Reaction of Phenyl-Substituted *o*-Quinodimethanes with Nitric Oxide. Are Benzocyclobutenes Suitable Precursors for Nitric Oxide Cheletropic Traps?

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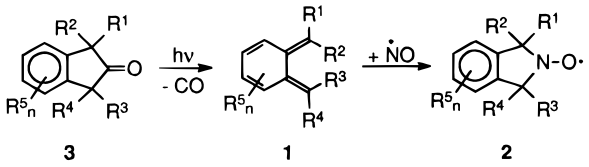
In order to elucidate the potential of substituted *o*-quinodimethanes as reagents for the trapping of nitric oxide (NO) in biological systems, the reaction of alkoxyl- and alkyl-substituted 7,8-diphenyl- and 7,7,8-triphenyl-*o*-quinodimethanes with nitric oxide in solution was investigated by ESR spectroscopic and UV/vis stopped-flow techniques. Photolytic decarbonylation of 1,3-diphenyl- and 1,1,3-triphenylindan-2-ones gave the corresponding phenyl-substituted benzocyclobutenes as the major products and low photostationary concentrations of *o*-quinodimethanes. During 266-nm laser flash photolysis (LFP) of 1,3-dimethoxy-1,3-diphenylindan-2-one and 1-methoxy-1,3,3-triphenylindan-2-one in acetonitrile, species absorbing in the 400−600 nm range were produced, which were attributed to configurational isomers of the corresponding 7,7,8,8-substituted *o*-quinodimethanes. The isomeric *o*-quinodimethanes decayed at significantly different rates, indicating a strong influence of the relative orientation of the terminal substituents on their stability. Reaction of the raw photolysates of the 2-indanones with NO produced strong ESR spectra of the corresponding cyclic nitroxide radicals, isoindolin-2-oxyls. The nitroxide radicals were generated in a two-phase process, the first, rapid phase being attributed to the reaction of NO with the photolytically formed *o*-quinodimethanes and the second, slow phase reflecting the reaction with small amounts of *o*-quinodimethanes, generated by thermal ring opening of the phenyl-substituted benzocyclobutenes and probably a direct reaction of NO with the benzocyclobutenes. The kinetics of both steps, as evaluated by stopped-flow UV/vis and ESR spectroscopy, revealed a strong dependence of the rate constants of the *o*-quinodimethane + NO reaction on the substitution pattern of the *o*-quinodimethanes, with rate constants spanning a range of 10−4000 M^{-1} s^{-1}. The rate constants ((0.4−7.5) × 10^{-4} s^{-1}) for the reaction of NO with the 7,7,8,8-tetrasubstituted benzocyclobutenes are much less influenced by the substitution pattern. The utility of phenyl-substituted benzocyclobutenes as "reservoirs" for *o*-quinodimethane-type nitric oxide traps is discussed.

Introduction

During the past decade, nitric oxide, NO, has emerged as an important signal molecule in living organisms, involved, for example, in the regulation of vascular tone, acting as a messenger in the central nervous system and as mediator in the immune system.[1] For the monitoring and quantitation of NO formation in biological systems a number of physicochemical and biochemical analytical methods have been developed.[2] Unfortunately, none of these methods fulfills the desirable requirements for general use with the variety of biological specimens, *viz.* specifity for NO, high sensitivity, tolerance for the various physiological conditions, easy structural modification, and the potential to monitor NO formation with temporal and spacial resolution. In order to overcome at least some of these obstacles, we[3−5] recently have begun to develop an alternative method, based on the reaction of NO with *o*-quinodimethane derivatives **1**, to yield persistent, cyclic nitroxide radicals **2**, reaction 1, which can easily be detected and quantitated by ESR spectroscopy.



3 **1** **2** (1)

Among the series of our so-called "nitric oxide cheletropic traps" (NOCTs),[6] the prototypal tetramethyl derivative NOCT-1[3] and the trimethylindenyl derivative NOCT-4[4] have been sucessfully applied in the trapping of NO from cultured macrophages under physiological conditions. Further, nonbiological applications of NOCTs included the trapping of NO produced from NO-releasing

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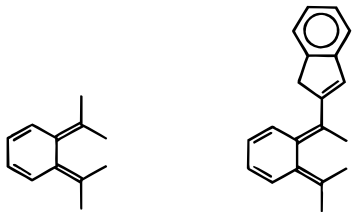
compounds (nitrovasodilators)[8,9] and in photochemical reactions.[10]



NOCT-1 **NOCT-4**

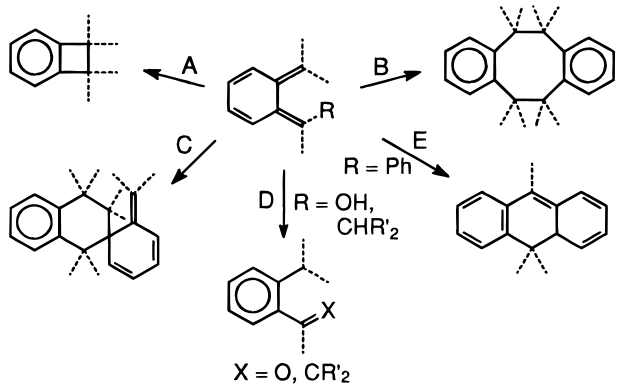
However, a serious disadvantage of NOCT-1 and other tetraalkyl-substituted NOCTs is the short lifetime (e.g., ca. 120 s for NOCT-1 at 37 °C[4,11]) at physiological temperature, a result of a rapid 1,5-hydrogen shift reaction. In marked contrast, the indenyl compound NOCT-4 was found to be very long-lived (several days) at 37 °C under similar conditions[4] though its concentration was very low. The increased lifetime of NOCT-4 has been tentatively attributed to the extension of the delocalized π-system by the indenyl substituent, thus thermodynamically stabilizing the *o*-quinodimethane structure.

We therefore proposed that also *o*-quinodimethanes carrying phenyl substituents at the exocyclic double bond(s) should exhibit longer lifetimes than alkyl-substituted ones, which might render them more suitable for biological applications. In addition, by replacing the terminal alkyl groups with alkoxy substituents an increase of the lifetime of *o*-quinodimethanes was expected due to suppression of possible 1,5-hydrogen shift reactions.

So far, we used as a convenient route to *o*-quinodimethanes the photolysis of the corresponding 2-indanones **3**,[12−14] reaction 1, because a variety of substituted indanones can easily be prepared from readily available starting materials.

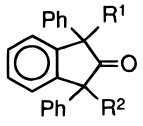
Unfortunately, due to their strong UV/vis absorption at wavelengths >350 nm *o*-quinodimethanes of type **1** are photolabile themselves, leading only to low photostationary concentrations in the range of 10^{-3}−10^{-6} M. Such concentrations, however, are still sufficient to generate strong ESR signals of the nitroxides **2**.

Scheme 1



General modes of decay of *o*-quinodimethanes[13] (Scheme 1) include electrocyclic ring closure to substituted benzocyclobutenes (path A), [4 + 4] cycloaddition to give dibenzocyclooctadienes (path B), formation of spiro compounds via [4 + 2] cycloaddition (Diels−Alder reaction; path C), 1,5-hydrogen shift if suitable hydrogen-donating substituents (alkyl, hydroxyl) are present (path D), and electrocyclic ring closure to 4a,10-dihydroanthracene derivatives in the case of R = phenyl (path E).

Since sterically congested benzocyclobutenes in solution may exist in thermal equilibrium with the corresponding *o*-quinodimethanes via electrocyclic ring opening/ring closure (reversibility of path A), we hypothesized that such benzocylobutenes may serve as convenient "reservoirs" for the actual NO trap. Therefore, we synthesized a series of phenyl-substituted 2-indanones and studied their photochemically induced decarbonylation and the reaction of their photoproducts with nitric oxide. Here, we present our results on the 1,3-diphenyl-2-indanones **3a**−**e** and 1,1,3-triphenyl-2-indanones **3h**−**l**.



3a: $R^1 = R^2 = OMe$
3b: $R^1 = R^2 = OCH_2CO_2Et$
3c: $R^1 = R^2 = OCH_2CO_2H$
3d: $R^1 = R^2 = OCH_2CO_2^- Na^+$
3e: $R^1 = R^2 = Me$
3f: $R^1 = R^2 = OH$
3g: $R^1 = R^2 = H$

3h: $R^1 = Ph$, $R^2 = OH$
3i: $R^1 = Ph$, $R^2 = OMe$
3j: $R^1 = Ph$, $R^2 = OCH_2CO_2Et$
3k: $R^1 = Ph$, $R^2 = H$
3l: $R^1 = Ph$, $R^2 = Me$

Results

Synthesis of Phenyl-Substituted 2-Indanones. 1,3-Diphenyl-substituted 2-indanones **3a**−**g** were conveniently prepared from ninhydrin monohydrate by standard procedures (Scheme 2).

According to the ^1H NMR spectrum (only one OCH_3 signal) ketal **4** was obtained in >99% yield as the *rac* diastereomer. During hydrolytic cleavage of **4** *meso*/*rac* isomerization occurred, producing mainly *meso*-**3f**, which could be isolated in pure form. Further conversion of *meso*-**3f** to compounds **3a**−**d** did not affect the stereochemistry.

(6) Although the cyclic nitroxides **2** represent the products of a formal cheletropic reaction, we do not imply that the mechanism for their formation is a truly cheletropic one in the sense of the Woodward−Hoffman rules, i.e., to proceed in a concerted fashion. Indeed, at least for the reaction of the unsubstituted *o*-quinodimethane in the gas phase there is evidence that the reaction with NO occurs in a stepwise manner.[7]

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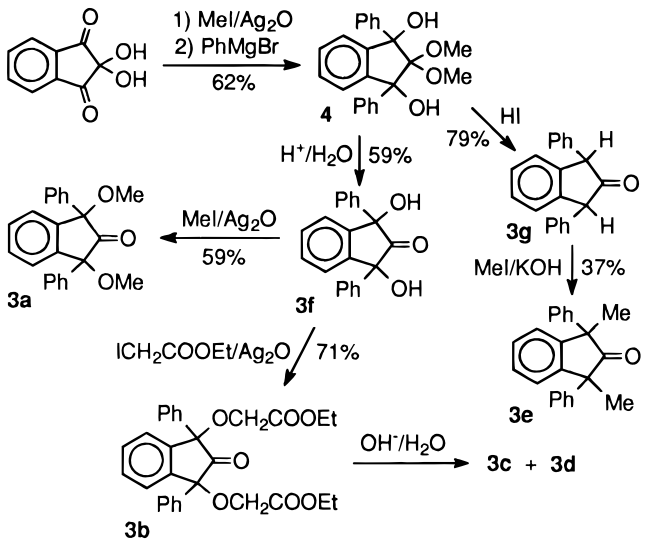
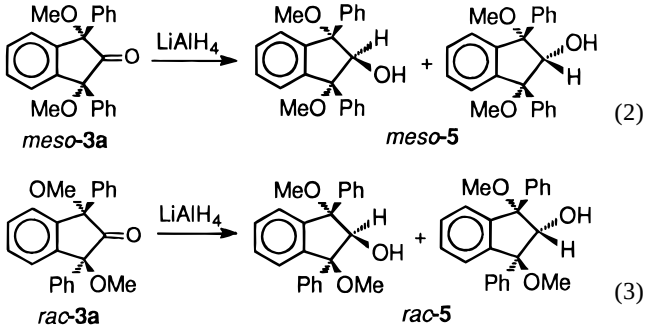
Scheme 2



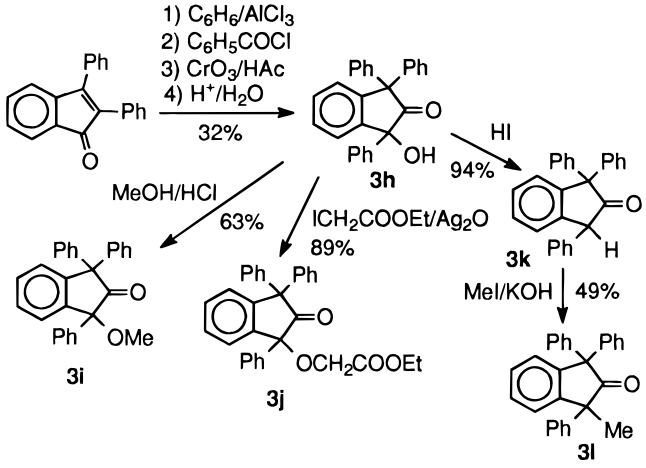
The assignment of stereochemistry of the 1,3-diphenylindan-2-ones **3a**−**e** by ^{1}H NMR spectroscopy was based on the $LiAlH_4$ reduction of *meso*-**3a** to the corresponding hydroxy compounds **5**, reaction 2, similar to the procedure reported by Quinkert et al.[15] The ^{1}H NMR spectrum of the reduction mixture showed two sets of signals in an intensity ratio of 1:1.3, in agreement with a mixture of the diastereomers of *meso*-**5**. From *rac*-**3a** only one set of NMR signals would have been expected, since the corresponding groups of the diastereomers of *rac*-**5**, reaction 3, are all chemically equivalent.



1,1,3-Triphenyl-indan-2-ones **3h**−**l** were obtained from 2,3-diphenylinden-1-one (Scheme 3).

