parison with authentic samples. The second and third fractions contained 25 mg (23%) of a colorless oil which was unidentified. The fourth fraction contained 17 mg (15%) of a colorless oil which was identified as a 1:1 mixture of (*E*)- and (*Z*)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butenes (**37**) by comparison with authentic samples.[53] The fifth fraction contained 10 mg (10%) of a colorless oil which was identified as a 1:1 mixture of diastereomeric 3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butenes (**38**) by comparison with authentic samples.[53]

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.

Registry No. **1**, 62907-47-5; **2**, 62955-52-6; **3**, 73377-53-4; **4**, 62907-49-7; **5**, 65086-18-2; **8**, 71956-73-5; **9**, 62907-50-0; **10**, 62907-51-1; **11**, 62907-52-2; **12**, 62907-53-3; **13**, 62907-54-4; **14**, 66221-08-7; **16**, 73377-54-5; **17**, 73377-55-6; **18**, 73377-56-7; **21**, 73377-57-8; (*E*)-**22**, 50555-64-1; (*Z*)-**22**, 50555-63-0; **23**, 73377-58-9; **26**, 73377-59-0; **27**, 73377-60-3; **28**, 58310-20-6; **33**, 66221-12-3; **34**, 66221-10-1; **35**, 73377-61-4; **36**, 73464-49-0; (*E*)-**37**, 66221-09-8; (*Z*)-**37**, 70840-44-7; **38**, isomer 1, 66221-07-6; **38**, isomer 2, 66221-06-5; (*E*)-1,2-diphenylbut-1-en-3-one, 38661-88-0; allyl bromide, 106-95-6; (*E*)-1,2-diphenyl-3-hydroxy-3-methyl-1,5-hexadiene, 73377-62-5; *tert*-butyl 1-methyl-2,3-diphenyl-2-cyclopropene-1-acetate, 73377-63-6; *tert*-butyl 2-methyl-1,3-diphenyl-2-cyclopropene-1-acetate, 73377-64-7; 3-methyl-2-phenylindanone, 62907-55-5; methyl bromide, 74-83-9.

Photochemical Reactions of Bicyclo[2.2.2]octadienones

Hans-Dieter Becker* and Bernd Ruge

Department of Organic Chemistry, Chalmers University of Technology and University of Gothenburg,
S-412 96 Gothenburg, Sweden

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A series of spirooxirano-substituted bicyclo[2.2.2]octadienones have been prepared by Diels–Alder addition of dimethyl acetylenedicarboxylate to 2,4-cyclohexadienones, and their photochemistry was investigated. Upon direct excitation, they were found to aromatize by elimination of 2-carbonyloxirane which was trapped by ethanol to give ethyl glycidate. The acetophenone-sensitized reaction of bicyclooctadienones gave tricyclic isomers whose formation by regiospecific di-π-methane rearrangement is discussed.

Substituted bicyclo[2.2.2]octadienones **3a–i** are conveniently accessible by reaction of dimethyl acetylenedicarboxylate with 2,4-cyclohexadienones **2** which, unless stabilized by bulky substituents,[1] can be generated by thermal dissociation of their Diels–Alder dimers **1**.[2] Consideration of bicyclooctadienones both as β,γ-unsaturated ketones and as homoconjugated dienes indicates that they may conceivably undergo a variety of photochemical reactions. Photochemical fragmentation of **3a** or **3f**, as known[3] for related bicyclooctadienones, gives **4** or **5** and the correspondingly substituted dimethyl phthalates **6**. Photochemical isomerization by skeletal rearrangement of **3** formally could lead to ten products. **7** and **8** are the two possible 1,3-acyl-migration products of **3**, and **9–12** may derive from oxa-di-π-methane rearrangements (see Scheme I) for which precedence exists in the triplet-sensitized reaction of benzobicyclo[2.2.2]octadienone.[4,5] The formation of **13-16** may be rationalized by conceivable di-π-methane rearrangements of **3** as outlined in Scheme II.[6] Moreover, intramolecular cycloaddition of **3**, analogous to that of norbornadiene, would give products of tetracyclane structure.[7]

Challenged by the multitude of formally conceivable excited-state reactions mentioned above, we have prepared bicyclooctadienones **3a–i** and studied their photochemistry.[8]

Results and Discussion

Structure and Spectral Properties of Bicyclooctadienones 3. The Diels–Alder reaction of acetylenedicarboxylate with 2,4-cyclohexadienones **2** afforded in one case, namely, that of 4-*tert*-butyl-2,4-cyclohexadienone, a mixture of the two possible diastereomers **3b** and **3c**, differing in the configuration of the substituents R^4 and R^5. In all other cases, only one isomer was isolated whose structural assignment rests on the ^{1}H NMR spectral data listed in Table I and the following evidence. For **3f–h**, structure was established by determining the configuration of the substituents R^4 and R^5 by chemical means as outlined in Scheme III. As for **3i**, its structure has been confirmed by X-ray analysis.[9] Thus, for all the established structures of bicyclooctadienones, R^5 is either a methylene or methyl group. In apparent analogy to the formation of Diels–Alder dimers **1**, the attack of 2,4-cyclohexadienones **2** by acetylenedicarboxylate is governed by steric factors; in the transition complex involved in the formation of **3**, the sterically less demanding substituent at the disubstituted sp^3 carbon of **2** is oriented towards the dienophile.

The ultraviolet spectral properties of bicyclooctadienones **3** are typical of β,γ-unsaturated ketones.[5] Thus, the UV spectra are characterized by an enhanced n-π^* absorption (ϵ ~400) at about 310 nm (see Table II). Unfortunately, we have not been able to separate the two

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[1] Becker, H.-D.; Bremholt, T.; Adler, E. *Tetrahedron Lett.* **1972**, 4205.

[2] For the formation of dimers 1, see the following references. **1a,e**: Adler, E.; Holmberg, K. *Acta Chem. Scand., Ser. B* **1974**, *28*, 465. **1d**: Becker, H.-D.; Ruge, B.; Westlöf, T. *Tetrahedron Lett.* **1975**, 253, footnote 4. **1f,h**: Adler, E.; Dahlén, J.; Westin, G. *Acta Chem. Scand.* **1960**, *14*, 1580. **1g**: Adler, E.; Brasen, S.; Miyake, H. *Ibid.* **1971**, *25*, 2055.

[3] Murray, R. K.; Hart, H. *Tetrahedron Lett.* **1968**, 4995. Hart, H.; Huang, I. C. *Tetrahedron Lett.* **1974**, 3245.

[4] Givens, R. S.; Oettle, W. F. *J. Am. Chem. Soc.* **1971**, *93*, 3963.

[5] For a comprehensive review on "The Photochemistry and Spectroscopy of β,γ-Unsaturated Carbonyl Compounds", see: Houk, K. N. *Chem. Rev.* **1976**, *76*, 1.

