radical ion pairs. There is also cyclic voltammetry evidence for rather slow deprotonation of the far longer lived 1^+ by (dimethylamino)phthalimide.[7] We believe that the above discussion suggests very strongly that R_3N is usually not a strong enough base to lead to extremely rapid deprotonation of its radical cation in competition with other modes of decomposition. Because the α-amino radical is so much more easily oxidized than the parent amine, it would seem impossible to devise conditions under which $R_3N^{\bullet+}$ and the α-amino radical derived from it by deprotonation could be equilibrated, which would be necessary for experimental determination of the thermodynamic acidity of $R_3N^{\bullet+}$. Hydrogen atom abstraction by $R_3N^{\bullet+}$ is known to be a fast process,[2] and abstraction from a neutral amine with the same R groups gives the same products as does proton transfer, but the hydrogen ends up on the other partner in the reaction. Sorting out electron, hydrogen atom, and proton transfer in an unsymmetrical case would be a most formidable task! Whitten and co-workers have very recently shown[22] that cleavage of weak CC bonds α to nitrogen occurs upon photooxidation of some tertiary amines, which fits in well with the great bond weakening for CH bonds α to nitrogen discussed above. **Note Added in Proof**: We thank Prof. von Sonntag for informing us of his recent pulse radiolytic determination of the pK_a of Me_3N as 8.0 in water, which agrees with the conclusions of this paper.[23]

Acknowledgment. We thank the National Institutes of Health for partial financial support of this work under Grant GM-29549 and Professors Alder and Asmus for preprints of their work.

Registry No. 6$^{\bullet}$, 102725-62-2; 7, 73321-02-5.

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Irradiation-Induced Transformations of Homoconjugated Dienones.[1] Highly Selective Photorearrangements in the Spiro[5.5]undeca-1,3-dien-7-one System[2]

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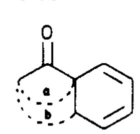
Abstract: We present a study of the photorearrangements in the homoconjugated ($\beta,\gamma,\delta,\epsilon$-unsaturated) ketone **1a** system, viz., derivatives of spiro[5.5]undeca-1,3-dien-7-one (**2**, **3**, **4**) which are of mechanistic interest and considerable synthetic potential because of their high *wavelength selectivity, regioselectivity, and diastereoselectivity*. Thus, in direct irradiation of **2–4** at 254 nm, electrocyclic opening of the cyclohexadiene ring to trienone products (**5**, **9**) occurs, along with some α-cleavage and β-H abstraction to give aromatic aldehydes (**10**, **11**). These are the main products at $\lambda \geq 300$ nm while at $\lambda \geq 340$ nm an oxa-di-π-methane (ODPM) rearrangement takes place to give exclusively the *trans*-tricyclo[5.4.0.0^{7,11}]undeca-9-en-2-ones (**12t**, **13t**, and **14t**). Sensitized irradiation of **2**, **3**, and **4** yielded the latter along with 1,2-acyl shift products of a second kind: *cis*- and *trans*-tricyclo[5.4.0.0^{7,9}]undeca-10-en-2-ones (**15–17**). Quantum yields, triplet sensitizer energy, quenching, and solvent effects were studied. The involvement of multiple excited states is inferred, and mechanistic models are discussed.

We have recently initiated a systematic investigation of homoconjugated dienones featuring fixed s-cis 1,3-dienes in judiciously directed geometry of juxtaposition to the homoconjugated carbonyl group (see below for a rationalization of this approach in the context of the well-documented β,γ-unsaturated carbonyl photochemistry[3]). After a relatively disappointing, even if eventful investigation of fused systems (**1b**),[5] we report now on the unusually interesting photochemical behavior of an **1a** type system, namely spiro[5.5]undeca-1,3-dien-7-one (**2**) and two of its methyl-substituted derivatives (**3** and **4**). Their synthesis recently has been described.[6]



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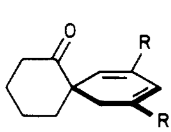

2; R = R' = H
3: R = Me; R' = H
4: R = H; R' = Me

Photochemistry: Product Isolation and Characterization

The first striking feature of their photochemical behavior is the high wavelength selectively on direct irradiation; this is generally depicted in Scheme I. Thus, as a rule, low wavelength (254 nm) irradiation induces electrocyclic opening of the cyclohexadiene ring, the isolated end products being substitution dependent: while the parent compound (**2**) yields the linear conjugated trienone (**6**), the 2-methyl derivative (**3**) leads to a mixture of isomeric cross-conjugated trienones (**8** and **9**), most likely following an initial (thermal or photochemical) 1,7-sigmatropic hydrogen shift in **5** to **7**. The reason for the diverse secondary reaction paths is believed to be the steric influence of the methyl group which

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[1] Photochemical Studies. 26. Part 25: Oren, J.; Viskin, R.; Fuchs, B. *Tetrahedron Lett.* **1985**, *26*, 2365.

[2] (a) Taken in part from the Ph.D. Thesis of J.O., Tel Aviv University 1984. (b) Presented in part at the Sendai Symposium on Organic Photochemistry, August 1985. (c) Some of the present results have been included in a preliminary communication: Zizuashvili, J.; Abramson, S.; Fuchs, B., *J. Chem. Soc., Chem. Commun.* **1982**, 1375.

[3] (a) de Mayo, P., *Rearrangement in Ground and Excited States*, Wiley: New York, 1980; Vol. 3. (b) Schuster, D. I. In ref 3a, p 232. (c) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1. (d) Schaffner, K. *Tetrahedron* **1976**, *32*, 641. (e) Dauben, W. G.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73. (f) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.

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[6] Zizuashvili, J.; Abramson, S.; Fuchs, B. *J. Org. Chem.* **1982**, *47*, 3473.

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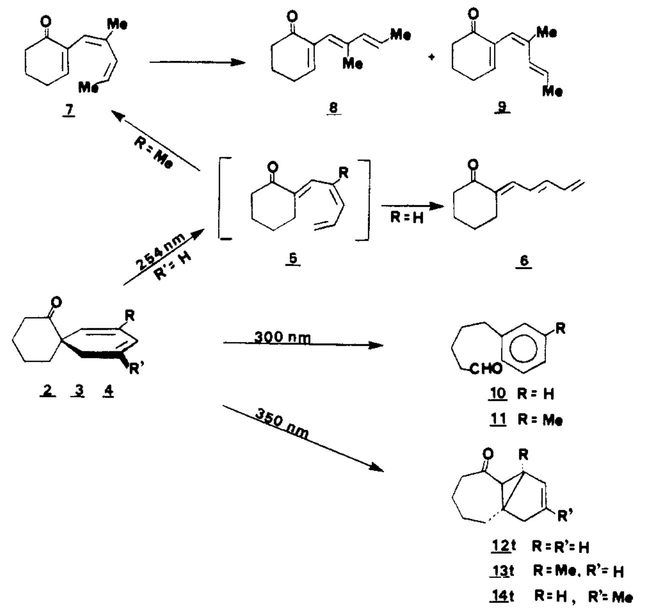
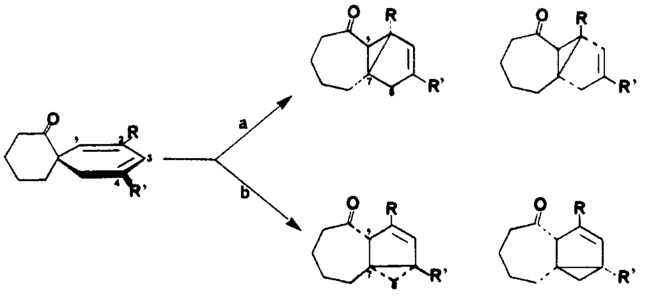
Scheme I



Scheme II



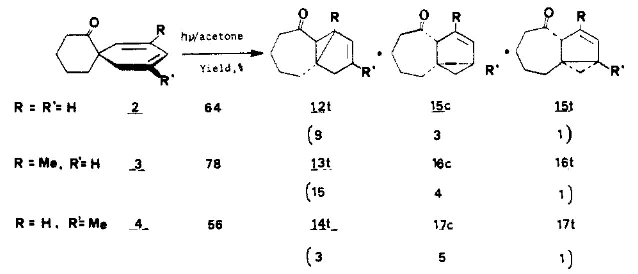
prevents the formation of a linear (**6**) analogue, allowing the more favorable hydrogen transfer to occur in a longer lived (**5**) intermediate. It should be noted that considerable deterioration of the sensitive trienone products is observed: **2** was photolyzed to 50% conversion and 10% of **6** was isolated, and **3** was photolyzed to 80% conversion, yielding 30% of **8** and **9**. The scarcity of **4** caused us to examine it only qualitatively at 254 nm, and after establishing that it behaves largely as **2**, it was not pursued in detail at this wavelength.

