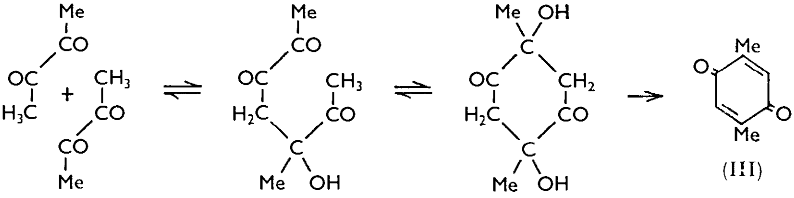
142. *The Action of Alkali on Diacetyl.*

By GREVILLE MACHELL.

The rapid dimerisation of diacetyl in dilute aqueous alkali is followed by partial rearrangement of the dimer to an acid, thought to be γ-acetyl-αγ-dihydroxy-α-methylvaleric acid. Competing with these reactions is one leading to the formation of acetic acid.

DURING an investigation [1] into the behaviour of carbohydrates towards alkaline reagents, it became clear that further information concerning the action of dilute aqueous alkali on simple aliphatic α-diketones could assist in its interpretation. The present study of diacetyl was therefore undertaken, the choice being made on the grounds of ready accessibility and the availability of previous work.

It is known [2] that in dilute aqueous potassium hydroxide diacetyl rapidly undergoes an aldol type of condensation, yielding a mixture of the open-chain (I) and the cyclic (II) dimer. Treatment with alkali at higher temperatures then converts at least part of this mixture into *p*-xyloquinone (III). In a more recent investigation von Euler and Hasselquist [3] reported the immediate formation of an enediol (IV), disclosed by decolorisation of dichlorophenylindophenol, and to account for this they proposed, without experimental support, the synchronous formation of acetic acid:


(I) (II) (III)

$$2\text{Me·CO·CO·Me} + 2\text{H}_2\text{O} \longrightarrow \text{HO·CMe=CMe·OH (IV)} + 2\text{CH}_3\text{·CO}_2\text{H}$$

The formation of acetic acid from diacetyl has also been reported by Evans and Dehn,[4] but under quite different experimental conditions. These workers treated ethereal diacetyl with potassium hydroxide, expecting to obtain α-hydroxy-α-methylpropionic acid by a benzilic acid type of rearrangement. They were unable to detect this rearrangement product, but claimed without experimental evidence that acetic acid and acetaldehyde were formed.

The primary object of the present investigation was to establish whether treatment of diacetyl with dilute aqueous alkali affords acetic acid and acetaldehyde. For the parallel investigation on carbohydrates, it was also desired to reveal any influence of the calcium ion.

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[1] Blears, Machell, and Richards, *Chem. and Ind.*, 1957, 1150.

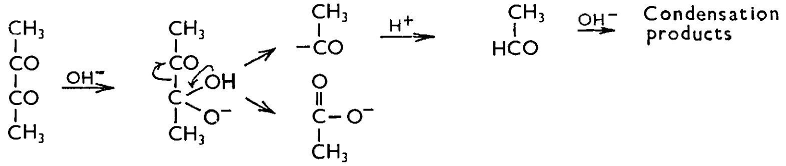
[2] von Pechmann, *Ber.*, 1888, **21**, 1419; von Pechmann and Wedekind, *Ber.*, 1895, **28**, 1845; Diels, Blanchard, and Heyden, *Ber.*, 1914, **47**, 2356.

[3] von Euler and Hasselquist, *Arkiv Kemi*, 1949, **1**, 325.

[4] Evans and Dehn, *J. Amer. Chem. Soc.*, 1930, **52**, 252.

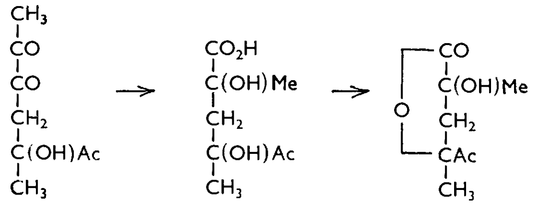
Acetaldehyde could not be detected in the neutral products obtained on treatment of diacetyl with lime-water or dilute aqueous sodium hydroxide at 25° in the absence of oxygen. If acetaldehyde is formed it presumably undergoes condensation due to the alkali. With 2,4-dinitrophenylhydrazine the neutral products afforded 4-hydroxy-2,5-dimethyl-2′,4′-dinitroazobenzene, arising from *p*-xyloquinone. Under similar conditions, *p*-benzoquinone affords 4-hydroxy-2′,4′-dinitroazobenzene instead of the expected hydrazone.[5]

The results reported in Table 1 show that diacetyl is converted into acid at similar rates in 0·05N-sodium hydroxide and 0·04N-lime-water. The acidic products were isolated by established ion-exchange resin technique, but separation of the individuals was complicated by the presence of acidic resins which were insoluble in dilute acid and accounted for about two-thirds of the total acids formed. Of the non-resinous acids the volatile portion was mainly acetic acid, arising as proposed by von Euler and Hasselquist or possibly, on analogy with the behaviour of aromatic α-diketones,[6] by hydrolysis:



A similar scission of the open-chain dimer (I) of diacetyl could also afford acetic acid.

