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# The Photochemical Behavior of 3,3-Dimethyl-1,2-indanedione toward Aromatic Aldehydes

Kazuhiro MARUYAMA, Yoshinori NARUTA, Atsuhiro OSUKA,*,† and Hitomi SUZUKI†
*Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606*
† *Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790*

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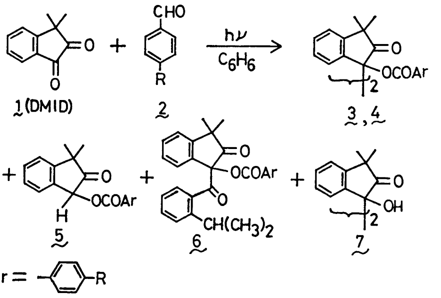
**Synopsis.** The photochemical reaction of 3,3-dimethyl-1,2-indanedione with aromatic aldehydes in benzene was found to give a mixture of two diastereoisomeric 2:2 adducts, a 1:1 adduct, a 2:1 adduct, and pinacol.

When photolyzed together with aldehydes, cyclic $\alpha$-diketones in both aliphatic[1] and aromatic systems[2] abstract the formyl hydrogen atom to give in-cage combination products predominantly. In contrast, open chain $\alpha$-diketones yield out-of-cage products mainly.[3] In the present work, we have investigated the photochemical reaction of 3,3-dimethyl-1,2-indanedione (**1**) (DMID) with several aromatic aldehydes and found a rather unexpected behavior of DMID toward these aldehydes.

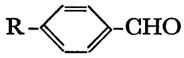
After a benzene solution of DMID and *p*-anisaldehyde **2a** had been irradiated in a Pyrex tube for 2 h, the separation of the products by TLC gave two diastereoisomeric 2:2 adducts, **3a** (11%) and **4a** (10%), a 1:1 adduct, **5a** (4%), and a 2:1 adduct, **6a** (7%). In addition, the $^1$H-NMR spectrum of this reaction mixture showed the presence of pinacol, **7** (15%).[4] The molecular weights of **3a** and **4a**, as determined by the vapor-pressure method, are 598±30 and 620±30 (Calcd, 618.25) respectively. The 2:2 adducts, **3a** and **4a**, show characteristic IR bands due to the unconjugated five-membered cyclic ketone and the aromatic ester at 1777 and 1729 cm$^{-1}$ and at 1768 and 1720 cm$^{-1}$, respectively. The $^1$H-NMR spectra show signals at 1.52 (s, 3H), 1.55 (s, 3H), and 3.76 (s, 3H), and at 0.82 (s, 3H), 1.52 (s, 3H), and 3.82 (s, 3H), respectively. The $^{13}$C-NMR spectrum of **4a** shows peaks at 213.2 (ketone), 164.1 (ester), 86.1 (s), 55.5 (q, $CH_3O$–), and 48.9 (s) ppm, besides two methyl carbons and twelve sp$^2$ carbons. These spectral data and the results of elemental analyses are consistent only with the formulation of **3a** and **4a** as two diastereoisomers of 1,1′-bis(4-methoxybenzoyloxy)-3,3,3′,3′-tetramethyl-1,1′-biindane-2,2′-dione. The molecular weight of **6a**, as determined by the vapor-pressure method, is 430±30 (Calcd, 456.6). The IR spectrum shows characteristic bands at 1757 (unconjugated five-membered cyclic ketone), 1716 (aromatic ester), and 1695 (conjugated ketone). The $^1$H-NMR and $^{13}$C-NMR spectra reveal that the framework of **6a** consists of a half-unit of the 2:2 adduct and the 2-isopropylbenzoyl group. Thus **6a** was identified as 1-(4-methoxybenzoyloxy)-1-(2-isopropylbenzoyl)-3,3-dimethyl-2-indanone. In similar reactions with other aromatic aldehydes, **2b**—**d**, the products were **3b**—**d**, **4b**—**d**, **5b**, **6b**—**d**, and **7**. The yields and physical properties of the products are summarized in Tables 1 and 2.



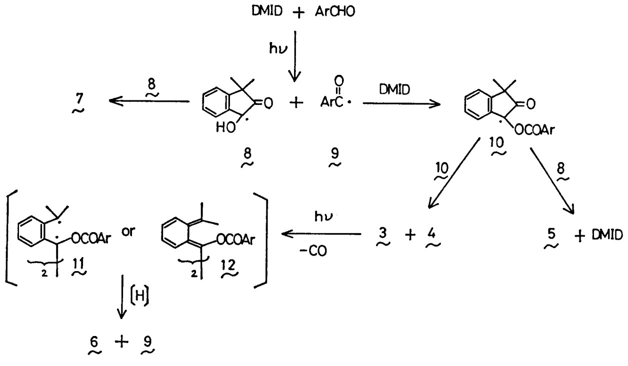
Scheme 1.