On irradiation at $\lambda \geq 300$ nm, **2**, **3**, and **4** yield exclusively, albeit slowly, the corresponding ω-aryl aldehydes (**10**, **11**), evidently as a result of α-cleavage and β-hydrogen abstraction. It should be noted that these aldehydes constitute byproducts (up to 5%) in both the lower (254 nm) and the higher (350 nm) wavelength irradiations.

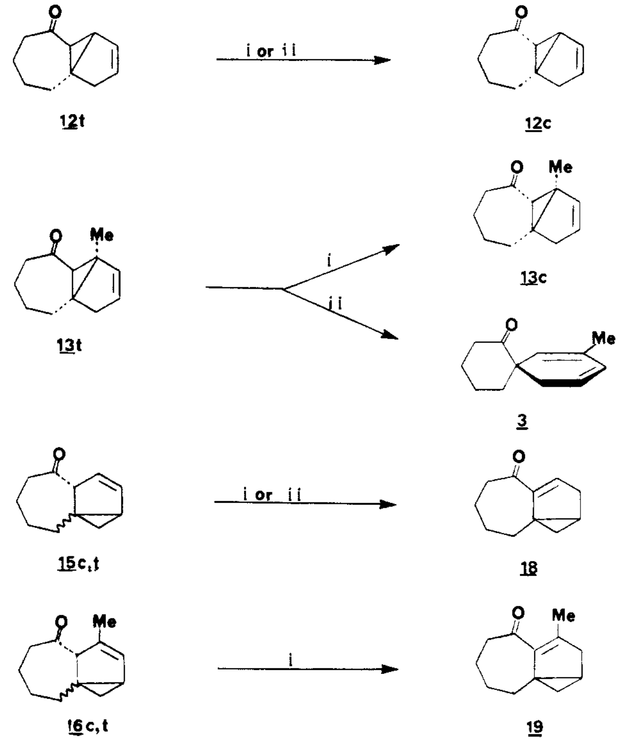
The highest wavelength direct irradiation was at about 350 nm, using a solution filter to cutoff below 340 nm or a monochromator. In these conditions, the main photoproducts from **2**, **3**, and **4** were invariably *trans*-tricyclo[5.4.0.$0^{7,11}$]undeca-9-en-2-one (**12t**) or its 11-methyl and 9-methyl derivatives (**13t** and **14t**, respectively), typical 1,2-acyl shift, i.e., oxadi-π-methane (ODPM)[3,4] rearrangement products. In fact, it was the latter process that we anticipated and which interested us most in this study; it should be noted in this context that (Scheme II), in principle, there are two available modes of ODPM rearrangement in systems of type **2**; ${}_\sigma 2 + {}_\pi 2$ and ${}_\sigma 2 + {}_\pi 4$, each yielding isomers in two possible (trans and cis) configurations (Scheme IIa, and b, respectively). Evidently, in the above, high-wavelength irradiation, we deal with a highly regio- and diastereoselective 1,2-acyl shift photorearrangement. Occasionally, traces of the corresponding cis isomers could be suspected from the NMR spectra, but they were not isolable and did certainly not exceed the (ca. 4%) limit of detection.

Sensitized irradiation (acetone, 300 nm) of **2**, **3**, and **4** turned out to be more complex, although complete selectively in the general 1,2-acyl shift is observed. Thus (Scheme III), both modes obtain, but the ${}_\sigma 2 + {}_\pi 2$ mode is still highly diastereoselective, viz., only the trans isomers (**12t**, **13t**, **14t**) could be isolated and less so the ${}_\sigma 2 + {}_\pi 4$ mode, by which the tricyclo[5.4.0.$0^{7,9}$]undeca-10-en-2-one (**15**, **16**, **17**) in both their trans (t) and cis (c) configurations are formed. Significantly, the variable substitution probe points to a clear dependence of regioselectivity as well as diastereoselectivity of the rearrangement on H vs. Me substitution (Scheme III), the yield ratios being **12**/**15** = 2.2, **13**/**16** = 3, **14**/**17** = 0.5, **15c**/**15t** = 3, **16c**/**16t** = 4, and **17c**/**17t** = 5.

Scheme III



Scheme IV



i : 1N CH_3ONa/CH_3OH.
ii: Al_2O_3(basic)/$CHCl_3$.

The structure and geometry of the photoproducts in the two tricyclic series were assigned on the strength of their spectroscopic data (mainly NMR) and were unequivocally confirmed by the reported X-ray diffraction analyses of two oxime derivatives (one of each series) namely of **12t** and **17c**,[2c] and supplemented by chemical interconversion and probing of the various isomeric pairs, as shown below.

Most of the tricyclic compounds of the above three substitution series was subjected to base and acids catalysis as well as to irradiation and thermal treatment. The following pattern obtains:

(i) **Base-Catalyzed Transformations (Scheme IV).** In the tricyclo[5.4.0.$0^{7,11}$] series, base treatment of the trans compounds (**12t**, **13t**) readily provided the hitherto elusive cis isomers (**12c**, **13c**) by using sodium methoxide in methanol.

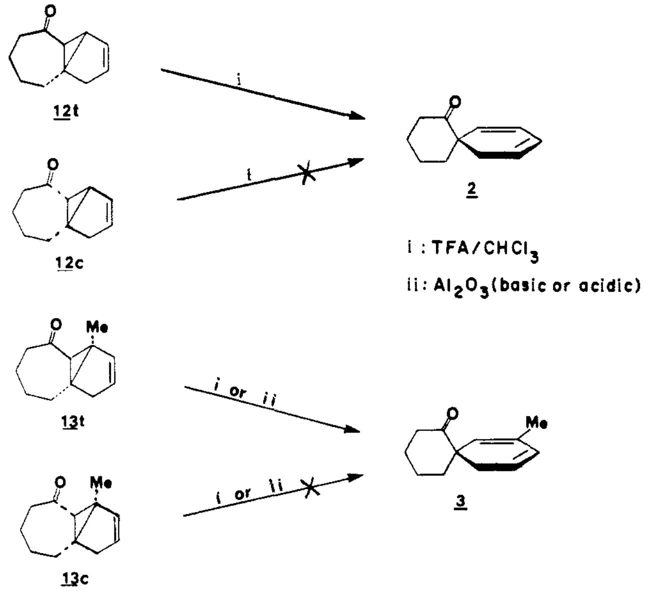
Attempts to accomplish this in milder conditions, viz., on basic alumina, succeeded in the unsubstituted series (**12t** → **12c**) but

Table I. Quantum Yields ($\phi \times 10^2$) of Disappearance and Corresponding Product Formation in Direct, Sensitized, and Quenched Irradiations of Dienones (**2** and **3**)[a]

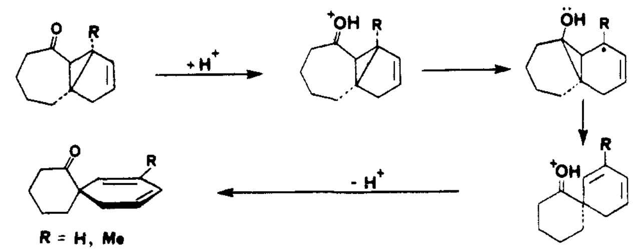
	ϕ_{disapp} dienone[e]		$\phi_{formation} \times 10^2$					
			aldehyde[e]		tricyclo-[5.4.0.0^{7,11}][e]		tricyclo-[5.4.0.0^{7,9}][e]	
λ[b], nm	**2**[f]	**3**[g]	**10**[f]	**11**[g]	**12t**[f]	**13t**[g]	**15c**[f]	**16c**[g]
310	9.4	14.0	1.6	5.0		0.5		
338	5.0	8.8	1.0	2.5		2.0		
338 + Q[c] (2.5 × 10^{-3} M)		5.0		2.4		1.6		
338 + Q[c] (5 × 10^{-3} M)		5.0		2.2		1.2		
338 + S[d]	17.3	26.0			11.0	18.0	3.7	3.0

[a] Taken in acetonitrile at concentrations which ensured total absorption at the respective wavelengths and measured by ^{1}H NMR after evaporation of the solvent and with use of the sensitizers as internal standard. The estimated accuracy in this procedure is ±20%. [b] The irradiation chromaticity is λ ± 7 nm. [c] Irradiation in the presence of quencher, viz., ferrocene at a given concentration. [d] Sensitized (2-acetonaphthone with OD ≥1) irradiation. [e] R' = H. [f] R = H. [g] R = Me.