Paper chromatography of the non-volatile acids precluded the presence of more than a trace of α-hydroxy-α-methylpropionic acid and indicated a single constituent. This is tentatively identified as γ-acetyl-αγ-dihydroxy-α-methylvaleric acid (V), formed by a benzilic acid type of rearrangement of the open-chain dimer (I).



(I) (V) (VI)

Dehydration (reversible) of the acid afforded two crystalline isomeric lactones, probably geometric isomers (VI).

Quantitative analysis yielded the results shown in Table 2. The "total" acid represents the sum of the non-resinous acids, *i.e.*, those acids whose individual yields are recorded in the Table; yields are expressed as a percentage of the total acid on an equivalent basis. It is clear that the acid yields are largely independent of the nature of the alkali. In the case of sodium hydroxide, increasing the temperature did not lead to a corresponding increase in the yield of total acid, while the amount of scission to acetic acid was reduced.

EXPERIMENTAL

Chromatography was carried out with Whatman No. 1 paper at 25° with ethyl acetate–acetic acid–water (10 : 1·3 : 1)[7] as solvent and, as sprays, (*a*) "B.D.H." 4·5 Indicator,[8] (*b*) hydroxylamine–ferric chloride,[9] and (*c*) a saturated solution of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid.

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[5] Borsche, Müller, and Bodenstein, *Annalen*, 1929, **472**, 201.

[6] Pfeil, Geissler, Jacquemin, and Lömker, *Chem. Ber.*, 1956, **89**, 1210; Lachman, *J. Amer. Chem. Soc.*, 1924, **46**, 779.

[7] Richtzenhain and Moilanen, *Acta Chem. Scand.*, 1954, **8**, 704.

[8] Nair and Muthe, *Naturwiss.*, 1956, **43**, 106.

[9] Abdel-Akher and Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 5859.

Action of Lime-water on Diacetyl.—(a) *Rate of acid formation.* Freshly distilled diacetyl (0·429 g.) was dissolved in 0·041N-lime-water (250 ml.) at 25° in the absence of oxygen; the solution quickly became dark brown. At intervals, aliquot portions were added to excess of 0·05N-hydrochloric acid, and the excess of acid was determined by titration with 0·05N-sodium hydroxide. After 48 hr. a brown precipitate was formed; results are shown in Table 1.

TABLE 1. *Rate of acid formation from diacetyl at 25°.*

(a) 0·04N-*Lime-water.*								
Time (hr.)	0	0·25	1	4	7	24	48	
Acid formed (equiv./mole)	0	0·17	0·21	0·26	0·28	0·31	0·38	
(b) 0·05N-*Sodium Hydroxide.*								
Time (hr.)	0	0·25	1	3	23	71	435	695
Acid formed (equiv./mole)	0	0·14	0·23	0·27	0·45	0·57	0·76	0·87

TABLE 2. *Yields of acids from action of alkali on diacetyl.*

Conditions	Total (equiv./mole)	γ-Acetyl-αγ-dihydroxy-α-methylvaleric (%)	Acetic (%)	Formic (%)
Lime-water, 25°, 6 hr.	0·124	76	17	7
Sodium hydroxide, 25°, 6 hr.	0·121	76	21	3
Sodium hydroxide, 100°, 7 hr.	0·158	87	11	2

(b) *Isolation of the products.* A solution of diacetyl (3·42 g.) in 0·042N-lime-water (2 l.) was kept at 25° for 6 hr. in the absence of oxygen. The solution was then saturated with carbon dioxide, whereupon a dark green solid (0·11 g.) was precipitated; this was filtered off, and not examined further. The filtrate was distilled under reduced pressure, and the distillate collected in successive receivers at 0° and −80°. When the volume of the residue was reduced to 200 ml., distillation was arrested, and the two distillates (A, 1600 ml. at 0°; B, 4 ml. at −80°) were separately tested for acetaldehyde by use of Schiff's reagent and piperidine–sodium nitroprusside.[10] Both tests gave negative results with both distillates. The distillates were each made 2N with respect to hydrochloric acid, and an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid was added. Flocculent orange precipitates were obtained in both cases and were collected. From A was produced a solid (0·42 g.), which on recrystallisation from chloroform afforded *4-hydroxy-2,5-dimethyl-2′,4′-dinitroazobenzene*, m. p. 222—223° (Found: C, 53·1; H, 4·0; N, 17·5. $C_{14}H_{12}O_5N_4$ requires C, 53·2; H, 3·8; N, 17·7%). Authentic *p*-xyloquinone and 2,4-dinitrophenylhydrazine gave the same compound, m. p. and mixed m. p. 222°. Distillate B afforded an inseparable mixture (0·06 g.), m. p. 80—150°.