Photolysis of 2-Indanones. The photolytic decarbonylation of the phenyl-substituted 2-indanones **3f,g,k** has been investigated by the groups of Quinkert[14] and Scaiano.[12] Quinkert also investigated the 1,1,3,3-tetraphenyl-2-indanone (**3m**; $R^1 = R^2 =$ Ph). With regard to the photoproducts and transients the results reported in this study are generally in line with their findings. All 2-indanones of this study were photolyzed in deoxygenated solution at concentrations of 5×10^{-2} M with $\lambda = 300$ nm light. The resulting photolysates were analyzed by ^{1}H NMR, ^{13}C NMR, and UV/vis spectroscopy and in part also by HPLC (see Experimental Section). The only products of the photolytic decarbonylation (Scheme 4) that could be detected by conventional 300-MHz ^{1}H NMR spectroscopy were the corresponding benzocyclobutenes **6** and, where possible, the products **9** of a 1,5-hydrogen shift. In some cases small amounts of dihydroanthracene **7** and/or anthracene derivatives **8** were also found. *o*-Quinodimethanes **1** could only be detected UV/vis-spectroscopically by their characteristic absorptions in the 400−600 nm wavelength range.[12,14,16,17] In agreement with literature reports,[12,14] no [4 + 2] or [4 + 4] cycloadducts (paths B and C of Scheme 1) were detected within the sensitivity limit (≤1%) of our 300

Scheme 3



Scheme 4

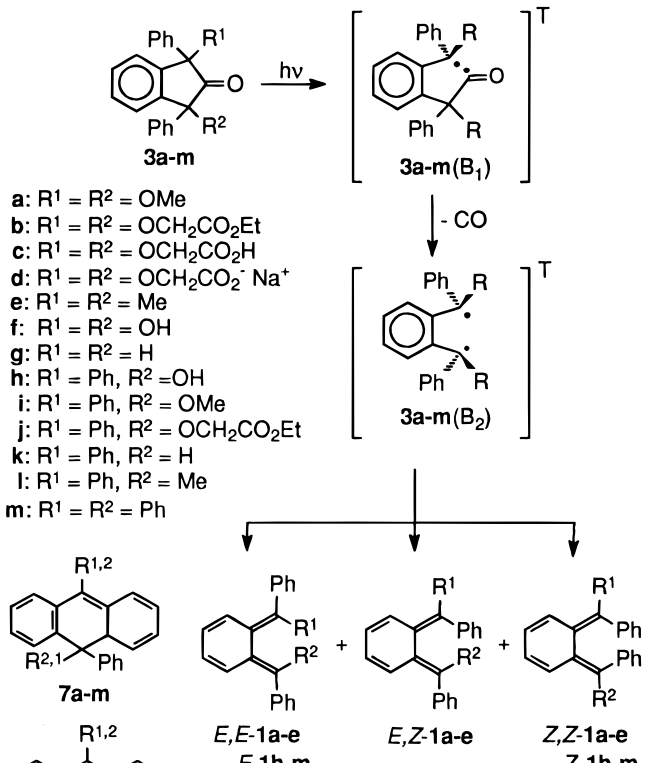


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Table 1. Photolysis (300 nm) of 1,3-Diphenyl- and 1,1,3-Triphenylindan-2-ones (^{1}H NMR analysis)[a]

indanone R	solvent	*T*/°C	photolysis time/h	conversion (%)	benzocyclobutene **6** (*meso*/*rac*) (mol %)	1,5-H shift product **9** (mol %)
3a[b]	CD_3CN	−7	4	100	95/5	
OMe	C_6D_6	12	3.5	100	93/7	
3b[b]	CD_3CN	10	4	87	95/5	
OCH_2COOEt						
3c[b]	CD_3CN	10	4	100	100/0	
OCH_2COOH						
3d[b]	D_2O	10	4	100	100/0	
OCH_2COONa						
3e[c]	CD_3CN	−10	5	9	33/67	
Me	CD_3CN	10	15	31	48/52	
	CD_3CN	20	17	68	47/53	
3h	CD_3CN	6	4	40		100
OH	CD_3CN	−20	2	33		100
3i	CD_3CN	15	7	65	100	
OMe	CD_3CN	10	24	100	96[d]	
3j	C_6D_6	10	5	96	100	
OCH_2COOEt						
3k	C_6D_6	10	1	15	100	
H	C_6D_6	10	48	100	95[e]	
3l	C_6D_6	10	2	14	57	43
Me						

[a] Products <1% not considered. [b] >99% *meso*. [c] 36/64 *meso*/*rac*. [d] 4% 9,10-diphenylanthracene (**8m**) by UV/vis analysis. [e] 5% 9,10-diphenylanthracene (**8m**).

MHz ^{1}H NMR analysis procedure or by HPLC (UV/vis) analysis. Conditions of the photolysis experiments and ^{1}H NMR-detected product yields are collected in Table 1.

In most cases, the detected benzocyclobutene and *o*-quinodimethane photoproducts appeared to be thermally unstable, converting slowly to 4a,10-dihydroanthracene **7** and further to anthracene derivatives **8**. Investigations focused on these reactions will be reported in a forthcoming paper.

***meso*-1,3-Dimethoxy-1,3-diphenylindan-3-one (3a).** In CD_3CN solution a complete conversion of *meso*-**3a** was achieved after 4 h photolysis at −7 °C to yield a 95:5 ratio of benzocyclobutenes *meso*-**6a** and *rac*-**6a** (Scheme 4). *meso*-**6a** could be isolated in pure form; its absolute stereochemistry was determined by X-ray diffraction analysis (to be reported in a following paper). ^{1}H NMR signals that might be assigned to the *o*-quinodimethanes **1a** (Scheme 4) could not be resolved. The orange-colored photolysate showed a broad UV/vis absorption at λ_{max} = 470 nm (see below) which was persistent for several days at room temperature. We assign this absorption to one of the three possible isomeric *o*-quinodimethanes **1a** because of the following arguments: (i) its similarity to the UV/vis absorption of other phenyl-substituted *o*-quinodimethanes,[12,14,16,17] (ii) the decay of the absorption and concomittant formation of an ESR-detectable nitroxide radical when the photolysate was reacted with nitric oxide (see below), (iii) its irreversible disappearance on heating the sample to 60 °C, and (iv) the results of the laser flash photolysis (LFP) experiments described below. Assuming an extinction coefficient for *o*-quinodimethanes in the range of ϵ(**1**) = 10^4 M^{-1} cm^{-1} (as found for 7,7,8,8-tetraphenyl-*o*-quinodimethane (**1m**)[14d], ϵ = 9170 M^{-1} cm^{-1}, 7,8-diphenyl-*o*-quinodimethane (**1g**)[14b], ϵ = 10 600 M^{-1} cm^{-1}, or 7,7,8,8-tetramethyl-*o*-quinodimethane (NOCT-1)[11c], ϵ = 13 700 M^{-1} cm^{-1}) we estimated from the stationary UV/vis absorption at λ = 470 nm a concentration of **1a** on the order of 10^{-4} M. Thus, it is not surprising that we were not able to detect **1a** by conventional ^{1}H NMR spectroscopy.

By HPLC (UV/vis detection) an additional trace component was detected, most likely the 9,10-substituted anthracene derivative **8a**, based on the similarity of its UV/vis spectrum to other 9,10-substituted anthracenes[12a,14d,16] (compare, e.g., 9,10-diphenylanthracene (**8m**), below).

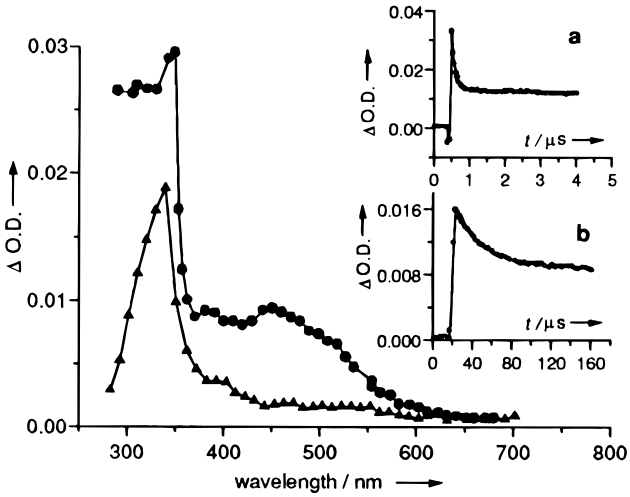


Figure 1. Time-resolved UV/vis spectra obtained during 266-nm LFP of a 10^{-2} M solution of **3a** in acetonitrile as observed 250 ns (●) and 1.6 μs (△) after laser excitation. Insets: decay traces of the absorptions at 320 nm for the first (a) and second (b) phase.

Further support for the formation of isomeric *o*-quinodimethanes **1a** was provided by LFP experiments. After excitation of **3a** (10^{-2} M in acetonitrile) with 266-nm laser light, a transient absorption spectrum characterized by a broad band in the 380−600 nm range (λ_{max} ca. 460 nm) and sharper, more intense bands in the 300−360 nm range were observed within the width (10 ns) of the laser pulse (Figure 1a). The 460-nm band and the absorptions > 330 nm decayed in a biphasic process, both steps showing first-order kinetics with lifetimes of τ = 0.16 μs (k = 7.3 × 10^6 M^{-1} s^{-1}) and 24 μs (k = 3.3 × 10^4 M^{-1} s^{-1}), respectively (Figure 1a, insets). A weak absorption in the 430−600 nm range and a stronger, sharp band at λ_{max} = 340 nm remained. We attribute the two transient and the persistent absorptions to the three isomeric *o*-quinodimethanes **1a** because of the characteristic wavelength range, their relatively (long)

lifetimes, and the fact that they could not be "quenched" by dissolved oxygen, as would be expected for biradical species.

Absorptions that might be related to the intermediate triplet acyl alkyl biradical **3a**(B_1) (Scheme 4) and the decarbonylated dialkyl biradical **3a**(B_2) (which can be regarded as a triplet state of **1a**) could not be observed, indicating that decarbonylation and rotational isomerization are very fast on the nanosecond time scale of our LFP experiments.[4,12] Likewise, significant formation of dihydroanthracene (**7a**) or anthracene species (**8a**), either in the photolytic process or in the decay of transient **1a**, can be excluded; such compounds are characterized by absorptions in the 350−400 nm range.[14−16]

***meso*-1,3-Bis[(ethoxycarbonyl)methoxy]-1,3-diphenylindan-2-one (3b).** The photolysis of *meso*-**3b** in CD_3CN at 10 °C gave very similar results to **3a**, only the decomposition occurred somewhat slower and the ratio of the benzocyclobutene products *meso*-**6b** and *rac*-**6b** was slightly changed to 93:7.

***meso*-1,3-Bis(carboxymethoxy)-1,3-diphenylindan-2-one (3c) and Disodium *meso*-1,3-Bis(carboxylatomethoxy)-1,3-diphenylindan-2-one (3d).** The photolysis of **3c** in CD_3CN and of **3d** in buffered D_2O (phosphate buffer, pH 7.5) at 10 °C was completed within 4 h with almost quantitative formation of *meso*-**6c** and *meso*-**6d**, respectively. The aqueous solution of **3d** became turbid during the photolysis, probably because traces of acid **3c** (which is almost insoluble in water) were formed.

1,3-Dimethyl-1,3-diphenylindan-2-one (3e). The photolysis of this ketone has already been studied.[14c] The photolytic decomposition of a 1:1.1 *meso*/*rac* mixture of **3e** in CD_3CN at 20 °C was less effective than with the above alkoxy-substituted 2-indanones; e.g., after 17 h 68% were converted, affording only *meso*- and *rac*-**6e** in approximately the same ratio as the starting material. Somewhat unexpected, the product of a 1,5-hydrogen shift reaction could not be detected by ^{1}H NMR spectroscopy. This is in agreement with observations made by Quinkert,[14c] who found evidence that the 1,5-hydrogen shift only occurred after complete decarbonylation of **3e**.

No detailed analysis of the photolytic decomposition of 1,3-dihydroxy-1,3-diphenylindan-2-one (**3f**) and 1,3-diphenylindan-2-one (**3g**) was performed because of their unfavorable properties for our purposes. Compound **3f** is very soluble in organic solvents and produces a variety of products, primarily 1,3-diphenylisobenzofuran, when photolyzed in DMSO solution; **3g** would produce only short-lived *o*-quinodimethanes and a thermally too stable benzocyclobutene.[18] Furthermore, reaction of the photolysates of both ketones produced only very weak, rapidly decaying ESR signals of nitroxide radicals not compatible with the structures expected from **1g** and **1h**.[18]

1-Hydroxy-1,3,3-triphenylindan-2-one (3h). After photolysis of **3h** in CD_3CN at 6 and −40 °C, respectively, the only NMR-detectable product was 2-diphenylmethylbenzophenone (**9h**), the formal 1,5-hydrogen shift product of (*E*)-**1h** (Scheme 4). If **9h** is indeed formed in a concerted 1,5-hydrogen shift process then one has to assume that either only (*E*)-**1h** is produced from **3h** or that (*E*)-**1h** and (*Z*)-**1h** exist in a rapid equilibrium (probably via **6h**). On the other hand, **9h** simply may have been formed by a proton-catalyzed keto−enol tautomerization, e.g., by traces of water or by the starting hydroxyl compound **3h**. There is some evidence for the latter interpretation from work by Porter and Tchir,[16] who showed that the decay of *o*-quinodimethanes deriving from 2,4-dimethylbenzophenone is faster in protic than in aprotic solvents.