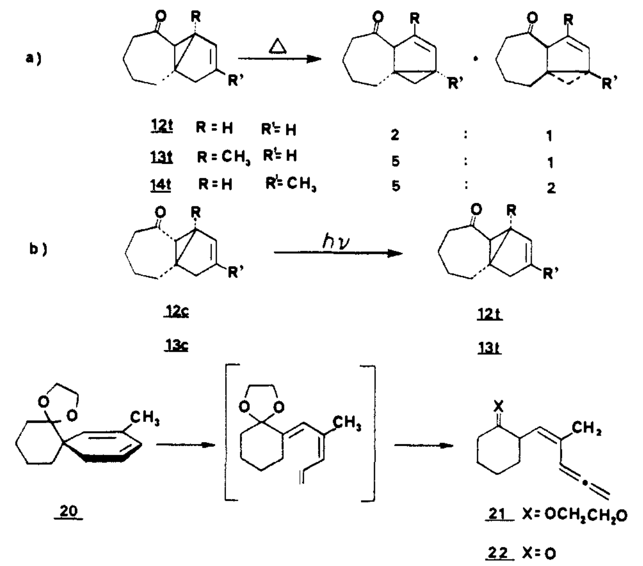
Scheme V



Scheme VI



Scheme VII



not in the 11-methyl one where a surprising reversal to the starting dienone (**13t** → **3**) was observed. This was readily rationalized after the acid catalyzed behavior became known (see below).

In the tricyclo[5.4.0.0^{7,9}] series, sodium methoxide in methanol causes rapid isomerization of both trans and cis isomers of **15** or **16** to the α,β-unsaturated isomers (**18** or **19**). This time, basic alumina induces the same isomerization, albeit more sluggishly, on the unsubstituted compounds (**15c,t**) as well as the 11-methyl derivatives (**16c,t**).

(ii) **Acid-Catalyzed Transformations (Scheme V).** The *trans*-tricyclo[5.4.0.0^{7,11}] photoproducts (**12t,13t**) readily undergo an acid (TFA/CHCl$_3$) catalyzed rearrangement to the dienone starting materials (**2** or **3**, respectively). The cis isomers as well as the tricyclo[5.4.0.0^{7,9}] isomers remain unchanged in these conditions.

The above rearrangement is plausibly rationalized in Scheme VI, where a stabilized C_{11}-carbenium ion intermediate plays a central role. At this point we can also suggest an explanation for the apparent discrepancy in (i) (Scheme IV), where C_{11}-methyl substitution prevents the alumina catalysed trans–cis isomerization (**13t** $\not\rightarrow$ **13c**), in contrast to **12t** → **12c**. Models indicate that the methyl group at C_{11} may well shield the α-position (C_1) from proton abstraction by the base in the alumina, allowing the latter to act as a Lewis acid and to initiate the rearrangement to **3** as depicted in Scheme VI. The same rationale is bound to hold for the observation (Scheme IV) that basic alumina fails to catalyze the β,γ-double-bond migration to α,β (**16** $\not\rightarrow$ **19**), as opposed to **15** → **18**.

(iii) **Thermal Transformations (Scheme VIIa).** On heating (in refluxing cyclohexane), only the *trans*-tricyclo[5.4.0.0^{7,11}] photoproducts (*12t, 13t, 14t*) undergo an all but quantitative vinyl–cyclopropane rearrangement to the respective [5.4.0.0^{7,9}] isomers (**15t, c**; **16t, c**; **17t,c**) albeit with moderate, substitution-dependent diastereospecificity, indicating diradical intermediacy, with preferred bonding at the center with increased charge density.

(iv) **Photochemical Transformations (Scheme VIIb).** In contrast to the above thermal behavior, only the *cis*-tricyclo[5.4.0.0^{7,11}] (**12c**, **13c**, **14c**) compounds photoisomerized slowly ($\phi < 10^{-2}$) but exclusively to the corresponding trans isomers (**12t**, **13t**, **14t**, respectively). The [5,4.0.0^{7,9}] system is photochemically (as well as thermally) reasonably stable. These results served also to confirm that the described photoreactions yield genuine primary photoproducts.

Photochemistry; Mechanistic Work

We present here the first steps we undertook toward the mechanistic elucidation of the photochemical behavior of the system under scrutiny, aiming to suggest a reasonable model for spectroscopic and flash-photolytic testing.

To start with, we reasoned that the electrocyclic opening occurs from a high (S_2) π,π* singlet. This implies the involvement of a "pure" diene chromophore, and to lend support to this assertion, we irradiated the ethylene ketal (**20**) of the 2-methyl spirodienone (**3**) and could observe *only* electrocyclic ring-opening, albeit leading to a different kind of end product namely the ketal (**21**) of the keto-allene (**22**).

Table II. Ratios of Yields of $_{\sigma}2 + _{\pi}2$ and $_{\sigma}2 + _{\pi}4$ Mode Products as a Function of Sensitizer (E_T) and of Solvent in Sensitized Irradiations of Dienones (**2**, **3**, and **4**).[a]

	2(H,H)[c] **12t**/**15c**[d]			**3**(Me,H)[c] **13t**/**16c**[d]			**4**(H,Me)[c] **14t**/**17c**[d]		
sensitizer (E_T)	MeCN[e]	Me_2CO[e]	C_6H_{12}[e]	MeCN[e]	Me_2CO[e]	C_6H_{12}[e]	MeCN[e]	Me_2CO[e]	C_6H_{12}[e]
(1) Acetone (78)		1.8			4			0.7	
(2) 9-xanthenone (74)				4		1.6[b]			
(3) phenanthrene (62)				5		1.7[b]			
(4) 2-acetonaphthone (59)	4		1	5		1.7	1		0.4
(5) 1-acetonaphthone (56)				5		2			
(6) fluorenone (53)				5					
(7) pyrene (49)				NR					

[a] Performed by irradiation at 338 nm in ca. 10^{-3} M solutions, evaporation of solvent and ^{1}H NMR measurement, using the sensitizer as internal standard for both δ and integration. GC was sometimes used for confirmation. The estimated accuracy is 20%. [b] Taken in benzene for solubility reasons. [c] Dienone (R,R'). [d] Product ratio. [e] Solvent.

The measured quantum yields of dienone (**2** and **3**) disappearance and product formation are displayed in Table I for direct, sensitized (2-acetonaphthone, λ_{max} 341 nm, E_T = 59 kcal/mol) irradiations (due to the scarce availability of **4**, it was not included in these elaborate studies).

