J. Org. Chem. 1981, 46, 5395–5398

(16′*R*,14′*R*, type B, $R_3 = C_2H_5$). Finally, no asymmetric induction from the vindoline could be detected as the dimeric compounds **9** and **12** were isolated in the same yield.

From a biogenetic point of view, this observation can be compared with the fact that the two series of dimeric compounds type A and type C that are isolated from *Catharanthus* species[13] probably arise from a common biogenetic pathway with antipodal pentacyclic ibogane alkaloids as precursors, although definitive proof of this point is lacking.

Interactions between compounds **9** and **12** and their receptor, tubulin,[15] have been tested in comparisom with vinblastine. Compound **9** showed an $I_{50}{}^{16} = 6 \times 10^{-6}$ M (vinblastine, $I_{50} = 2 \times 10^{-6}$ M) and $S_{50}{}^{16} = 4 \times 10^{-5}$ M (vinblastine, $S_{50} = 3 \times 10^{-5}$ M), while compound **12** was inactive.

These in vitro experiments must be completed by in vivo tests using L1210 and P-388 leukemias.

Experimental Section

Infrared spectra (ν cm^{-1}, $CHCl_3$) were recorded on a Perkin-Elmer 257, ultraviolet spectra [EtOH, λ_{max}, nm (ϵ)] on a Bausch and Lomb Spectronic 505, and CD curves (EtOH, λ_{max}, nm ($\Delta\epsilon$)] on a Roussel-Jouan Dichrograph II. ^{1}H NMR spectra were obtained ($CDCl_3$, Me_4Si, $\delta = 0$ ppm) on an IEF_{400} spectrometer (coupling constants, *J*, are given in hertz; s, d, t, dd, and m indicate singlet, doublet, triplet, doublet of doublets, and multiplet, respectively). Mass spectra were measured on an MS 50. Preparative layer chromatography (preparative TLC) was performed with Kieselgel HF 254 (Merck).

(±)-Deethylcatharanthine N_b-Oxide. *m*-Chloroperoxybenzoic acid (17 mg, 0.1 mmol) in CH_2Cl_2 (2.4 mL) was added at 0 °C to a stirred solution of (±)-20-deethylcatharanthine (**7** (20.0 mg, 0.065 mmol) under argon. After 10 min, the reaction mixture was poured into a saturated solution of Na_2CO_3 and the N_b-oxide was extracted with CH_2Cl_2 (90%): UV 223, 274, 283, 292; mass spectrum, *m/z* 324 ($M^{+\cdot}$), 307, 265, 226, 220, 218, 204, 194, 167; ^{1}H NMR 7.88 (1 H, N_a-H), 7.5–7.0 (4 H, aromatic), 6.57 (m, 2 H, C_{15}-H and C_{20}-H), 5.0 (1 H, d, $J_{20,21} = 5$, C_{21}-H), 3.74 (3 H, CO_2CH_3).

Coupling of (±)-Deethylcatharanthine N_b-Oxide with Vindoline at −78 °C. Trifluoroacetic anhydride (24 μL, 0.15 mmol) was added to a stirred solution of (±)-deethylcatharanthine N_b-oxide (**8**, 15.5 mg, 0.048 mmol) and vindoline (**2**; 24.8 mg, 0.054 mmol) in 0.3 mL of dichloromethane under argon at −78 °C. After 1 h, excess solvent and TFAA were distilled off in vacuo. The residue was dissolved in MeOH (1 mL) and excess $NaBH_4$ was added at 0 °C. After 30 min, the reaction mixture was poured into H_2O and extracted with $CHCl_3$. Preparative TLC ($CHCl_3$–MeOH, 9:1) of the residue afforded **9** (1.0 mg 2.7%), **10** (1.4 mg, 3.6%), and **11** (2.0 mg, 5.2%).