A plausible mechanism to account for the formation of the photoproducts, **3**, **4**, **5**, **6**, and **7**, is outlined in Scheme 2. The photoexcitation of DMID and the subsequent formyl hydrogen abstraction afford two radicals, **8** and **9**, a large portion of which escape from the solvent cage. The escaped radical, **8**, has earlier been shown to dimerize to yield pinacol **7**.[4] The aroyl radical, **9**, out of the cage attacks the oxygen atom of C-1 carbonyl group of DMID, leading to the formation of the **10** radical; the two radicals then couple with each other to give **3** and **4**. This reaction path is in agreement with the fact that the anisoyl radical, **9a**, generated by the thermal decomposition of di-*t*-butyl diperoxyoxalate,[5] reacted with DMID to give **3a** and **4a**, but neither **5a** nor **6a**. Hydrogen transfer from **8** to **10** will result in the formation of

TABLE 1. PHOTOCHEMICAL REACTION OF DMID WITH AROMATIC ALDEHYDES

| Aromatic aldehydes | Isolated yields of photoadducts (%)a),b) | | | | |
|---|---|---|---|---|---|
| | 3 | 4 | 5 | 6 | 7 |
|  | | | | | |
| **2a**, R=MeO– | 11 | 10 | 4 | 7 | (15) |
| **2b**, R=Me– | 12 | 6 | 6 | trace | (17) |
| **2c**, R=H– | 9 | 9 | — | 8 | (19) |
| **2d**, R=Cl– | 8 | 13 | — | trace | (20) |

a) Based on unrecovered DMID. b) Numerals in parentheses refer to the yields determined by $^1$H-NMR analysis.



Scheme 2.

Table 2. Some physical properties of the photoproducts obtained

| Photo-adducts | Molecular formula | Found (%) | Calcd (%) | Mp/°C | IR spectra (C=O) cm$^{-1}$ | $^1$H-NMR spectra (CCl$_4$; ppm) |
|---|---|---|---|---|---|---|
| **3a** | $C_{38}H_{34}O_8$ | C; 73.02<br>H; 5.87 | 73.77<br>5.54 | 232—233 | 1724 1777 | 1.52(s, -Me), 1.55(s, -Me), 3.76(s, -OMe), 6.5—6.7(m, 2H$_{\text{arom.}}$) 7.1—7.2(m, 2H$_{\text{arom.}}$), 7.2—7.6(m, 4H$_{\text{arom.}}$). |
| **4a**[a)] | $C_{38}H_{34}O_8$ | C; 73.41<br>H; 5.81 | 73.77<br>5.54 | 214—215 | 1720 1768 | 0.82(s, -Me), 1.52(s, -Me), 3.82 (s, -OMe), 6.8—6.9(m, 2H$_{\text{arom.}}$), 6.9—7.4(m, 4H$_{\text{arom.}}$), 8.0—8.1(m, 2H$_{\text{arom.}}$). |
| **3b** | $C_{38}H_{34}O_6$ | C; 77.79<br>H; 6.02 | 77.79<br>5.84 | 231—232 | 1723 1773 | 1.56(s, -Me), 1.60(s, -Me), 2.30(s, Ar-Me), 7.0(m, 4H$_{\text{arom.}}$), 7.3—7.7(m, 4H$_{\text{arom.}}$). |
| **4b** | $C_{38}H_{34}O_6$ | C; 77.39<br>H; 5.87 | 77.79<br>5.84 | 250—251 | 1727 1763 | 0.76(s, -Me), 1.52(s, -Me), 2.41(s, Ar-Me), 6.8—7.4(m, 4H$_{\text{arom.}}$), 7.1—7.2(m, 2H$_{\text{arom.}}$), 7.9—8.0(m, 2H$_{\text{arom.}}$). |
| **3c** | $C_{36}H_{30}O_6$ | C; 76.79<br>H; 5.59 | 77.40<br>5.41 | 229—231 | 1727 1767 | 1.52(s, -Me), 1.57(s, -Me), 7.1—7.7 (m, 4H$_{\text{arom.}}$), 7.16(m, 5H$_{\text{arom.}}$). |
| **4c** | $C_{36}H_{30}O_6$ | C; 77.12<br>H; 5.62 | 77.40<br>5.41 | 235—236 | 1728 1774 | 0.75(s, -Me), 1.60(s, -Me), 7.3—7.8 (m, 4H$_{\text{arom.}}$), 7.1—7.3(m, 5H$_{\text{arom.}}$) |
| **3d** | $C_{36}H_{28}O_6Cl_2$ | C; 68.42<br>H; 4.62<br>Cl; 11.27 | 68.91<br>4.50<br>11.30 | 223—224 | 1736 1775 | 1.50(s, -Me), 1.55(s, -Me), 6.5—6.9 (m, 4H$_{\text{arom.}}$), 7.1—7.4(m, 4H$_{\text{arom.}}$) |
| **4d** | $C_{36}H_{28}O_6Cl_2$ | C; 68.99<br>H; 4.50<br>Cl; 11.26 | 68.91<br>4.50<br>11.30 | 223—224 | 1722 1767 | 1.21(s, -Me), 1.58(s, -Me), 7.1—7.8 (m, 4H$_{\text{arom.}}$), 7.4—8.0(m, 4H$_{\text{arom.}}$) |
| **6a**[b)] | $C_{29}H_{28}O_5$ | C; 76.45<br>H; 6.18 | 76.29<br>6.18 | 129—130 | 1695 1716<br>1757 | 1.22(d, -Me, $J$=7 Hz), 1.25(d, -Me, $J$=7 Hz), 1.48(s, -Me), 1.63(s, -Me), 3.00(m, 1H), 3.76(s, -OMe), 7.2—7.5(m, 8H$_{\text{arom.}}$), 6.7(m, 2H$_{\text{arom.}}$), 7.6—7.7(m, 2H$_{\text{arom.}}$) |
| **6c** | $C_{28}H_{26}O_4$ | C; 78.80<br>H; 6.14 | 78.85<br>6.14 | 111 | 1692 1720<br>1750 | 1.20(d, -Me, $J$=7 Hz), 1.24(d, -Me, $J$=7 Hz), 1.48(s, -Me), 1.47(s, -Me), 1.65(s, -Me), 7.1—7.5(m, 8H$_{\text{arom.}}$), 7.4(m, 5H$_{\text{arom.}}$), 2.99(m, 1H). |