[6] For a review of the di-π-methane rearrangement, see: Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.

[7] Concerning the stability of tetracyclanes derived from bicyclo[2.2.2]octadienes, see: Miller, R. D.; Dolce, D. L.; Merrit, V. Y. *Tetrahedron Lett.* **1976**, 1845. Liu, R. S. *Tetrahedron Lett.* **1969**, 1409. Prinzbach, H.; Eberbach, W.; Philippossian, G. *Angew. Chem.* **1968**, *80*, 910.

[8] For a preliminary communication of part of the results, see: Becker, H.-D.; Ruge, B. *Angew. Chem.* **1975**, *87*, 782. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 761.

[9] Becker, H.-D.; Ruge, B.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1979**, *32*, 1231.

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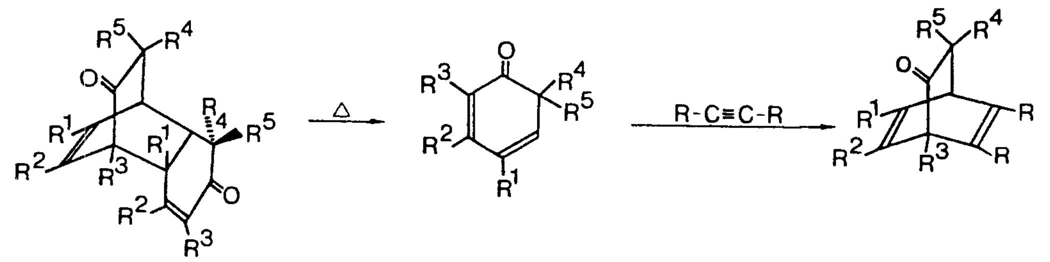
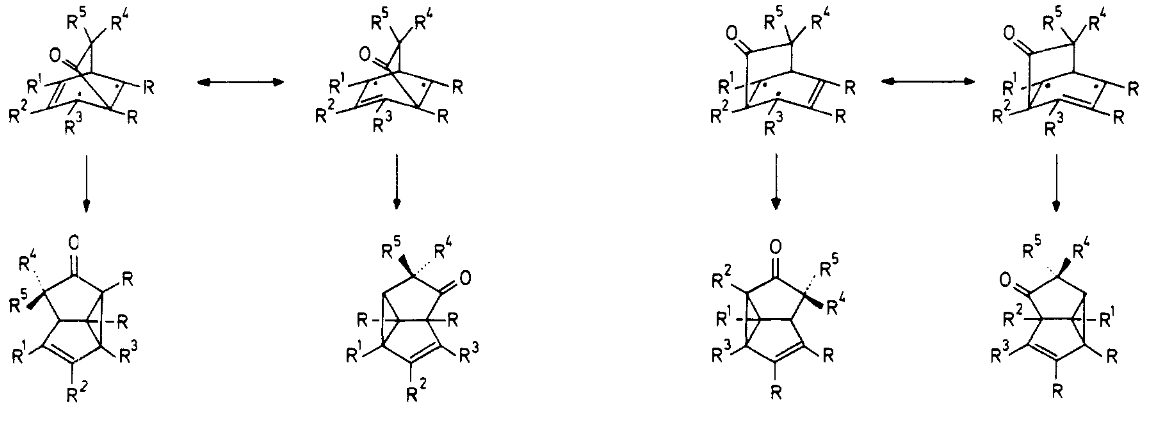


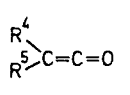
1a-i **2a-i** **3a-i**

1-3	R^1	R^2	R^3	R^4	R^5	R
a	CH_3	H	H	O—	CH_2	$COOCH_3$
b	t-butyl	H	H	O—	CH_2	$COOCH_3$
c	t-butyl	H	H	CH_2—	O	$COOCH_3$
d	CH_3	CH_3	H	O—	CH_2	$COOCH_3$
e	H	H	CH_3	O—	CH_2	$COOCH_3$
f	H	H	CH_3	OH	CH_3	$COOCH_3$
g	CH_3	H	CH_3	O—	CH_2	$COOCH_3$
h	CH_3	H	CH_3	OH	CH_3	$COOCH_3$
i	t-butyl	H	CH_3	O—	CH_2	$COOCH_3$

Scheme I. Conceivable Oxa-di-π-methane Rearrangement Products 9–12 and Their Diradical Precursors

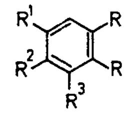


9 **10** **11** **12**

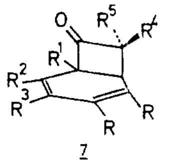

$R^4R^5C{=}C{=}O$

4: R^4-R^5 = O-CH_2

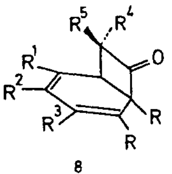
5: R^4 = OH; R^5 = CH_3



6



7



8

isomers **3b** and **3c**, so we do not know to what extent the oxygen of R^4 affects the absorption enhancement. In order to assess the degree of absorption enhancement in bicyclooctadienones **3**, we prepared in the case of **3f** the correspondingly substituted bicyclooctanone **17f** as well as the two bicyclooctenones **22** and **25**. As summarized in Table III, compared to the n–π* absorption of the saturated ketone, the enhancement in **3f** is considerable. Remarkably, however, the enhancement in the case of bicyclooctenone **22** was found to exceed that of bicyclooctadienone **3f**. According to the X-ray structure analyses of **3f**, **22**, and **25**, there are no significant differences detectable in the geometry of the β,γ-unsaturated carbonyl moieties.[10] We believe, therefore, that the decrease in the n–π* absorption enhancement in **3f** compared to that of **22**, in conjunction with the noticeable bathochromic shift of the π–π* absorption, is indicative of homodiene interaction.