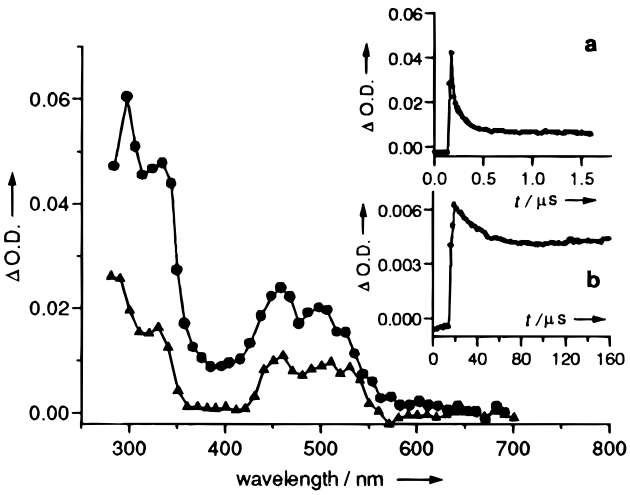


Figure 2. Time-resolved UV/vis spectra obtained during 266-nm LFP of a 10^{-2} M solution of **3i** in acetonitrile as observed 200 ns (●) and 1.6 μs (△) after laser excitation. Insets: decay traces of the absorptions at 320 nm for the first (a) and second (b) phase.

1-Methoxy-1,3,3-triphenylindan-2-one (3i). Photolysis of **3i** in CD_3CN for 7 h (65% conversion) gave benzocyclobutene **6i** as the only ^{1}H NMR-detectable product. When the photolysis was driven to complete conversion of **3i** (24 h) small amounts (ca. 4%) of 9,10-diphenylanthracene (**8m**) were also detected by HPLC and UV/vis spectroscopy by comparison with authentic material. The yellow photolysate showed only a very weak absorption in the 400−500 nm region, from which we estimated, again assuming $\epsilon(\mathbf{1}) = 10^4\ M^{-1}\ cm^{-1}$, a low concentration of *o*-quinodimethanes **1i** in the range of 10^{-5} to 10^{-6} M. Attempts to purify product **6i** by chromatography or crystallization were not successful due to partial decomposition of the compound during the purification procedures.

Ketone **3i** was also subjected to LFP experiments. Very similar to **3a** (see above), 266-nm LFP of a 10^{-2} M solution of **3i** in acetonitrile produced within the width of the laser pulse a transient absorption spectrum characterized by a broad band in the 400−600 nm range with maxima at ca. 460 and 500 nm and stronger absorptions at 330 and 280 nm (Figure 2a). The 460, 500, and 280-nm absorptions, which we attribute to the isomeric *o*-quinodimethanes **1i**, again decayed in a two-phase process with first-order rate constants of $k = 5 \times 10^6\ s^{-1}$ and $4.5 \times 10^4\ s^{-1}$ for the first and second stage, respectively (Figure 2a, inset). The decay rates were the same in nitrogen- and oxygen-saturated solution. Decay of the *o*-quinodimethane bands, however, did not occur completely (Figure 2b). Since in this system only two isomeric *o*-quinodimethanes **1i** are possible, this would imply the onset of an equilibrium **6i** ⇌ **1i**.

1-[(Ethoxycarbonyl)methoxy]-1,3,3-triphenylindan-2-one (3j). This ketone was decarbonylated to about 96% on 5 h photolysis at 10 °C, giving almost exclusively benzocyclobutene **6j** and traces of 9,10-diphenylanthracene. By HPLC another trace component was detected, most probably the corresponding dihydroanthracene derivative **7j**.

(18) Paul, T. Diploma thesis, Universität − GH Essen, 1993.

Table 2. ESR Spectroscopic Data[a] at 20 ± 2 °C of Cyclic Nitroxide Radicals from the Reaction of 7,8-Diphenyl- and 7,7,8-Triphenyl-*o*-quinodimethanes with Nitric Oxide

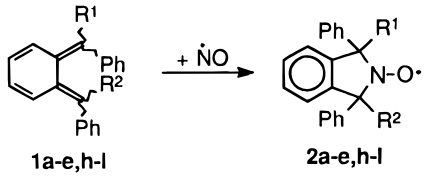
			hyperfine splittings/mT		
nitroxide	solvent	*g* factor	$a(^{14}N)$	$a(^{13}C)$	$a(^{15}N)$
2a	acetonitrile	2.006 29(3)	1.185(3)	0.43(1) (4C)	1.66(1)
	benzene	2.006 34(3)	1.150(3)	0.42(1) (4C)	1.61(1)
2b	acetonitrile	2.006 33(3)	1.168(3)	0.40(1) (2C)	1.62(1)
				0.41(1) (2C)	
2c	acetonitrile	2.006 27(4)	1.173(3)	0.39(1) (4C)	1.65(1)
2d	buffer pH7.4	2.006 03(4)	1.292(5)	0.40(1) (2C)	1.65(1)
				0.42(1) (2C)	
2e(1)[b]	acetonitrile	2.006 02(5)	1.422(5)	0.54(1) (4C)	1.995(5)
2e(2)	acetonitrile	2.005 93(5)	1.405(5)	n.a.[c]	n.a.
2h	acetonitrile	2.006 16(3)	1.267(4)	n.a.	n.a.
2i	acetonitrile	2.006 15(3)	1.267(4)	0.52(1) (3C)	1.79(1)
				0.72(1) (1C)	
	DMSO	2.006 06(4)	1.264(4)	n.a.	n.a.
	benzene	2.006 17(3)	1.234(3)	0.51(1) (3C)	1.738(5)
				0.72(1) (1C)	
2j	acetonitrile	2.006 15(3)	1.252(3)	0.52(1) (3C)	1.790(5)
				0.63(1) (1C)	
2k	benzene	2.006 15(3)	1.385(3)	0.56(1) (2C)	n.a.
			1.851(3)[d]	0.68(1) (3C)	
2l	benzene	2.006 06(3)	1.380(3)	0.53(1) (3C)	1.94(1)
				0.72(1) (2C)	

[a] Estimated errors in the last digit given in parentheses. [b] Two radicals, initial ratio 73:27. [c] Not analyzed. [d] β-Hydrogen splitting.

1,1,3-Triphenylindan-2-one (3k). Photolytic decarbonylation of **3k** has been investigated by Scaiano et al.[12] who reported the formation of 7,7,8-triphenylbenzocyclobutene (**6k**) and 9,10-diphenylanthracene (**8m**) in various ratios, depending on the light source (laser or mercury lamp). In agreement, we observed a complete destruction of **3k** on 48 h photolysis in benzene-d_6 at 10 °C with formation of **6k** and 9,10-diphenylanthracene (**8m**) in a 95:5 ratio.

1-Methyl-1,3,3-triphenylindan-2-one (3l). The products identified by ^{1}H NMR after 8 h photolysis of **3l** in benzene-d_6 at 10 °C (72% conversion) were benzocyclobutene **6l** (68%) and α-phenyl-*o*-diphenylmethylstyrene (**9l**) (32%); i.e., some 1,5-hydrogen shift had occurred (in contrast to the dimethyl compound **3e**). The given percentage of **9l**, however, might not reflect the true relative ratio of the stereoisomers of the intermediate *o*-quinodimethanes **1l** as produced photolytically, because a photolytically induced back-reaction (1,5-hydrogen shift) of the styrene compound **9l** to reform **1l** cannot be excluded.[19]

Reaction of the Photolysis Products of 1,3-Diphenyl- and 1,1,3-Triphenylindan-2-ones with Nitric Oxide. As mentioned above, even small concentrations (10^{-4}−10^{-6} M) of *o*-quinodimethanes are sufficient to produce strong ESR signals of cyclic nitroxides **2** (isoindolin-2-oxyls) on reaction with nitric oxide.[3,4] The ability of the phenyl-substituted *o*-quinodimethanes **1a**−**e,h**−**l** produced, or expected to be produced, in the photolytic decompositions of ketones **3a**−**e,h**−**l** was checked by reaction of the raw photolysates with solutions of nitric oxide, reaction 4, in the same solvent and ESR-spectroscopic detection of the resulting nitroxide radicals. From all photolysates of ketones **3**, except **3h**, good-to-excellent ESR were obtained (note that in most cases the ^{13}C and ^{15}N isotope satellite lines could be easily analyzed), indicating that *o*-quinodimethanes **1** had reacted with NO. The ESR spectroscopic data (Table 2) are in full agreement with the cyclic structure of nitroxides **2**;[4,20] in particular, the analysis of the ^{13}C satellite hyperfine lines confirms their structure.



(4)

1a-e,h-l **2a-e,h-l**

a: $R^1 = R^2$ = OMe
b: $R^1 = R^2 = OCH_2COOEt$
c: $R^1 = R^2 = OCH_2COOH$
d: $R^1 = R^2 = OCH_2COO^-\ Na^+$
e: $R^1 = R^2$ = Me
h: R^1 = Ph, R^2 = OH
i: R^1 = Ph, R^2 = OMe
j: R^1 = Ph, $R^2 = OCH_2COOEt$
k: R^1 = Ph, R^2 = H
l: R^1 = Ph, R^2 = Me

The kinetics of formation of nitroxides **2a**−**e,h**−**l** (Table 3) was measured by following the time evolution of the ESR spectra. For comparison with the *o*-quinodimethane concentrations estimated from the UV/vis spectra, the absolute radical concentrations given in Table 3 were determined via double integration of the ESR spectra. With one exception (**2k**), the ESR signal intensities of nitroxides **2** measured "initially" (i.e., after 2−5 min, the time to prepare the sample and to tune the spectrometer) after mixing the photolysates of **3** with NO solution increased slowly with time (within hours). However, the rates of this increase would not account for the "initial" radical concentration. When the formation of radicals **2** was followed kinetically under first-order conditions it became evident that the nitroxides were formed in a biphasic process; i.e., after an initial "jump" (on the time scale of minutes) their signal intensities increased steadily by a slower process to achieve either a constant "plateau" value or going through a maximum. Extrapolation of the least-squares fit to the concentration−time data of the "slow" process to zero time gave a radical concentration that we set equal to the concentration of the *o*-quinodimethane derivatives in the respective photolysate (Table 3, column 9) at the time of reaction with NO. This procedure seems to be justified, since, with the exception of **2e**, the formation of only one nitroxide radical was monitored by ESR in the respective trapping experiments.

(19) Hornback, J. M.; Russell, R. D. *J. Org. Chem.* **1982**, *47*, 4285−4291.

(20) Forrester, A. R. In *Landolt-Börnstein, New Series, Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K. H., Eds.; Springer: Berlin, 1979; Vol. 9, Part c1; Vol. 17, Parts d1, d2.

Table 3. Kinetic Data for the Reaction of 7,8-Diphenyl- and 7,7,8-Triphenyl-*o*-quinodimethanes and 7,8-Diphenyl- and 7,7,8-Triphenylbenzocyclobutenes with Nitric Oxide in Solution

compd	solvent	*T*/°C	λ^a/nm	$10^6 c(\mathbf{1})^b$/ mol L^{-1}	$k^{sf}(\mathbf{1})^c$/ s^{-1}	$k_2^{sf}(\mathbf{1})^d$/ M^{-1} s^{-1}	$10^4 k^{ESR}(\mathbf{2})^e$/ s^{-1}	$10^6 c(\mathbf{2})_0^f$/ mol L^{-1}	$10^6 c(\mathbf{2})_{max}^g$/ mol L^{-1}
1a/6a	acetonitrile	23	470	140	0.061 ± 0.01	10 ± 1	1.8	570	1335
1a/6a	benzene	23	470	6	0.16 ± 0.04	20 ± 5	0.4	17	623
6a^h	acetonitrile	23					4.6	0	1958
1b/6b	acetonitrile	24	490	6	1.6 ± 0.1	230 ± 15	1.0	32	869
1c/6c	acetonitrile	23	450	4	1.1 ± 0.4	160 ± 60	n.a.^{i}	20	54
1e/6e	benzene	23	490	4	15.0 ± 3.2	2140 ± 460	2.7	14	41
1i/6i	acetonitrile	24	490	0.6	0.39 ± 0.10	60 ± 15	*j*	346	1246
1j/6j	acetonitrile	23			n.a.		1.0	52	660
1k/6k	benzene	23	490	18	17.0 ± 3.9	2430 ± 560	*k*	15	15^k
1l/6l	benzene	23	490	90	29.0 ± 2.7	4140 ± 390	7.5	71	125

^{a} Wavelength of stopped-flow kinetic measurement. ^{b} Estimated concentration of *o*-quinodimethane from change of the long-wavelength absorption, assuming an extinction coefficient of $\epsilon = 10^4$ M^{-1} cm^{-1}. ^{c} Experimental pseudo-first-order rate constant from spectrophotometric stopped-flow experiment. ^{d} Estimated second-order rate constant (rounded to the next decimal number) for **1** + NO reaction, calculated from k^{sf}(**1**) and 7×10^{-3} M NO concentration. ^{e} Rate constant for the slow growth of the ESR signal of nitroxide **2**. ^{f} Extrapolated "initial" ($t = 0$) concentration of nitroxide **2** for slow growth. ^{g} Maximum concentration of nitroxide **2** produced in the slow process. ^{h} Purified *meso*-**6a** employed. ^{i} Not analyzed, sigmoid concentration/time profile. ^{j} Linear growth. ^{k} Constant ESR signal, no growth.

