Unusual Photorearrangements of Homoconjugated Diacylcyclohexa-2,4-dienes[1]

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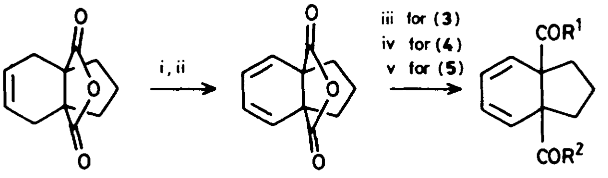
The unprecedented triplet sensitized electrocyclic ring opening of various 3a,7a-diacyl-3a,7a-dihydroindans (**3**)—(**5**) to the corresponding cyclononatriene derivatives (**7**)—(**11**) is reported, direct irradiation at all absorbing wavelengths of the keto-ester (**5**) resulting in a diastereoselective oxa-di-π-methane (ODPM) rearrangement to the tricyclic product (**6**); dimethyl 1,2-dimethyl-1,2-dihydrophthalate (**15**) reacted similarly to give dimethyl *E,E,E*-2,7-dimethyl-2,4,6-octatrienoate (**16**), whose structure has been determined by single crystal *X*-ray diffraction analysis.

It is generally accepted that cyclohexa-1,3-dienes undergo photoinduced electrocyclic opening to hexatriene products *via* the directly excited singlet state whereas triplet sensitization gives dimers,[2,3] and that β,γ-unsaturated ketones[4] as well as β,γ,δ,ε- ones[5] undergo oxa-di-π-methane (ODPM) rearrangements *via* the lowest excited triplet (π,π*) state and α-cleavage and/or 1,3-acyl shifts from higher, usually singlet excited states. In the framework of our photochemical studies of systems with directed geometry involving juxtaposition of two homoconjugated chromophores, in particular homoconjugated ketones in spiro[5] and in condensed[6] systems, we report now on some novel and surprising results in the 3a,7a-diacyl-3a,7a-dihydroindan series.

We prepared the desired compounds as shown (Scheme 1), starting with the known anhydride (**1**),[7] from which was obtained the diene (**2**), which in a simple sequence of reactions was converted into any of the compounds (**3**)—(**5**).† On direct irradiation (Scheme 2) of the keto-ester (**5**) [λ_{max}/nm (ε): 262(3200), 269(3100), 300(1000)] at three wavelengths in acetonitrile, only the ODPM rearrangement product (**6**) was isolated, with complete diastereoselectivity, as follows: at 254 nm in 15% yield, at 300 nm in 8% yield (slow, 18% conversion), and at 350 nm in 32% yield.†

The most surprising outcome, however, was that of triplet sensitization of (**5**) (Scheme 2): a mixture of the all-*cis*-cyclonona-1,3,6-triene derivatives (**7**) and (**8**) (*ca.* 1:1) was isolated. Ordinarily, one would take this to be a result of electrocyclic ring opening in (**5**) at the ring fusion, followed by a sigmatropic 1,5-hydrogen shift in the *trans,cis,cis*-1,3,5-triene (**X**), which is considered to be the orbital symmetry control allowed primary product.[2,8,9] Moreover, when the monoester (**3**) and the diester (**4**) were submitted to triplet sensitization as above, the corresponding cyclonona-1,4,6-triene dicarboxylic acid derivatives (**9**), (**10**) and (**11**), respectively, were obtained.†



(**1**) (**2**)

	R^1	R^2
(**3**)	OH	OMe
(**4**)	OMe	OMe
(**5**)	Me	OMe

Scheme 1. *Reagents and conditions*: i, *N*-bromosuccinimide (NBS)/CCl_4; ii, heat/dimethylformamide (DMF); iii, MeOH/room temp.; iv, MeOH/H^+/heat, v (a) MeMgBr/Et_2O, (b) CH_2N_2/Et_2O.

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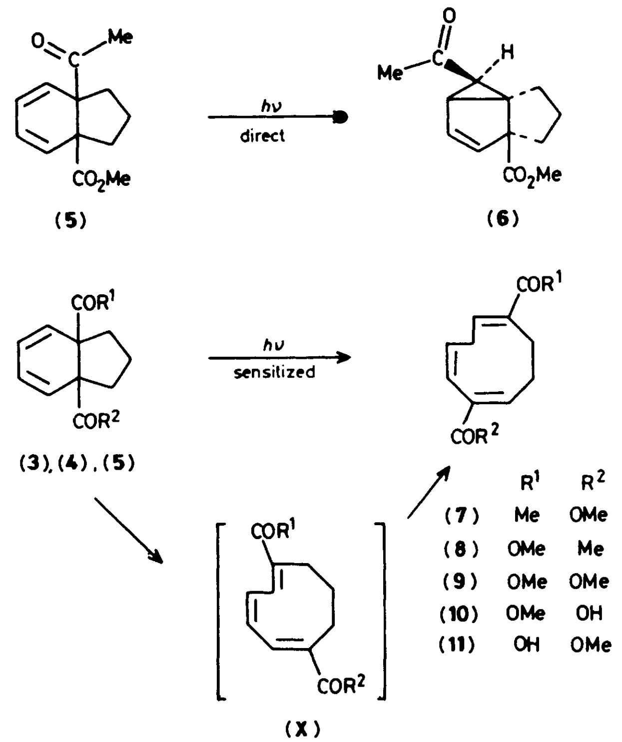
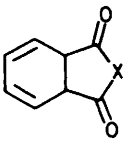
† All new compounds were fully characterized by spectroscopic (i.r., u.v., mass, n.m.r.) methods and by chemical correlation; all these data will be provided in the full paper or, in the meantime, on request from the authors.