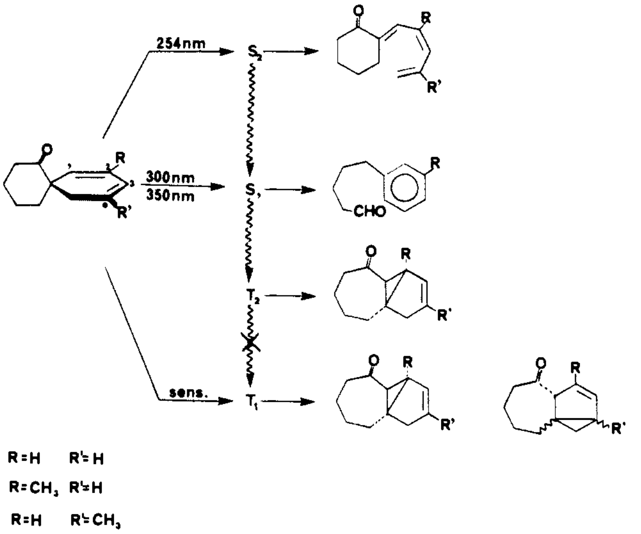
Having established that the tricyclic products are formed via triplet excited state(s), we proceeded to examine in more detail (E_T and solvent effect) the sensitized transformations of **3**. Table II shows that the lowest sensitizer to induce efficient photoconversions **3** → **13t** + **16c**,**t** was fluorenone with E_T = 53 (pyrene with E_T = 49 failed completely), allowing for the estimate of the triplet energy of **3** at about 51 kcal. Furthermore, the product ratio is largely unaffected by the sensitizers triplet energy. It is, however, very clearly solvent dependent, as shown in Table II; due to the mechanistic significance of these results, all three dienones were examined and showed consistent behavior, viz., increased solvent polarity causes the $_{\sigma}2 + _{\pi}2$ mode products to be preferred over the $_{\sigma}2 + _{\pi}4$ ones or, in other words, a higher ratio of tricyclo[5.4.0.$0^{7,11}$]/tricyclo[5.4.0.$0^{7,9}$].

Discussion

It is fitting to start the discussion of the results of this investigation by giving its "raison d'etre". As mentioned in the introduction, the basic approach was to examine if and how the variation in geometry of juxtaposition of the two homoconjugated chromophores, the carbonyl and 1,3-diene, affects the photochemical behavior of the system (**1**), *with particular attention to the ODPM* rearrangement.[3,4] The reason for extending the β,γ-unsaturation to a 1,3-diene was multiple: (i) to facilitate intersystem crossing for attainment of triplet excited states, (ii) to provide a lower energy $^3\pi,\pi^*$ level and to be thus more confident as to the character of the lowest excited triplet, and (iii) to offer an additional mode of rearrangement to the known $_{\sigma}2 + _{\pi}2$ mode,[4] namely the $_{\sigma}2 + _{\pi}4$ mode; in fact, it is worth mentioning that earlier observations on such unique $_{\sigma}2 + _{\pi}4$ 1,2-acyl shifts, albeit involving imide carbonyls,[7-9] initiated among other things this investigation. The s-cis conformation of the diene was deemed necessary in order to ensure good orbital overlap for bonding between its terminus and the saturated (quaternary) α-carbon and was imposed by its incorporation in a six-membered ring.

The spiro-dienone system (**1a**) was anticipated to provide the geometry with perpendicular chromophores (without considering conformational effects at this stage), to exclude energy wastage by spurious processes, and to prevent even generally expected reaction pathways such as the 1,3-acyl shift (the latter is excluded via both concerted and diradical pathways, on stereochemical grounds). On the other hand, we were aware of two obvious photoreactivity channels, namely, α-cleavage and electrocyclic ring opening while our principal interest was in the oxadi-π-methane (ODPM) rearrangement in its two modes (vide supra) with its intriguing mechanism and attractive synthetic potential.

Scheme VIII



While a thorough discussion of the detailed mechanism of the above reported photochemistry must be deferred to when the photophysical work will be completed, we can draw some preliminary conclusions and mechanistic hypotheses from the available data. First (Scheme VIII), we consider the excited states involved in the above described photoprocesses, as inferred from the striking wavelength selectivity observed. It stands to reason that the highest energy process, viz., the electrocyclic opening of the cyclohexadiene ring,[10] occurs via a high $^1\pi,\pi^*$ singlet (S_2) while the lower ^{1}n,π^* singlet (S_1) affords α-cleaved aldehyde products (the possibility that some of the latter occurs also from the ^{3}n,π^* cannot be excluded since the ferrocene quenching results for **3** leave some room for it) (Table I).

As with the structural outcome, the most interesting and, in a way, intriguing behavior is that involving the 1,2-acyl shifts. From literature evaluations[11,12] (as also critically discussed in Houk's comprehensive review[4a]) a $\beta,\gamma,\delta,\epsilon$-unsaturated ketone may be expected to exhibit a lowest (T_1) π,π^* triplet of ca. 54 kcal/mol and a (T_2) n,π^* triplet of about 77 kcal/mol, all these below the vertical (S_1) n, π^* of about 83 kcal/mol. At this stage of knowledge of our system, the most plausible scheme appears, hence, to involve two discrete excited triplet processes (Scheme VIII): (i) the higher (^{3}n, π^*) triplets attained by intersystem crossing from S_1 give exclusively the trans $_{\sigma}2 + _{\pi}2$ (ODPM) rearrangement products (**12t**, **13t**, **14t**); (ii) the lowest ($^3\pi,\pi^*$) triplets attained by energy transfer, with E_T around 51 kcal/mol, lead to a (solvent dependent) mixture of the same trans $_{\sigma}2 + _{\pi}2$ along with cis and trans $_{\sigma}2 + _{\pi}4$ rearrangement products (**15t**, **16t**, **17t**).

Turning to the other mechanistic features of the rearrangement involving the carbonyl chromophore (Scheme IX), it is compelling that excitation to S_1 be followed by α-cleavage (path i) to a diradical in which the carbonyl abstracts a β-hydrogen to give

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(7) (a) Fuchs, B.; Scharf, G. *J. Org. Chem.* **1979**, *44*, 604. (b) Scharf, G.; Fuchs, B. *J. Chem. Soc., Chem. Commun.* **1975**, 244.

(8) Ben-Bassat, J. M.; Ginsburg, D. *Tetrahedron* **1974**, *30*, 483.

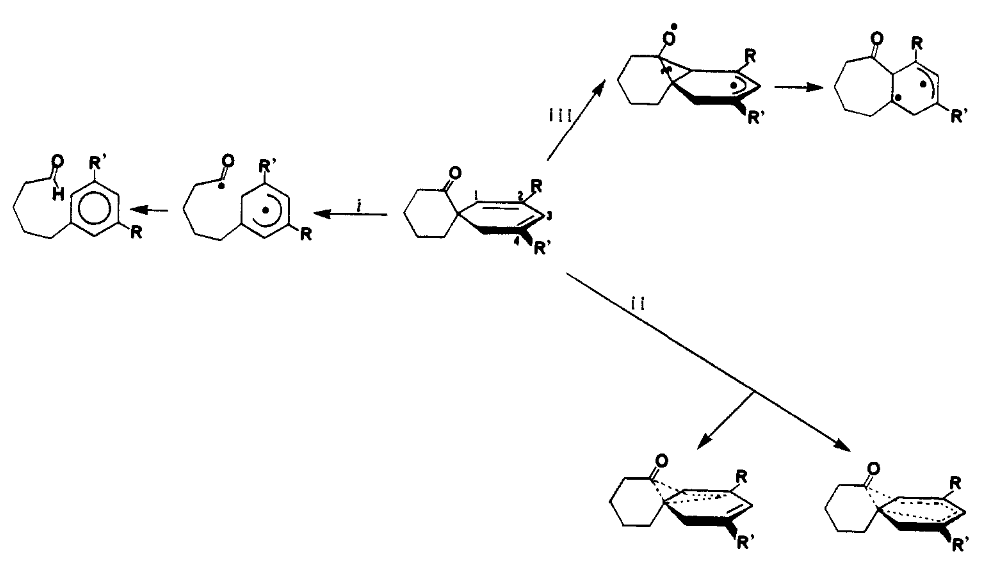
(9) Jones, D. W.; Kneen, G. *J. Chem. Soc., Perkin Trans. 1* **1975**, 171.

(10) Dauben, W. G. In ref 3a, pp 91-166 and pertinent references cited there.