The rates of reaction of **1a**−**e,h**−**l** with NO were determined by spectrophotometric stopped-flow measurements, monitoring the decay of the characteristic *o*-quinodimethane absorptions in the 400−600 nm range. The concentration of our phenyl-substituted *o*-quinodimethanes were estimated from the maxima of these UV/vis absorptions by assuming an extinction coefficient of $\epsilon = 10^4$ M^{-1} cm^{-1}. In some cases, however, the 400−600 nm absorptions did not decay to zero values (see, e.g., Figure 7, below), indicating that also other, nonreactive products exhibited some absorptions in this region. Therefore, the estimated *o*-quinodimethane concentrations given in Table 3, column 5, were calculated only from the change of the UV/vis absorptions after reaction with excess NO. The sometimes large difference in the *o*-quinodimethane concentration estimated from the UV/vis absorptions and the "initial" ESR signal intensities of radicals **2** (see above) accounts for the fact that most of our *o*-quinodimethanes are thermally unstable. Note that in the ESR experiments generally "fresh" photolysates, i.e., always stored on dry ice, were rapidly mixed with NO solutions when still at temperatures below ambient temperature, whereas the stopped-flow experiments required handling of the samples at room temperature for several minutes. Of course, significant differences in the *o*-quinodimethane concentrations, probably up to a factor of 10, may simply derive from a larger deviation of the true extinction coefficient of **1** from the assumed number of 10^4 M^{-1} cm^{-1}, combined with the fact that the ESR determination of absolute radical concentration normally is subject to large systematic errors (100% and more).

The orange color of the photolysate from 1,3-dimethoxy-1,3-diphenylindan-2-one (**3a**) in CD_3CN or benzene disappeared rapidly when a ca. 10^{-2} M solution of NO in the same solvent was added. At the same time a strong three-line ESR spectrum (Figure 3), assigned to nitroxide radical **2a,** was observed when the reaction was carried out in the cavity of the ESR spectrometer. The number and intensities of the ^{13}C satellite lines confirm a symmetrical structure with respect to the nitroxide group and indicate that the hyperfine splittings of the α-carbon atoms and the *ipso*-carbon atoms of the phenyl substituents are accidentally equivalent within the line width. The initial signal intensity of **2a** further increased slowly to reach after ca. 10 h a constant level corresponding to a concentration of **2a** of about 1335 μM (Figure 4). Least-squares fit to a (pseudo) first-order rate law gave a rate constant of k^{ESR}(**2a**) = 1.8×10^{-4} s^{-1} for the "slow" process

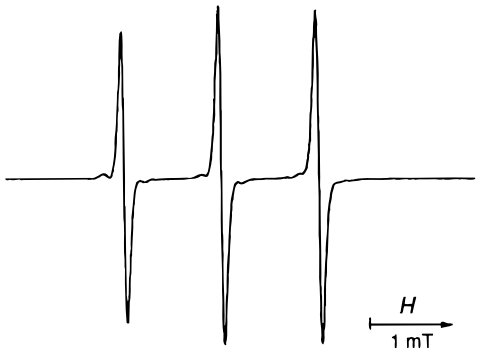


Figure 3. ESR spectrum of **2a** in acetonitrile at 20 °C, recorded 15 min after mixing of the photolysate of **3a** with NO solution.

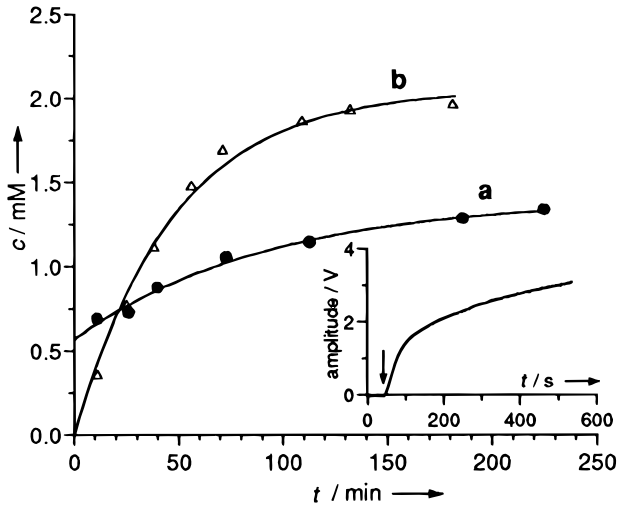


Figure 4. Time dependence of the ESR signal of **2a** obtained from mixing an acetonitrile solution of NO with (a) the raw photolysate from **3a** and (b) pure *meso*-**6b** in acetonitrile at 23 °C. Inset: Time evolution of the ESR signal of **2a** in benzene recorded by the rapid-mixing technique. The arrow marks point of injection.

and an extrapolated "initial" concentration of c(**2a**) = 570 μM (Table 3). This value is higher by about a factor of 4 compared to the spectrophotometrically estimated concentration of **1a** (150 μM). In benzene-d_6 solution the "initial" ESR concentration of **2a** was lower by a factor of ca. 35 (17 μM), indicating a significantly lower photostationary concentration of *o*-quinodimethane **1a** in this solvent. This was nicely confirmed by the ratio of the

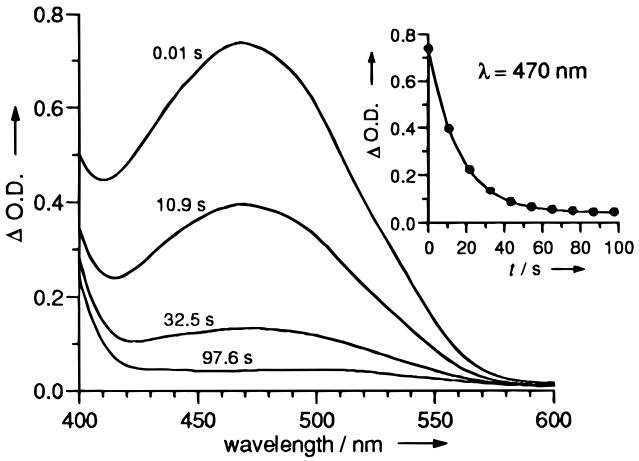
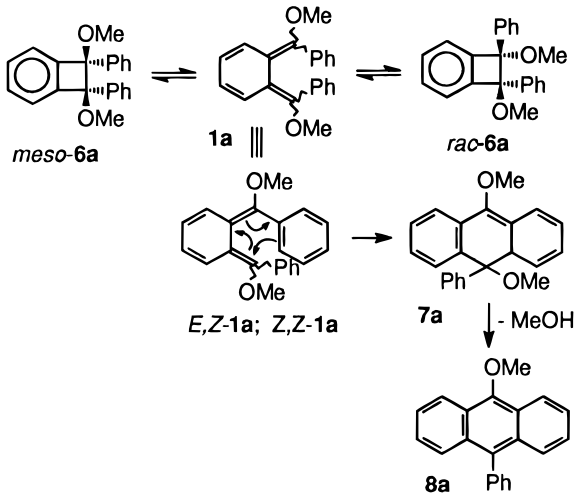


Figure 5. Spectrophotometric stopped-flow measurement of the decay of the absorption of **1a** in the reaction with NO in acetonitrile solution at 23 °C. Inset: First-order decay trace of the absorption at 470 nm.

concentration of **1a** in both solvents as estimated from the UV/vis absorption intensity (140 and 6 μM, ratio 23; Table 3). In benzene, the rate constant for the further, "slow" buildup of the ESR signal was lower by a factor of 4.5 compared to the acetonitrile solution; i.e., there is a small solvent effect. In order to extend the time evolution of the kinetics of formation of the ESR signal we performed "rapid"-mixing ESR experiments with a time resolution in the range of seconds. These experiments qualitatively confirmed the biphasic kinetic behavior of the nitroxide-forming process (Figure 4, inset). The concentration/time profile for the first minute after rapid mixing of the photolysate with NO solutions was identical with the inherent time constant of the mixing device (ca. 27 s); i.e., the rapid radical-forming process must have occurred faster. We attributed the "fast" process to the reaction of NO with the persistent isomer of *o*-quinodimethane **1a** (tentatively assigned to (*E*,*E*)-**1a**). To support this assignment, we measured the kinetics of the reaction of the *o*-quinodimethane **1a** with saturated (1.4×10^{-2} M)[21] solutions of NO in acetonitrile and benzene by the spectrophotometric stopped-flow method by monitoring the decay of the UV/vis absorption at $\lambda_{max} = 470$ nm (Figure 5). The decay obeyed a clean pseudo-first-order rate law in both solvents with rate constants of k^{sf}(**1a**) = 0.061 and 0.16 s^{-1} in acetonitrile and benzene, respectively, in good agreement with the number evaluated from the "fast" growth of the ESR signal. Thus, the rate data indeed describe the reaction of the persistent isomer of **1a** with nitric oxide. Taking the known concentration of NO after mixing (7×10^{-3} M) we calculated the second-order rate constants for this process to be k_2(**1a**) = 10 and 20 M^{-1} s^{-1} in acetonitrile and in benzene, respectively.

Further support for the presence of a (relatively) persistent *o*-quinodimethane species was provided by experiments where the photolysates were "aged" at 40 °C for various periods of time before mixing with NO solutions. With increasing aging time the initial "jump" of the ESR signal of **2a** became less and less pronounced, in agreement with a slow, irreversible decay of the corresponding *o*-quinodimethane. After 30 h at 40 °C only the "slow" growth of the ESR signal could be monitored.

Scheme 5



Because the "fast" growth of the ESR signal of **2a** is certainly due to the *o*-quinodimethane + NO reaction, the subsequent "slow" increase of the signal must be due to a reaction of NO with another component of the photolysis mixture, most likely benzocyclobutene **6a**. To check on this, we mixed equal volumes of a 10^{-2} M solution of purified, colorless *meso*-**6a** in acetonitrile (which showed no UV/vis absorption above 300 nm) with a 1.4×10^{-2} M solution of NO in the same solvent in the cavity of the ESR spectrometer. As expected, no initial "jump" of the ESR signal was observed now, but we subsequently monitored the slow buildup of the ESR signal of **2a** (Figure 4, trace b) with a rate constant (k^{ESR}(**2a**) = 4.6×10^{-4} s^{-1}) in reasonable agreement with the number obtained from the experiment with the raw photolysate.

We attributed the slow formation of nitroxide **2a** to the reaction of NO with (a) reactive isomer(s) of *o*-quinodimethane **1a**, formed by electrocyclic ring opening of *meso*-**6a**. (Scheme 5). Justification for this interpretation was based on the following observations: We found that *meso*-**6a** undergoes a slow thermal isomerization to its thermodynamically more stable diastereomer *rac*-**6a**. (Note that if this reaction would occur as a concerted process it must involve symmetry-forbidden disrotatory ring-opening/ring-closure processes). It is hard to believe that the *meso*/*rac* isomerization does not proceed via (an) *o*-quinodimethane intermediate(s), as does the symmetry-allowed conrotatory ring opening of benzocyclobutenes. However, we were unable to detect the buildup of the characteristic UV/vis absorptions in the 400−600 nm range of the corresponding *o*-quinodimethanes during the isomerization of carefully purified *meso*-**6a**. Thus, the steady-state concentration of the intermediate *o*-quinodimethane(s) must be very low ($\leq 10^{-7}$ M). This conclusion agrees with the above-mentioned detection of two rather short-lived *o*-quinodimethane species formed in the laser flash photolysis of **3a**. Further evidence for the presence of (a) reactive *o*-quinodimethane(s) was provided by the observation that in competition to the isomerization process *meso*- and/or *rac*-**6a** are irreversibly converted to a 4a,10-dihydroanthracene derivative, most likely **7a**. The latter further decomposed to give finally a 9,10-substituted anthracene, namely **8a**. The most reasonable explanation for such a reaction to occur is an electrocyclic ring closure of the *o*-quinodimethane isomer(s) having at least one phenyl group in *Z*-orientation.

(21) (a) *IUPAC Solubility Data Series Vol. 8*; Young, C. L., Ed.; Pergamon Press: Oxford, 1981; pp 260−351. (b) Wisniak, J.; Herskowitz, M. *Solubility of Gases and Solids, Part B, Physical Sciences Data 18;* Elsevier: Amsterdam, 1984; p 1635.

Thus, the time evolution of the "slow" build-up of the ESR signal of **2a** would appear to be governed by the rate of ring opening of *meso*-**6a** rather than the rate of reaction of the *o*-quinodimethane with NO. A detailed investigation of the mechanism of the *meso*/*rac* isomerization and the accompanying reactions is beyond the scope of the present paper and will be reported in a separate publication.

