

## Participation of Hydrocarbons in the Photodimerization of 3,4-Dichlorocinnamic Acid

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*Summary* Crystals of the  $\beta$ -form of 3,4-dichlorocinnamic acid photodimerize with incorporation of various hydrocarbons into the crystalline dimer.

SINCE the extensive study on the photodimerization of cinnamic acid<sup>1</sup> there has been a growing interest in organic reactions in the solid state. We now report a new type of solid-state photodimerization which proceeds with participation of hydrocarbons.

Crystals of the  $\beta$ -form of 3,4-dichlorocinnamic acid (0.3 g) were dispersed in hexane (100 ml) in a Pyrex flask and irradiated with a 450 W high-pressure mercury lamp at 35–40 °C. Upon irradiation for 1 h, the cinnamic acid was almost completely consumed. The i.r. and n.m.r. spectra of the photo-product indicated the formation of a dimer [disappearance of the  $\nu_{\text{C}=\text{C}}$  i.r. band at 1640  $\text{cm}^{-1}$ ; n.m.r.  $\delta$  ( $\text{CD}_3$ )<sub>2</sub>SO 6.8–7.4 (m, 6H, ArH) and 3.8–4.5 (m, 4H, cyclobutane ring-H)].

Careful examination of the cyclobutane ring proton n.m.r. patterns confirmed that the photo-product was *t*-3,4-bis-(3,4-dichlorophenyl)cyclobutane-*r*-1,2-dicarboxylic acid (a  $\beta$ -truxinic acid-type dimer). Schmidt and his co-workers obtained the same steric configuration of the dimer without the use of a dispersant.<sup>1</sup> However, it should be noted that the dimer obtained in hexane has significantly different properties from those of the dimer obtained without dispersant. One of the characteristics of this dimer is the inclusion of hexane molecules, which was confirmed by n.m.r. spectroscopy, differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.). N.m.r. signals corresponding to hexane protons were observed at  $\delta$  0.8–1.3. In the d.s.c. curve, a broad endothermic peak which was accompanied by 7.2% weight loss was found at *ca.* 110 °C. I.r. and n.m.r. spectra confirmed that the weight loss was due to the loss of hexane molecules from the dimer. The amount of hexane lost (calculated from this weight loss) was *ca.* 0.4 mol per mol of dimer. Elemental analysis also supported this result. This dimer melts at 198 °C accompanied by formation of an anhydride from the carboxylic acid residues, while the dimer obtained without the use of a dispersant is amorphous and shows no clear m.p. Neither dimer could be recrystallized from hexane but each could be recrystallized from hexane-ethanol (19:1) giving almost identical m.p.s. However, these recrystallized dimers included ethanol rather than hexane. They could also be recrystallized from nonane but without incorporation of nonane. Neither the hexane-free dimer, which was obtained by heating the hexane-

containing dimer *in vacuo*, nor the dimer obtained without dispersant incorporated hexane when they were dispersed in hexane. Irradiation of a saturated solution of 3,4-dichlorocinnamic acid in hexane ( $1.6 \times 10^{-5} \text{ mol l}^{-1}$ ) led to *cis-trans* isomerization and no dimer was found in the solution. These facts suggest that the hexane was incorporated into the dimer during the photoreaction as in the case of the photodimerization of *p*-formylcinnamic acid in water dispersant,<sup>2</sup> and not subsequent to formation of the dimer.

TABLE. Hydrocarbons incorporated into the dimers

| Hydrocarbon | Amounts of hydrocarbon <sup>a</sup><br>(mol : mol of dimer) |
|-------------|---|
| Pentane     | 1 : 2   |
| Hexane      | 2 : 5   |
| Heptane     | 1 : 4   |
| Octane      | 1 : 4   |
| Nonane      | 1 : 4   |
| Cyclohexane | 1 : 2   |
| Benzene     | 1 : 2   |

<sup>a</sup> Determined by t.g.a.-d.s.c. and elemental analysis.

Different hydrocarbons were incorporated into the dimer in a similar way as hexane when they were used as dispersants (Table). These hydrocarbons are released slowly when the dimers are kept in air. On heating, these hydrocarbons were lost completely from the dimer in the range 100–130 °C, and all the dimers melt at the same temperature (198 °C) after loss of hydrocarbons. Though the crystal structure of the dimers containing hydrocarbons has not been established yet, they seem to be a type of inclusion compound.

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<sup>2</sup> F. Nakanishi, H. Nakanishi, T. Tasai, Y. Suzuki, and M. Hasegawa, *Chem. Letters*, 1974, 525; F. Nakanishi, H. Nakanishi, M. Tsuchiya, and M. Hasegawa, *Bull. Chem. Soc. Japan*, 1976, 49, 3096.