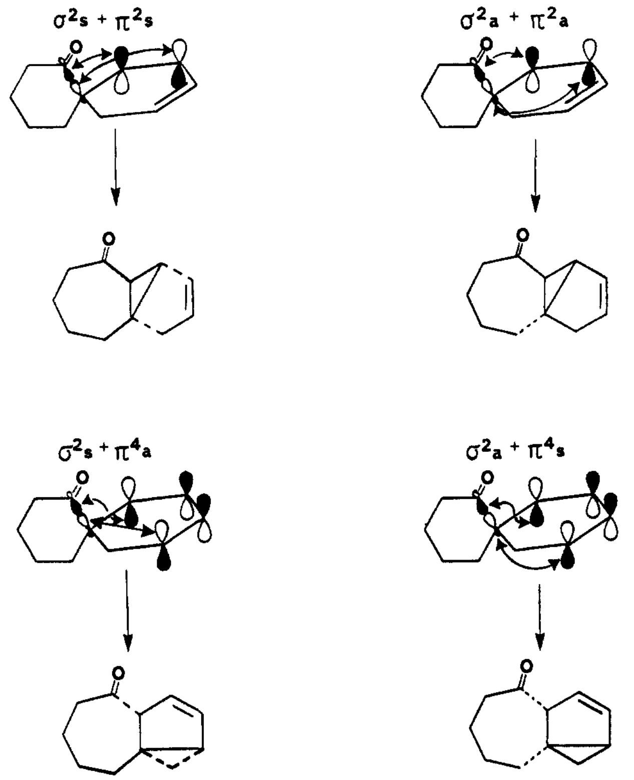
(11) Schexnaider, M. A.; Engel, P. S. *Tetrahedron Lett.* **1975**, *1153*.

(12) Meier A. J.; Mulliken, R. S. *Chem. Rev.* **1969**, *69*, 639.

Scheme IX



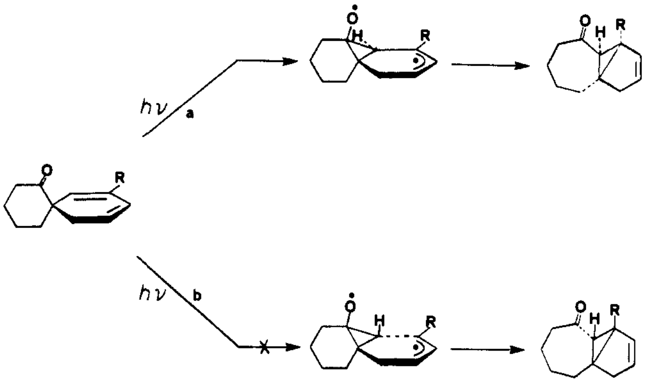
Scheme X



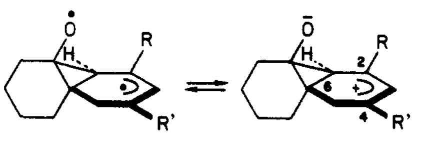
the aromatic ω-aldehyde (**10**, **11**). It is equally apparent that the above diradical is not involved in any of the 1,2-acyl shifts: the arguments for its rejection in the regular ${}_{\sigma}2 + {}_{\pi}2$ case are based on those convincingly put forward by Zimmerman,[4d] and for the ${}_{\sigma}2 + {}_{\pi}4$ mode they are in part the same and reinforced by the fact that no accompanying aldehyde (or any other aromatic) product is observed in the sensitized irradiation. The two remaining pathways, ii and iii (Scheme IX), present, respectively, the Zimmerman–Givens[3f,4b] and concerted pericyclic[13] mechanisms for the 1,2-acyl shifts and cannot really be told apart at this moment (if ever). It is worth mentioning that the latter, with its strict stereochemical bias, is still very much possible from a triplet excited state.[14]

While it is difficult to account for the virtually complete regio- and stereoselectivity in the direct irradiation ODPM rearrangement, we attempted to rationalize the outcome of the sensitized one in molecular orbital terms (Scheme X). Thus, the regioselectivity appears to be governed by the relative electron densities on the C_2 and C_4 of the diene moiety and is strongly substituent dependent. As to stereoselectivity, it is evident that for reasons of avoidance of charge density accumulation in the available small space element, the ${}_{\sigma}2_{a} + {}_{\pi}2_{a}$ mode leading to the trans isomer is totally preferred over the ${}_{\sigma}2_{s} + {}_{\pi}2_{s}$ one, but this constraint is less severe in the second case, where the ${}_{\sigma}2_{a} + {}_{\pi}4_{s}$ prevails, to give the favored cis isomer.

Scheme XI



Scheme XII



For good measure it should be pointed out that careful analysis of the Zimmerman–Givens mechanism gives similar results for, say, the ${}_{\sigma}2 + {}_{\pi}2$ process (Scheme XI) where, on stereochemical grounds (an improbable trans-fused intermediate), path b is excluded and path a implies not only complete stereoselectivity but also enantiospecificity. This was very recently shown to be indeed the case (for R = CO_2Me).[1] It is here also adequate to point out the rationale for the observed solvent effect. Indeed, polar solvents may well induce charge separation in the diradical intemediate (Scheme XII) along with bias in the subsequent bonding step.

Finally, we should give due credit to other contributions in this area. Only a small number of β,γ,δ,ε-unsaturated ketones have been investigated. Of these, the open chain systems behave rather indiscriminately and uncharacteristically. Thus, the diastereomeric s-cis dienic systems (**23**) underwent either electrocyclic ring closure or internal Paterno–Büchi cycloaddition[15a,b] whereas the s-trans

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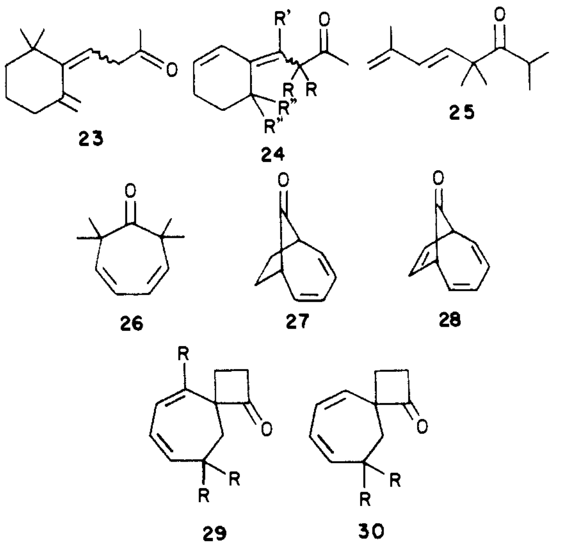
(13) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1969.

(14) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57.

(15) (a) van Wageningen, A.; Cerfontain, H. *Tetrahedron Lett.* **1972**, 367. (b) Roof, A. M.; van Wageningen, A.; Kuruk, C.; Cerfontain, H. *Ibid.* **1972**, 376. (c) van Wageningen, A.; van Nort, P. C. M.; Cerfontain, H. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1662.

Chart I



dienones (**24**) gave 1,3- and 1,5-acyl shifts.[15c] The latter were observed also in direct irradiations of the dienone (**25**), and only sensitized irradiation caused some ${}_{\sigma}2 + {}_{\pi}2$ ODPM rearrangement.[17] All those were accompanied by "free rotor"[16] energy wasting processes, and in no case was a ${}_{\sigma}2 + {}_{\pi}4$ process observed. This is, in fact, true also for more recent and elaborate studies of ring dienones (**26**, **27**, **28**) by Schuster and Eriksen[18] which provided, however, valuable information about the photophysics and reaction mechanism of such systems. Thus, e.g., **26** was reported to undergo electrocyclic diene closure and 1,3-acyl shift from S_2 ($^1\pi,\pi^*$), decarbonylation from S_1 ($^1n,\pi^*$), and ODPM (${}_{\sigma}2 + {}_{\pi}2$ only) rearrangement by sensitization to T_1 ($^3\pi,\pi^*$).

In the context of our study, two significant contemporary reports have to be mentioned, namely, the irradiation induced transformations of the spirocyclobutanones **29** and **30** (R = H, Me) where only on sensitization *both* ${}_{\sigma}2 + {}_{\pi}2$ and ${}_{\sigma}2 + {}_{\pi}4$ ODPM rearrangement products were isolated but no further, mechanistic probes were reported.

