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THE PHOTODECOMPOSITION AND PHOTORACEMIZATION OF METHYL (+)-O-METHYLMANDELATE[1]

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Abstract—Irradiation at 254 nm of the bichromophoric molecule methyl (+)-O-methylmandelate ((+)-3) in methanol has been found to lead to photodecomposition and photoracemization. The major monomeric product isolated, methyl phenylacetate (**1b**), is shown to arise by a mechanism totally different from that responsible for racemization. The high efficiency of the direct irradiation, the very short singlet lifetime of 3 (*ca* 1 nsec), and the inability to sensitize the formation of **1b** with acetone triplets implicate the singlet state of 3 as the reactive species. Mechanistic models to account for the products are discussed.

The photolyses of phenylacetic acid (**1a**),[3] esters (**1b**–**1d**),[3–7] and sodium salts (**1e**, **1f**),[3,8] have been reported. Direct irradiation of the acid or its methyl ester[3] yield products derived almost exclusively from homolytic cleavage of the carboxylate–methylene bonds. The benzyl esters of α- and β-naphthylacetate, by contract, are extremely stable to 254 nm irradiation.[9] Sodium phenylacetate and sodium (nitrophenyl)acetates yield significant quantities of toluenes, products of heterolytic cleavage.[3,9] When esters in which the β-carbon is substituted with at least one hydrogen are irradiated, Norrish Type II processes are observed.[4–6] Recently, (−)-carbomethoxy[2.2]paracyclophane (2) was photoracemized via a mechanism in which the benzylic–carboxylate bond did not participate.[10]

To determine if recombination of benzyl radicals with their carbomethoxy radical partners is an important energy wasting step, to further elucidate the photochemistry of arylacetates, and as an extension of our interest in photoracemization of benzylic carbons,[11] we have irradiated methyl (+)-O-methylmandelate ((+)-3) at 254 nm. Since the benzylmethoxy radical from (+)-3 should be planar or be racemized very rapidly at room temperature, the appearance of (−)-3 would offer good evidence for recombination *provided that racemization does not arise via some other process.* Herein, we report that photoracemization and photodecomposition of (+)-3 do occur and that radical recombination is almost certainly the source of racemic 3.†

RESULTS AND DISCUSSION

The major monomeric product from photolyses at 254 nm of 3 in methanol, cyclohexane, or t-butyl alcohol is methyl phenylacetate (**1b**), identical in all respects to an authentic sample. No analyses for formaldehyde, another probable product, were conducted. At low conversions, no evidence for toluene, benzaldehyde, acetophenone, benzyl methyl ether, or methyl α-phenethyl ether (**4**) was found. Both the rate of disappearance of 3 and appearance of **1b** are zero order in 3 (for O.D. ≥3) and exhibit $\Phi_3 = 0{\cdot}17 \pm 20\%$ and $\Phi_{1b} = 0{\cdot}084 \pm 25\%$ in 10^{-2} M solutions of deoxygenated methanol (Table 1). In addition, after 69% disappearance of (+)-3, $[\alpha]_D^{26} + 123°$ (MeOH), the recovered starting material exhibited $[\alpha]_D^{26} + 85{\cdot}3°$ (MeOH) or 31% photoracemization. From this, lower limits of $\Phi_{rac} \simeq \Phi_{recom} \simeq 0{\cdot}09$ for racemization of 3 and diradical recombination, respectively, can be calculated.‡ The correction for back reaction (i.e., $(R) \xrightleftharpoons{h\nu} (S)$) by the method of Lamola and Hammond[13] is made assuming Φ_3 is constant to 70% conversion. Obviously, the rate of conversion of 3 decreases with time as competitive absorption of light by products increases. However, we have noted that the rate of reaction of 3 is nearly linear to 69% conversion due to its high absorptivity as compared with other simple phenylated molecules (Fig. 1). By contrast, methyl (+)-α-phenethyl

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†(−)-Mandelic acid has been reported to be racemized during γ-irradiolysis.[12]