The bulk transformation of benzocyclobutene **6a** on reaction with NO was confirmed by an experiment in which we bubbled gaseous NO through a solution of **6a** in CD_3CN for 1 min. After a 4 min reaction period ^1H NMR analysis revealed a ca. 36% decrease of the concentration of **6a**. After several days, all of **6a** had disappeared; no formation of dihydroanthracene or anthracene derivatives was detected.

Reaction of the photolysates from 1,3-bis[(ethoxycarbonyl)methoxy]-1,3-diphenylindan-2-one (**3b**), 1,3-bis(carboxymethoxy)-1,3-diphenylindan-2-one (**3c**), and disodium-1,3-bis(carboxylatomethoxy)-1,3-diphenylindan-2-one (**3d**) with a solution of NO in the same solvent similarly produced strong ESR signals of the corresponding nitroxides **2b**−**d** (Table 1). The spectroscopic data of these radicals are, as expected, very similar to those of **2a**. The slightly different ^{14}N hyperfine splitting of **2d** reflects the stronger solvation effect in water. The initial ESR signal intensities of **2b**−**d** again all increased slowly with time, giving very strong spectra, persistent for several days, corresponding to radical concentrations that were much larger than the estimated *o*-quinodimethane concentrations. The concentration−time dependence of **2b** could be satisfactoryly fitted to a first-order rate law, yielding a photostationary concentration of **1b** in the photolysate of about 32 μM. The rate constant for this slow process was virtually identical to that of **1a**. In agreement with the ESR observations, the UV/vis spectra of the photolysate of **2b** showed only a minor change of the absorption in the wavelength range of the *o*-quinodimethanes when reacted with NO solution in the stopped-flow apparatus. Notably, the rate constant (k_2^{sf}(**1b**) = 230 M^{-1} s^{-1}) for the **1b** + NO reaction in acetonitrile was found to be higher by approximately a factor of 25 than that of the **1a** + NO reaction.

The slow growth of the ESR signal of nitroxide **2c** obtained from the photolysate of ketone **3c** occurred on a time scale similar to that of **2a** and **2b**. The concentration−time profile, however, could not be analyzed straightforwardly because for unknown reasons it followed a sigmoid time dependence. The extrapolated, initial **2c** concentration (20 μM) again was significantly higher than the concentration of **1c** as estimated from the UV/vis absorption. The rate constant for the fast **1c** + NO reaction differed by only a factor of 2 from that of **1b**.

The buffered aqueous photolysis mixture from **3d** could not be investigated by UV/vis spectroscopy because of its turbidity, which could not be removed by filtration or centrifugation. However, the strong ESR signal of **2d** that was obtained on mixing of the aqueous photolysate from **3d** and a saturated solution of NO in phosphate buffer (pH 7.5) indicated a concentration of *o*-quinodimethane **1d** comparable to the other systems.

The photolysate from **3e** represented the only case where more than one nitroxide radical was detected on reaction with NO solution. Immediately after mixing two overlapping ESR spectra exhibiting very similar spectral data were observed. The intensity of both signals increased with a rate constant again in the order of 10^{-4} s^{-1}. Whereas the "plateau" intensity of one of the ESR spectral components had not changed after 3 days, the spectrum of the other nitroxide radical had completely disappeared. Because of the similarity of the ESR data we tentatively assign the two ESR spectra to the *meso* and *rac* diastereomers of nitroxide **2e**. This would be the only case where the diastereomers of the symmetrically 1,3-diphenyl-substituted nitroxide radicals **2** exhibited differences in the spectral data exceeding the natural line widths.[22] The *o*-quinodimethane concentration in the photolysate of **3e** was as low as for most of the other photolysates; however, the rate of the reaction of **1e** with NO was about 100 times faster than the reaction of **1a** in the same solvent.

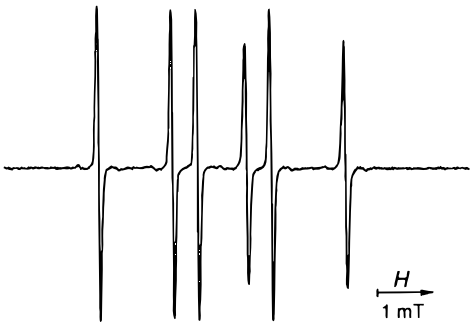


Figure 6. ESR spectrum of **2k** in acetonitrile at 20 °C, recorded 30 min after mixing of the photolysate of **3k** with NO solution.

The spectroscopic and kinetic data for the photolysate of 1,1,3-triphenyl-3-methoxyindan-2-one (**3i**) were, with one exception, very similar to the photolysate of the dimethoxy system **3a**. The extrapolated, initial signal intensity of the ESR spectrum of **2i** was similarly high, indicating a photostationary concentration of *o*-quinodimethane **1i** of about 350 μM. The ESR signal reached more or less the same high level as **2a** but showed an almost linear growth for several hours. Therefore, no rate constant for this growth is given. Markedly different to **1a**, however, was the very low concentration of 0.6 μM as estimated from the UV/vis absorption of the stopped-flow experiment. This fact indicated that, contrary to the dimethoxy system **1a**, the isomers of **1i**, namely (*Z*)-**1i** and (*E*)-**1i**, either both have relatively short lifetimes at room temperature or a probable long-lived isomer had been produced only in minor amounts. On the other hand, the stopped-flow experiments gave a rate constant for the **1i** + NO reaction not much different to that of **1a**. As with **6a**, the reaction of benzocyclobutene **6i** with excess NO led to a complete conversion of **6i** after a few hours.

The ESR investigation of the reaction of NO with the photolysate from 1-[(ethoxycarbonyl)methoxy]-1,3,3-triphenylindan-2-one (**3j**) paralleled the results obtained from the diester-substituted analogue **2b**. A stopped-flow experiment was not performed.

When the photolysate from 1,1,3-triphenylindan-2-one (**3k**) was mixed with a benzene solution of NO the six-line ESR spectrum of **2k** (Figure 6) was formed "instantaneously". The large doublet hyperfine splitting of a(H) = 1.851 mT is very characteristic for conformationally fixed β-hydrogen atoms in 5-membered cyclic nitroxides,[20] reflecting a favorable orientation of the β-C−H bond with

(22) Slight differences in the ESR parameters of *meso* and *rac* diastereomers of cyclic nitroxides are, in principle, generally expected, e.g., due to structural differences (extent of pyramidalization of the central nitrogen or bond length alterations) and/or solvent effects (as induced by the different dipole moments of both diastereomers).

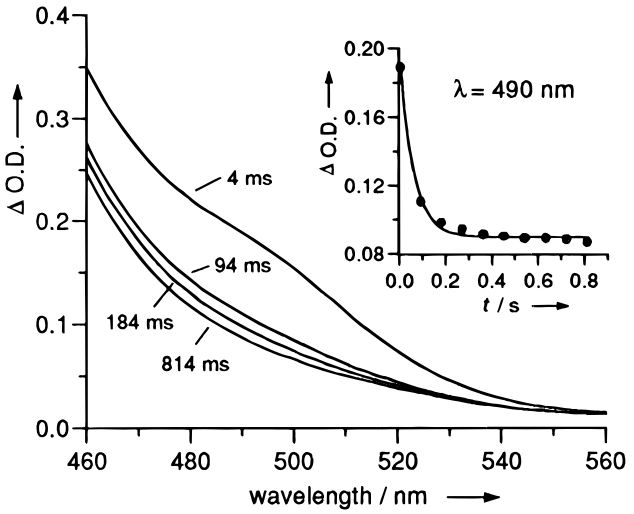


Figure 7. Spectrophotometric stopped-flow measurement of the decay of the absorption of **1k** in the reaction with NO in benzene at 23 °C. Inset: First-order decay trace of the absorption at 490 nm.

respect to the SOMO of the radical. This spectrum provided further evidence for the general structure of the nitroxide radicals generated in this study. The **3k/1k** system is the only one in which no further increase of the ESR signal intensity of **2k** was observed, showing (also in agreement with UV/vis and NMR observations) that the corresponding benzocyclobutene **6k** is stable under the applied conditions, i.e., does not undergo ring opening to the corresponding *o*-quinoid structure. A good correspondence between the ESR- and UV/vis-spectroscopically detected concentration of **1k** was found, which implies a sufficient thermal stability of this *o*-quinodimethane. Interestingly, the rate of reaction of **1k** with NO [k_2^{sf}(**1k**) = 2430 M^{-1} s^{-1}] (Figure 7) is at least 1 order of magnitude higher than measured for the alkoxy-substituted counterparts **1i** and **1j** and almost identical to that of **2e**.

Compound **1l** was found to be the most reactive *o*-quinodimethane of the present study, as revealed by the stopped-flow experiment [k_2^{sf}(**1l**) = 4140 M^{-1} s^{-1}] with the photolysate from 1,1,3-triphenyl-3-methylindan-2-one (**3l**). The UV/vis-determined concentration of **1l** corresponded well with the extrapolated initial ESR signal intensity of nitroxide **2l**. Though still in the same order of magnitude, the rate of the slow growth of the ESR signal of **2l** [k^{ESR}(**2l**) = 7.5×10^{-4} s^{-1}] was the highest among our series; i.e., benzocyclobutene **6l** should have a slightly lower thermal stability than the other benzocyclobutenes mentioned here. On the other hand, nitroxide **2l** appeared to be less persistent than the other nitroxides, as its ESR signal intensity only increased for about 40 min after mixing of the reactants, after which it slowly decayed again.

Discussion

Photolytic Decarbonylation of 2-Indanones. The photolytic decarbonylation of the alkyl- and alkoxyl-substituted 2-indanones **3** investigated in this paper occurred in high yields to produce the corresponding 7,8-diphenyl- or 7,7,8-triphenylbenzocyclobutenes **6** as by far the major products, in agreement with literature reports on other phenyl-substituted 2-indanones.[12,14] In two cases (**3f** and **3l**) products **9**, deriving from of a 1,5-hydrogen shift reaction of the intermediate *o*-quinodimethanes **1**, were also formed. The desired *o*-quinodimethanes were produced only in very low amounts (0.1−0.001% relative to **3**), thus rendering the photolysis of 2-indanones not a particularly good method for the production of *o*-quinodimethanes as nitric oxide cheletropic traps (NOCTs).

It is interesting to note that in case of the 1,3-diphenyl-1,3-dialkoxyl-substituted 2-indanones **3a**−**d** the *meso*-configuration of the starting ketone is largely (>90%) preserved in the benzocylobutene products **6a**−**d**. This implies that the decay of the intermediate triplet biradicals **3a**−**e**(B_2) (Scheme 4) to the *o*-quinodimethanes **1a**−**e** should proceed primarily to the *E,Z* configurational isomers of **1a**−**e**, which would produce the corresponding *meso*-benzocylcobutenes **6a**−**e** thermally via a symmetry-allowed conrotatory ring closure. (The direct collapse of triplet diradicals **3a**−**e**(B_2) to **6a**−**e** is a spin-forbidden process and, therefore, rather unlikely). However, due to their strong UV/vis absorptions the *o*-quinodimethanes are photolytically unstable species; hence, if the *Z,Z*- and *E,E*-isomers of **1a**−**e** also would have been produced from **3a**−**e**(B_2) they might have been further converted to *meso*-**6a**−**e** via a photolytically allowed disrotatory process in the course of the photolyses. Sound evidence for the formation of configurationally isomeric *o*-quinodimethanes is provided by the LFP experiments on **3a** and **3i**. The results from **3a** are particularly enlightening. Here, similar, overlapping absorption spectra of three photolytically generated species were detected, two of which decayed rather rapidly with rate constants in the range of 10^6 and 10^4 s^{-1}, respectively, whereas the third was very persistent, only decaying within 30 h at 40 °C. We attribute the three absorbing species observed in the LFP experiment to the three stereoisomers of **1a** by the arguments given above. In particular, the insensitivity of the decay rates of the transient absorptions on the presence of molecular oxygen dismissed the intermediate triplet diradicals **3a**(B_1) and **3a**(B_2) as the absorbing species. Our results are in line with observations made by Quinkert et al.,[14b] who determined for the 7,7,8,8-tetraphenyl-*o*-quinodimethane (**1m**) a decay rate constant of k^{296}(**1m**) = 2.8×10^4 s^{-1} and in case of the 7,8-diphenyl-*o*-quinodimethane (**1g**) also observed three similarly absorbing, transient species of markedly different lifetimes.

With regard to the time resolution of the LFP experiment (ca. 20 ns), the lifetime of the secondary triplet diradical **3a**(B_2) must be <20 ns, about 2 orders of magnitude shorter than found for corresponding 7,7,8,8-tetraalkyl-*o*-quinodimethane systems.[4,11] This fact is in agreement with observations reported by Scaiano.[12] The persistency of the third stereoisomer of **1a** was confirmed by the UV/vis spectrum of the photolysate from **3a**, which exhibits a rather strong absorption in the 400−600 nm range. Since decay of this absorption occurred at 40 °C within 30 h (from which we estimate a rate constant in the range of 10^{-6} s^{-1} at 20 °C), the activation barrier for decay of the corresponding *o*-quinodimethane is roughly estimated to be about 12−15 kcal mol^{-1} higher than the barrier for reaction of the two other isomers. We assume that the long-lived isomer of **1a** is the one having the (*E,E*)-diphenyl ((*Z,Z*)-dialkoxy) configuration. The reason for this assignment is based on the observations made with the triphenylalkoxy systems **3h**−**j**, where no "kinetically stabilized" (*Z,Z*)-dialkoxy configuration is possible, and therefore, only minor amounts of *o*-quinodimethanes could be detected in the photolysates by conventional UV/vis spectroscopy. Support for this view

is also provided by Jefford *et al.*,[23] who showed that the concerted, conrotatory ring opening of donor-substituted benzocylobutenes occurs preferably by rotation of the donor subtituents into the *trans* positions of the related *o*-quinodimethanes. Vice versa, the conrotatory ring closure of (*Z,Z*)-dialkoxy-*o*-quinodimethanes appears to be unfavorable. The ca. 35 times lower photostationary yield of **1a** in benzene-d_6 compared to CD_3CN might be explained by a strong solvent effect on the distribution of the diastereomers of **1** (e.g., by quenching of the excited states) and/or a more effective photochemical destruction of **1a** in benzene solution.