In conclusion, we have unravelled a homoconjugated dienone system which shows significant photochemical selectivity, the most remarkable transformation being a regioselective and diastereoselective ODPM type rearrangement. Substituent and solvent effects show clear directive behavior and tentative mechanistic conclusions could be drawn. While the full scope and ultimate mechanism of this photochemistry are still being explored, we are looking also into another potentially valuable aspect, namely, to use its versatility in working out methods for achieving synthons for stereoselectivity synthesis.[21]

Experimental Section

Melting points are uncorrected. IR spectra were measured on a Perkin-Elmer 297 spectrophotometer and UV spectra on a Cary 219 spectrophotometer. NMR spectra were taken on Brucker WH-90 and AM-360 WB spectrometers and are given in ppm downfield of Me_4Si. Mass spectra were taken on a DuPont 21-491 B mass spectrometer. Gas chromatography was performed on a Packard 427 instrument equipped with a capillary column (SE 30, 25 m) and a computing integrator (Spectra-Physics System I). HPLC work was done on a Waters Associates M-4000-A instrument with Merck 7734 prepacked columns.

Irradiations were carried out in two modes: (i) preparative, in Rayonet photoreactors (16 8 W lamps) or similar, locally built ones (32 lamps) with germicidal (254 ± 15 nm), cool-white (300 ± 30 nm), or black-light blue (350 nm) lamps, as well as a HANOVIA 679 A36, 450-W, medium-pressure Hg lamp in immersion reactors; and (ii) analytical, using a JASCO CRM-FA Spectroirradiator, at 257, 311, or 338 nm (band width 2–15 nm, according to filters used), equipped with a photoncounter. The latter was periodically calibrated by chemical actinometry (using mostly the Aberchrome 540 actinometer).

Quantum yields were measured only at 311 nm (1.24×10^{-8} einstein/count) or 338 nm (2.13×10^{-8} einstein/count) with about 100 counts/min, using ^{1}H NMR or GC monitoring.

Irradiations were performed on deoxygenated (N_2 or Ar) solutions in quartz (254 nm) or Pyrex (300 and 350 nm).

The following cutoff filters were used: Corex(for $\lambda > 280$ nm), a solution of NaBr (375 g) and $Pb(NO_3)_2$ (4 g) in water (500 mL) (for $\lambda > 340$ nm). In sensitized reactions it was made sure that the sensitizers absorb at least 95% of the relevant radiation.

Preparative Irradiations: **General Procedure**, A solution (ca. 0.1%) of spirodienone in purified cyclohexane (unless otherwise specified) was irradiated at the appropriate wavelength at ca. 35 °C. The solution was then evaporated to dryness and the mixture was analyzed by TLC and/or GC and accordingly chromatographed (Silica gel) to yield the pure products.

The spirodienones (**2**, **3**, **4**) were prepared by published procedures.[6]

Irradiations of Spiro[5,5]undeca-1,3-dien-7-one (**2**), (a) **Direct Irradiations of 2**, (i) **254 nm** (**Rayonet**). After 2 h (50% conversion) the process was stopped to prevent extensive decomposition. Workup and chromatography gave starting material (**2**) (30%), and electrocyclic ring-opening product (10%) which was assigned the structure 2-(*E*)-((*E*)-pentadienylene)cyclohexanone (**6**) [*m*/*z* 162 (M^+, $C_{11}H_{14}O$); ν_{max} (neat) 1680 cm^{-1} (CO); λ_{max} (cyclohexane) 306 nm; ^{1}H NMR ($CDCl_3$) δ 6.7 (m, 4 =CH), 5.3–4.9 (m, =CH_2) 2.1–2.7 (m, =CH_2, $COCH_2$), 1.6–2.0 (m, 2 CH_2); ^{13}C NMR ($CDCl_3$) δ 200.6, 141.5, 136.8, 135.3, 135.0, 127.4, 121.1, 40.0, 26.8, 23.3, 23.1] and, finally, ω-phenylpentanal (**10**) (4%) [*m*/*z* 162 (M^+, $C_{11}H_{14}O$); ν_{max}(neat) 1730 cm^{-1} (CO); ^{1}H NMR (CCl_4) δ 9.7 (br s, OCH), 6.9 (m, arom CH) 2.1–2.7 (m, $COCH_2$, $PhCH_2$), 1.6–2.0 (m, CH_2)]. The order of elution was (petroleum ether/dichloromethane): **10**, **2**, **6**.

(ii) **300 nm** (**Rayonet**), After seven days (50% conversion) and similar workup, only the aldehyde (10) was obtained (35%).

(iii) **>340 nm** (**HANOVIA**, **Solution Filter**), After 80 h, the solvent was evaporated and the residue chromatographed to give the aldehyde (**10**) (5.2%) followed by a product which was assigned the structure *trans*-tricyclo[5.4.0.0.^{7,11}]undeca-9-en-2-one (**12t**) (19.2%): *m*/*z* 162 (M^+, $C_{11}H_{14}O$); ν_{max} (neat) 1710 cm^{-1} (CO); λ_{max} (cyclohexane) (ϵ) 288 nm (100); ^{1}H NMR ($CDCl_3$) δ 5.95 (dddd, *J* = 6.0, 2.0, 2.0, 2.0 Hz, $C^{10}H$), 5.52 (ddd, *J* = 6.0, 2.5, 2.5 Hz, C^9H), 1.5–2.7 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 202.0, 128.9, 128.2, 42.6, 41.7, 38.3, 38.35, 37.1, 23.2, 28.9, 24.6. The crystalline oxime of **12t** was obtained from its reaction with hydroxylamine hydrochloride and sodium acetate in water: mp 165 °C (from ether); *m*/*z* 177 (M^+, $C_{11}H_{15}NO$). The X-ray diffraction analysis and structure were reported.[2c]

(b) Sensitized Irradiations of 2, (i) **>280 nm (Rayonet, Corex) in Acetone**, After 36 h (70% conversion) the solvent was removed and the residue chromatographed to give starting material (**2**) (20%) followed by *cis*-tricyclo[5.4.0.0^{7,9}]undeca-10-en-2-one (**15c**) (15%) [*m*/*z* 162 (M^+, $C_{11}H_{14}O$); ν_{max} (neat) 1705 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 6.27 (ddd, *J* = 5.8, 2.5, 2.0 Hz, $C^{10}H$), 5.30 (dd, *J* = 5.8, 2.6 Hz, $C^{11}H$), 3.37 (dd, *J* = 2.6, 2.5 Hz, C^1H), 1.0–2.5 (m, 9 H), 0.95 (dd, *J* = 7.5, 3.6 Hz, C^8H), 0.29 (dd, *J* = 3.6, 3.6 Hz, C^8H)] next *trans*-tricyclo]5.4.0.0^{7,9}]-undeca-10-en-2-one (**15t**) (5%) [*m*/*z* 162 (M^+, $C_{11}H_{14}O$); ν_{max} (neat) 1700 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 5.99 (ddd, *J* = 5.8, 2.0, 2.0 Hz, $C^{10}H$), 5.44 (dd, *J* = 5.8, 2.0 Hz, $C^{11}H$), 4.04 (dd, *J* = 2.0, 2.0 Hz, C^1H), 2.6 (m, 2 H), 0.9–2.4 (m, 7 H), 0.60 (dd, *J* = 7.5, 4.0 Hz, C^8H), 0.14 (m, C^8H)] and finally the tricyclic product (**12t**) (25%).

(ii) 350 nm (Rayonet) in Acetonitrile (100 mL) and 2-Acetonaphthone (65 mg), After 3 h, full conversion was reached and the reaction mixture was worked up as usual to give a mixture of similar products as above but with a ratio of **12t**/**15c** = 4. A similar irradiation in cyclohexane gave a ratio **12t**/**15c** = 1.