‡From the optical rotations at 0 per cent and 69 per cent conversion of 3, the % racemization of 3 is ≃(123–85·3)/123 = 30·6% (i.e., 15·3 per cent of the remaining 3 is (S) at *ca.* 70 per cent conversion). Although Φ_3 is a constant, $\Phi_{S\text{-}3}$, the quantum yield for production of (S)-3 from (R)-3 is a function of the relative concentrations of (R) and (S) since back reaction, $(S) \xrightarrow{h\nu} (R)$, occurs. In fact, $\Phi_{S\text{-}3}$ at 0 per cent conversion of (R) to (S) is the quantity sought. By definition, $\Phi_3 = (d[3]/dt)/I$ and $\Phi_{S\text{-}3} = (d[(S)\text{-}3]/dt)/I$ where I is the intensity of the absorbed light. Then, $\Phi_{S\text{-}3}/\Phi_3 = (d[(S)\text{-}3]/dt)/(d[3]/dt)$. The 15·3 per cent of (S)-3 calculated above at 69 per cent conversion of 3 cannot be used in this equation since d[(S)-3]/dt is a non-linear function. However, correction for back reaction can be made by the method of Lamola and Hammond.[13]

$$\beta = 2{\cdot}303\,\alpha \log[\alpha/(\alpha - \beta')]$$

where α is the fraction of (S) present at the photostationary state, β′ is the measured fractional conversion of (R) to (S), and β is the fraction of (S) present were no back reaction to have occurred. Then,

$$\beta = 2{\cdot}303\,.\,0{\cdot}5 \log[0{\cdot}5/(0{\cdot}5\text{–}0{\cdot}153)] \simeq 18{\cdot}3\%$$

and $\Phi_{S\text{-}3} \simeq (0{\cdot}183/0{\cdot}694)0{\cdot}17 \simeq 0{\cdot}045$. Since $\Phi_{recom.} = 2\Phi_{S\text{-}3}$, $\Phi_{recom.} \simeq 0{\cdot}09$.

Table 1. Quantum yields for photolyses of 3 and related compounds

Compound	Concn. $M \times 10^2$	Solvent	Φ_3[a]	Φ_{1b}[a]	Φ_{dis}
3	1·04	MeOH	0·17	0·084	
	1·84	MeOH, O_2	0·11	0·042	
	1·34	t-BuOH	0·12	~0·03	
	1·04	cyclohexane	0·21	0·058	
	1·27	1:7: acetone: cyclohexane	<0·04	<0·005[b,c]	
4		MeOH			<0·02[c]
1a[d]		MeOH			0·131
1b[d]		MeOH			0·099
1c[e]		MeOH			0·12

[a] Errors are estimated to be 20% for diappearance of 3 and 25% for appearance of **1b**.

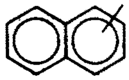
[b] No **1b** was detected.

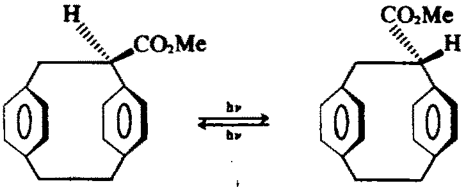
[c] Quantum yield represents estimated limit of detection.

[d] Ref. 3.

[e] Ref. 6.

$ArCO_2R$
$\mathbf{I}_x$

X	Ar	R
a	Ph	H
b	Ph	Me
c	Ph	CH_2CH_2OEt
d	Ph	CH_2Ph
e	Ph	Na
f	O_2N–Ph	Na
g		CH_2Ph



(−)-**2** (+)-**2**

ether ((+)-**4**) had $\Phi_4 = <0{\cdot}02$ in methanol although it, too, slowly underwent partial photoracemization. Under similar conditions, Grossweiner *et al.*[3] determined the quantum yield for disappearance of **1b** to be 0·099.