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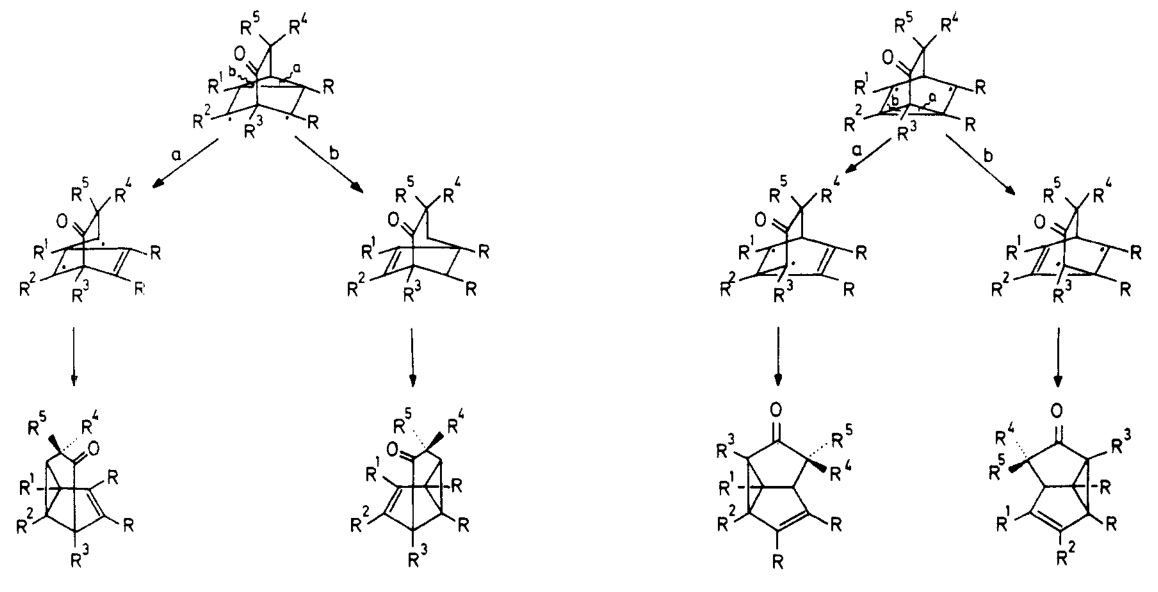
[10] Becker, H.-D.; Ruge, B.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1979**, *32*, 1687.

Scheme II. Conceivable Di-π-methane Rearrangements of 3



13 14 15 16

Table I. ^{1}H NMR Spectral Data (δ) of Bicyclooctadienones 3a–i[a]

compd	R^1	R^2	R^3	R^4	R^5	H	R
a	2.05 (d, 1.5 Hz)	6.24 (m)	4.45 (d, 6 Hz)		3.01 (d, 5.5 Hz), 3.07 (d, 5.5 Hz)	3.56 (d, 2 Hz)	3.85 (s)
b	1.13 (s)	6.23 (dd, 6 and 2.5 Hz)	4.52 (d, 6 Hz)		AB centered at 3.03 (5.5 Hz)	~3.85[c]	3.86 (s)
c	1.13 (s)	6.23 (dd, 6 and 2.5 Hz)	4.52 (d, 6 Hz)	AB centered at 3.03 (5.5 Hz)		~3.85[c]	3.86 (s)
d	1.92 (s)		4.27 (s)		3.00 (d, 5 Hz), 3.10 (d, 5 Hz)	3.48 (s)	3.84 (s)
e	6.80 ("t", 7 Hz)	6.31 (dd, 7 and 1.7 Hz)	1.58 (s)		2.96 (d, 5.5 Hz), 3.10 (d, 5.5 Hz)	4.00 (dd, 7 and 1.7 Hz)	3.82 (s), 3.87 (s)
f	6.60 ("t", ~7 Hz)	6.10 (dd, 7.2 and 1.8 Hz)	1.50 (s)[b]	2.9 (br s)	1.37 (s)[b]	4.38 (dd, 7 and 1.8 Hz)	3.79 (s), 3.83 (s)
g	2.02 (d, 1.7 Hz)	5.80 (m)	1.50 (s)		3.02 (d, 6 Hz), 3.10 (d, 6 Hz)	3.70 (d, 2.2 Hz)	3.81 (s), 3.86 (s)
h	2.05 (d, 1.8 Hz)	5.74 (m)	1.47 (s)[b]	2.9 (br s)	1.39 (s)[b]	4.15 (d, 2.5 Hz)	3.87 (s), 3.91 (s)
i	1.12 (s)	5.82 (d, 2 Hz)	1.55 (s)		2.99 (d, 5.5 Hz), 3.15 (d, 5.5 Hz)	4.05 (d, 2 Hz)	3.86 (s), 3.89 (s)

[a] The integrations are consistent with the number of protons in the proposed structures. Values in parentheses are multiplicities and coupling constants, *J*. [b] Uncertain assignment. [c] Signal partly hidden under other peaks.

Table II. Ultraviolet Spectral Data of 3 in Ethanol Solution

compd	λ_{max}, nm (ε)				
a	330 (230, sh)	313 (390)	306 (395)	245 (3700, sh)	227 (4500, sh)
b,c	325 (250, sh)	310 (385)		250 (3340, sh)	225 (4500, sh)
d	330 (365, sh)	313 (575)	306 (570)	239 (4900)	
e	326 (275, sh)	314 (405)	305 (390, sh)	240 (4200, sh)	
f	327 (250, sh)	312 (380)	305 (380)	243 (3250)	225 (4000, sh)
g	328 (310, sh)	315 (440)	305 (400, sh)	244 (4750, sh)	232 (5200)
h	325 (320, sh)	312 (420)		245 (3800, sh)	222 (5500, sh)
i	325 (340, sh)	314 (470)	305 (430, sh)	242 (4700, sh)	227 (5550, sh)

Table III. Comparison of n–π Carbonyl Absorption Enhancement in Bicyclic Ketones[a]

	17f	25	3f	22
ε	30	100	380	510
λ_{max}, (nm)	308	309	312	307

[a] In ethanol.

Direct Irradiations. Irradiation (high-pressure Hg lamp, Pyrex filter) of spirooxirano-substituted bicyclooctadienones such as **3d**, **3g**, and **3i** in chloroform containing 1–2% ethanol smoothly gave the corresponding dimethyl phthalates **6** by elimination of carbonyloxirane (**4**) which was characterized as ethyl glycidate. Likewise, direct irradiation of 3-hydroxy-3-methyl-substituted bicyclooctadienones **3f** and **3h** gave the dimethyl phthalates **6f** and **6h**, respectively, and the corresponding ketene **5**, trapped as ethyl lactate.