Irradiations of 2-Methylspiro[5,5]undeca-1,3-dien-7-one (**3**), **(a) Direct Irradiations of 3**, (i) **254 nm** (**Rayonet**), After 5 h (80% conversion) the solvent was evaporated and the residue was resolved by HPLC (1.5% ethylacetate/cyclohexane). Two main fractions were collected, the first consisting of a mixture of starting material (**3**) and aldehyde (**11**) (10%) and the second of trienones (**8**, **9**) (30%). Rechromatography (HPLC) of the latter provided the pure electrocyclic ring-opening products, 2-((*E*,*E*)-2′-methylpenta-1′,3′-dienyl)cyclohex-2-en-1-one (**8**) [*m*/*z* 176 (M^+, $C_{12}H_{16}O$); ν_{max}(CCl_4) 1680 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 6.81 (t, *J* = 4.5 Hz, =C^3H), 6.21 (d, *J* = 16.0, =$C^{3'}H$), 6.11 (br s, =$C^{1'}H$), 5.73 (dq, *J* = 16.0, 7.0 Hz, =$C^{4'}H$), 2.5 (m, 4 H), 1.4–2.2 (m, 8 H), 1.82 (d, *J* = 1.0 Hz, CH_3), 1.79 (d, *J* = 7.0, $C^{5'}H_3$)] and 2-((*Z*,*E*)-2′-methylpenta-1′,3′-dienyl)cyclohex-2-en-1-one (9) [*m*/*z* 176 (M^+,

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(21) Cf., for example: Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820.

$C_{12}H_{16}O$); ν_{max} (CCl_4) 1680 cm^{-1} (CO); λ_{max} (cyclohexane) (ϵ) 290 (4500), 233 (18 500); ^{1}H NMR ($CDCl_3$) δ 6.84 (t, J = 4.0 Hz, C^3H), 6.39 (d, J = 15.6 Hz, $=C^{3'}H$), 6.00 (br s, $C^{1'}H$). 5.81 (dq, J = 15.6, 6.5 Hz, $=C^{4'}H$), 2.48 (m, 4 H), 1.5–2.2 (m, 8 H), 1.92 (d, J = 1.1 Hz, CH_3), 1.79 (d, J = 6.5 Hz, $C^{5'}H_3$)].

Irradiation of the ethylene ketal (**20**) of the above spirodienone (**3**) at the same wavelength (254 nm) in acetonitrile, provided, after 8 h (80% conversion) and chromatographic separation, the allene (**21**) (47%): ν_{max} (neat) 1940 cm^{-1} ($-CH{=}C{=}CH_2$); λ_{max} (acetonitrile) 234 nm; ^{1}H NMR ($CDCl_3$) δ 6.13 (t, J = 6.5 Hz, $-CH{=}C{=}C$), 5.15 (m, $HC{=}C{<}$), 4.85 (m, $C{=}C{=}CH_2$), 3.8 (m, 4 H), 2.6 (m, COCH), 1.3–2.0 (m, 11 H), 1.75 (d, CH_3).

Hydrolysis of the ethylene ketal (**20**) was carried out by adding it (140 mg) to a suspension of SiO_2 (3 g) + H_2SO_4 (15%, 2 mL) in methylene chloride (8 mL) and stirring the mixture for 3 h, followed by filtration, drying on K_2CO_3, and chromatography. The keto-allene (**21**) was isolated (80 mg, 70%): ν_{max} (neat) 1710 (CO), 1940, 835 ($-CH{=}C{=}CH_2$) cm^{-1}; λ_{max} 230 nm; ^{1}H NMR ($CDCl_3$) δ 6.04 (t, J = 6.5, $HC{=}C{=}C$), 5.45 (m, $HC{=}C{<}$), 4.96 (m, $C{=}C{=}CH_2$), 3.34 (m, COCH), 1.5–2.8 (m, 11 H), 1.81 (d, CH_3).

(ii) **300 nm (Rayonet)**, After 3 days (80% conversion) the reaction mixture was worked up a usual to give only ω-(*m*-toluyl)pentanal (**11**) (48%): m/z 176 (M^+, $C_{12}H_{16}O$; ν_{max} (CCl_4) 1735 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 9.75 (t, J = 1.8 Hz, OCH), 6.9–7.3 (m, 4 H), 2.35–2.6 (m, 4 H), 2.33 (s, CH_3), 1.55–1.80 (m, 4 H).

(iii) **>340 nm (Hanovia, Solution Filter)**, After 12 days (65% conversion) and the usual workup, the only isolated product was *trans*-11-methyltricyclo[5.4.0.0^{7,11}]undeca-9-en-2-one (**13t**) (45%): m/z 176 (M^+, $C_{12}H_{16}O$); ν_{max} 1715 cm^{-1} (CO); λ_{max}(cyclohexane) (ϵ) 295 nm (90); ^{1}H NMR ($CDCl_3$) δ 5.82 (ddd, J = 5.6, 2.0, 2.0 Hz, $=C^{10}H$), 5.48 (ddd, J = 5.6, 2.2, 2.2 Hz, $=C^9H$), 2.05–2.70 (m, 4 H), 2.00 (s, C^1H), 1.35–1.95 (m, 6 H), 1.32 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 201.9, 133.4, 127.1, 47.7, 45.2, 43.3, 39.9, 38.5, 34.6, 28.9, 24.9, 16.3.

(b) Sensitized Irradiations of 3, **(i) >280 (Rayonet, Corex) in Acetone**, After 60 h (90% conversion) and the usual workup and chromatography the following products were isolated (after some starting material): *cis*-11-methyltricyclo[5.4.0.0^{7,9}]undeca-10-en-2-one (**16c**) (15.4%) [m/z 176 (M^+, $C_{12}H_{16}O$); ν_{max}(neat) 1705 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 5.86 (m, $C^{10}H$), 3.15 (s, C^1H), 1.2–2.9 (m, 12 H), 1.53 (br s, CH_3), 0.84 (dd, J = 7.0, 3.4 Hz, C^8H), 0.32 (t, J = 3.4 Hz, C^8H)], *trans*-11-methyltricyclo[5.4.0.0^{7,9}]undeca-10-en-2-one (**16t**) (3.9%) [m/z 176 (M^+, $C_{12}H_{16}O$); ^{1}H NMR ($CDCl_3$) δ 5.61 (m, $C^{10}H$), 3.92 (brs, C^1H), 2.55 (m, 2 H), 1.1–2.4 (m, 10 H), 1.62 (br s, CH_3),0.52 (dd, J = 7.0, 3.8 Hz, C^8H), 0.25 (m, C^8H)] and finally the already characterized tricyclo[5.4.0.0^{7,11}] isomer (**13t**) (58%).

(ii) **350 nm (Rayonet, Solution Filter) in Acetonitrile, in the Presence of Various Sensitizers, to Full Conversion**, The mixtures were worked up and analyzed by ^{1}H NMR. The results are given in Table II.

Irradiations of 4-Methylspiro[5,5]undeca-1,3-dien-7-one (**4**), **(a) Direct Irradiations of 4**, (i) **300 nm (Rayonet)**, After 68 h (90% conversion) and the usual workup and chromatography, the only isolated product was the aldehyde (**11**) (40%) (vide supra).

(ii) **> 340 nm (Rayonet, Solution Filter)**, After 65 h and the usual workup and chromatography, two products were isolated: the aldehyde (**11**) (13%) and *trans*-9-methyltricyclo[5.4.0.0^{7,11}]undeca-9-en-2-one (**14t**) (65%): m/z 176 (M^+, $C_{12}H_{16}O$); ν_{max} (neat) 1705 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 5.50 (m, $C^{10}H$), 1.2–2.6 (m, 15 H), 1.62 (br s, CH_3); ^{13}C NMR ($CDCl_3$) δ 202.8, 140.0, 121.7, 43.1, 42.6, 42.3, 39.6, 37.4, 34.6, 29.1, 24.8, 15.9.