Compound 9: IR 1740, 1615; UV 218, 261, 288, 296; CD: 214 (−), 225 (+), 259 (+), 304 (+); mass spectrum 764, 733, 605, 497, 282, 136, 135, 122, 121, 107; ^{1}H NMR 8.05 (1 H, C_{16}-OH), 7.88 (1 H, $N_{a'}$-H, 7.5–7.0 (aromatic), 6.49 (1 H, s, C_9-H), 6.11 (1 H, s, C_{12}-H), 5.89 (3 H, C_{14}-H, C_{15}-H, and $C_{20'}$-H), 5.43 (1 H, s, C_{17}-H), 5.29 (1 H, C_{15}-H), 3.83 (3 H, s), 3.80 (3 H, s), 3.65 (3 H, s, C_{11}-OCH_3, C_{16}-CO_2CH_3, and $C_{16'}$-CO_2CH_3), 2.74 (3 H, s, N_a-CH_3), 2.11 (3 H, s, $OCOCH_3$), 0.79 (3 H, t, $J_{18,19} = 7$, C_{18}-H).

Compound 10: UV 218, 263, 288, 296; CD 214 (−), 227 (+), 260 (+); mass spectrum, 796, 765, 737, 637, 529, 469, 341, 282, 135, 122, 121, 107; ^{1}H NMR 7.98 (1 H, $N_{a'}$-H), 7.5–7.0 (aromatic), 6.48 (1 H, s, C_9-H), 6.07 (1 H, s, C_{12}-H), 5.84 (1 H, dd, $J_{14,15} = 9.4$ and $J_{3,14} = 4$, C_{14}-H), 5.41 (1 H, s, C_{17}-H), 5.3 (1 H, d, $J_{14,15} = 9.4$, C_{15}-H), 3.79 (3 H, s), 3.77 (3 H, s), 3.63 (3 H, s, C_{11}-OCH_3, C_{16}-CO_2CH_3, and $C_{16'}$-CO_2CH_3), 3.08 (3 H, s, OCH_3), 2.69 (3 H, s, N_a-CH_3), 2.10 (3 H, s, $OCOCH_3$), 0.79 (3 H, t, $J_{18,19} = 7$, C_{18}-H).

Compound 11: UV 222, 258, 292, 297; CD 222 (−), 258 (+), 304 (−); mass spectrum, 796, 765, 737, 637, 529, 469, 341, 282, 135, 122, 121, 107.

Coupling of (±)-Deethylcatharanthine N_b-Oxide with Vindoline at −20 °C. Trifluoroacetic anhydride (0.2 mmol) was added to a stirred solution of **8** (0.06 mmol) and **2** (0.063 mmol) in 0.3 mL of CH_2Cl_2 under argon at −20 °C. After 1 h excess solvent and TFAA were distilled off in vacuo. The residue was dissolved in THF (1 mL), excess $NaBH_4$ was added at 0 °C, and the mixture was stirred at 0 °C for 1 h. After the usual workup, the residue was dissolved in EtOH and the solution was heated under reflux for 1 h. The residue was purified by preparative TLC ($CHCl_3$–MeOH, 90:10) and gave 20′-deethylanhydrovinblastine (**9**, 16%) and compound **12** (16%).

Dimeric compound 12: IR 1740, 1615; UV 220, 257, 288, 296; CD 223 (−), 260 (+), 306 (−); mass spectrum, 764, 733, 705, 605, 497, 282, 135, 122, 121, 107; ^{1}H NMR 8.07 (1 H, $N_{a'}$-H), 7.5–7.0 (aromatic), 6.67 (1 H, s), 6.15 (1 H, s, C_9-H and C_{12}-H), 5.79 (3 H, m, C_{14}-H, $C_{15'}$-H, and $C_{20'}$-H), 5.46 (1 H, s, C_{17}-H), 5.23 (1 H, $J_{14,15} = 9.4$, C_{15}-H),3.81 (3 H, s), 3.80 (3 H, s), 3.56 (3 H, s, C_{11}-OCH_3, C_{16}-CO_2CH_3, and $C_{16'}$-CO_2CH_3), 2.73 (3 H, s, N_a-CH_3), 2.07 (3 H, s, $OCOCH_3$), 0.37 (3 H, t, $J_{18,19} = 7$, C_{18}-H).