Sensitized Photoreactions. Irradiation of aceto-

Table IV. Infrared and Ultraviolet Spectral Data of Photoproducts 16

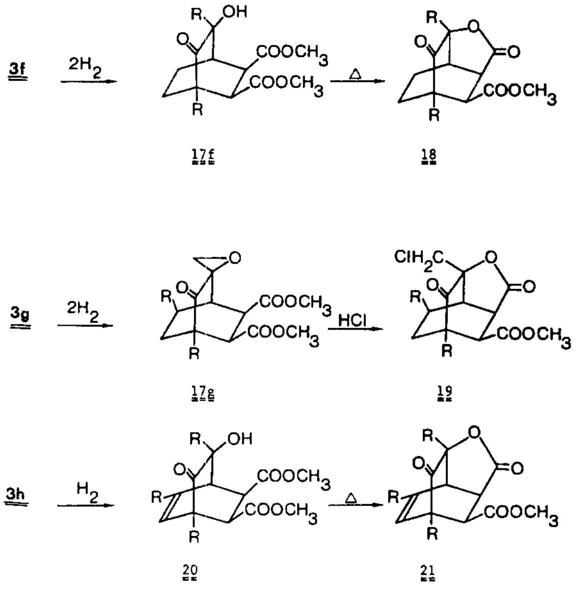
compd	$\bar{\nu}_{C=O}$, cm^{-1}	λ_{max}, nm (ϵ)			
a	1743, 1733, 1718 (s)	340 (sh, 25)	327 (sh, 50)	312 (sh, 60)	252 (sh, 520)
b	1757, 1730, 1720 (s)	340 (sh, 20)	327 (sh, 40)		250 (sh, 740)
c	1750 (br, s)			315 (sh, 50)	250 (sh, 770)
d	1750, 1735 (s)	341 (sh, 25)	326 (sh, 55)	313 (sh, 65)	258 (sh, 400)
e	1748, 1710 (s)	339 (sh, 30)	326 (sh, 60)	312 (sh, 70)	250 (sh, 580)
f	1733 (s)			310 (sh, 40)	245 (sh, 700)
g	1745, 1720 (s)	340 (sh, 30)	325 (sh, 70)	313 (sh, 90)	255 (sh, 485)
h	1745, 1725 (s)			310 (sh, 50)	250 (sh, 720)
i	1760, 1735 (s)	337 (sh, 30)	323 (sh, 65)	312 (sh, 85)	256 (sh, 530)

Table V. ^{1}H NMR Spectral Data of Photoproducts 16a-i[a]

compd	R^1	R^2	R^3	R^4	R^5	H	R
a	1.82 (m)	5.75 (q, 1.5 Hz)	3.72 (s)		3.09 (d, 5 Hz), 3.29 (d, 5 Hz)	3.54 (br s)	3.82 (s)
b	1.12 (s)	5.83 (s)	3.74 (s)[b]		3.25 (d, 4.5 Hz), 3.45 (d, 4.5 Hz)	3.75–3.85[b,c]	3.82 (s)
c	1.14 (s)	5.79 (s)	3.66 (s)[b]	2.99 (d, 6.5 Hz), 3.13 (d, 6.5 Hz)		3.75–3.90[b,c]	3.76 (s) 3.81 (s) 3.79 (s) 3.82 (s)
d	1.73 (d, ~1 Hz)	1.70 (s, 3)	3.62 (s)		3.09 (d, 5 Hz), 3.25 (d, 5 Hz)	3.53 (br s)	3.78 (s) 3.82 (s)
e	5.75 (dd, 5.3 and 2.5 Hz)	6.03 (d, 5.3 Hz)	1.67 (s)		2.92 (d, 5 Hz), 3.24 (d, 5 Hz)	3.67 (d, 2.5 Hz)	3.78 (s) 3.81 (s)
f	5.64 (dd, 5.5 and 2.5 Hz)	5.96 (d, 5.5 Hz)	1.68 (s)	2.93 (s)	1.17 (s)	~3.75 (d, 2.5 Hz?)[c]	3.76 (s) 3.81 (s)
g	1.79 (dd, 1.5 and 0.6 Hz)	5.61 (q, 1.5 Hz)	1.65 (s)		3.10 (d, 5 Hz), 3.34 (d, 5 Hz)	3.48 (br s)	3.77 (s) 3.80 (s)
h	1.82 (d, 1.5 Hz)	5.56 (q, 1.5 Hz)	1.66 (s)	2.94 (s)	1.23 (s)	3.49 (br s)	3.76 (s), 3.81 (s)
i	1.10 (s)	5.70 (d, 0.5 Hz)	1.64 (s)		3.23 (d, 4.3 Hz), 3.43 (d, 4.3 Hz)	3.70 (br s)	3.77 (s), 3.80 (s)

[a] The integrations are consistent with the number of protons in the proposed structures. Values in parentheses are multiplicities and coupling constants, *J*. [b] Uncertain assignment. [c] Signal partly hidden under other peaks.

Scheme III. Structure Elucidation of 3f–h by Intramolecular Transesterification (R = Methyl)



phenone solutions of bicyclooctadienones **3a–i** afforded, in each case, only one well-defined isomeric product. Out of the ten conceivable structures **7–16** discussed in Schemes I and II, eight (**7**, **8**, **10–15**) could be ruled out on the basis of the spectral data of the photoproducts summarized in Tables IV–V. However, a clear-cut distinction between the remaining two structures, namely, that of an oxa-di-π-methane rearrangement product **9** and that of di-π-methane rearrangement product **16**, was possible in favor of **16** only for the photoisomers derived from **3a–c**. Their substitution pattern, R^2 and R^3 being hydrogen, facilitated unambiguous analysis by ^{1}H NMR spectroscopy because, in contrast to the oxa-di-π-methane rearrangement of **3** leading to **9**, the di-π-methane rearrangement leading **16** is associated with a disruption of the 1,4-cyclohexadiene moiety in bicyclooctadienones between the R^2- and R^3-substituted carbons.

By X-ray analysis the photoproduct deriving from **3d** (R^2 = methyl, R^3 = H) was shown to have structure **16d**.[11] The remaining bicyclooctadienones (**3e–i**) undergoing photosensitized isomerization differ from **3a–d** insofar as their bridgehead substituent R^3 is a methyl group. However, experimental evidence available suggests that structure **16**, rather than **9**, also applies to the photoproducts derived from **3e–i**. In the case of the photoisomer derived from **3f**, the structure of the oxa-di-π-methane rearrangement product **9** was excluded as follows. Selective hydrogenation of **3f** gave the bicyclo[2.2.2]octenone **22** which was isomerized by an acetophenone-sensitized oxa-di-π-methane rearrangement. The resulting compound **23** was not identical with compound **24** which we prepared by hydrogenation of the product obtained in the acetophenone-sensitized isomerization of **3f**. Finally, the structure of the **3i** photoisomer was ascertained by X-ray analysis to be that of the di-π-methane rearrangement product **16i**.[9] Unambiguous structure determination was necessary in this case because thermolysis of the photoproduct derived from **3i** afforded an isomeric bicyclo[2.2.2]octadienone in which R^2 and R^3, unexpectedly, were adjacent substituents.[12]

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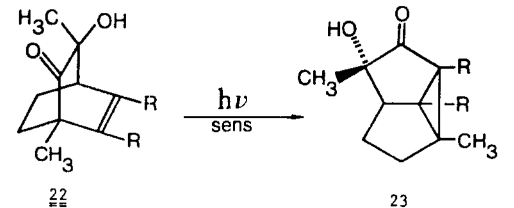
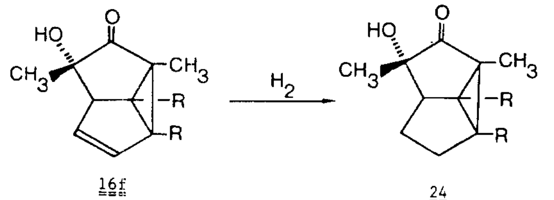
[11] Lindgren, O. *Acta Crystallogr., Sect. B* **1978**, *34*, 2638.