NO Trapping Experiments. The ESR spectroscopic monitoring of the buildup of the nitroxide radicals **2** after mixing of the photolysates from the indanones **3** with solutions of NO revealed that the nitroxide radicals are formed in a "two-phase" process; i.e., two different precursors are present in the photolysates, which react with NO at significantly different rates to give the same radical product. Kinetic stopped-flow experiments, by monitoring the decay of the UV/vis absorptions in the 400−500 nm range, showed that the fast nitroxide-forming reaction is indeed the reaction of the *o*-quinodimethanes with NO. The estimated second-order rate constants (Table 3) for this reaction cover the range of 10−4000 M^{-1} s^{-1}, markedly dependent on the substitution pattern of the *o*-quinoid system. Though only a limited number of rate data are currently available, it seems that the alkoxyl-substituted 7,8-diphenyl- and 7,7,8-triphenyl-*o*-quinodimethanes generally tend to react slower with NO by roughly 2 orders of magnitude than the unsubstituted or alkyl-substituted ones; compare, e.g., the rate constants of **1a** vs **1e** and **1i** vs **1l**. The higher reactivity of the methyl-substituted systems **1e, 1l** versus the methoxyl-substituted ones **1a, 1e** is unlikely due to a more pronounced steric destabilization of the *o*-quinodimethane structure by the methyl substitutents, as, for example, the 7,7,8-triphenyl-*o*-quinodimethane (**1k**) is much more reactive than the sterically more congested methoxyl system **1i** . These relationships imply a pronounced electronic influence on the reactivity of our *o*-quinodimethanes. The rate constant of $k = 310$ M^{-1} s^{-1} for reaction of NO with our first NO trap, 7,7,8,8-tetramethyl-*o*-quinodimethane (NOCT-1; see Introduction), also falls in the above range.[24] This would mean that there is no special "phenyl effect" on the reactivity toward NO. The differences in the rate constants of the alkoxyl systems **1a** and **1b** or **1c**, on the other hand, reveal some other influence of the substituents rather than a purely electronic one. One should keep in mind, however, that we do not know what the actual configuration or distribution of possible configurations of the active NO traps might be in our photolysates. The reactivity of the *o*-quinodimethanes toward NO certainly is governed by steric and electronic influences of the terminal substitutents; however, at the present point even a qualitative judgement on the relative importance of both effects is not possible.

The ESR experiments with the purified *meso*-7,8-dimethoxy-7,8-diphenylbenzocyclobutene (**6a**) (Figure 4) as well as the complete consumption of this and other benzocyclobutenes in the long-term reaction with NO proved that those phenyl-substituted benzocyclobutenes that are thermally unstable (as indicated by the slow conversion into 4a,10-dihydroanthracene and anthracene derivatives) react with nitric oxide to produce the corresponding nitroxide radicals **2**. This reaction is most easily explained by the trapping (with rate constants as discussed above) of the small amounts of the corresponding *o*-quinodimethanes in equilibrium with the benzocyclobutene; i.e., the rates of the "slow" formation of nitroxides **2** would indeed represent the rate of ring-opening of the benzocyclobutenes. Very recently, Roth and co-workers[7] have shown that the formally symmetry-forbidden *meso/rac* isomerization of 7,8-diphenylbenzocyclobutene (**6g**) has an activation barrier only 1 kcal mol^{-1} above the barrier of the symmetry-allowed conrotatory ring opening. The isomerization is believed to proceed via an orthogonal biradical intermediate. A similar situation, therefore, is very likely for our our systems. Thus, the rates of the **6** + NO reactions might also include the trapping of the corresponding biradical intermediates. However, a direct reaction of NO with the benzocyclobutenes cannot be completely ruled out presently because at least the **6a** + NO reaction is much faster than the thermal *meso/rac* isomerization. Investigations to clarify this point are in progress. The rate data (Table 3) show that the slow nitroxide-forming process is somewhat influenced by the substitution pattern of the tetrasubstituted benzocyclobutenes, the rate constants varying by a factor of 20. Steric interactions should provide the major contribution to the stability of our benzocyclobutene systems, as is evident from the stability of the trisubstituted benzocyclobutene **6k**, which is completely stable at room temperature and, hence, does not react with NO to produce nitroxide radicals **2k**.

***o*-Quinodimethanes and Benzocyclobutenes as Nitric Oxide Cheletropic Traps (NOCTs).** The formation of strong ESR signals of nitroxides **2** demonstrates that the small concentrations of the *o*-quinodimethanes **1** are sufficient for the application of the photolysates as NO trapping reagents in solution, as has been demonstrated before.[3−5]

In view of the desired (see Introduction) thermodynamic stabilization of *o*-quinodimethanes by introduction of terminal phenyl substitutents combined with the suppression of 1,5-hydrogen shift reactions by alkoxyl substituents, most of the *o*-quinodimethanes generated in this study disappointingly appeared to be rather unstable species. This is due to the now-opened route to form stable benzocyclobutene derivatives, the exception being the (probably kinetically stabilized) *Z,Z*-conformer of **1a**. Of course, one would prefer a synthetic method by which persistent, reactive *o*-quinodimethanes would be produced in preparative yields without the production of large amounts of byproducts. The unfavorable cyclization to benzocyclobutenes as well as the 1,5-hydrogen shift can be avoided by generating bicyclic *o*-quinodimethanes in which the terminal carbon atoms of the quinoid system are fixed by the ring structure. Related work is in progress.[24]

As has been demonstrated by the *o*-quinodimethanes NOCT-1 and NOCT-4 (see Introduction), a rate constant of about 300 M^{-1} s^{-1} for the reaction with NO is sufficient to trap some NO in biological environment.[3−5] However, this has been done with a line of cells, macrophages, which are known to produce high levels (nmol range) of NO. For the trapping of NO from low-level biological sources (e.g., brain; pmol NO levels) such rate constants are too low in order to compete with the destruction of NO by other reactions such as oxidation, addition to iron

(23) Jefford, C. W.; Bernardinelli, G.; Wang, Y.; Spellmeyer, D. C., Buda, A.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1157−65.

(24) Bätz, T., Korth, H.-G.; Sustmann, R. Universität − GH Essen, unpublished results.

complexes, and so forth.[1] Currently, our rate constants are far below the absolute desirable optimum, i.e., a diffusion-controlled rate constant for the *o*-quinodimethane + NO reaction. However, the fact that the simple exchange of methoxy goups by methyl groups is connected with an increase of the rate constants by a factor of 10−100 gives some hope that the reactivity of our NOCTs can be increased further by suitable structural variations. We estimate that a rate constant in the range of 10^6 M^{-1} s^{-1} will be sufficient for a useful NO trap for biological applications.

The low rate of reaction of our benzocyclobutenes with NO certainly renders them to be useless as preparatively easily accessible "reservoirs" for NOCTs under physiological conditions. Of course, one might further destabilize the benzocyclobutene ring in order to increase the rate of formation of the *o*-quinodimethanes. On the other hand, this would probably defacilitate the synthetic preparation of the benzocyclobutenes. Substituted benzocylobutenes of the present type, however, can be advantageously applied as NO traps for situations where the generated NO is long-lived enough and/or the NO is generated at high rates, e.g., in the screening for NO-releasing drugs or investigations concerning NO-related chemistry. For example, this has been demonstrated in the investigation of the oxygen-dependence of the cytotoxicity of NO-releasing compounds.[9]

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra (internal standard TMS): Varian Gemini-200 and Bruker AMX-300. IR (KBr pellet): Perkin-Elmer 1600 series FTIR. UV/vis: Varian Cary 219, modified for use with light pipes and thermostatable sample holders. GC/MS (70 eV): Hewlett-Packard HP 5971A mass-sensitive detector and HP5890 GC, capillary column HP 1; 50 m × 0.2 mm; SF 0.33 μm. High-resolution MS (70 eV): Fisons Instrument VG Pro Spec 300. HPLC: Varian LC 5000 and Hewlett-Packard 1040 diode array UV detector, Varian MCH-10 column (10 μm; 4 × 300 mm). Stopped-flow UV/vis measurements (time range 2 ms to minutes): Hi-Tech Scientific SF 40 instrument and Hewlett-Packard 9153c computer. ESR (9.4 GHz): Bruker ER-420 X-band spectrometer. ESR data acquisition: 486 PC equipped with a Microstar DAP 1200/4 data acquisition board and DigiS (GfS Aachen, Germany) software. Melting points (uncorrected): Büchi 510.

Materials. For the synthesis of 1,3-diphenyl-substituted 2-indanones ninhydrin was used as starting material. Ketalization of ninhydrin monohydrate (Aldrich) according to Kuhn and Trischmann[25] gave **2,2-dimethoxyindan-1,3-dione** in 81% yield, mp 69 °C (lit.[25] 70−71 °C).

1,3-Dihydroxy-2,2-dimethoxy-1,3-diphenylindan (**4**) was obtained via Grignard reaction of 2,2-dimethoxyindan-1,3-dione following the procedure of Holland and Jones,[17b] yield 76%, mp 114 °C (lit.[17b] mp 116−118 °C). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.85 (s, 6H), 4.28 (s, 2H, OH), 7.57−7.15 (m, 14H).

***meso*-1,3-Dihydroxy-1,3-diphenylindan-2-one (3f)**[26] was prepared by hydrolysis of **4** in 16% hydrochloric acid/acetic acid (9:8) to give 59% **3f**, mp 230−235 °C dec (lit.[26] mp 225−240 °C dec). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 6.67 (s, 2H, OH), 7.15−7.05 (m, 10 H), 7.60−7.53 (m, 4H, AA′BB′). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 79.3, 125.5, 126.8, 127.5, 127.7, 129.6, 141.0, 143.0, 214.0.

***meso*-1,3-Dimethoxy-1,3-diphenylindan-2-one (3a).** A mixture of **3f** (5.0 g, 15.8 mmol), iodomethane (20 mL, 321 mmol), and silver(I) oxide (7.51 g, 54.5 mmol) in DMF (120 mL) was stirred for 2 d at room temperature. The mixture was poured into trichloromethane (250 mL) and the precipitate filtered off and washed once with trichloromethane. The combined filtrate was washed three times with a 5% aqueous solution of sodium cyanide (100 mL each) and three times with water (100 mL each). After being dried over magnesium sulfate the solvent was evaporated and the oily residue dried under vacuum at 50 °C and recrystallized from ethanol to afford 3.19 g **3a** (59%), mp 131 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.32 (s, 6H, OCH_3), 7.10 (m, 10H), 7.65 (m, 4H, AA′BB′). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 53.6, 85.6, 126.6, 126.8, 127.5, 128.1, 128.3, 130.2, 138.1, 140.5, 221.5. IR (KBr, cm^{-1}): 3060, 3039, 2954, 2923, 2833, 1761, 1185, 1092, 762, 746, 700. UV/vis (acetonitrile, nm) λ_{max} (lg ϵ): 269 (3.45), 277 (3.36), 344 (2.60), 355 (2.60). MS (GC/MS, 70 eV) m/z: 316 (M^+ − CO, 38), 301 (M^+ − $COCH_3$,100), 239 (14), 165 (12) , 105 (13) , 77 (18). HRMS (70 eV): calcd (M^+) 344.1412, obsd 344.1419.

***meso*-1,3-Bis[(ethoxycarbonyl)methoxy]-1,3-diphenylindan-2-one (3b).** To a solution of **3f** (3.0 g, 9.48 mmol) in DMF (50 mL) were added ethyl iodoacetate (12.0 mL, 101 mmol) and silver(I) oxide (10.0 g, 43.25 mmol). The mixture was stirred for 3 d at room temperature and was then poured into trichloromethane (200 mL). The precipitated silver salts were filtered off, and the filtrate was washed three times with a 5% aqueous solution of sodium cyanide (50 mL each) and five times with water (50 mL each). After the filtrate was dried over magnesium sulfate the solvent was evaporated and the oily residue recrystallized from pentane/benzene (6:1) to give 3.28 g of **3b** (71%), mp 93−94 °C. ^{1}H NMR (300 MHz, CD_3CN) δ: 1.19 (t, ^3J = 7.1 Hz, 6H), 3.97 (d, ^3J = 15.4 Hz, 2H), 4.10 (q, ^3J = 7.1 Hz, 4H), 4.12 (d, ^3J = 15.4 Hz, 2H), 7.21−7.07 (m, 10H), 7.72−7.63 (m, 4H, AA′BB′, arom H of indanone). ^{13}C NMR (75 MHz, CD_3CN) δ: 14.2, 61.5, 64.4, 86.3, 127.5, 128.4, 129.1, 129.7, 131.9, 138.4, 140.5, 169.9, 211.9. IR (KBr, cm^{-1}): 3062, 2924, 1761, 1743 ($\nu_{C=O}$), 1120, 768, 698. UV/vis (acetonitrile, nm) λ_{max} (lg ϵ) 270 (3.45), 277 (3.36), 344 (2.61), 354 (2.55). MS (70 eV) m/z: 488 (1, M^+), 460 (4, M^+ − CO), 373 (70), 269 (100). HRMS (70 eV): calcd (M^+) 488.1835, obsd 488.1830.