Acknowledgment. We thank Dr. D. Guénard for the tubulin tests of compounds **9** and **12** and Dr. P. Potier for his continuous interest.

Registry No. 2, 2182-14-1; **7**, 74194-98-2; **8**, 79681-29-1; **9**, 79703-87-0; **10**, 79703-88-1; **11**, 79733-72-5; **12**, 79733-73-6.

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[15] F. Zavala, D. Guénard, and P. Potier, *Experientia*, **34**, 1498 (1978).

[16] I_{50}, concentration inducting 50% of the rate of inhibition of polymerization of tubulin. S_{50}, concentration inducing 50% of the maximum of spiralization of tubulin.

Photochemical Studies.[1] On the Photofragmentation of Substituted 1,2-Dihydrophthalic Anhydrides

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The irradiation-induced transformations of 4,5-diphenyl-1,2-dihydrophthalic anhydride (**2b**) as well as those of the 3,6-dimethyl-4,5-diphenyl and 3,4,5,6-tetraphenyl derivatives (**2c,d**) are elaborated. All undergo photofragmentation, viz., CO + CO_2 ejection to give aromatic hydrocarbons, while only **2b** also closes electrocyclically to the bicyclo[2.2.0]hex-5-ene product **5**. The quantum yields for fragmentation are indicative in this respect. The rearrangement accompanying the fragmentation of **2d** to give 1,2,3,5-tetraphenylbenzene (**11**) was shown to occur via a triplet excited state, populated by benzene sensitization.

We had discovered,[2] while working on the photodecarbonylation of substituted norbornen-7-ones (**1**), that the resulting 1,2-dihydrophthalic anhydrides (**2**) undergo a surprisingly facile extrusion of CO and CO_2 to give the

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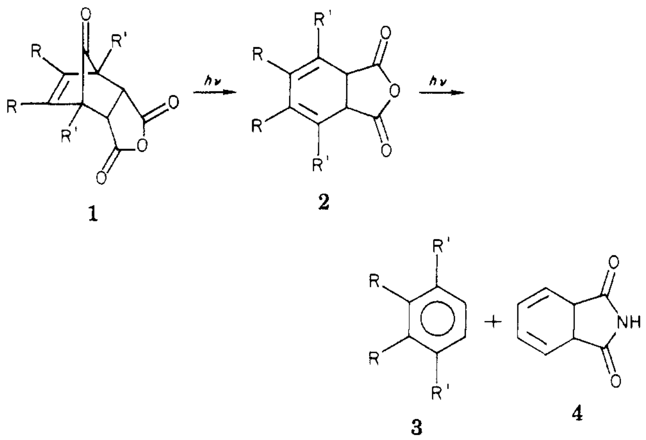
Scheme I[a]



[a] a, R = R' = H; b, R = Ph, R' = H; c, R = Ph, R' = Me; d, R = R' = Ph; e, R = 2,2'-biphenylylene, R' = Me.

Table I. Quantum Yields for Formation of Benzene Derivatives 3 by Photofragmentation of the Corresponding 1,2-Dihydrophthalic Anhydrides 2 or (in Parentheses) of Their Norbornen-7-one Precursors (1)[a]

	compd				
λ, nm	4[b]	2a[c]	2b	2c	2d
230	0.016	0.24 (0.05)	0.12 (0.01)	0.14	0.03 (0.008)
257	0.009	0.12 (0.07)	0.07 (0.03)	0.15 (0.02)	0.03 (0.006)
284	0.002	0.07	0.007	0.10	0.004

[a] The details of the procedures are given in the Experimental Section. [b] Values for comparison taken from ref 7. [c] Values for comparison taken from ref 6.

corresponding aromatic products (**3**; cf. Scheme I). This was, in fact, corroborated in other laboratories,[3,4] and other analogous systems were also found to behave similarly, while certain inconsistencies, e.g., as in the photolysis of 3,4,5,6-tetraphenyl-1,2-dihydrophthalic anhydride (**2d**),[2-4] were registered.