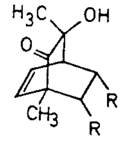
[12] The results of the thermolysis of **16i** are suggestive of the thermal reversibility of the di-π-methane rearrangement (cf. ref 9).



22 23



16f 24



25

Mechanism of Photoreactions. Under the experimental conditions of direct irradiation, the carbonyl chromophore in bicyclooctadienones **3** absorbs the light, so we presume the carbonyl n–π* excited singlet state to be involved in the observed fragmentation reaction. This assumption is in line with previous findings on excited-singlet-state reactions of β,γ-unsaturated ketones, i.e., intersystem crossing to the excited triplet state is an inefficient process. As to whether the fragmentation of **3** to give **4**/**5** and **6** actually proceeds by 1,3-acyl migration and intermediates **7** and/or **8** has not been investigated.

Concerning triplet-sensitized reactions of β,γ-unsaturated ketones, the oxa-di-π-methane rearrangement is the commonly encountered chemical deactivation path.[5] By contrast, we find that triplet-sensitized reaction of "β,γ-unsaturated bicyclooctenones" **3** gives rise to di-π-methane photochemistry leading to **16**. Consequently, we believe the excited triplet state of the homodiene moiety, energetically presumably resembling that of butadiene, to be the lowest lying excited state of **3**. In support of this conclusion, we find that the conversion of **3f** into **16f** (benzene solution, Pyrex filter) can also be sensitized by benzophenone, flavone, and Michler's ketone, having triplet energies of 69, 62, and 61 kcal/mol, respectively. With benzophenone as sensitizer, **16f** was formed with a quantum yield of 0.3. (By contrast, the oxa-di-π-methane rearrangement of benzobicyclo[2.2.2]octadienone cannot be sensitized by benzophenone.[4]) Neither benzil (E_T = 54 kcal/mol) nor β-acetonaphthone (E_T = 59 kcal/mol) sensitized the formation of **16f**, leaving **3f** unchanged. If energy transfer is assumed to be operative as the principal mode of sensitization, the lowest excited triplet energy of bicyclooctadienones, consequently, could be about 60 kcal/mol.

In order to explain the regiospecificity of the di-π-methane rearrangement of bicyclooctadienones **3**, we assume that the formation of the carbonyl-substituted cyclopropyldicarbinyl diradical leading to **15** and **16** is favored because of its stabilization by overlap of the carbonyl π orbitals with those of the cyclopropane bond orbitals.[13] By contrast, as pointed out by a referee, in diradical precursors of **13** and **14**, the carbonyl group will have a destabilizing effect. The formation of **16** rather than **15** may be rationalized by the regeneration of the olefinic double bond of higher energy. As to whether the substituents R, being methoxycarbonyl in the case of **3a–i**, may play a role in bringing about the described di-π-methane rearrangement of bicyclo[2.2.2]octadienones remains to be investigated.

Experimental Section

Melting points (uncorrected) were determined on a hot-stage microscope. Infrared spectra, in KBr disks, and electronic absorption spectra, in ethanol, were taken on Beckman IR9 and Beckman DK2 instruments, respectively. ^{1}H NMR spectra were obtained on a Varian A-60 spectrometer by using chloroform-*d* as solvent with Me_4Si as internal standard. Chemical shifts are reported in parts per million (δ). Catalytic hydrogenations were carried out in ethyl acetate with $Pd/CaCO_3$ catalyst. Elemental analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark.

General Procedure for Preparation of Bicyclo[2.2.2]octadienones 3a–i. Cyclohexadienones[1] (**2b**/**c**, **2i**) or cyclohexadienone dimers were heated in excess dimethyl acetylenedicarboxylate, the temperature (70–160 °C) and reaction time (5 min to 6 h) depending on the reactivity of the substrates.

Dimethyl 8′-Methyl-2′-oxospiro[oxirane-2,3′-bicyclo[2.2.2]octa[5,7]diene]-5′,6′-dicarboxylate (3a): yield 49%; mp 108–110 °C (from methylene chloride/petroleum ether). Anal. Calcd for $C_{14}H_{14}O_6$ (mol wt 278.26): C, 60.43; H, 5.07. Found: C, 60.52; H, 5.19.

Dimethyl 8′-*tert*-Butyl-2′-oxospiro[oxirane-2,3′-bicyclo[2.2.2]octa[5,7]diene]-5′,6′-dicarboxylate (3b,c): yield 81%; oil (distilled at 5 × 10^{-2} torr, bp ~125 °C). Anal. Calcd for $C_{17}H_{20}O_6$ (mol wt 320.35): C, 63.74; H, 6.29. Found: C, 63.70; H, 6.33.

Dimethyl 7′,8′-Dimethyl-2′-oxospiro[oxirane-2,3′-bicyclo[2.2.2]octa[5,7]diene]-5′,6′-dicarboxylate (3d): yield 50%; mp 148–151 °C (from methylene chloride/ether). Anal. Calcd for $C_{15}H_{16}O_6$ (mol wt 292.30): C, 61.64; H, 5.52. Found: C, 61.68; H, 5.63.

Dimethyl 1′-Methyl-2′-oxospiro[oxirane-2,3′-bicyclo[2.2.2]octa[5,7]diene]-5′,6′-dicarboxylate (3e): yield 53%; mp 110–112 °C (from methylene chloride/ether). Anal. Calcd for $C_{14}H_{14}O_6$ (mol wt 278.26): C, 60.43; H, 5.07. Found: 60.34; H, 5.08.

Dimethyl 1,3-Dimethyl-3-hydroxy-2-oxobicyclo[2.2.2]octa-5,6-diene-5,6-dicarboxylate (3f): yield 84%; mp 130–131 °C (from methylene chloride/*n*-hexane). Anal. Calcd for $C_{14}H_{16}O_6$ (mol wt 280.28): C, 59.99; H, 5.75. Found: C, 59.80; H, 5.75.

Dimethyl 1′,8′-Dimethyl-2′-oxospiro[oxirane-2,3′-bicyclo[2.2.2]octa[5,7]diene]-5′,6′-dicarboxylate (3g): yield 56%, mp 147–148 °C (from ethanol/hexane). Anal. Calcd for $C_{15}H_{16}O_6$ (mol wt 292.30): C, 61.64; H, 5.52. Found: C, 61.69; H, 5.61.

Dimethyl 1,3,8-Trimethyl-3-hydroxy-2-oxobicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate (3h): yield 62%; mp 140–141 °C (from methylene chloride/*n*-hexane). Anal. Calcd for $C_{15}H_{18}O_6$ (mol wt 294.31): C, 61.22; H, 6.16. Found: C, 61.02; H, 6.08.