An excited singlet of **3** appears to be the reactive species since oxygen suppressed by less than half the destruction of **3** *and* appearance of **1b**. A partial reason for this was found in the lifetime of the singlet state: Berlman's method[14] yielded a τ_s for **3** of *ca.* 1 nsec (vs 34 nsec for toluene[15]). In addition, it was not possible to photosensitize the production of **1b** with acetone triplets. These results do not rigorously exclude a triplet reaction especially since energy transfer from acetone triplets ($E_T \simeq 78$ kcal) to **3** may be slightly endothermic. However, they, in combination with data for photolyses of other arylacetates,[4-6,8] strongly implicate the singlet state as being responsible.

The presence of free radicals during irradiation of **3** was demonstrated by the production of bicyclohexyl with cyclohexane solvent. A careful search for CIDNP signals by Drs. Angelo Lamola and Heinz Roth at Bell Labs was unsuccessful.[16]

Various reasonable mechanisms can be envisioned for the production of **1b** and racemization of (+)-**3**. Since benzylic, rather than phenyl–carbon, bonds are usually cleaved photochemically,[10,11,17] photoracemization most likely arises via scission of the benzylic bonds to hydrogen, methoxyl, or carboxyl (Scheme 1). Homolysis of the methoxyl-benzyl bond followed by recombination or intracage disproportionation (mechansim 1) offers one alternative. Another attractive explanation for racemization involves tautomerization of the benzylic–hydrogen bond to yield the enol of **3** (mechanism 2). The mechanism appeared plausible in view of the observations that acetophenone forms an enol when irradiated in the presence of phenol,[18a] and acetone forms an enol when irradiated in isopropyl alcohol.[18b] A reversible Norrish Type I process, homolysis of the benzylic–carboxyl bond followed by radical recombination (mechanism 3), also accounts for the photoracemization of **3**.*

To test these hypotheses, we irradiated **3** in methanol-O-d. Were mechanism 1 occurring, no deuterium should appear in **1b** or recovered **3** after prolonged irradiation. Mechanism 2 predicts that deuterium should appear at the benzylic carbon of **3**. The opposite should be found if mechanism 3 is operative. When a 0·61 M solution of **3** in methanol-O-d was irradiated to 35 per cent conversion, reisolated starting material contained no discernible deuterium by NMR analyses—the photoenolization mechanism is clearly eliminated. However, the product **1b** contained *ca.* one deuterium per molecule at the benzylic carbon (NMR analysis). Irradiation of **1b** in methanol-O-d under conditions similar to those employed with **3** did not result in detectable deuterium incorporation. Thus, deuteration occurs after excitation of **3** but before formation of **1b**: mechanism 1 of Scheme 1 is not

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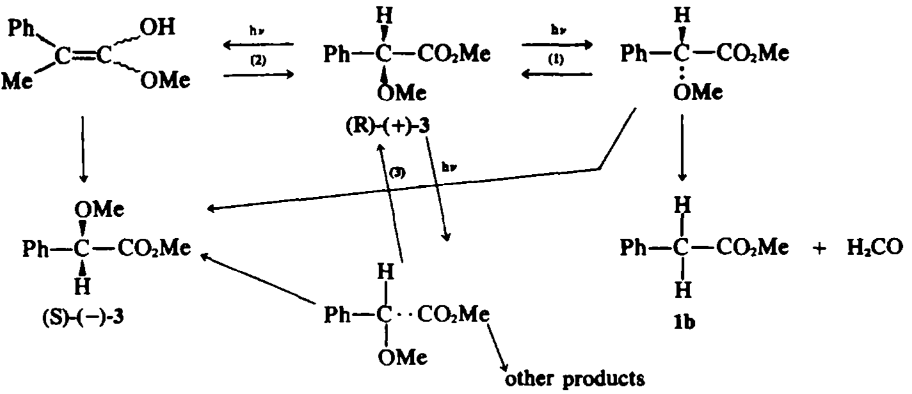
*A referee has pointed out that reversible intermolecular abstraction of the benzylic hydrogen of ground state **3** by excited **3** is another possible route to racemization. The very short singlet lifetime of **3** and the dilute concentration employed in the experiment where racemization was observed (*ca.* 10^{-2} M) require that the abstracting agent not be the excited singlet of **3**. If such a mechanism were important, we would have expected Φ_3 to have been much greater than 0·04 in the acetone sensitized irradiation since acetone triplets are efficient hydrogen abstractors.