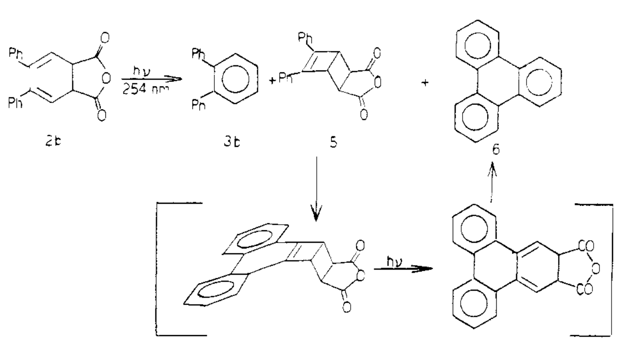
As a sequel to our recent detailed study of unsubstituted 1,2-dihydrophthalic anhydride,[6] we decided to investigate in detail the photochemical behavior of the substituted derivatives (**2b–d**). This was justified by the subsequent findings as described below.

Results and Discussion

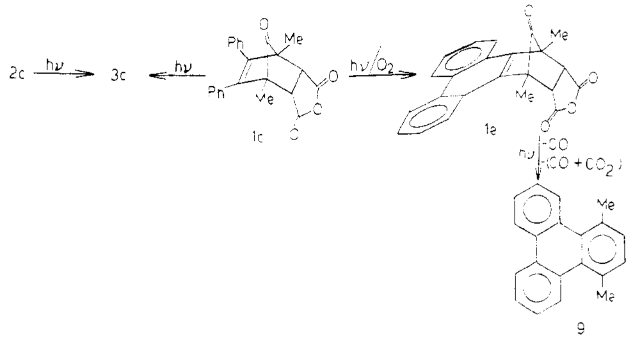
The anhydrides **2b–d** were irradiated in acetonitrile solution at three wavelengths in two modes, viz., preparatively and in analytical runs at low conversion. The latter served for quantum yield determination, the results of which are given in Table I, for aromatic hydrocarbon formation by photofragmentation of the 1,2-dihydrophthalic anhydrides or of their norbornen-7-one precursors (**1**).

At once we see that the efficiency of photofragmentation drops sharply around 300 nm, and this is matched by a drastic reduction in chemical yield as has, in fact, also been observed in case of the unsubstituted 1,2-dihydrophthalic anhydride[6] (**3a**) as well as for its imide analogue (**4**).[7] This is understandable in view of the involvement of n,π^* excited singlet states in the process.[5-7] For nonconjugated carboxylic acid derivatives these are high-energy excited states, uniformly below 280 nm.

Scheme II

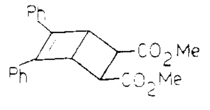


Scheme III

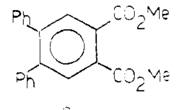


Careful examination of the data in Table I reveals another interesting feature: in contrast to **2c** and **2d** which undergo photofragmentation at 230 and 257 nm with practically the same quantum yields, **2b** shows a ratio of nearly 2 for ϕ_{230}/ϕ_{257}, in striking similarity to the photochemical behavior of **2a**[6] and **4**.[7] Hence, we decided to look for competing photochemical processes by investigating the irradiation of **2b** at 254 nm using ^{1}H NMR monitoring techniques. We were thus able to see the *concurrent* formation of *o*-terphenyl (**3b**) by CO + CO_2 loss and of *anti*-5,6-diphenylbicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic anhydride (**5**) by electrocyclic closure of the diene in **2b** (cf. Scheme II). The anti geometry was assigned to **5** on the strength of the arguments used for the unsubstituted anhydride[6] and imide[7] analogues.