Dimethyl 1′-Methyl-8′-*tert*-butyl-2′-oxospiro[oxirane-2,3′-bicyclo[2.2.2]octa[5,7]diene]-5′,6′-dicarboxylate (3i): yield 58%; mp 135–136 °C (from 2-propanol/hexane). Anal. Calcd for $C_{18}H_{22}O_6$ (mol wt 334.37): C, 64.66; H, 6.63. Found: C, 64.69; H, 6.62.

General Procedure for Photochemical Fragmentation of 3. Solutions of bicyclooctadienones **3d** and **3f–i** (2 g) in 175 mL of chloroform containing ethanol (about 1–2%) were irradiated through Pyrex for 1 h under nitrogen at 12–20 °C (450-W high-pressure Hg lamp). The solvent was then evaporated (rotary evaporator), and the residue was distilled in vacuo (0.01 mm). Ethyl glycidate (yield 66%), deriving from **4**, and ethyl lactate, deriving from **5**, were collected in a dry ice trap and redistilled before analysis. The ^{1}H NMR spectra of the substituted dimethyl phthalates are in agreement with the assigned structures.

Ethyl Glycidate: ^{1}H NMR δ 1.37 (t, *J* = 7 Hz, 3 H), 2.97 ("d", *J* = 3 Hz, 2 H), 3.45 ("t", *J* = 3 Hz, 1 H), 4.29 (q, *J* = 7 Hz, 2 H). With shift reagent Eu(fod)$_3$, the signals at 2.97 gave two

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[13] A similar argument has been used previously in the discussion of the photorearrangement of 5,6-benzo-2-azabicyclo[2.2.2]octa-5,7-dien-3-ones; see: Paquette, L. A.; Meisinger, R. H. *Tetrahedron Lett.* 1970, 1479.

double doublets (J = 6.4 and 4 Hz, 1 H, and J = 6.4 Hz and 2.5 Hz, 1 H) and the signal at 3.45 gave one double doublet (J = 4 Hz and 2.5 Hz, 1 H). IR 1750 cm^{-1} (s). Anal. Calcd for $C_5H_8O_3$ (mol wt 116.12): C, 51.72; H, 6.94. Found: C, 51.67; H, 6.98.

Ethyl Lactate: ^{1}H NMR δ 1.29 (t, J = 7 Hz, 3 H), 1.41 (d, J = 7 Hz, 3 H), 3.56 (s, 1 H), 4.25 (q, J = 7 Hz, 2 H), 4.30 (q, J = 7 Hz, 1 H).

Dimethyl 4,5-Dimethylphthalate (6d): yield 95%; mp 52–53 °C (from hexane) (lit.[14] mp 56 °C).

Dimethyl 3-Methylphthalate (6f): yield 60%; liquid. Anal. Calcd for $C_{11}H_{12}O_4$ (mol wt 208.17): C, 63.45; H, 5.81. Found: C, 63.17; H, 5.94.

Dimethyl 3,5-Dimethylphthalate (6g): yield 90%; mp 53–56 °C (from hexane) (lit.[15] mp 54 °C).

Dimethyl 3-Methyl-5-*tert*-butylphthalate (6i): yield 88%; mp 55–56 °C (from ethanol/water). Anal. Calcd for $C_{15}H_{20}O_4$ (mol wt 264.32): C, 68.16; H, 7.63. Found: C, 68.40; H, 7.71.

General Procedure for Acetophenone-Sensitized Rearrangement of 3a–i. Solutions of 3 (2 g) in acetophenone (175 mL) were irradiated through Pyrex for 1–2 h under nitrogen at 20 °C (450-W high-pressure Hg lamp). Acetophenone was distilled off in vacuo (0.01 mm). The photoproducts were isolated by column chromatography on silica gel (epoxy-substituted products: methylene chloride/ethyl acetate 9:1; hydroxy-substituted products: methylene chloride/methanol 95:5) and/or crystallization. Bicyclooctadienones 3b and 3c were inseparable and, therefore, irradiated as a mixtutre. The photoproducts 16b and 16c were separable by column chromatography.

Dimethyl 6′-Methyl-3′-oxospiro[oxirane-2,4′-tricyclo[3.3.0.0^{2,8}]oct[6]ene]-1′,8′-dicarboxylate (16a): yield 42%; mp 138–140 °C (from ethanol/hexane). Anal. Calcd for $C_{14}H_{14}O_6$ (mol wt 278.26): C, 60.43; H, 5.07. Found: C, 60.56; H, 5.19.

Dimethyl 6′-*tert*-Butyl-3′-oxospiro[oxirane-2,4′-tricyclo[3.3.0.0^{2,8}]oct[6]ene]-1′,8′-dicarboxylates (16b and 16c): yield 7%, mp 107–110 °C, and 9%, mp 108–109 °C (from ether petroleum ether). Anal. Calcd for $C_{17}H_{20}O_6$ (mol wt 320.35): C, 63.74; H, 6.29. Found: C, 63.93; H, 6.32; and C, 63.67; H, 6.30.

Dimethyl 6′,7′-Dimethyl-3′-oxospiro[oxirane-2,4′-tricyclo[3.3.0.0^{2,8}]oct[6]ene]-1′,8′-dicarboxylate (16d): yield 73%; mp 123–124 °C (from propanol). Anal. Calcd for $C_{15}H_{16}O_6$ (mol wt 292.29): C, 61.64; H, 5.52. Found: C, 61.59; H, 5.54.

Dimethyl 2′-Methyl-3′-oxospiro[oxirane-2,4′-tricyclo[3.3.0.0^{2,8}]oct[6]ene]-1′,8′-dicarboxylate (16e): yield 46%; mp 114–116 °C (from methylene chloride/hexane). Anal. Calcd for $C_{14}H_{14}O_6$ (mol wt 278.26): C, 60.43, H, 5.07. Found: C, 60.32; H, 5.19.

Dimethyl 2,4-Dimethyl-4-hydroxy-3-oxotricyclo[3.3.0.0^{2,8}]oct-6-ene-1,8-dicarboxylate (16f): yield 57%; mp 100–102 °C (from methylene chloride/petroleum ether). Anal. Calcd for $C_{14}H_{16}O_6$ (mol wt 280.28): C, 59.99; H, 5.75. Found: C, 59.88; H, 5.78.

Dimethyl 2′,6′-Dimethyl-3′-oxospiro[oxirane-2,4′-tricyclo[3.3.0.0^{2,8}]oct[6]ene]-1′,8′-dicarboxylate (16g): yield 53%; mp 130–131 °C (from methylene chloride/ether). Anal. Calcd for $C_{15}H_{16}O_6$ (mol wt 292.29): C, 61.64; H, 5.52. Found: C, 61.84; H, 5.64.

Dimethyl 2,4,6-Trimethyl-4-hydroxy-3-oxotricyclo[3.3.0.0^{2,8}]oct-6-ene-1,8-dicarboxylate (16h): yield 40%; mp 101–103 °C (from ether/petroleum ether). Anal. Calcd for $C_{15}H_{18}O_6$ (mol wt 294.31): C, 61.21; H, 6.17. Found: C, 61.42; H, 6.22.