Anal. Calcd for $C_{29}H_{28}O_7$ (488.18): C, 71.30; H 5.78. Found: C, 71.67; H, 7.20.

***meso*-1,3-Bis(carboxylmethoxy)-1,3-diphenylindan-2-one (3c).** A solution of **3b** (2.50 g, 5.1 mmol) in a mixture of ethanol (50 mL) and 10% aqueous sodium hydroxide (50 mL) was stirred for 5 h at room temperature and then acidified with 2 M hydrochloric acid and extracted three times with trichloromethane (50 mL each). The combined organic layers were dried over magnesium sulfate, the solvent was evaporated, and the oily residue was recrystallized from pentane/benzene (5:2) to give 1.42 g (3.3 mmol, 63%) of **3c**, mp 185−195 °C dec. ^{1}H NMR (200 MHz, DMSO-d_6) δ: 3.97 (d, ^2J = 15.8 Hz, 2H), 4.12 (d, ^2J = 15.8 Hz, 2H), 7.23−7.02 (m, 10H) 7.75−7.63 (m, 4H, AA′BB′). ^{13}C NMR (50 MHz, CD_3CN) δ: 63.8, 86.3, 127.5, 128.3, 129.1, 129.5,131.9, 138.2, 140.3, 170.3, 211.6. IR (KBr, cm^{-1}): 3421 (ν_{OH}), 3062, 2924, 1761, 1743 ($\nu_{C=O}$), 1448, 1120, 768, 698. UV/vis (acetonitrile) λ_{max} (lg ϵ): 270 (3.32), 277 (3.23), 344 (2.47) nm. MS (70 eV) m/z: 404 (1, M^+), 328 (45), 270 (100). HRMS (70 eV) calcd 404.1260 (M^+ − CO), obsd 404.1281. Anal. Calcd for $C_{25}H_{20}O_7$ (404.13): C, 69.44; H, 4.66. Found: C 69.25; H, 4.68.

Disodium *meso*-1,3-Bis(carboxylatomethoxy)-1,3-diphenylindan-2-one (3d). A solution of **3c** (0.35 g, 0.81 mmol) in ethanol (15 mL) was neutralized (pH meter control) by dropwise addition of a solution of sodium ethanolate (from dissolution of 0.2 g sodium in 30 mL of ethanol). The solvent was evaporated and the residue dried at 50 °C under vacuum for 3 d to give 0.35 g of **3d** (88%), mp 219−230 °C dec. ^{1}H NMR (200 MHz, D_2O) δ: 3.79 (d, ^2J = 14.7 Hz, 2H), 3.97 (d, ^2J = 14.9 Hz, 2H), 7.13 (m, 10H) 7.79 (m, 4H, AA′BB′). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.84 (d, ^2J = 14.7 Hz, 2H), 4.01 (d, ^2J = 14.7 Hz, 2H), 7.04 (m, 4H), 7.21 (m, 6H), 7.70 (m, 4H). IR (KBr, cm^{-1}): 3057, 2965, 2907, 1760 ($\nu_{C=O}$), 1491, 1219, 1126, 765, 697. UV/vis (phosphate buffer pH 7.8, nm) λ_{max} (lg ϵ): 342 (2.62).

1,3-Diphenylindan-2-one (3g) was prepared from **4** by a literature procedure,[17b] yield 79%, mp 153−156 °C dec (lit.[17b] mp 155 °C dec). ^{1}H NMR (200 MHz, CD_3CN) δ: 4.95 (s, 2H), 7.41−7.06 (m, 14H). IR (KBr, cm^{-1}): 3054, 3026, 2884, 1754 ($\nu_{C=O}$), 1598, 759, 742,700. UV/vis (acetonitrile, nm) λ_{max} (lg ϵ): 268 (3.17), 276 (3.12), 303 (2.62), 313 (2.56), 325 (2.25).

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1,3-Dimethyl-1,3-diphenylindan-2-one (3e). To a vigorously stirred suspension of powdered sodium hydroxide (4.20 g, 74.9 mmol) in DMSO (15 mL) was added at 60 °C within 1 h a suspension of **3g** (2.0 g, 7.0 mmol) in a mixture of iodomethane (6.0 mL, 95.4 mmol) and DMSO (10 mL). After further addition of iodomethane (2.0 mL, 31.8 mmol) the mixture was stirred for 3 h at 60 °C and 2 h at room temperature. The solution was poured into ice−water (100 mL) and extracted five times with petroleum ether (boiling range 40−60 °C; 50 mL each), and the combined organic phases were dried with magnesium sulfate. After evaporation of the solvent the orange-colored, oily residue was dissolved in diethyl ether and the solution filtered over neutral alumina (30 × 4.4 cm column). The solvent was evaporated from the eluate and the yellow residue stirred for 3 d with pentane. The colorless precipitate was filtered off and dried under vacuum to give 0.81 g of **3e** (2.6 mmol, 37%) as a 1:1.1 mixture of the *meso* and *rac* diastereomers. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.68, 1.78 (s, 6H), 7.45−7.03 (m, 14H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 6.0, 26.4, 57.3, 57.7, 125.2, 125.5, 126.5, 126.8, 126.9, 127.2, 128.1, 128.3, 128.4, 142.1, 143.1, 144.5, 145.3, 218.2, 219.1. IR (KBr, cm^{-1}): 3063, 3032, 2973, 2929, 1744 ($\nu_{C=O}$), 1596, 1492, 766, 729, 700. UV/vis (acetonitrile, nm) λ_{max} (lg ϵ): 261 (3.22), 267 (3.24), 274 (3.18), 284 (2.77), 302 (2.64), 313 (2.70), 323 (2.52).

1-Hydroxy-1,3,3-triphenylindan-2-one (3h). This compound was prepared in four steps starting from diphenylinden-1-one (Aldrich) according to the procedure reported by Koelsch,[27] overall yield 25%, mp 160 °C (lit.[17b] mp 161 °C). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.34 (s, 1H, OH), 7.59−6.97 (m, 19H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) δ: 58.1, 68.8, 125.8, 127.0, 127.4, 128.2, 128.3, 128.4, 128.5, 128.7, 129.0, 129.2 u. 129.5, 137.7, 139.6, 141.4, 143.1, 144.8, 214.0. IR (KBr, cm^{-1}): 3414, 3057, 3026 , 1754 ($\nu_{C=O}$), 1596, 1046, 1032, 746, 696. UV/vis (acetonitrile, nm) λ_{max} (lg ϵ): 269 (3.30), 277 (3.18), 329 (2.56). MS (70 eV) *m*/*z*: 376 (5, M^+), 360 (11), 348 (100, $M^+ - CO$), 271 (44). HRMS (70 eV): calcd 376.1463 (M^+), obsd 376.1474.

1-Methoxy-1,3,3-triphenylindan-2-one (3i). This compound was prepared by the method of Oku et al.,[28] yield 63%, mp 165−166 °C (lit.[28] mp 168 °C). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.22 (s, 3H), 7.54−6.93 (m, 19H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 53.5, 68.6, 88.0, 126.4, 126.9, 127.1, 127.6, 127.9, 128.1, 128.6, 129.3, 130.0, 138.5, 138.9, 141.0, 143.1, 145.5, 212.8. IR (KBr, cm^{-1}): 3060, 3031, 2932, 2830, 1754 ($\nu_{C=O}$), 1597, 1087, 752, 697. UV (acetonitrile, nm) λ_{max} (lg ϵ): 269 (3.35), 278 (3.22), 327 (2.47).

1-[(Ethoxycarbonyl)methoxy]-1,3,3-triphenylindan-2-one (3j). To a solution of **3h** (3.0 g, 7.97 mmol) in DMF (45 mL) were added ethyl iodoacetate (9.0 mL, 67.5 mmol) and silver(I) oxide (14.4 g, 62.1 mmol). The mixture was stirred for 3 d at room temperature and was then poured into trichloromethane (150 mL). The precipitated silver salts were filtered off, and the filtrate was washed three times with a 5% aqueous solution of sodium cyanide (50 mL each) and five times with water (50 mL each). After the filtrate was dried over magnesium sulfate the solvent was evaporated and the oily residue recrystallized from hexane/benzene (3:1 v/v) to give 3.30 g of **3j** (89%), mp 153−155 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.22 (t, ^3J = 7.2 Hz, 3H), 3.96 (d, ^2J = 15.3 Hz, 1H), 4.07 (d, ^2J = 15.3 Hz, 1H), 4.15 (q, ^3J = 7.2 Hz, 4H), 7.62−6.97 (m, 19H). ^{13}C NMR (75 MHz, C,H-COSY, $CDCl_3$) δ: 14.1 (CH_3), 60.9 (CH_2CH_3), 63.7 (OCH_2), 66.8 (CPh_2), 87.8 [$CPh(OCH_2CO_2Et)$], 126.4, 127.1, 127.2, 127.6, 127.7, 128.0, 128.2 (2C), 128.3, 128.7, 128.9, 129.3, 130.3 (tert arom C), 138.0, 138.2, 140.3, 143.1, 145.1 (quart arom C) 169.4 (*C*O(OEt)), 212.4 (C=O). IR (KBr, cm^{-1}): 3063, 2912, 2856, 1764 ($\nu_{C=O}$), 1593. UV/vis (acetonitrile, nm) λ_{max} (lg ϵ): 270 (3.45), 278 (3.34), 329 (2.64). MS (70 eV) *m*/*z*: 462 (1, M^+), 434 (10, $M^+ - CO$), 418 (30), 330 (100). HRMS (70 eV): calcd 462.1830 (M^+), obsd 462.1793. Anal. Calcd for $C_{31}H_{26}O_4$ (462.18): C, 80.49; H, 5.68. Found: C, 80.53; H, 5.69.

1,1,3-Triphenylindan-2-one (3k). By deoxygenation of **3h**;[27] yield 94%, mp 103 °C (lit.[27] mp 105−109 °C). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.83 (s, 1H), 7.40−7.00 (m, 19 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 58.1, 68.8, 125.8, 127.0, 127.4, 128.2, 128.3, 128.4, 128.5, 128.7, 129.0, 129.2, 129.5, 137.7, 139.6, 141.4, 143.1, 144.8, 214.0. IR (KBr, cm^{-1}) 3054, 3026, 2883, 1754 ($\nu_{C=O}$), 1598, 1494, 1060, 759, 741, 699. UV/vis (acetonitrile, nm) λ_{max} (lg ϵ): 277 (3.07), 328 (2.50).

1-Methyl-1,3,3-triphenylindan-2-one (3l). A solution of **3k** (2.0 g, 5.54 mmol) and iodomethane (3.0 mL, 48.0 mmol) in DMSO (10 mL) was added to a stirred suspension of potassium hydroxide (6.80 g, 121 mmol) in DMSO (20 mL). After being heated to 50 °C the mixture was stirred for 3 h, cooled, and poured into ice−water (150 mL). The precipitate was filtered off and dried under vacuum. The product then was refluxed with trichloromethane (50 mL) for 15 min, the solution was cooled to room temperature, and insoluble byproducts were removed by filtration. The solvent was evaporated and the residue recrystallized from pentane, affording 1.04 g of **3l** (2.78 mmol, 50%), mp 107−110 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.78 (s, 3H), 7.45−6.95 (m, 19H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 26.1, 57.9, 68.2, 125.4, 126.7, 126.8, 126.9, 127.2, 127.3, 128.0, 128.2, 128.4, 128.8, 129.1, 141.9, 142.0, 143.7, 143.8, 144.8, 217.0. IR (KBr, cm^{-1}): 3062, 3031, 2962, 2923 , 1746 ($\nu_{C=O}$), 1600, 1031, 769, 746, 700. UV/vis (acetonitrile, nm) λ_{max} (lg ϵ): 261 (3.28), 268 (3.28), 275 (3.17), 308 (2.74), 317 (2.76), 330 (2.47). MS (70 eV) *m*/*z*: 374 (10, M^+), 356 (51, $M^+ - H_2O$), 346 (64, $M^+ - CO$), 331 (100). HRMS (70 eV): calcd 374.1671 (M^+), obsd 374.1681.