The distillation residue of calcium salts and non-volatile neutral products was filtered to remove calcium carbonate, and treated with Amberlite IR-120 (H) resin (40 ml.). A copious brown precipitate was produced; this was removed and the acidic filtrate stirred for 24 hr. with Amberlite IR-A400 carbonate resin (20 g.). The resin was washed with water (250 ml.), the filtrate and washings containing any neutral compounds being discarded. Acids were eluted from the resin with N-ammonium carbonate (3 l.) during 20 hr., and the eluate was then evaporated to dryness at 65°/20 mm. to decompose the excess of eluant. The residue of ammonium salts was taken up in water (50 ml.) and passed through a column of Amberlite IR-120(H) resin (40 ml.). The acidic effluent was decolorised with charcoal, and the acids separated into volatile and non-volatile components.

From the volatile acid was prepared *p*-bromophenacyl acetate, m. p. and mixed m. p. 84—85° (from acetone–light petroleum). Paper chromatography of the non-volatile acid with spray *a* revealed an unknown acid, R_L 0·79, with a trace of (?) α-hydroxy-α-methylpropionic acid, R_L 1·15 (L = lactic acid). Application of spray *b* showed lactones, R_L 0·97 and R_L 1·18. The remaining solution of non-volatile acid was concentrated to a syrup and converted into crystalline lactone by drying over phosphoric oxide at 50°/0·01 mm. Paper chromatography of this lactone followed by application of spray *b* gave two spots, R_L 0·96 and 1·15 severally, of similar intensity, which also reacted with spray *c*. Recrystallisation of the mixture of lactones from ethyl acetate–light petroleum gave three fractions, which were examined by paper chromatograpy as above: (i) *γ-acetyl-α-hydroxy-α-methyl-γ-valerolactone*, m. p. 135—137°, R_L

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[10] Lewin, *Ber.*, 1899, **32**, 3388.

1·18 (Found: C, 55·6; H, 7·0%; equiv., 172·8. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%; equiv., 172·2); (ii) ~1 : 1 mixture of lactones, R_L 0·97 and 1·18; (iii) m. p. 126—127°, R_L 0·97 (Found: C, 55·9; H, 6·9%). A portion of fraction (ii) was converted into the free acids through the sodium salt, and the acids on paper chromatography as described gave a single spot of R_L 0·80; there were also traces of re-formed lactones, R_L 0·98 and 1·17.

A further portion of fraction (ii) was converted into *calcium γ-acetyl-αγ-dihydroxy-α-methylvalerate monohydrate*, which recrystallised from methanol–acetone (1 : 3) [Found: C, 44·3; H, 6·5; Ca, 9·3. $(C_8H_{13}O_5)_2Ca,H_2O$ requires C, 44·0; H, 6·4; Ca, 9·2%]. An aqueous solution of this calcium salt was freed from calcium by using Amberlite IR-120(H) resin, and the resulting acidic solution heated with excess of brucine at 100° for 4 hr. After removal of unchanged brucine, the solution was evaporated to dryness, and the residue crystallised from a little ethanol. Subsequent recrystallisation from the same solvent afforded *brucine γ-acetyl-αγ-dihydroxy-α-methylvalerate*, m. p. 211—213° (decomp.) (Found: C, 63·6; H, 6·6; N, 4·7. $C_{31}H_{40}O_9N_2$ requires C, 63·7; H, 6·85; N, 4·8%).

(c) *Quantitative analysis of acidic products.* Diacetyl (3·44 g.) was treated with lime-water as above. The acidic and the non-volatile neutral products were separated by stirring the acidic solution for 24 hr. with De-Acidite FF resin (micro-bead; 2% cross-linked) (20 g.) in the carbonate form.[11] Sorbed acids were eluted with N-ammonium carbonate (500 ml.), and the free acids (4·95 milliequiv.) recovered as described. A portion (4·65 milliequiv.) of the acid mixture was separated into volatile (1·09 milliequiv.) and non-volatile (3·42 milliequiv.) fractions. The solution of volatile acids was heated with excess of red mercuric oxide for 2·5 hr. at 100°, conditions under which formic acid is quantitatively oxidised.[12] Titration of the residual acid established that the solution had contained formic acid (0·32 milliequiv.). The composition of the acid mixture on an equivalent basis is recorded in Table 2; it is assumed that the remainder of the volatile acid is acetic acid.