a) $^{13}$C-NMR of **4a**(CDCl$_3$); 24.41(q), 28.32(q), 48.99(s), 55.50(q), 86.10(s), 114.09(d), 122.23(d), 123.37(d), 125.97(s), 127.44(d), 131.18(d), 132.48(d), 134.44(s), 149.57(s), 164.06(s), 163.00(s), and 213.22(s). b) $^{13}$C-NMR of **6a** (CDCl$_3$); 24.08(q), 24.41(q), 26.04(q), 27.34(q), 30.76(d), 50.61(s), 55.00(q), 91.30(s), 113.90(d), 121.09(d), 123.04(d), 125.32(s), 126.46(d), 128.25(d), 130.69(d), 132.32(s), 137.04(d), 138.18(d), 147.13(s), 149.73(s), 163.57(s), 164.22(s), 201.66(s), and 213.22(s).

**5.** The 2:1 adduct, **6**, is apparently the secondary photoproduct derived from **3** and **4**, since it was not formed upon irradiation with light of wavelength above 400 nm, to which **3** and **4** were transparent. The facile photodecarbonylation of 2-indanone derivatives is a well-known process.[6)] Hydrogen transfer to a possible intermediate, the diradical, **11** or *o*-xylylene, **12**, will lead to the formation of **6**. In accord with this, the photochemical conversion of **3** and **4** to **6** occurs in the presence of aromatic aldehydes.

Noteworthy is the finding that the out-of-cage products are formed exclusively in the photochemical reaction of DMID with aldehydes, in spite of the DMID's cyclic structure.

## Experimental

The apparatus and equipment used in this study were described in a preceding paper.[4)]

A degassed benzene solution of DMID[7)] (33 mM) and aldehyde (33 mM) was irradiated for 2 h in a Pyrex tube, using a 300 W high-pressure Hg lamp. After the removal of the solvent, the products were separated by preparative TLC, developing three times with benzene/dichloromethane. The 2:1 adduct, **6**, developed at $R_f \approx 0.7$, the 1:1 adduct, **5**, at ≈0.5, and the 2:2 adducts, **3** and **4**, at ≈0.2—0.3. The 2:1 adduct, **6**, was purified once more by preparative TLC, developing with benzene, and by recrystallization from dichloromethane/hexane. The 2:2 adducts, **3** and **4**, were recrystallized from chloroform.

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