Dimethyl 6′-*tert*-Butyl-2′-methyl-3′-oxospiro[oxirane-2,4′-tricyclo[3.3.0.0^{2,8}]oct[6]ene]-1′,8′-dicarboxylate (16i): yield 61%; mp 111–112 °C (from methylene chloride/petroleum ether). Anal. Calcd for $C_{18}H_{22}O_6$ (mol wt 334.37): C, 64.66; H, 6.63. Found: C, 64.52; H, 6.62.

Dimethyl 1,3-Dimethyl-3-hydroxy-2-oxobicyclo[2.2.2]octane-5,6-dicarboxylate (17f): obtained by hydrogenation of 3f; yield 88%; mp 130–133 °C; NMR δ 1.00 (s, 3 H), 1.37 (s, 3 H), 1.5–2.1 (m, 4 H), 2.8 (m, 1 H), 3.19 (s, 2 H), 3.71 (s, 3 H), 3.79 (s, 3 H), 4.77 (s, 1 H); IR 3410 (s), 1730 (s), 1692 cm^{-1} (s); UV (ϵ) 307 nm (30). Anal. Calcd for $C_{14}H_{20}O_6$ (mol wt 284.32): C, 59.14; H, 7.09. Found: C, 59.41; H, 7.11.

Dimethyl 1′,8′-Dimethyl-2′-oxospiro[oxirane-2,3′-bicyclo[2.2.2]octane]-5′,6′-dicarboxylate (17g): yield 37%; mp 145–146 °C (from methylene chloride/petroleum ether); NMR δ 1.09 (s, 3 H), 1.1–1.6 (m, 4 H), 1.9–2.5 (m, 3 H), 2.86 (d, AB, J = 7 Hz, 1 H), 3.25 (s, 2 H), 3.38 (d, AB, J = 7 Hz, 1 H), 3.66 (s 3 H), 3.71 (s, 3 H); IR 1750 cm^{-1} (s).

Methyl 1,6-Dimethyl-4,10-dioxo-5-oxatricyclo[4.3.1.0^{3,7}]decane-2-carboxylate (18): obtained by heating 17f to 150 °C for 10 min; yield 86%; mp 141–142 °C (from methylene chloride/ether); NMR δ 1.07 (s, 3 H), 1.56 (s, 3 H), 1.6–2.2 (m, 4 H), 2.77 (m, 1 H), 3.15 (s, 1 H), 3.20 (s, 1 H), 4.67 (s, 3 H); IR 1785 (s), 1740 cm^{-1} (s). Anal. Calcd for $C_{13}H_{16}O_5$ (mol wt 252.27): C, 61.89; H, 6.39. Found: C, 61.94; H, 6.42.

Methyl 1,8-Dimethyl-6-(chloromethyl)-4,10-dioxo-5-oxatricyclo[4.3.1.0^{3,7}]decane-2-carboxylate (19): obtained by refluxing 17g in methanol/HCl for 24 h; yield 78%; mp 202–204 °C (from chloroform/ether); NMR δ 1.09 (s, 3 H), 1.16 (d, J = 7 Hz, 3 H), 0.9–2.7 (m, 3 H), 3.18 (s, 3 H), 3.60 (d, 13.5 Hz, 1 H), 3.70 (s, 3 H), 4.44 (d, 13.5 Hz, 1 H); IR 1780 (s), 1742 cm^{-1} (s). Anal. Calcd for $C_{14}H_{17}O_5Cl$ (mol wt 300.74): C, 55.91; H, 5.70. Found: C, 55.94; H, 5.70.

Dimethyl 1,3,8-Trimethyl-3-hydroxy-2-oxobicyclo[2.2.2]oct-7-ene-5,6-dicarboxylate (20): yield 80%; mp 145–147 °C; NMR δ 1.22 (s, 3 H), 1.33 (s, 3 H), 1.92 (d, J = 1.5 Hz, 3 H), 3.05 (br s, 2 H), 3.32 (m, 1 H), 3.72 (s, 3 H), 3.81 (s, 3 H), 4.77 (s, 1 H), 5.36 (m, 1 H); IR 3430 (s), 1730 cm^{-1} (s). Anal. Calcd for $C_{15}H_{20}O_6$ (mol wt 296.33): C, 60.80; H, 6.80. Found: C, 60.91; H, 6.84.

Methyl 1,6,8-Trimethyl-4,10-dioxo-5-oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-2-carboxylate (21): obtained by refluxing 20 in ethanol for 30 min; mp 98–100 °C; NMR δ 1.27 (s, 3 H), 1.48 (s, 3 H), 1.93 (d, J = 1.5 Hz, 3 H), 2.7–3.4 (m, 3 H), 3.68 (s, 3 H), 5.7 (m, 1 H); IR 1785 (s), 1740 (s), 1650 (w) cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_5$ (mol wt 264.28): C, 63.62; H, 6.10. Found: C, 63.61; H, 6.12.

Dimethyl 1,3-Dimethyl-3-hydroxy-2-oxobicyclo[2.2.2]oct-5-ene-5,6-dicarboxylate (22): obtained by partial hydrogenation of 3f; yield 42%; mp 150–151 °C (from ethanol); NMR δ 1.26 (s, 3 H), 1.37 (s, 3 H), 1.4–2.1 (m, 4 H), 2.67 (br s, 1 H), 3.5 (m, 1 H), 3.80 (s, 3 H), 3.83 (s, 3 H); IR 3480 (s), 1728 (s), 1703 (s), 1627 cm^{-1} (m); UV (ϵ) 327 (sh, 315), 313 (505), 307 (510), 245 nm (3350). Anal. Calcd for $C_{14}H_{18}O_6$ (mol wt 282.30): C, 59.56; H, 6.43. Found: C, 59.44; H, 6.31.

Dimethyl 4,8-Dimethyl-4-hydroxy-3-oxotricyclo[3.3.0.0^{2,8}]octane-1,2-dicarboxylate (23): yield 37%; mp 93–96 °C (from chloroform/petroleum ether). Anal. Calcd for $C_{14}H_{18}O_6$ (mol wt 282.30): C, 59.56; H, 6.43. Found: C, 59.46; H, 6.42.

Dimethyl 2,4-Dimethyl-4-hydroxy-3-oxotricyclo[3.3.0.0^{2,8}]octane-1,8-dicarboxylate (24): yield 35%; mp 116–118 °C (from ether); NMR δ 1.18 (s, 3 H), 1.60 (s, 3 H), 1.3–2.7 (m, 5 H), 3.1 (m, 1 H), 3.74 (s, 3 H), 3.82 (s, 3 H); IR 3490 (s), 1725 cm^{-1} (s). Anal. Calcd for $C_{14}H_{18}O_6$ (mol wt 282.30): C, 59.56; H, 6.43. Found: C, 59.59; H, 6.44.

