

product (4) was extracted with ether and crystallized as colourless plates from Et<sub>2</sub>O: CHCl<sub>3</sub> mixture (yield 250 mg) (Found C; 71.59, H: 7.00; C<sub>27</sub>H<sub>32</sub>O<sub>6</sub> required C; 71.68, H: 7.07%); IR: 3445, 1735, 1722, 1640, 1510, 910, 875 and 822; <sup>1</sup>H-NMR: 0.93, 1.00, 1.05, 1.08, 1.20-1.90, 3.25, 3.65, 3.70, 4.90, 5.10, 5.60, 6.15, 6.39, 6.90, 7.20 and 7.40.

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## CLAY-CATALYSED KNOEVENAGEL CONDENSATION

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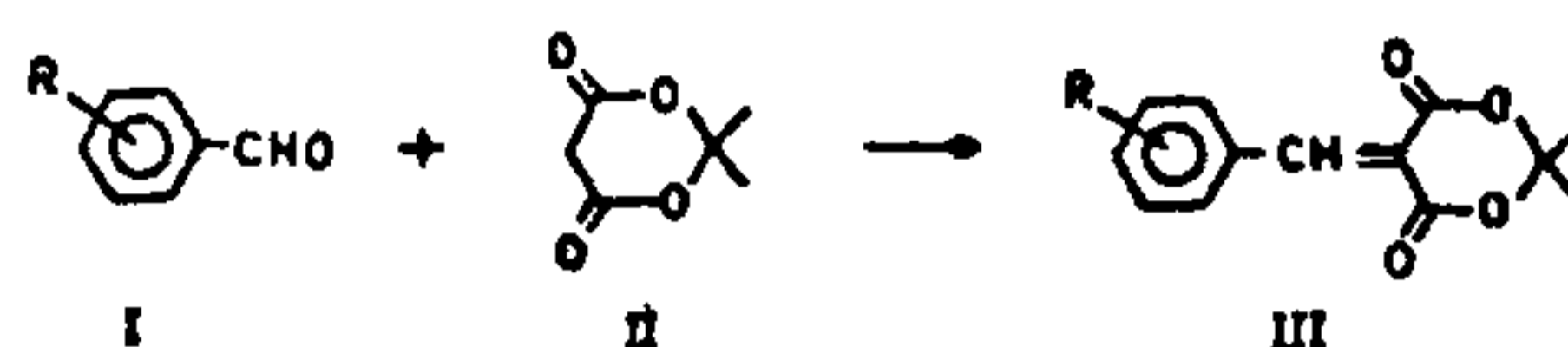
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MELDRUM'S acid (2,2-dimethyl-1,3-dioxan-4,6-dione) is an attractive alternative to acyclic esters in organic synthesis<sup>1</sup> and it has a strong tendency to undergo bis-alkylation<sup>2</sup>. Meldrum's acid is a good source of malonate carbanion and has an acidity (pK = 4.83) very close to that of acetic acid which is used with acetate as a catalyst in Knoevenagel and related condensations. In continuation of our work on solid-supported reactions<sup>3-6</sup>, and in view of the importance of alkylated Meldrum's acid in phar-

maceuticals, we report here a simple method for a Knoevenagel condensation of Meldrum's acid with aldehydes in the presence of clay, Kaolin (Kaylene Chemicals Ltd., London) at room temperature, in the absence of a solvent. The advantage of the method is its simplicity and high yields of the pure product.

An equimolar mixture of aldehydes (I) and Meldrum's acid (II) was melted and adsorbed on kaolin at room temperature without the use of solvent. It was observed that complete condensation took place within 20-25 hr after mechanical stirring.



### General procedure for condensation

An aldehyde or ketone (I) was mixed with Meldrum's acid (II) in equimolar (0.01 mol each) quantity. This mixture whether it contained solid or liquid carbonyl compound, was carefully melted and adsorbed on 4 g of kaolin and mechanically stirred for 20-25 hr at room temperature. The product (III) was eluted by dichloromethane (3 × 30 ml). Evaporation of the solvent under reduced pressure generally gave a pure crystalline product. Purity was assured by TLC. If necessary, the product was crystallized from an appropriate solvent, i.e. CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> or benzene. Products were characterized by PMR, IR and compared with authentic samples.

