Electronic Control of Stereoselectivity in Photocycloaddition Reactions. 4. Effects of Methyl Substituents at the Donor Olefin[1]

Axel G. Griesbeck* and Stefan Stadtmüller

Contribution from the Institut für Organische Chemie der Universität Würzburg Am Hubland, D-8700 Würzburg, FRG. *Received August 24, 1990. Revised Manuscript Received April 29, 1991*

Abstract: The photocycloaddition reaction of benzaldehyde with a series of methyl-substituted cycloalkenes (1-methyl- and 1,2-dimethylcyclopentene, 1-methyl- and 1,2-dimethylcyclohexene, and 5-methyl-2,3-dihydrofuran) was investigated and compared with the results of the corresponding parent hydrocarbons. In all cases, the incorporation of methyl groups led to inversion of stereoselectivity (e.g. for cyclopentene, endo/exo = 61:39; for 1,2-dimethylcyclopentene, endo/exo = 20:80). No influence on regioselectivity could be observed for the alicyclic cases 1-methylcyclopentene and 1-methylcyclohexene, whereas 5-methyl-2,3-dihydrofuran gave only one regioisomer. The reactive conformations of the intermediate 1,4-triplet biradicals are used to rationalize the observed diastereoselectivity.

The factors controlling the regio- and stereochemistry of photoreactions via triplet states are not well-understood. In contrast to the corresponding transformations via singlet excited states, pure steric parameters could not be the only ones crucial for predicting or explaining stereoselectivity phenomena. It has been known for a long time that [2 + 2] cycloaddition reactions (or Paternò-Büchi reactions) of electronically excited singlet carbonyl compounds occur with high *stereospecifity* (using Zimmerman's terminology[2]), e.g. (*E*)- and (*Z*)-1-methoxybutene react with S_1-acetone to give predominantly photoadducts (oxetanes) with retained cis and trans configurations, respectively.[3]

T_1-benzophenone on the other hand leads to a mixture of diastereomeric oxetanes of identical proportions from either *cis*- or *trans*-2-butene.[4] A (relatively long lived) triplet 1,4-biradical can serve as a logical explanation (rotation around single bonds) for the second experimental result. The case where two prochiral trigonal centers have to combine in the product-forming step makes the prediction of product stereochemistry more complicated. If intersystem crossing (ISC) from the triplet 1,4-biradical leads to the same singlet 1,4-biradical formed in the reaction between the substrate and an S_1-carbonyl compound, and if this transient species has a lifetime long enough for certain rotations around single bonds, the *stereoselectivity* of T_1 and S_1 reactions should be determined by the same factors (mostly by the size of the substituents and a proper alignment of p orbitals for bond formation).

Recently we have shown that the product stereoselectivity of simple Paternò-Büchi reactions between aromatic aldehydes and monoolefins such as cyclopentene, cyclohexene, 2,3-dihydrofuran, or 2,3-dihydropyran can be explained by the reactive conformations of the intermediate triplet 1,4-biradicals.[5,6] This concept corresponds to spin inversion control as postulated by Shaik[7] for concerted triplet reactions. The assumption of two-step processes is essential for our explanation, however. Analyzing the data set of reactions between aromatic aldehydes with unsubstituted cycloalkenes, a "masochistic" steric effect on product stereoselectivity could be deduced: the higher the size of the carbonyl substituent, the higher the amount of thermodynamically unfavored stereoisomer in the product mixture. At first sight, this tendency should also be valid for substituted cycloalkenes; steric repulsion (in the intermediary triplet 1,4-biradical conformation) between the substituent at the carbonyl carbon and the cycloalkene is greater, and consequently the amount of endo diastereomer is expected to increase. To investigate the applicability of this idea we used mono- and dimethyl-substituted cycloalkenes[8] as donor olefins. All photoreactions were performed in benzene as the solvent with olefins having oxidation potentials high enough to exclude efficient competition of electron-transfer processes and the formation of solvent-separated ion pairs.[9] Following the Rehm-Weller equation,[10] electron transfer is expected to be highly exothermic in the cases investigated here. As the triplet carbonyl source we employed benzaldehyde, in which intersystem crossing is fast enough (for benzophenone, $k_{ST} \approx 10^{11}$ s^{-1} and $\Delta E_{ST} = 5$ kcal; for benzaldehyde, $\Delta E_{ST} = 4$ kcal) to exclude singlet reactivity.[11]