Since the electrocyclic process is reversible, the yield of **5** diminishes with increasing conversion, and optimization of preparative runs demands careful monitoring of the extent of reaction. Furthermore, the isolation of **5** is tedious (in presence of starting material **2b**), and we preferred to characterize it by converting it to the diester **7** side by side with **8** (which means that **2b** underwent dehydrogenation prior to or along with the esterification step; eq 1).



7



8

$$5 \xrightarrow{H^+/MeOH} 7 \text{ and } 2b \xrightarrow{O_2,\ H^+/MeOH} 8 \qquad (1)$$

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[1] (a) Part 22. (b) Part 21: Fuchs, B.; Pasternak, M. *Tetrahedron* **1981**, *37*, 2501.

[2] Fuchs, B. *J. Chem. Soc. C* **1968**, 68. Cf. also: *Isr. J. Chem.* **1965**, *3*, 44.

[3] Warrener, R. N.; Bremner, J. B. *Tetrahedron Lett.* **1966**, 4265.

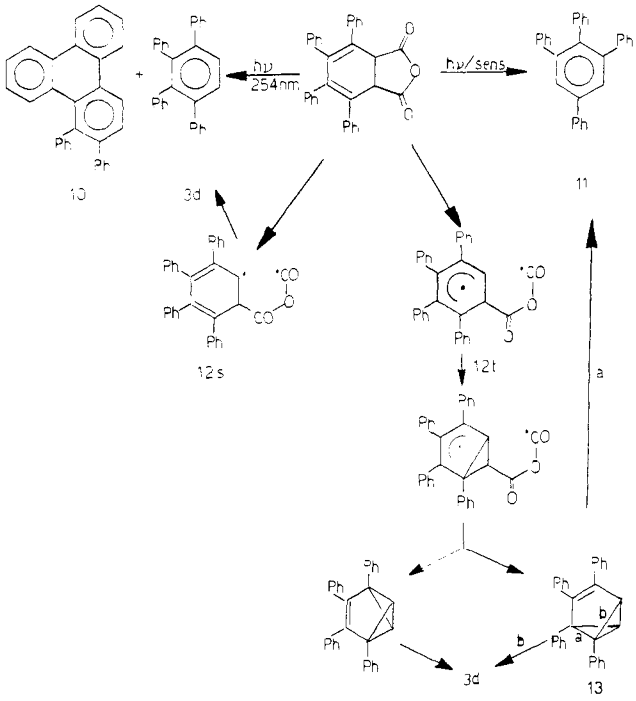
[4] Kitzing, R.; Prinzbach, H. *Helv. Chim. Acta* **1970**, *53*, 158. Cf. also: Prinzbach, H.; Kitzing, R.; Druckrey, E.; Achenbach, H. *Tetrahedron Lett.* **1966**, 4265.

[5] Zweig, A.; Huffman, K. R.; Gallivan, J. B.; Orloff, M. K.; Halverson, F. *J. Am. Chem. Soc.* **1974**, *96*, 1449.

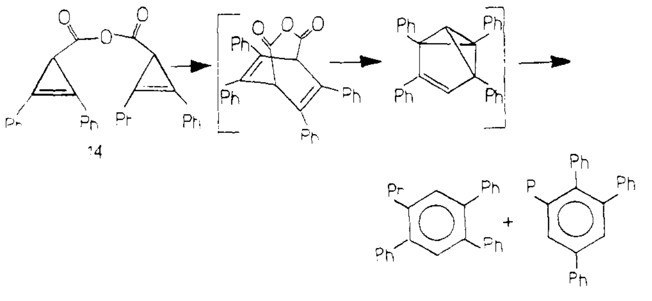
[6] Fuchs, B.; Scharf, G. *Isr. J. Chem.* **1977**, *16*, 335.

[7] Fuchs, B.; Scharf, G. *J. Org. Chem.* **1979**, *44*, 604.