Kaolin gave a good result similar to basic alumina<sup>7</sup> (Merck 1076) and chromatographic neutral alumina<sup>7</sup> (Woelm-N, 2087) and more active

Table 1 Condensation of Meldrum's acid with aldehydes

Aldehyde (I)	Yield (III) (%)	m.p (°C)
Benzaldehyde	89	85
Cinnamaldehyde	80	109
<i>m</i> -hydroxybenzaldehyde	80	175
<i>p</i> -hydroxybenzaldehyde	85	197
<i>p</i> -methoxybenzaldehyde	91	126
<i>p</i> -N-dimethylamino- benzaldehyde	95	174
Vanillin	85	129
<i>p</i> -methylbenzaldehyde	87	159
<i>p</i> -chlorobenzaldehyde	82	182

catalyst than silica gel<sup>7</sup> (Merck 7734), Fluorosil<sup>®</sup> and Montmorillonite K10<sup>®</sup>. Slight excess of kaolin did not give any side products and showed no effect on percentage yield. However condensation with ketones did not give satisfactory results, even after heating at 50°C for 10 hr.

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## FORMATION OF H<sub>2</sub>O<sub>2</sub> ON RUTILE TiO<sub>2</sub> DURING PHOTO-ILLUMINATION OF OXYGEN

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PREVIOUS studies<sup>1,2</sup> on the adsorption of water on titanium dioxide have shown that molecularly adsorbed water is bound to the surface in addition to hydroxyl groups. Sufficient evidence is available to support the strong relationship existing between surface bound hydroxyl groups and photoactivity of titanium dioxide<sup>3</sup>. The presence of these OH groups may lead to their combination in pairs to form hydrogen peroxide. But there is little evidence available to show that H<sub>2</sub>O<sub>2</sub> is formed during photoadsorption of O<sub>2</sub> on TiO<sub>2</sub>. However, its participation during photocatalytic reaction on TiO<sub>2</sub> has been reported<sup>4-6</sup>. This communication investigates further to show the formation of H<sub>2</sub>O<sub>2</sub> as an intermediate through the photostudy of O<sub>2</sub> on TiO<sub>2</sub> surfaces.

The adsorption-desorption experiments were performed in a conventional high vacuum system. The samples were irradiated with UV light using water-cooled medium pressure mercury arc (Hanovia, 500 W). The temperature programmed desorption (TPD) experiments were performed in conjunction with a proportional temperature controller. The desorbed species were analysed by a mass spectrometer (VG Micromass 2A).

It is reported<sup>7</sup> that the decrease in photouptake of O<sub>2</sub> with increasing outgassing temperature between 273 K and 693 K is due to the decrease in surface OH groups. The participation of OH groups in photo-adsorption of oxygen on TiO<sub>2</sub> is further supported by the observation that the strongly bound OH groups on TiO<sub>2</sub> are affected under normal illumination in the presence of oxygen while, in the absence of oxygen, the OH groups remain unaffected<sup>8</sup>.

Temperature has a pronounced effect on oxygen photo-adsorption on TiO<sub>2</sub>. The effect observed is shown in figure 1 which indicates a complex behaviour with a maximum around 323 K. The equilibrium uptake of O<sub>2</sub> increases from 273 K to 323 K, having a maximum at 323 K and then decreases abruptly. The gradual increment of O<sub>2</sub> uptake between 273 K and 323 K reflects the conversion of OH ions into OH radicals on TiO<sub>2</sub> since evidence for the photocatalytic formation of surface hydroxyl radicals on TiO<sub>2</sub> has been reported<sup>9,10</sup>. The existence of these OH radicals may lead to their combination to form H<sub>2</sub>O<sub>2</sub>. The increase in the surface concentration of H<sub>2</sub>O<sub>2</sub> remains thermally