Results

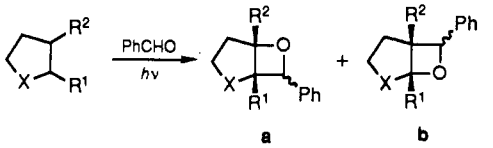
The results are shown in Table I; regioselectivity, expressed by the **a**/**b** ratio is not induced by a methyl group at the 1-position of cyclopentene (**1**) or cyclohexene (**4**). In contrast to these results, 2,3-dihydrofuran (**7**) as well as 5-methyl-2,3-dihydrofuran (**8**) gave only one regioisomer in the Paternò-Büchi reaction with benzaldehyde. The additional methyl group in **8** does not alter the regioselectivity. If the methyl group is expected to have an additional stabilizing effect on one center of the triplet 1,4-biradical, this effect is not visible because of the already exclusive attack at C-5 in compound **7**.

The stereoselectivity, however, is strongly influenced by substituents at the C-C double bond. Whereas the addition of benzaldehyde to cyclopentene (**1**) or cyclohexene (**4**) is endo selective (de: 22% and 48%, respectively), in the presence of methyl groups the stereochemical preference is less pronounced. In the 1-methylcyclopentene (**2**) case, the stereoselectivity is inverted (16:84) for the regioisomer **a**, and no selectivity (49:51) could be observed in the formation of regioisomer **b**. The same trend appeared in the cyclohexene series; the diastereoselectivity (favoring the endo photoproduct) decreases from 74% for the unsubstituted case **4** to 67% for 1-methylcyclohexene (**5**) (both

(1) Electronic Control of Stereoselectivity in Photocycloaddition Reactions. 4. Part 3: Griesbeck, A. G.; Mauder, H.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Chem. Ber.* **1991**, *124*, 407.
(2) Zimmerman, H. E.; Singer, L.; Thyagarajan, B. S. *J. Am. Chem. Soc.* **1959**, *81*, 108 and ref 16.
(3) Turro, N. J.; Wriede, P. A. *J. Am. Chem. Soc.* **1970**, *92*, 320.
(4) Arnold, D. R.; Hinman, R. L.; Glick, A. H. *Tetrahedron Lett.* **1964**, 1425.
(5) Griesbeck, A. G.; Stadtmüller, S. *Chem. Ber.* **1990**, *123*, 357.
(6) Griesbeck, A. G.; Stadtmüller, S. *J. Am. Chem. Soc.* **1990**, *112*, 1281.
(7) Shaik, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 3184.
(8) Paternò-Büchi reactions were reported with cyclopentene: (a) Jones, G., II. *Org. Photochem.* **1981**, *5*, 1. (b) Mattay, J.; Buchkremer, K. *Heterocycles* **1988**, *27*, 2153. Reported with cyclohexene: (a) Bradshaw, J. S. *J. Org. Chem.* **1966**, *31*, 237. (b) Borrell, P.; Sedlar, *J. Chem. Soc., Faraday Trans.* **1970**, *66*, 1670. (c) Jones, G. II; Acquadro, M. A.; Carmody, M. A. *J. Chem. Soc., Chem. Commun.* **1975**, 206. Reported with 1,2-dimethylcyclohexene: Cantrell, T. S.; Allen, A. C. *J. Org. Chem.* **1989**, *54*, 135.
(9) Gersdorf, J.; Mattay, J.; Görner, H. *J. Am. Chem. Soc.* **1987**, *109*, 1203.
(10) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(11) Data from: Wilkinson, F. *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1975.

0002-7863/91/1513-6923$02.50/0

Table I. Photocycloaddition of Benzaldehyde to Cycloalkenes: Regio- and Diastereoselectivity[a,b]

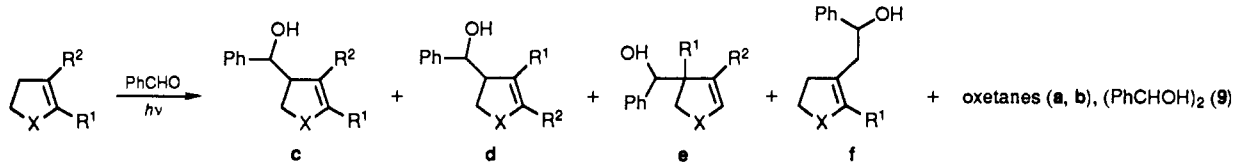


a b

no.	X	R^1	R^2	endo/exo, a	a/b	endo/exo, b	yield[c] (%)
1	CH_2	H	H	61:39			55
2	CH_2	CH_3	H	16:84	49:51	49:51	47
3	CH_2	CH_3	CH_3	20:80			48
4	$(CH_2)_2$	H	H	74:26			34
5	$(CH_2)_2$	CH_3	H	67:33	52:48	66:34	73
6	$(CH_2)_2$	CH_3	CH_3	44:56			60
7	O	H	H	88:12	>98:2		98
8	O	CH_3	H	65:35	>98:2		68

[a] 250-MHz ^{1}H NMR integration of crude product mixture. [b] Error limits ±2%. [c] Yield of [2 + 2] cycloadducts.