(b) Sensitized Irradiations of 4, **(i) >280 nm (Rayonet, Corex) in Acetone**, After 20 h and the usual workup and chromatography the following products were obtained: *cis*-9-methyltricyclo[5.4.0.0^{7,9}]undeca-10-en-2-one (**17c**) (34%): [m/z 176 (M^+, $C_{12}H_{16}O$); ν_{max} (neat) 1710 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 5.9 (dd, J = 5.5, 2.0 Hz, $C^{11}H$), 5.4 (dd, J = 5.5, 2.0 Hz, $C^{10}H$), 4.02 (br s, C^1H), 1.3–2.6 (m, 8 H), 1.21 (s, CH_3), 0.2–0.4 (m, C^8H_2); ^{13}C NMR($CDCl_3$) δ 213.6, 144.6, 125.4, 67.9, 40.2, 34.5, 32.2, 31.9, 30.9, 27.7, 26.1, 16.1]. The oxime of **16c** was prepared as described above: mp 162 °C (from ether); m/z 191 (M^+, $C_{12}H_{17}NO$). Its single-crystal X-ray diffraction analysis has been reported.[2c] The isomer *trans*-9-methyltricyclo[5.4.0.0^{7,9}]undeca-10-en-2-one (**17t**) (6%) was obtained only in impure state and no further effort was spent for purification, but its ^{1}H NMR spectrum could be readily taken [δ 5.9 (dd, J = 5.5, 2.0 Hz, $C^{11}H$), 5.4 (dd, J = 5.5, 2.0 Hz, $C^{10}H$), 4.02 (br s, C^1H), 1.3–2.6 (m, 8 H), 1.21 (s, CH_3), 0.2–0.4 (m, C^8H_2)] and finally the already described isomer (**14t**) (19%).

(ii) **>340 nm (Rayonet, Solution Filter)** in **Cyclohexane, in the Presence of 2-Acetonaphthone**. After 6 h, the solvent was evaporated. The ^{1}H NMR spectrum of the residue showed the occurrence of the three products **14t**:**17c**: **17t** in the ratio 7:3:18; a similar experiment in acetonitrile was over after 1 h and gave a ratio of 5:1:5.

Transformations of the Irradiation Products, (i) **Base-Catalyzed Transformations (Scheme IV)**, The *trans*-tricyclo[5.4.0.0^{7,11}] product **12t** (100 mg) was stirred in a NaOMe/MeOH solution (3 mL, 0.3 N) for 3 h. The solvent was removed in vacuo, cold water was added, and the mixture was extracted with chloroform. After the solvent was dried ($MgSO_4$) and evaporated, the residue was chromatographed to give the corresponding *cis*-tricyclo[5.4.0.0^{7,11}]isomer (**12c**) (60%) (which was obtained also by stirring **12t** in a suspension of basic alumina in chloroform): m/z 162 (M^+, $C_{11}H_{14}O$); ν_{max}($CHCl_3$) 1665 cm^{-1} (CO); λ_{max} (MeCN) (ϵ) 282 nm (180); ^{1}H NMR ($CDCl_3$ δ 5.98 (dddd, J = 5.6, 1.5, 1.5, 1.5 Hz, $C^{10}H$), 5.53 (ddd, J = 5.6, 2.3, 2.3 Hz, C^9H), 2.3–2.8 (m, 4 H), 1.2–2.2 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 211.0, 133.4, 129.9, 49.3, 45.6, 42.1, 37.8, 36.3, 33.1, 26.8, 24.9. By the same procedure, the 11-methyl derivative **13t** gave the cis isomer **13c** (55%): m/z 176 (M^+, $C_{12}H_{16}O$); ν_{max}($CHCl_3$) 1695 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 5.81 (ddd, J = 5.8, 2.0, 2.0 Hz,$C^{10}H$), 5.46 (ddd, J = 5.8, 2.3, 2.3 Hz, C^9H), 2.75 (ddd, J = 17.5, 2.3, 2.0 Hz, C^8H), 2.41 (ddd, J = 17.5, 2.3, 2.0 Hz, C^8H), 2.2–2.5 (M, 2 H), 1.4–2.0 (M, 6 H), 1.31 (s, CH_3), 1.22 (s, C^1H); ^{13}C NMR ($CDCl_3$) δ 210.0, 139.9, 126.5, 45.8, 44.3, 43.2, 39.2, 31.6, 29.8, 25.7, 24.8, 15.0.

By using the same experimental procedure with either one (or a mixture) of the diastereoisomeric tricyclo[5.4.0.0^{7,9}] products (**15c**, **15t**), the isomeric α,β-unsaturated ketone (**18**) (ca. 57%) was isolated: m/z 162 (M^+, $C_{11}H_{14}O$); ν_{max} (neat) 1675 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 6.29 (dd, J = 4.0, 2.5 Hz, $C^{11}H$), 2.6 (m, 4 H), 1.1–2.2 (m, 7 H), 0.85 (dd, J = 8.0, 4.0 Hz, C^8H), 0.23 (dd, J = 4.0, 4.0 Hz, C^8H). The same applies to the base-catalyzed isomerization of the 11-methyl derivatives (**16c**, **16t**) which gave in 50% yield **19**: m/z 176 (M^+, $C_{12}H_{16}O$); ν_{max} (neat) 1680 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 2.2–2.8 (m, 4 H), 1.0–2.2 (m, 10 H), 1.95 (s, CH_3), 0.8 (dd, J = 8.0, 4.0 Hz, C^8H), 0.28 (dd, J = 4.0, 4.0 Hz, C^8H).

(ii) **Acid-Catalyzed Transformations (Scheme V)**, A solution of *trans*-tricyclo[5.4.0.0^{7,11}] product **12t** (50 mg) in chloroform (2 mL) containing two drops of trifluoroacetic acid was stirred for 4 h, after which it was diluted with chloroform (10 mL) and neutralized on K_2CO_3 (anhydrous). After filtration and removal of the solvent, the residue contained only the spiroketone (**2**). A similar treatment of the 11-methyl derivative (**13t**) gave, as expected,[6] a mixture of the 2-methyl- and 4-methylspiro[5.5]undeca-1,3-dien-7-ones (**3**,**4**) along with some of the 2-methylene-3-en-7-one isomer.[6] When this isomerization was carried out by stirring (2 h) a chloroform solution of **13t** on alumina (acid or basic!), only the unrearranged spiroketone (**3**) was isolated (40%).

(iii) **Thermal Transformations (Scheme VIIa)**, A solution of *trans*-tricyclo[5.4.0.0^{7,11}]undeca-9-en-2-one (**12t**) (50 mg) in 0.5–0.6 mL of CD_3CN in an NMR tube was kept at 70 °C overnight and then analyzed by ^{1}H NMR to show that complete isomerization had occurred to a 2:1 mixture of *trans*- and *cis*-tricyclo[5.4.0.0^{7,9}]undeca-10-en-2-one (**15t**:**15c**). Similarly, **13t** gave a 5:1 mixture of **16t**:**16c** and **14t** gave a 5:2 mixture of **17t**:**17c**.

(iv) **Photochemical (Sensitized) Transformations (Scheme VIIb)**, An acetone (20 mL) solution of *cis*-tricyclo[5.4.0.0^{7,11}]undeca-9-en-2-one (**12c**) (20 mg) was irradiated (300 nm) for 20 h. The solvent was removed and the residue chromatographed to give only the trans isomer (**12t**). Similarly, **13c** gave **13t** exclusively. Yields: ca. 50%.

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Registry No, **2**, 82390-19-0; **3**, 82390-25-8; **4**, 82390-27-0; **6**, 102696-55-9; **8**, 102683-35-2; **9**, 102683-36-3; **10**, 36884-28-3; **11**, 102683-34-1; **12c**, 102735-18-2; **12t**, 85679-33-0; **12t** (oxime), 85679-36-3; **13c**, 102735-19-3; **13t**, 85679-29-4; **14t**, 85679-31-8; **15c**, 85679-34-1; **15t**, 85718-03-2; **16c**, 85679-30-7; **16c** (oxime), 102683-38-5; **16t**, 85718-01-0; **17c**, 85679-32-9; **17t**, 85718-02-1; **18**, 102683-39-6; **19**, 102683-40-9; **20**, 82390-24-7; **21**, 102683-37-4; **22**, 103190-39-2; 10-Methylenespiro[5.5]undec-8-en-1-one, 82390-28-1.