide, which probably has the structure (III), an unstable substance which regenerates selenanthren when it is kept in air, heated, or treated with sodium hydroxide.

Experimental.—Selenanthren 5 : 10-*dioxide*. Selenanthren was prepared by heating a mixture of thianthren tetroxide and selenium (Krafft and Kaschau, *loc. cit.*; Cullinane, Rees, and Plummer, *J.*, 1939, 151); its m. p. was 180°. It gradually dissolved in concentrated sulphuric acid, the liquid becoming blue-violet, then deep blue, and finally pale blue. Ferric chloride or syrupy phosphoric acid gave no colour (contrast thianthren).

The method of oxidation was a modification of that used by Krafft and Kaschau. To finely powdered selenanthren (8 g.) nitric acid (*d* 1·2; 230 c.c.) was added and the whole was boiled until evolution of brown fumes had ceased (about 15 minutes). Excess of 2N-sodium hydroxide was introduced and the whole kept for 12 hours in a stoppered flask, whereafter it was made acid by passing in carbon dioxide. The water was then completely driven off *in vacuo* at a low temperature, and the solid extracted with a large volume of boiling alcohol, on evaporation of which the dioxide, mixed with a little sodium carbonate, remained. After being washed with small portions of water the dioxide (6 g.) was obtained. It crystallised from hot water, in which it was moderately soluble, in colourless plates with water of crystallisation which was removed at 130° during 3 hours. The first crop of crystals separating from the aqueous solution consisted of plates, in very small amount, which after being heated at 130° to constant weight decomposed sharply at 249° with loss of oxygen and complete conversion into selenanthren. The main product from the mother liquors melted at 265° with rapid decomposition to selenanthren. It was slightly soluble in ethanol, somewhat more in acetic acid, and insoluble in carbon disulphide or benzene [Found (compound, m. p. 265°) : C, 42·2, H, 2·4. (Compound, m. p. 249°) : C, 42·2, H, 2·4. $C_{12}H_8O_2Se_2$ requires C, 42·1, H, 2·3%].

Addition of concentrated sulphuric acid caused the crystals to become bluish-violet, then as they slowly dissolved the solution became reddish-violet; when heated, the solution became purplish-red, and then pink on storage. Further heating caused the colour to become purple and finally violet. In syrupy phosphoric acid the dioxide gave a pale pink solution, gradually becoming pale blue.

Treatment of selenanthren in acetic solution with excess of perhydrol gave only a very small yield of the dioxide, most of the initial material being recovered. The dioxide could not be oxidised to a selenone by perhydrol or chromic acid.

Conversion of selenanthren dioxide into selenanthren. Selenanthren was obtained in quantitative yield when the dioxide was heated to its m. p. and when it was ground in a mortar with a concentrated solution of sodium pyrosulphite and then kept with occasional shaking for 12 hours in a stoppered bottle, and the product was washed with water and crystallised from carbon disulphide.

Selenanthren dioxide dihydrochloride. A solution of the dioxide in hot water was cooled to about 35° and then, before precipitation occurred, excess of concentrated hydrochloric acid was added rapidly. Immediately a copious white precipitate was formed; the *salt* was quickly dried and melted at 213° with brisk decomposition (Found : Cl, 17·3, 17·0. $C_{12}H_8O_2Se_2,2HCl$ requires Cl, 17·1%).

Selenanthren dibromide. To a solution of selenanthren (1·7 g.) in carbon disulphide (20 c.c.) bromine (1·2 g., 1·5 mols.) was slowly added with shaking and cooling. Crystals separated during the addition. After 30 minutes the *dibromide* was collected and washed with dry carbon disulphide; it formed brownish-red prisms, m. p. 140° (decomp.) (Found : Br, 34·9. $C_{12}H_8Se_2Br_2$ requires Br, 34·0%), and gave with concentrated sulphuric acid a rose-pink colour, which gradually became purplish-pink, purple, permanganate-coloured, and finally deep blue. On addition of dilute aqueous sodium hydroxide the crystals became white, the process being accelerated by rubbing; the product was extracted with hot water, from which a very small quantity of the dioxide was isolated; the residue was taken up in carbon disulphide and found to consist of selenanthren (yield over 90%). When kept in air or heated the dibromide was eventually transformed entirely into selenanthren.

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