Scheme 1. Possible mechanisms for the photoracemization of (+)-3.

operative, also, and mechanism 3 appears to be responsible for photoracemization. Although none of the mechanisms of Scheme 1 accounts for the deuteration of 3 derived **1b**, the result is accommodated very well by a Norrish Type II like abstraction of hydrogen from the ether methyl of 3. The biradical intermediate should lose formaldehyde rapidly to form the enol of **1b**. Proton–deuteron exchange followed by tautomerization will yield **1b** deuterated at the benzylic position. At no point along this reaction path would deuteration of 3 be expected.

If mechanism 3 of Scheme 1 and Norrish Type II abstraction are the only photolysis processes, it is obvious that *ca.* 50% of the radical pairs do not recombine and the quantum yield for cleavage is $\Phi_3 - \Phi_{1b} + \Phi_{racem.} \simeq 0{\cdot}18$. The other paths responsible for destruction of 3 probably involve decomposition of the carbomethoxy radical (to CO_2 and methyl) and diffusion of the radical pair out of its solvent cage. If this analysis is correct, recombination is at least as fast as decarboxylation and escape from the solvent cage.

When compared with the absorption spectrum of **1b** or **4**, the spectrum of 3 has significantly higher molecular extinction coefficients at all wavelengths and its second transition extends much farther toward the red.* Furthermore, spectra of dilute solutions of methyl acetate and toluene are additive (indicating no intermolecular ground state interaction between the phenyl and carboxyl chromophores). All of these data are compatible with the chromophores of 3 behaving independently (but being perturbed by auxochromes) or interacting strongly in the ground state.

It is apparent from the fluorescence spectrum of 3 that those singlets which do emit are essentially excited benzyl chromophores: the maxima for emission and excitation for 3 are λ_{em} 282 nm and λ_{ex} 268 nm in cyclohexane and λ_{em} 284 nm and λ_{ex} 270 nm in methanol; λ_{em} of toluene in cyclohexane is 284 nm.[14] This indicates that at least some of the time (or in some of the excited 3), virtually all of the excitation energy resides in the phenyl chromophore.

These results compare well with those obtained by Brainard and Morrison[6] with **1c**, whose fluorescence spectrum is very similar in shape to that of toluene and which also undergoes a Norrish Type II cleavage. The τ_s for **1c**, as determined by Berlman's method, was reported to be 12 nsec. That τ_s of 3 is *ca.* 1 nsec indicates that the role of its methoxy is not just to serve as a source of hydrogen radicals for the excited carboxyl: since $\tau_s = k_f/\sum_i k_i$ (where k_f is the rate constant for fluorescence and $\sum_i k_i$ is the sum of the unimolecular rate constants responsible for the disappearance of the singlets of 3) and τ_s of anisole is 8·3 nsec,[13] there must be k_i of 3 which are not available to or much slower in **1b**. It may be that

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*On the basis of analyses of the CD spectrum of 3 and related molecules, this band has been assigned to a carboxyl absorption.[19]