Scheme IV



Scheme V[12]



In addition to *o*-terphenyl (**3b**) the aromatic hydrocarbon fraction in the chromatographic workup of the irradiation mixture of **2b** shows small amounts (up to 1%) of triphenylene **6**. Since we were able to show that **6** is not an irradiation artifact from **3b**, we are compelled to attribute its formation to the closure of the *cis*-stilbene moiety in **5**[8] as outlined in Scheme II. It is worth mentioning that **6** is isolated in similarly small yields along with **3b** in preparative irradiations of **1b** at 254 nm.

Turning to the diphenyldimethyl derivative **2c**, its irradiation is indeed the most efficient (cf. Table I and Scheme III), giving **3c** in 97% yield at all wavelengths below 300 nm.[2-4] It does not undergo electrocyclic closure at any wavelength and shows no dimethyltriphenylene (**9**) formation. Understandably, however, the latter is isolated in small yields (ca. 2%) in the irradiation of **1c**. This is readily explained by the intermediate formation and then double photofragmentation of 5,6-(2,2′-biphenylylene)-1,4-dimethylnorbornen-7-one-2,3-dicarboxylic anhydride (**1e**). An authentic sample of the latter was secured[1b,9] and irradiated, whereby dimethyltriphenylene (**9**) was indeed obtained as indicated (Scheme III).

The last but not least interesting item in this series is the photochemistry of 3,4,5,6-tetraphenyl-1,2-dihydrophthalic anhydride (**2d**). Earlier work performed in our[2] and other[3,4] laboratories provided, as it turns out, only partial answers. Thus we[2] and Prinzbach[3] obtained by irradiation of **2d** only 1,2,3,4-tetraphenylbenzene (**3d**) whereas Warrener reported[4] the formation of 1,2,3,5-tetraphenylbenzene (**11**). We can now draw a detailed picture of what is really happening: irradiation of **2d** in acetonitrile causes ejection of CO + CO$_2$ to give an aromatic product in low quantum yield but good chemical yield, both of which diminish with increasing wavelength until this product is reduced to traces at or above 300 nm. The low-efficiency photodecomposition at low wavelength, e.g., 100 h at 254 nm, yields, however, *two* aromatic hydrocarbons, 1,2,3,4-tetraphenylbenzene (**3d**, 60%) and 1,2-diphenyltriphenylene (**10**, 9%). The latter is evidently another case of stilbene–phenanthrene closure in **2d** prior to CO + CO$_2$ expulsion[8] (see Scheme IV).

A careful analysis showed only minute amounts of 1,2,3,5-tetraphenylbenzene (**11**) in the 254-nm irradiation in acetonitrile. When, however, benzene was used as the solvent, as Warrener did[3] but with largely monochromatic irradiation, **11** constituted 10% of the aromatic product obtained at 254 nm and 94% of it at 350 nm (cf. Experimental Section) with a quantum yield ϕ_{350} (benzene) $\approx 10^{-5}$. Irradiation at 300 nm in acetone failed to cause any decomposition of **2d**.

There are two main issues to be concerned with in an interpretative discussion of these results. The excited state involved in the rearrangement mechanism by which **11** is obtained is one of them. Concerning the excited state, the n,π^* singlet state is apparently involved in the regular photofragmentation of all **2** derivatives,[5-7] including **2d**. We think that no concerted (CO + CO$_2$) formation is likely, and the only way to envisage such a (low quantum yield) fragmentation is by starting with α cleavage of **2** through a diradical species, **12**.

The formation of 1,2,3,5-tetraphenylbenzene (**11**), however, seems to occur via a triplet state populated only by sensitization with benzene. Interestingly, it appears that this is attained by irradiation of benzene into the spectroscopic (forbidden) $S_0 \rightarrow T_1$ transition and not by the intersystem crossing route, $S_1 \rightarrow T_1$. The latter may well be to slow and inefficient[10] to compete with the singlet S_1 state for a fast energy transfer to **2d**. This could trigger the α cleavage to give the same *singlet* diradical species (**12s**) as the one attained by direct irradiation (vide supra), which quickly decomposes with little chance to rearrange. The spectroscopic triplet of benzene, poorly populated as it may be,[10] is still bound to transfer energy to a triplet state of **2d**, to be followed by α cleavage to a *triplet* diradical (**12t**). The latter should then be sluggish enough to allow rearrangement prior to fragmentation, as put forward in Scheme IV,[11] and after fragmentation with formation of the substituted benzvalene **13**.