	R^1	R^2
(7)	Me	OMe
(8)	OMe	Me
(9)	OMe	OMe
(10)	OMe	OH
(11)	OH	OMe

Scheme 2



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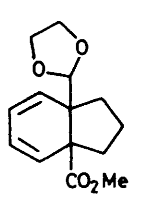

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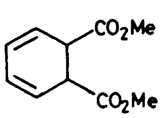

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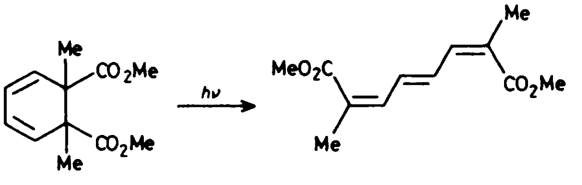

Scheme 3

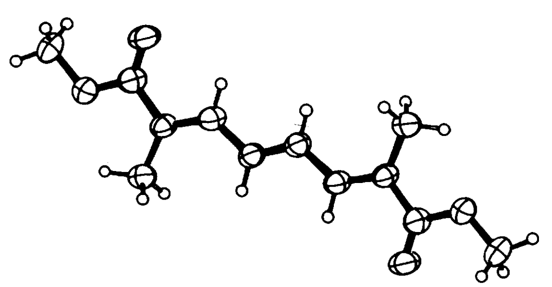

Figure 1. Molecular structure of the ester (**16**).

Monochromatic low-conversion irradiation of (**5**) at 340 nm followed by careful analysis revealed that the electrocyclic ring opening products (**7**) and (**8**) were, in fact, formed in the direct mode along with the ODPM rearrangement product (**6**); this should also be the case at lower wavelengths, but the highly sensitive and strongly absorbing diacyltrienes would photoreact extremely efficiently to give ill-defined products. Quantum yields in the direct photolysis at 340 nm were 0.05 for disappearance of (**5**) and 0.015 and 0.01 for formation of (**7**) and (**8**) and of (**6**), respectively; in the sensitized process, they were 0.02 for disappearance of (**5**) and 0.01 for ring opening to (**7**) and (**8**). Sensitization experiments with compounds of various triplet energies (E_T) [acetone (78 kcal mol^{-1}; cal = 4.184 J), 2-acetonaphthone (59), 1-acetonaphthone (56), and pyrene (49)] showed that the starting materials (**3**)—(**5**) have triplet energies of $49 < E_T < 56$. Quenching of (**5**) excited at 340 nm with ferrocene (E_T 42) indicated that both rearrangement products (**6**), and (**7**) and (**8**), are formed *via* excited triplets.

The above photochemical behaviour is highly unusual, especially in that triplet sensitization of the cyclohexadiene derivatives (**3**)—(**5**) caused them to undergo electrocyclic ring opening, rather than dimerization.[2,10,11] In fact, cyclopentane annelation has been assumed to inhibit ring opening, albeit not to suppress it altogether.[11] While 1,2-dihydrophthalic anhydride derivatives (**12**) do not undergo irradiation induced electrocyclic ring opening (for obvious strain reasons),[10,11] cyclohexa-1,3-dienes condensed to saturated (five or six membered) rings have been shown[2,9] to open readily *via* singlet excited states. Sensitized irradiation of the ethylene acetal (**13**) of (**5**) did not lead to analogous ring opening, and neither did that of the ester (**14**); however, the dimethyl analogue (**15**)[12] of the ester (**14**) slowly opened on sensitized irradiation (Scheme 3), to give the octatrienedioate (**16**).† Compound (**16**) was also rapidly and quantitatively formed and isolated from the direct (254 nm) irradiation of (**14**) and shown, by single crystal *X*-ray diffraction analysis, to have the all-*E* structure (Figure 1).‡

In conclusion, the novelty of these results resides in the fact that electrocyclic opening of, for example, cyclohexa-1,3-dienes can occur from the triplet excited state, provided a carbonyl and/or a carboxy function is located in *each* of the two *tertiary*, homoconjugated positions in the cyclohexadiene ring. Evidently, the weak, hexasubstituted, doubly allylic 1,2-bond has high propensity for cleavage, possibly owing to intramolecular electron transfer in an initial diradical, because of the presence of two flanking C=O functionalities. The photochemical behaviour of the keto-ester (**5**) seems to involve two excited triplets (π,π* and n,π*). Further experimental (on various cyclohexadiene derivatives) and theoretical work (molecular mechanics and MO calculations) is in progress, to probe the conformational dependence[13] and the excited states involved.

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‡ *Crystal data for* (**16**): $C_{12}H_{16}O_4$, $M = 224$, monoclinic, space group $P2_1/n$, $a = 8.290$, $b = 7.390$, $c = 9.915$ Å, $\beta = 93.89°$, $Z = 2$, 1222 measured reflections, 645 independent reflections, $I > 3\sigma(I)$, $R = 0.067$, $R_w = 0.076$, number of parameters = 73. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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