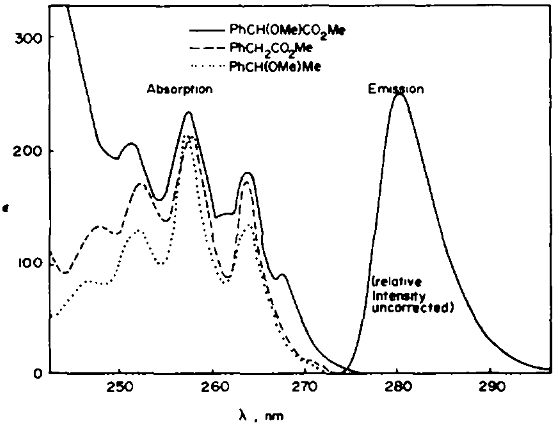
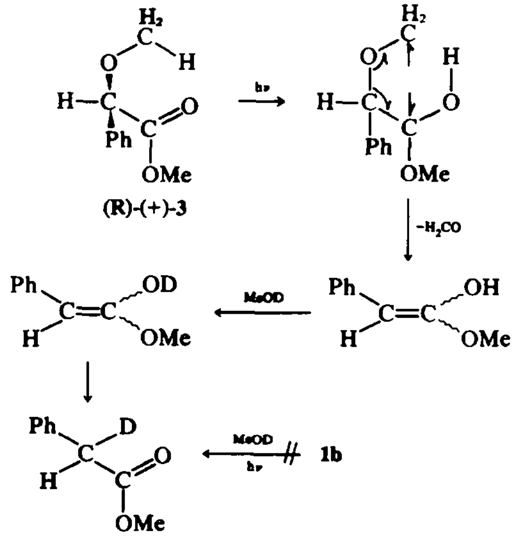


Fig. 1. UV spectra of some related aromatic molecules in cyclohexane.



Scheme 2. Photochemical formation of **1b**.

methoxyl, by decreasing the energy required for homolytically cleaving the benzyl–carboxylate bond, increases the rate of mechanism 3 over that observed when **1b** is the substance. The fact that the quantum yield for disappearance of **1b** is about the same as (if not greater than) $\Phi_3 - \Phi_{1b}$ argues against this explanation.

Another attractive explanation for the short τ_s of **3** is that the methoxyl alters the conformational preference of **3** to one in which phenyl and carboxyl interact strongly. The enhanced absorption of **3** over **1b** certainly is in accord with this hypothesis. Whether deactivation of the phenyl is concurrent with excitation of the carboxyl and *vice versa* (i.e. intramolecular energy transfer), leads to enhanced intersystem crossing and internal conversion, or is responsible for formation of an intramolecular "exciplex" cannot be answered with the information in hand.*

It is quite possible that a detailed study of the photochemistry of **3** at various wavelengths and temperatures would resolve these uncertainties.†

EXPERIMENTAL

UV spectra were recorded on a Cary 14 spectrophotometer. Emission spectra were determined with a Perkin–Elmer MPF-2 spectrofluorometer equipped with a xenon lamp. Gas–liquid phase chromatography was conducted on a Varian Aerograph 1800 gas chromatograph equipped with flame ionization detectors and using a 5 ft × $\frac{1}{8}$ in 3 per cent SE 52 on $\frac{100}{200}$ mesh Varaport 30 column at 80°. Quantitative data were obtained by weighing peaks and comparing them to the peak weights for a standard. Irradiations were performed on samples in quartz tubes using PCQ–XI and Pen–Ray UV Products low pressure Hg lamps.

MeOH (Carlos Erba, *pro analysi*) was dried over 3A molecular sieves and distilled before use. Cyclohexane was purified by the method of Murray and Keller.[21] t-BuOH (Aldrich, 99·5 per cent) and acetone (Merck, spectrograde) were used as received.

Methyl phenylacetate (**1b**), b.p. 78° (1 mm) [lit:[3b] b.p. 78° (1 mm)], was prepared from phenylacetic acid by a standard method.[22] Compound (+)-**4**, b.p. 60° (12 mm) and $[\alpha]_D^{24\cdot5} + 141\cdot5°$ (cyclohexane), was prepared from the corresponding alcohol by treating it sequentially with NaH and MeI in anhyd ether. Compound (+)-**3**, b. p. 79–82° (1 mm), $[\alpha]_D^{26}$ 123° (MeOH), and $[\alpha]_D^{25} + 86\cdot7°$ (acetone) [ref:[23] b.p. 79–88° (1 mm), $[\alpha]_D^{23}$ 88·7 (acetone)] was synthesized from (+)-mandelic acid (Norse Chemical Co., $[\alpha]_D^{26} + 148\cdot1°$ (MeOH)) by the method of Bonner.[23] Racemic **3** was synthesized from racemic acid using the same procedure.

