

could not be determined owing to the insolubility in the common solvents available. The  $\alpha$ - and  $\beta$ -protons in these esters absorb at lower fields than do those in the corresponding open chain compounds, and this is not due to a solvent effect (Table II). Only one  $\beta$ -proton signal was observed for both the axial and equatorial  $\text{CH}_3$  groups in isopropylidene dimethylmalonates, indicating rapid chair-chair interconversion of the six-membered ring. Another, but less likely, explanation could be that the ring is almost planar in these compounds. Again, no evidence of enolization was discernible in isopropylidene ethylmalonate, in agreement with the conclusions reached on the basis of the infrared spectra of Meldrum's acid and its derivatives (2).

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## Dianils of *o*-Hydroxyaldehydes as Potential Photochromes

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Several diamine-aldehyde anils have been prepared and examined for crystalline photochromism.

A NUMBER of crystalline anils of *o*-hydroxy aromatic aldehydes have been reported to be photochromic (2). This photochromism has been ascribed to a topochemical phenomenon determined by the packing of the anil molecules in the crystal lattice which permits or inhibits internal photohydrogen transfer to a colored enol (1). Since very

tallized from methanol to analytical purity. Yields and melting points are reported in Table I.

The dianils were irradiated as crystalline films on the walls of fused quartz vessels positioned 4 cm. from a Hanovia No. 30620 mercury vapor lamp. Because photochromism can sometimes be eradicated by light absorbed in the region

Table I. Diamine-Aldehyde Anils

| Amine                            | Aldehyde                        | Formula  | Yield,<br>% | M.P., °C.            | Analysis, % N |       |
|----------------------------------|---------------------------------|--|-------------|----------------------|---------------|-------|
|                                  |                                 |  |             |                      | Calcd.        | Found |
| 1,4-Cyclohexanebis (methylamine) | 2-Hydroxy-3-methoxybenzaldehyde | $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_4$ | 76          | 153-155              | 6.82          | 6.86  |
|                                  | 2-Hydroxybenzaldehyde           | $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2$ | 45          | 109                  | 7.99          | 7.92  |
| 4,4'-Diaminodiphenylmethane      | 2-Hydroxy-1-naphthaldehyde      | $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_2$ | 65          | 203-204              | 6.21          | 6.21  |
|                                  | 2-Hydroxy-3-methoxybenzaldehyde | $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_4$ | 70          | 192                  | 6.00          | 6.06  |
| Diethylenetriamine               | 2-Hydroxybenzaldehyde           | $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_2$ | 70          | 214-215              | 6.89          | 6.90  |
|                                  | 2-Hydroxy-1-naphthaldehyde      | $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_2$ | 73          | 153-154              | 10.21         | 10.25 |
| Ethylenediamine                  | 2-Hydroxy-3-methoxybenzaldehyde | $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$ | 70          | 161-162              | 8.53          | 8.20  |
| <i>p</i> -Phenylenediamine       | 2-Hydroxybenzaldehyde           | $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$ | 94          | 212-213 <sup>a</sup> | 8.86          | 8.80  |

<sup>a</sup> Although this compound has been previously reported (3), it was synthesized for inclusion in this photochemical study.

few of the larger molecular species, typified by symmetrical dianils, have been examined for crystalline photochromism, the authors have prepared the following diamine-aldehyde anils and investigated them in this regard. None of these compounds gave evidence of visually detectable photochromism.

#### EXPERIMENTAL

The anils employed in this study were prepared by refluxing a 0.20 to 0.10 mole ratio of the aldehyde to the diamine in 350 ml. of anhydrous methanol for 4 hours. The solvent was removed in vacuo and the product recryst-

allized from methanol to analytical purity. Yields and melting points are reported in Table I.

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