***meso*-2-Hydroxy-1,3-dimethoxy-1,3-diphenylindan (5).** To a stirred solution of **3a** (66.7 mg, 0.19 mmol) in dry diethyl ether (10 mL) was added $LiAlH_4$ (0.10 g, 2.6 mmol) under nitrogen, and the mixture was refluxed for 1 h. After the mixture was cooled to room temperature hydrolysis was performed by careful addition of 1 M sulfuric acid. Diethyl ether (20 mL) was added, and the organic layer was separated and washed three times with water. Drying over magnesium sulfate and evaporation of the solvent gave 59 mg (90%) of the diastereomeric mixture of *meso*-**5** in a 1:1.3 ratio. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.82 (d, ^3J = 2.9 Hz, 1H, OH), 3.16 (s, 6H), 3.21 (s, 6H), 3.60 (d, ^3J = 12.1 Hz, 1H, OH), 3.87 (d, ^3J = 12.1 Hz, 1H), 4.33 (d, ^3J = 2.9 Hz, 1H), 7.58−7.25 (m). The signals at δ 0.82 and 3.60 as well as the splitting of the signals disappeared on addition of D_2O.

Photolysis of 2-Indanones (General Procedure). All reactions were carried out with careful exclusion of oxygen under argon (Messer-Griesheim 99.999%). Typically, 5×10^{-2} M solutions of the 2-indanones in the deoxygenated solvent (acetonitrile, water, benzene) were transferred into a long-necked, septum-capped 1-cm UV quartz cell, and the cell was placed in an externally cooled methanol bath in a double-walled quartz jacket. Irradiation was performed in a Rayonet photoreactor (# RPR-100; The Southern New England Ultraviolet Co.) at 300 nm (RPR 3000 lamps) with continuous stirring of the solution by a slow stream of argon that was passed through the solution via a hypodermic needle. After photolysis the photolysates were rapidly transferred to dry, argon-flushed septum-capped vials by means of a gas-tight syringe and stored at −78 °C (dry ice). The photolysates were analyzed by GC/MS and ^{1}H and ^{13}C NMR spectroscopy as soon as possible after completion of the photolysis. With the exception of **6a** the photoproducts were not isolated. The conditions of the photolyses are given in Table 1. Spectroscopic data of the photoproducts are reported below.

Photolysis of 3a. A solution of **3a** (90.0 mg, 0.26 mmol) in acetonitrile (5 mL) was photolyzed (λ = 300 nm) at −7 °C for 4 h. The solution was transferred to a Schlenck tube, approximately half of the volume of the solvent was removed under vaccuum, and the tube was stored at −18 °C for 7 d during which time colorless *meso*-7,8-dimethoxy-7,8-diphenylbenzocyclobutene (*meso*-**6a**) crystallized; yield 26.1 mg (31%), mp 106−107 °C. ^{1}H NMR (300 MHz, CD_3CN) δ: 3.33 (s, 6H), 7.08−6.94 (m, 10H), 7.62 (m, 4H, AA′BB′). ^{13}C NMR (75 MHz, CD_3CN) δ: 53.9, 95.2, 126.4, 127.6, 128.0, 128.6, 130.6, 140.0, 146.1. UV/vis (HPLC, nm) λ_{max}: 258, 264, 269. MS (GC/MS, 70 eV) *m*/*z*: 316 (1, M^+), 301 (7, $M^+ - CH_3$), 285 (53), 270 (8), 254 (100), 238 (48), 165 (10), 77 (5). *rac*-7,8-Dimethoxy-7,8-diphenylbenzocyclobutene (*rac*-**6a**): ^{1}H NMR (300 MHz, CD_3CN) δ: 2.97 (s, 6H), 7.39−7.33 (m, 10H), 7.66−7.58 (m, 4H,

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AA′BB′). ^{13}C NMR (75 MHz, CD_3CN) δ: 53.0, 94.3, 126.0, 128.4, 128.6, 129.3, 130.3, 139.7, 145.7. UV/vis (HPLC, nm) λ_{max}: 258, 263, 269. Anthracene derivative (**8a**): UV/vis (HPLC, nm) λ_{max} 258, 357, 374, 396.

Photolysis of 3b. *meso*-7,8-Bis[(ethoxycarbonyl)methoxy]-7,8-diphenylcyclobutene (*meso*-**6b**). ^{1}H NMR (200 MHz, CD_3CN) δ: 1.16 (t, ^3J = 7.0 Hz, 6H), 4.09 (q, ^3J = 7.0 Hz, 4H), 4.27 (d, ^2J = 16.6 Hz, 2H), 4.37 (d, ^2J = 16.6 Hz, 2H), 6.99 (m, 10H), 7.70−7.50 (m, 4H, AA′BB′). ^{13}C NMR (50 MHz, CD_3CN) δ: 14.2, 61.2, 65.6, 95.9, 126.4, 127.9, 128.1, 128.4, 131.2, 139.8, 145.5, 171.2.

Photolysis of 3c. *meso*-7,8-Bis(carboxylmethoxy)-7,8-diphenylbenzocyclobutene (*meso*-**6c**). ^{1}H NMR (200 MHz, CD_3CN) δ: 4.21 (d, ^2J = 16.4 Hz, 2H), 4.31 (d, ^2J = 16.4 Hz, 2H), 7.00 (m, 10H), 7.68−7.63 (m, 4H AA′BB′). ^{13}C NMR (50 MHz, CD_3CN) δ: 64.8, 95.3, 126.4, 128.3, 128.6, 131.7, 138.8, 144.9, 171.5.

Photolysis of 3d. Disodium *meso*-7,8-bis(carboxylatomethoxy)-7,8-diphenylbenzocyclobutene (*meso*-**6d**): ^{1}H NMR (200 MHz, CD_3CN) δ: 3.89 (d, ^2J = 15.3 Hz, 2H), 4.09 (d, ^2J = 15.2 Hz, 2H), 7.01 (m, 10H), 7.66 (m, 4H, AA′BB′). ^{13}C NMR (50 MHz, D_2O, DMSO) δ: 66.2, 94.2, 126.3, 128.4, 128.5, 129.0, 131.4, 138.3, 144.7, 178.0. UV/vis (HPLC, nm) λ_{max}: 278, 283, 290.

Photolysis of 3e. *meso*/*rac*-7,8-Dimethyl-7,8-diphenylbenzocyclobutene (**6e**). ^{1}H NMR (200 MHz, CD_3CN) δ: 1.16/1.83 (s, 6H, CH_3), 7.50−6.80 (m, 19H). ^{13}C NMR (75 MHz, CD_3CN) δ: 24.1/27.5, 61.3/61.9, 123.8, 124.6, 125.9, 126.1, 127.2, 127.7, 127.8, 128.2, 128.7, 128.9, 129.1,129.4, 145.2/145.9, 149.7/150.6.

Photolysis of 3h. 2-(Diphenylmethyl)benzophenone (**9h**). ^{1}H NMR (200 MHz, C_6D_6) δ: 5.87 (s, 1H), 7.69−6.99 (m,19H). UV/vis (HPLC, nm) λ_{max}: 252, 285 (sh). MS (70 eV) *m*/*z*: 348 (100, M^+), 330 (40), 271 (63), 165 (38).

Photolysis of 3i. 7-Methoxy-7,8,8-triphenylbenzocyclobutene (**6i**). ^{1}H NMR (300 MHz, CD_3CN) δ: 3.13 (s, 3H, OCH_3), 8.00−6.80 (m, 19H). ^{13}C NMR (75 MHz, CD_3CN) δ: 53.7, 72.8, 95.0, 125.2, 126.0, 126.5, 126.8, 127.6, 127.7, 128.1, 128.6, 128.7, 128.8, 129.7, 130.5, 139.7, 142.9, 143.2, 144.1, 148.5. UV/vis (HPLC, nm) λ_{max}: 264, 271. 9,10-Diphenylanthracene (**8m**). UV/vis (HPLC, nm) λ_{max}: 353, 372, 392. 4a,-10-Dihydroanthracene derivative (**7i**?): UV/vis (HPLC, nm) λ_{max}: 383.

Photolysis of 3j. 7-[(Ethoxycarbonyl)methoxy]-7,8,8-triphenylbenzocyclobutene (**6j**). ^{1}H NMR (300 MHz, CD_3CN) δ: 1.06 (t, ^3J = 7.1 Hz, 3H), 3.70 (s, 2H), 3.95 (q, ^3J = 7.1 Hz, 2H), 7.95−6.82 (m, 19H). ^{13}C NMR (75 MHz, CD_3CN) δ: 14.0, 61.2, 64.7, 73.1, 95.3, 125.4, 126.2, 126.9, 127.9, 128.0, 128.3, 128.5, 128.8, 129.0, 129.5, 129.6, 131.2, 140.1, 142.8, 143.0, 143.5, 148.5, 170.3. UV/vis (HPLC, nm) λ_{max}: 230, 259, 265, 272. 9,10-Diphenylanthracene (**8m**). UV/vis (HPLC, nm) λ_{max}: 354, 372, 392. 4a,10-Dihydroanthracene derivative (**7j**?). UV/vis (HPLC, nm) λ_{max}: 378.

Photolysis of 3k. 7,7,8-Triphenylbenzocyclobutene (**6k**). ^{1}H NMR (300 MHz, C_6D_6) δ: 5.48 (s, 1H, CH), 7.64−6.78 (m, 19H). ^{13}C NMR (75 MHz, DEPT, C_6D_6) δ: 62.3 (*C*HPh), 68.2 (*C*Ph_2), 124.2, 124.4, 126.1, 126.4, 126.7, 127.6, 128.0 (2C), 128.4, 128.5, 128.6, 129.1, 129.4 (tert arom C), 139.6, 142.3, 145.0, 147.0, 149.9 (quart arom C). UV/vis (HPLC, nm) λ_{max}: 259 (sh), 265, 273. 9,10-Diphenylanthracene (**8m**). UV/vis (acetonitrile, nm) λ_{max}: 338, 354, 373, 393.

Photolysis of 3l. 7-Methyl-7,8,8-triphenylbenzocyclobutene (**6l**). ^{1}H NMR (200 MHz, C_6D_6) δ: 1.55 (s, 3H, CH_3), 7.33−6.74 (m, 15H), 7.67−7.61 (m, 4H). UV/vis (HPLC) λ_{max}: 261, 268, 271 nm. α-Phenyl-*o*-(diphenylmethyl)styrene (**9l**). ^{1}H NMR (200 MHz, C_6D_6) δ: 4.89 (d, ^2J = 1.3 Hz, 1H), 5.54 (d, ^2J 1.3 Hz, 1H), 5.71 (s, 1H), 7.33−6.74 (m, 19H). UV/vis (HPLC, nm) λ_{max}: 250, 222.

Reaction of the Photolysates with NO Solution for ESR Experiments (General Procedure). NO from a cylinder (Messer-Griesheim 2.8; 99.8% NO) was purified by passing through a column of Ascarite (Aldrich) and 20% potassium hydroxide solution using an all-stainless steel line. Saturated NO solutions (typically 1.4×10^{-2} M)[21] were prepared by bubbling NO for 30 min through a deoxygenated (by bubbling with argon for 1 h) solvent in a septum-capped vial by means of hypodermic needles. Typically, 0.2−0.5 mL of cold (≤0 °C) solution from the photolysis of the indanones was transferred using a hypodermic syringe into an argon-flushed septum-capped quartz ESR tube (external diameter 3 mm for acetonitrile, 4 mm for benzene) or a 0.4 mm quartz flat cell (for water). A total of 0.02−0.1 mL of the NO solution was then rapidly added using a gas-tight hypodermic syringe, the solutions were briefly mixed by the Ar stream, and the ESR tube was placed in the cavity of the ESR spectrometer.

ESR Measurements. ESR experiments were performed at ambient temperature in a double cavity at microwave power levels of 1−10 mW and 0.4−1 G modulation amplitude. The second cavity contained a calibrated spin concentration standard. (Varian strong pitch; $c = 4.68 \times 10^{-5}$ M). ESR spectra were recorded as fast as possible (2−5 min) after addition of the NO solution. ESR parameters were refined by computer simulation using the LMB simulation program.[29] Spin concentrations were determined by double integration of the digitized spectra of the nitroxide radicals and comparison with the double integration of the signal from the spin standard. The spin standard was recorded with the same instrument settings (except, when necessary, for the signal gain) as the nitroxide signal. For the rapid-mixing ESR experiments a flow tube was developed[30] that allowed rapid mixing of the photolysate and the NO solution in the cavity of the ESR spectrometer. Solutions were injected into the mixing part of the flow tube via stainless steel tubes by 500 μL syringes, which were driven by a Hamilton digital diluter. The kinetics of formation of the nitroxide radical **2a** was evaluated by monitoring the growth of the $M_s = +1$ hyperfine line of its ESR signal.

Laser Flash Photolysis. LFP (Nd:YAG laser, Lumonics HY-750) (266 nm) experiments were carried out employing oxygenated and deoxygenated 10^{-2} M acetonitrile solutions of indanones **3a** and **3i** in 7 × 7 mm quartz cuvettes. Details of the equipment and experimental procedures have been described elsewhere.[31]

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Supporting Information Available: Copies of ^{1}H NMR spectra of *meso*-**3a**, *meso*-**3b**, *meso*-**3c**, *meso*-**3d**, *meso*/*rac*-**3e**, **3j**, **3l**, *meso*-**5**, *meso*-**6a**, *meso*-**6b**, *meso*-**6c**, *meso*-**6d**, **6i**, the photolysis mixtures **3e** → **6e**, **3h** → **9h**, and **3l** → **6l**, and the mixture of the thermal rearrangement *meso*-**6a** → *rac*-**6a** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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