Irradiations of methyl O-*methylmandelate* (3)

(A) Argon was bubbled through a refluxing soln of 165 mg ($1\cdot15 \cdot 10^{-2}$ M) of methyl (+)-O-methylmandelate and a drop of n-decane (as glpc standard) in 8 ml MeOH for 10 min. The quartz tube was capped rapidly with a rubber septum and argon bubbling was continued via a needle inserted through the septum until the soln had returned to ambient temp. Constant volumes were maintained by adding solvent as needed. Irradiation with a bank of 4 PCQ–XI lamps was continued to 69·4 per cent conversion of **3**. Aliquots were removed periodically via syringe and were compared by glpc with the "zero"-time chromatogram. Unreacted mandelate, 34 mg, reisolated by preparative thin layer chromatography (silica HF) by eluting with a 6:4 mixture of benzene–chloroform, was distilled twice pot-to-pot under vacuum. It was found to exhibit $[\alpha]_D^{26} + 85\cdot3°$ (MeOH). A sample of **1b**, isolated as above, was shown to be identical to independently synthesized **1b** by NMR, IR and GLPC analyses. At least four other minor products were detected by GLPC.

(B) N_2 was bubbled for 5 min through two solns of 223 mg of racemic **3** and 12 mg of n-decane in 2 ml of MeOH-O-d (Baker). Their tubes were capped and one soln was irradiated as before while the other was kept in the dark. After 8 hr, the irradiated and dark tube displayed 35 per cent and 0 per cent conversions, respectively, by GLPC. Unreacted **3** and product **1b** from the irradiated tube and **3** from the dark tube were isolated by TLC. NMR spectra of the samples of **3** were identical to each other and to that of unreacted **3**. The NMR spectrum of the **1b** from the irradiated tube in $CDCl_3$ displayed singlets at δ 7·27 ppm (Ph) and at 3·67 ppm (Me). The methylene singlet normally at 3·6 ppm (Methylene) was replaced by a broad, unresolved multiplet centered at 3·6 ppm.

Irradiation of methyl phenylacetate (**1*b***) *in methanol-O-d*. Argon was bubbled through a soln of 200 mg of **1b** in 10 ml MeOH-O-d for 10 min. The sample was capped, irradiated, and analyzed as before. After 6 hr of irradiation, the remaining 46 per cent of **1b** was reisolated by TLC. Its NMR spectrum was identical to that of an unreacted sample.

Irradiation of methyl (+)-*α-phenethyl ether* ((+)-**4**). A soln of 14·7 mg of (+)-**4** in 10 ml MeOH was refluxed for 30 min. The soln was capped with a rubber septum and argon was bubbled through until the liquid returned to ambient temp. Irradiation for 1 hr resulted in 10·3 per cent conversion. An ord spectrum in MeOH of reisolated **4** was similar in shape to, but less intense than an ORD spectrum of non-irradiated material. Due to the presence of small amounts of optically active impurities, it was not possible to determine quantitatively the degree of racemization: absolute rotations of non-irradiated (+)-**4** were 13 per cent greater at 2800 Å and 31 per cent greater at 2650 Å than those of irradiated material.

Quantum yields and actinometry. Ferrioxalate actinometry by the method of Parker and Hatchard[24] was performed at the beginning and end of sample irradiation periods on a Pen–Ray lamp placed in the center of a "merry-go-round" apparatus.[25] The intensity of its 2537 Å emission was calculated by subtracting the actinometer conversion in pyrex tubes from that in quartz tubes.

Tubes with racemic **3** and (+)-**4** were prepared as noted above and in Table 1 and were irradiated on the "merry-go-round". The oxygenated methanol soln of **3** was prepared by bubbling O_2 through for 10 min. Analyses were performed by GLPC using n-decane as reference. Quantum yields reported in Table 1 represent values extrapolated to zero conversion.

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*For another discussion of this problem (see Ref. 6).

†An analysis of the conformational preferences of **3** based on IR absorptions has been made. [20a] In acetonitrile, the most stable conformation of phenylacetaldehyde has the phenyl and carboxyl eclipsed.[20b]

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