Dimethyl 1,3-Dimethyl-3-hydroxy-2-oxobicyclo[2.2.2]oct-5-ene-7,8-dicarboxylate (25). 1f (10 mmol) in dimethyl maleate (200 mmol) was refluxed for 15 min. Excess maleate was distilled off in vacuo; yield 83%; mp 119–121 °C (from methylene chloride/hexane); NMR δ 1.23 (s, 3 H), 1.33 (s, 3 H), 3.0 (br s, 1 H), 3.19 (dd, J = 11.3 and 1 Hz, 1 H), 3.30 (m, 1 H), 3.62 (s, 3 H), 3.66 (s, 3 H), 3.92 (dd, J = 11.3 and 2.2 Hz, 1 H), 5.86 (d, J = 8 Hz, 1 H), 6.67 (dd, J = 8 and 7 Hz, 1 H); IR 3530, 3470 (s), 1747 (s), 1725 (s), 1620 cm^{-1} (w); UV (ϵ) 309 nm (100). Anal. Calcd for $C_{14}H_{18}O_6$ (mol wt 282.30): C, 59.57; H, 6.43. Found: C, 59.32; H, 6.34.

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Registry No. 1a, 53543-55-8; **1d**, 55794-36-0; **1e**, 53543-52-5; **1f**, 35018-89-4; **1g**, 55822-28-1; **1h**, 35018-92-9; **2b**, 39117-94-7; **2c**, 39117-94-7; **2i**, 39117-93-6; **3a**, 73245-17-7; **3b**, 73245-73-5; **3c**, 73195-00-3; **3d**, 73245-18-8; **3e**, 73245-19-9; **3f**, 73245-20-2; **3g**,

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73245-21-3; **3h**, 73245-22-4; **3i**, 73245-23-5; **6d**, 17649-59-1; **6f**, 21483-46-5; **6g**, 50919-64-7; **6i**, 73195-01-4; **16a**, 73245-24-6; **16b**, 73195-02-5; **16c**, 73245-25-7; **16d**, 73245-26-8; **16e**, 73245-27-9; **16f**, 73245-28-0; **16g**, 73245-29-1; **16h**, 73245-30-4; **16i**, 73245-31-5; **17f**, 73195-03-6; **17g**, 73198-06-8; **18**, 73195-04-7; **19**, 73195-05-8; **20**, 73195-06-9; **21**, 73195-07-0; **22**, 73245-32-6; **23**, 73245-33-7; **24**, 73245-34-8; **25**, 73195-08-1; dimethyl acetylenedicarboxylate, 762-42-5; ethyl glycidate, 4660-80-4; ethyl lactate, 97-64-3.

Photodegradation of Some Alkyl *N*-Arylcarbamates[1]

John E. Herweh* and Charles E. Hoyle

Armstrong Cork Company, Research and Development Center, Lancaster, Pennsylvania 17604

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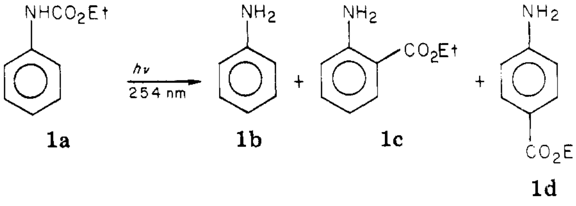
The UV photodegradation of a number of alkyl *N*-arylcarbamates in solution has been investigated. A mechanism for the photodegradation process is proposed. The initial excitation of the carbamate moiety involves a π,π^* transition into an excited singlet state. Chemical change from this excited state proceeds primarily via homolytic cleavage of the nitrogen to alkoxycarbonyl bond to provide a radical pair in a solvent cage. The quantum efficiency for carbamate disappearance is low. The major identifiable products are amines and photo-Fries rearrangement products (where formation is possible). The arylaminyl radical is proposed as a major reaction intermediate. It is suggested that the failure for the sum of quantum yields of formation for degradation products (amines and photo-Fries rearrangement products) to coincide with quantum yields for carbamate disappearance is due to reactions (e.g., coupling) of the aminyl radicals. The quantum yield for carbamate disappearance is independent of both methyl group substitution on the phenyl ring and excitation wavelength. In contrast, the quantum yield for the disappearance of the parent arylamine, a carbamate photodegradation product, does show dependence on these factors.

The photodegradation of urethanes based on aryl isocyanates has been the subject of a number of reports.[2-14] The earliest studies directed toward identification of the products formed were reported by Trecker et al.[2] and Bellus and Schaffner.[3] The latter found that irradiation of ethyl *N*-phenylcarbamate (**1a**) at 254 nm yielded ethyl *o*-aminobenzoate (**1c**), ethyl *p*-aminobenzoate (**1d**), and aniline (**1b**) (Scheme I). More recently, Beachell and Chang[4] also reported on the photodegradation of **1a**. In addition to products **1b**, **1c**, and **1d** they found CO_2. An intramolecular (concerted) rearrangement was proposed to account for the photo-Fries products (**1c** and **1d**).

Schwetlick and co-workers[5-10] confirmed the results of earlier workers with respect to the primary photodegradation products of **1a** in solution. They proposed, however, that the products were formed by N–C bond cleavage resulting in a solvent-caged radical pair. Within the solvent cage the ethoxycarbonyl radicals attacked the benzene ring at the ortho and para positions to give the reported photo-Fries products. Similarly, aniline was formed by diffusion of the anilinyl radical from the solvent cage followed by hydrogen abstraction. The existence of a cage effect was given credence when, upon photolysis of **1a** in the vapor phase, no photo-Fries products were detected.

Scheme I



Added support for a cage mechanism was obtained by Osawa et al.,[14] who reported ESR spectra as evidence for an anilinyl radical upon photolysis of the carbamate **1a**. Schwetlick et al.[8] determined the disappearance quantum yield of **1a** ($\Phi_D = 0.023$) and the quantum yield for formation of **1b** ($\Phi_{1b} = 0.009$), **1c** ($\Phi_{1c} = 0.008$), and **1d** ($\Phi_{1d} = 0.006$). The formation of **1b**, however, was not measured directly but was determined from the difference in the quantum yield of disappearance for **1a** and the sum of the quantum yields of formation for **1c** and **1d** [$\Phi_{1b} = \Phi_D(\mathbf{1a}) - (\Phi_{1d} + \Phi_{1c})$].

The current investigation is directed toward the photodegradation of simple urethanes **2a**–**5a** based upon aryl isocyanates bearing ring-substituted methyl groups. The effect of methyl-group ring placement on the photodegradation process and reaction products is of particular interest with respect to any analogies one may draw to the photodegradation of polymeric systems based on methyl phenylene diisocyanates.

Photolysis of carbamates **1a**–**5a** under a variety of conditions should yield interesting information concerning the

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