Alternatively,[16] one may invoke a weak ground-state DA complex[17] between benzene and the anhydride (**2d**) as the responsible absorbing species for formation of the triplet excited **2d** which leads eventually via **13** to **11**.

The preferred path of aromatization of **13** is understandably started by cleavage of bond "a". This rearrangement, as observed in the process **2d** → **11**, gains in verisimilitude from the occurrence of a rather similar rearrangement in a somewhat related photochemical sequence of events starting with **14** (Scheme V).[12]

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(8) Muszkat, A. K. *Top. Curr. Chem.* **1980**, *88*, 99.

(9) Fuchs, B.; Pasternak, M.; Scharf, G. *J. Chem. Soc., Chem. Commun.* **1976**, 53.

(10) Cundall, R. B.; Ogilvie, S. M. In "Organic Molecular Photophysics"; Birks, J. B., Ed.; Wiley: London, 1975; Vol. 2, Chapter 2.

(11) The proposed rearrangement scheme is inherently different from that proposed by Warrener and Bremner[3] both by its mechanism and the key intermediate (**13**).

We hope that in due time, this interesting behavior will be better understood and our interpretation further substantiated by results of flash-photolytical measurements.

Finally, a word about the fact that electrocyclic closure was observed only in **2b** and not at all in **2c**,**d**. We attribute this behavior to the strong steric strain experienced by a cyclobutene tetrasubstituted on the saturated carbons. Indeed, this is related to the cis effect in the mode of opening of cyclobutenes[13] and should account for the reluctance of **2c**,**d** to close in contrast to **2b**.

Experimental Section

Melting points are uncorrected. IR spectra were taken in KBr pellets unless otherwise specified. UV spectra were taken on a Cary 17 or Cary 219 spectrophotometer in 1,4-dioxane, unless otherwise specified. NMR spectra were measured on JEOL JNM-C-60 HL and Brucker WH-90 spectrometers in $CDCl_3$ solutions with Me_4Si as an internal standard, unless otherwise specified. Mass spectra were measured on a Du Pont 21-491B mass spectrometer.

Irradiations on a preparative scale were performed in Rayonet photoreactors fitted with lamps emitting at 254, 300, or 350 nm or by using a medium-pressure Hanovia 679A-36 Hg immersion lamp. Quartz or Pyrex vessels were used according to the wavelength range needed. Solutions were swept prior to irradiations with oxygen-free nitrogen or argon. Irradiations on analytical scales for quantum yield determinations were performed on a JASCO CRM-FA Spectro-Irradiator equipped with an electronic integrator. The latter was periodically calibrated by potassium ferrioxalate actinometry.

GLC analyses were performed either on a Varian 1800 gas chromatograph equipped with 3% SE-30 (1.5 m × 0.25 in.) or Carbowax 20M (1.5 m × 0.25 in.) columns or on a Packard 427 gas chromatograph equipped with a capillary column (SE-30, 25 m) and a Spectraphysics System I electronic integrator.

Preparative Work. The norbornen-7-one and dihydrophthalic anhydrides (**1** and **2**, respectively) were prepared according to literature procedures, as follows: **1b** and **2b**,[3] **1c** and **2c**,[14] **1d** and **2d**,[15] and **1e**.[1,4]

Photochemical Work. Chemical and quantum yields of formation of the aromatic hydrocarbons **3** were determined by suitable irradiation followed by passing the solution through a short column of basic alumina. Only the aromatic hydrocarbons were eluted and determined by gas chromatography or by quantitative isolation using chromatographic resolution on neutral alumina. Quantum yields are given in Table I (see text). Chemical yields were as shown in eq 2–7.