Action of Sodium Hydroxide on Diacetyl at 25°.—(a) *Rate of acid formation.* Diacetyl (0·432 g.) was treated with 0·05N-sodium hydroxide (250 ml.) at 25° in the absence of oxygen. The solution became dark brown within a few minutes but no precipitation occurred; samples were withdrawn for acid determinations as described above. Results are given in Table 1.

(b) *Isolation of the neutral products.* Diacetyl (3·40 g.) was added to 0·05N-sodium hydroxide (2·5 l.) at 25° in the absence of oxygen. After 6 hr., the reaction was arrested by the addition of concentrated hydrochloric acid (12 ml.), the final solution having pH 3. A rapid stream of nitrogen was then passed through the solution for 36 hr. and the effluent gas bubbled through traps containing a saturated solution of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid;[13] no significant precipitate of hydrazone resulted. The acid solution was then partially distilled at 30°/15 mm. and the distillate collected in two portions (A, 100 ml. at 0°; B, 5 ml. at −80°). These fractions were treated separately with the 2,4-dinitrophenylhydrazine reagent, and after two days the hydrazones were filtered off and dried. The *product* (0·24 g.) from A, crystallised twice from ethanol, had m. p. 66—67°; that from B (0·145 g.) had an identical m. p., undepressed on admixture with A (Found: C, 54·5; H, 6·4; N, 17·85. $C_{14}H_{20}O_4N_4$ requires C, 54·6; H, 6·5; N, 18·15%).

(c) *Isolation and determination of the acidic products.* Diacetyl was treated with sodium hydroxide as in (b), but the reaction was terminated by the addition of Amberlite IR-120(H) resin (200 ml.). When the pH of the solution had fallen to 5, a copious brown precipitate was produced, and this was then filtered off together with the resin. The solution was made slightly alkaline (pH 8) by the addition of 0·1N-sodium hydroxide, and the volume reduced to 200 ml. by distillation under reduced pressure. The concentrate was passed through a column of Amberlite IR-120(H) resin (40 ml.), and the acids (4·83 milliequiv.) isolated from the acidic effluent by means of DeAcidite FF resin (200—400 mesh; 2% cross-linked) carbonate as described above. Proportions of volatile and non-volatile acid, and the formic acid in the former, were then determined, with the results given in Table 2. From the volatile acid remaining after decomposition of the formic acid with mercuric oxide was prepared *p*-bromophenacyl acetate, which had the properties recorded above.

Paper chromatography of the non-volatile acid showed that it was the same as that formed in the lime-water treatment. The acid was converted into lactone by drying over phosphoric

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[11] Machell, *J.*, 1957, 3389.

[12] Richards and Sephton, *J.*, 1957, 4492.

[13] Cf. Bell and Smith, *J.*, 1958, 1691.

oxide *in vacuo*, and the lactone crystallised from ethyl acetate–light petroleum, giving three fractions as before.

Action of Sodium Hydroxide on Diacetyl at 100°.—To 0·05N-sodium hydroxide (2·5 l.) at 100° in the absence of oxygen, diacetyl (4·3 g.) was added. After 7 hr. at 100° the mixture was cooled, and stirred with Amberlite IR-120(H) resin (70 ml.) until the pH had fallen to 8. The resin was then filtered off, the filtrate evaporated to *ca.* 100 ml. under reduced pressure, and the concentrate stirred with Amberlite IR-120(H) resin (50 ml.) and charcoal for 1 hr. After filtration, the colourless solution was freed from remaining cations by passage through a column of Amberlite IR-120(H) resin (10 ml.). The acids (7·88 milliequiv.) were then isolated from the acidic effluent by using DeAcidite FF(200—400 mesh; 2% cross-linked) carbonate, and separated by distillation into volatile and non-volatile portions. Formic acid in the volatile portion was then determined; results are shown in Table 2.

Paper chromatography of the non-volatile acid portion established that its composition was similar to that of the non-volatile acid produced at 25°.

Action of Sodium Hydroxide on γ-Acetyl-α-methyl-γ-valerolactone.—The mixed lactones (0·1 g.) were treated with 6N-sodium hydroxide (4 ml.) at 100° for 16 hr. in the absence of oxygen. The colourless solution of sodium salts was then cooled, diluted to 50 ml., and run through a column of Amberlite IR-120(H) resin (30 ml.). Paper chromatography of the acidic effluent as described above revealed only the unchanged acids, R_L 0·78, and traces of re-formed lactones.

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British Rayon Research Association, Heald Green Laboratories,
Wythenshawe, Manchester, 22.
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