

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

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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.

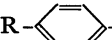
When photolyzed together with aldehydes, cyclic α -diketones in both aliphatic¹⁾ and aromatic systems²⁾ abstract the formyl hydrogen atom to give in-cage combination products predominantly. In contrast, open chain α -diketones yield out-of-cage products mainly.³⁾ In the present work, we have investigated 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 ¹H-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 ¹H-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 ¹³C-NMR spectrum of **4a** shows peaks at 213.2 (ketone), 164.1 (ester), 86.1 (s), 55.5 (q, CH₃O-), and 48.9 (s) ppm, besides two methyl carbons and twelve sp² 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 ¹H-

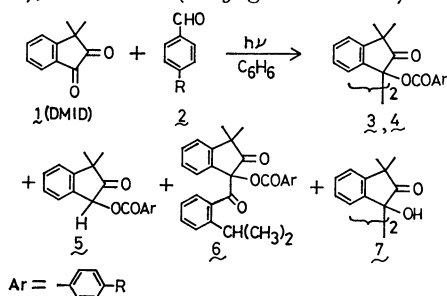
NMR and ¹³C-NMR spectra reveal that the framework of **6a** consists of a half-unit of the 2:2 adduct and the 2-isopropylbenzoyl group. Thus **6a** was identified as 1-(4-methoxybenzoyloxy)-1-(2-isopropylbenzoyl)-3,3-dimethyl-2-indanone. In similar reactions with other aromatic aldehydes, **2b–d**, the 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.

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 aryl 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

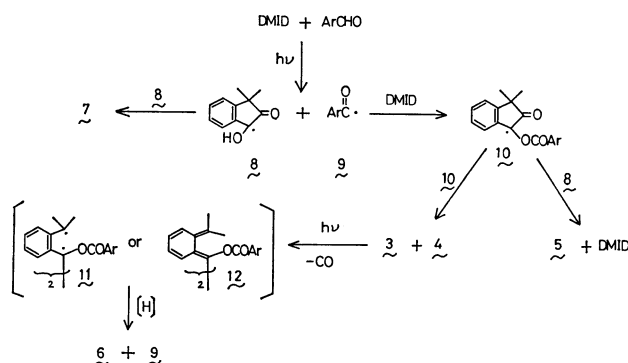
TABLE 1. PHOTOCHEMICAL REACTION OF DMID WITH AROMATIC ALDEHYDES

Aromatic aldehydes	Isolated yields of photoadducts (%) ^{a), b)}				
	3	4	5	6	7
R-  -CHO					
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 ¹H-NMR analysis.



Scheme 1.



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 H; 5.87	73.77 5.54	232—233	1724 1777	1.52(s, -Me), 1.55(s, -Me), 3.76(s, -OMe), 6.5—6.7(m, 2H _{arom.}), 7.1—7.2(m, 2H _{arom.}), 7.2—7.6(m, 4H _{arom.}).
4a^a	C ₃₈ H ₃₄ O ₈	C; 73.41 H; 5.81	73.77 5.54	214—215	1720 1768	0.82(s, -Me), 1.52(s, -Me), 3.82 (s, -OMe), 6.8—6.9(m, 2H _{arom.}), 6.9—7.4(m, 4H _{arom.}), 8.0—8.1(m, 2H _{arom.}).
3b	C ₃₈ H ₃₄ O ₆	C; 77.79 H; 6.02	77.79 5.84	231—232	1723 1773	1.56(s, -Me), 1.60(s, -Me), 2.30(s, Ar-Me), 7.0(m, 4H _{arom.}), 7.3—7.7(m, 4H _{arom.}).
4b	C ₃₈ H ₃₄ O ₆	C; 77.39 H; 5.87	77.79 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 _{arom.}), 7.1—7.2(m, 2H _{arom.}), 7.9—8.0(m, 2H _{arom.}).
3c	C ₃₆ H ₃₀ O ₆	C; 76.79 H; 5.59	77.40 5.41	229—231	1727 1767	1.52(s, -Me), 1.57(s, -Me), 7.1—7.7 (m, 4H _{arom.}), 7.16(m, 5H _{arom.}).
4c	C ₃₆ H ₃₀ O ₆	C; 77.12 H; 5.62	77.40 5.41	235—236	1728 1774	0.75(s, -Me), 1.60(s, -Me), 7.3—7.8 (m, 4H _{arom.}), 7.1—7.3(m, 5H _{arom.}).
3d	C ₃₆ H ₂₈ O ₆ Cl ₂	C; 68.42 H; 4.62 Cl; 11.27	68.91 4.50 11.30	223—224	1736 1775	1.50(s, -Me), 1.55(s, -Me), 6.5—6.9 (m, 4H _{arom.}), 7.1—7.4(m, 4H _{arom.}).
4d	C ₃₆ H ₂₈ O ₆ Cl ₂	C; 68.99 H; 4.50 Cl; 11.26	68.91 4.50 11.30	223—224	1722 1767	1.21(s, -Me), 1.58(s, -Me), 7.1—7.8 (m, 4H _{arom.}), 7.4—8.0(m, 4H _{arom.}).
6a^b	C ₂₉ H ₂₈ O ₅	C; 76.45 H; 6.18	76.29 6.18	129—130	1695 1716 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 _{arom.}), 6.7(m, 2H _{arom.}), 7.6—7.7(m, 2H _{arom.}).
6c	C ₂₈ H ₂₆ O ₄	C; 78.80 H; 6.14	78.85 6.14	111	1692 1720 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 _{arom.}), 7.4(m, 5H _{arom.}), 2.99(m, 1H).

a) ¹³C-NMR of **4a**(CDCl₃); 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) ¹³C-NMR of **6a** (CDCl₃); 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 DMID⁷⁾ (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* ≈ 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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