Table II. Total and Relative Yields in Various Solvents at Particular Wavelengths

		MeCN		C_6H_6		
		254 nm	300/350 nm	254 nm	350 nm	Me_2CO, 300 nm
tot yield, %		69	traces	90	16	traces
rel yield, %	**3d**	89	traces	89	6	traces
	11	3	traces	11	94	none
	10	8	none	traces	traces	none

$$\mathbf{2b} \xrightarrow{254\text{ nm}} \mathbf{3b}\ (42\%) + \mathbf{5}\ (\text{see below}) + \mathbf{6}\ (0.2\%) \tag{2}$$

$$\mathbf{2c} \xrightarrow{254\text{ nm}} \mathbf{3c}\ (97\%) \tag{3}$$

$$\mathbf{1b} \xrightarrow{254\text{ nm}} \mathbf{3b}\ (30\%) + \mathbf{6}\ (0.6\%) \tag{4}$$

$$\mathbf{1c} \xrightarrow{254\text{ nm}} \mathbf{3c}\ (46\%) + \mathbf{9}\ (0.5\%) \tag{5}$$

$$\mathbf{1e} \xrightarrow{254\text{ nm}} \mathbf{9}\ (40\%) \tag{6}$$

$$\mathbf{1c} \xrightarrow{254\text{ nm}} \mathbf{3c}\ (70\%) + \mathbf{9}\ (2.2\%) \tag{7}$$

4,5-Diphenyl-1,2-dihydrophthalic anhydride (**2a**) was also irradiated in acetonitrile-d_3 solution (ca. 5%) in a quartz NMR tube at 254 nm. The formation of *trans*-5,6-diphenylbicyclo[2.2.0]-hex-5-ene-2,3-dicarboxylic anhydride (**5**) was followed by ^1H NMR spectrometry, scrutinizing the H_1,H_4 and H_2,H_3 proton-pairs at δ 3.60 and 3.95, respectively. Eventually, the mixture was added to methanol containing a trace of H_2SO_4 and left overnight. Evaporation and chromatography on basic alumina provided, after elution of the hydrocarbon fraction, the corresponding dimethyl ester (**7**): 13.5% yield; mp 116–118 °C (ether); IR ν_{max} 1735, 1720 (CO) cm^{-1}; NMR δ 3.45 (d, 2 H), 3.85 (s, 6 H), 4.0 (d, 2 H), 7.2–7.8 (m, 10 H); mass spectrum, m/z 348 (M^+).

3,4,5,6-Tetraphenyl-1,2-dihydrophthalic anhydride (**2c**) was also irradiated in parallel experiments in 6×10^{-3} M solutions under various conditions (see Table II), and the hydrocarbon products were analyzed by gas chromatography (capillary column, SE-30, 220 °C, flow rate 100 mL/min; T_R (**3d**) = 1480 s, T_R (**11**) = 2500 s). The results were as shown in Table II.

Acknowledgment. Mrs. Sarah Weinman provided valuable technical assistance.

Registry No. 1b, 79465-36-4; **1c**, 79465-37-5; **1d**, 62117-02-6; **1e**, 59274-03-2; **2b**, 18636-39-0; **2c**, 34835-61-5; **2d**, 6971-41-1; **3b**, 84-15-1; **3c**, 13102-23-3; **3d**, 1487-12-3; **5**, 79421-22-0; **10**, 79421-23-1; **11**, 912-61-8.

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(12) Hoyt, E. B.; Reineberg, E. J.; Goodman, P.; Vaughan, P.; Georgian, V. *Tetrahedron Lett.* **1972**, 1579.

(13) Kaupp, G. *Angew. Chem.* **1974**, *86*, 741.

(14) Allen, C. F. H.; VanAllan, J. A. *J. Am. Chem. Soc.* **1942**, *64*, 1261.

(15) Allen, C. F. H.; Sheps, L. J. *Can. J. Chem.* **1934**, *11*, 171.

(16) We thank a referee for pointing this possibility out to us.

(17) Birks, J. B., in ref 10, p 517.