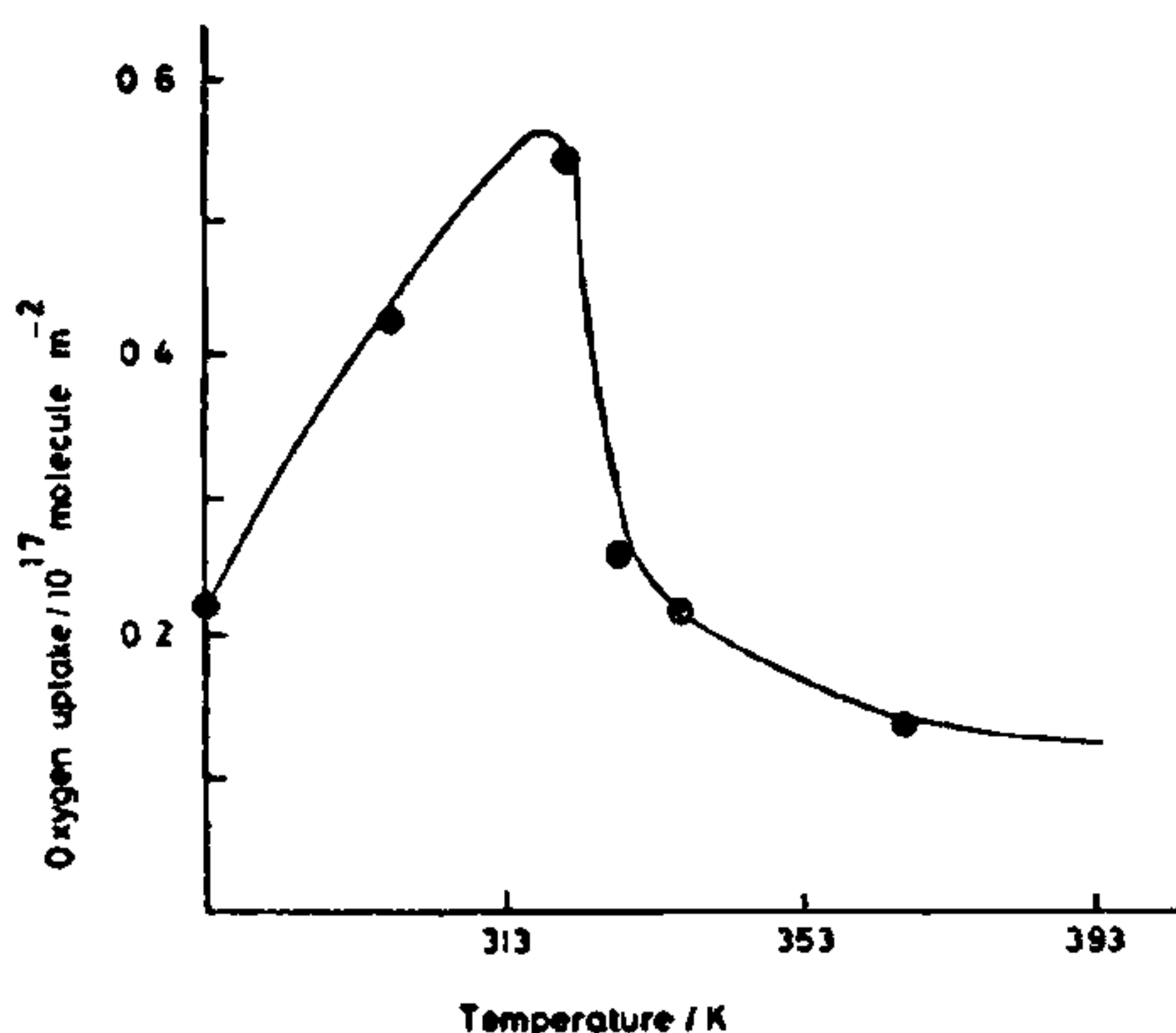


Figure 1. Effect of temperature on the photo-adsorption of oxygen on titanium dioxide.