Table II. Photocycloaddition of Benzaldehyde to Cycloalkenes: Product Distribution (%)[a]

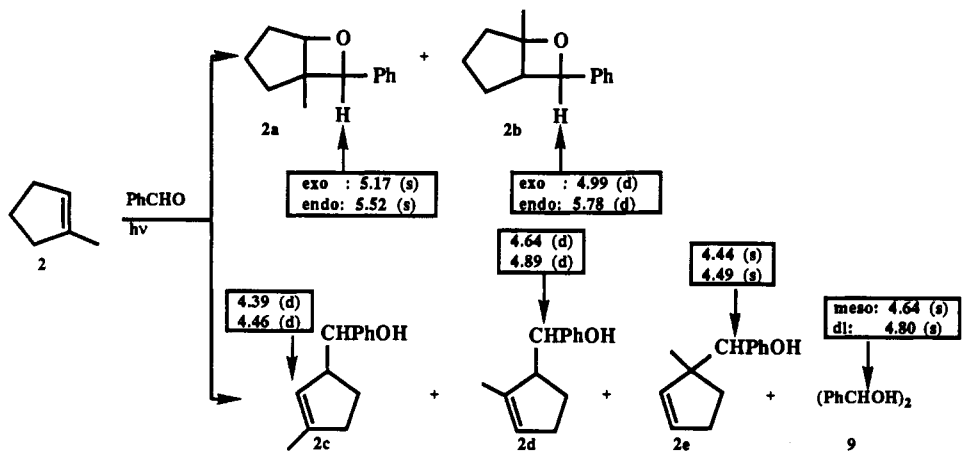


c d e f

no.	X	R^1	R^2	a + b	c[b]	d[b]	e[b]	f	g[c]
1	CH_2	H	H	55	33				12
2	CH_2	CH_3	H	47	16	5	11		21
3	CH_2	CH_3	CH_3	48	17		8	3	24
4[d]	$(CH_2)_2$	H	H	68	17				9
5	$(CH_2)_2$	CH_3	H	73	7	1	4		15
6	$(CH_2)_2$	CH_3	CH_3	60	1			11	28
8	O	CH_3	H	68					32

[a] Determined by ^{1}H NMR integration (250 and 400 MHz) of the crude reaction mixture. [b] Diastereomeric ration in all cases 50:50 (±3–5%). [c] DL- and *meso*-1,2-Diphenylglycol were formed in a 60:40 (±5%) ratio in all cases. [d] Additional product bicyclohex-2-ene (**10**, 6%).

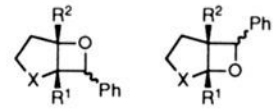
Scheme I. ^{1}H NMR Signals Used for Product Determination (**2**/PhCHO)



regioisomers) and 44% for the dimethyl compound **6**. A clear drop in endo selectivity also is observed for 2,3-dihydrofuran (**7**, ds = 88%) versus the corresponding 5-methyl compound (**8**, ds = 65%). Besides the 2,3-dihydrofuran case, the relative yields in [2 + 2] cycloadducts (type selectivity) were in the range of 45–65%, with photoreduction products (*meso*- and DL-1,2-diphenylglycol (**9**) and photodehydrodimerization products) and radical coupling products as byproducts. By the use of column and flash column chromatography the tertiary alcohols **c–f** could be separated from each other and from the [2 + 2] photoproducts (oxetanes **a**, **b**) and the diol **9**. Further separation of the regioisomeric coupling products **c–f** into their individual diastereomers was not carried out; the compounds (always formed as 1/1 mixtures, as one would expect off hand from radical recombination products) were characterized by using 2D NMR as H,H- and C,H-COSY techniques. Overall product ratios (Table II) were determined by repeated electronic integration of well-separated signals in the ^{1}H NMR spectra of the crude reaction mixtures. This procedure is illustrated for the 1-methylcyclopentene (**2**) case, where the maximum number of cycloaddition and radical recombination products is produced (Scheme I). All ^{1}H NMR signals given in Scheme I (250 MHz) were base line separated and could be used to determine the exact product ratio with the help of an internal standard (benzene).

Especially valuable for the determination of the endo/exo ratios of oxetanes **1a–8a** and **1b–8b** were the ^{1}H NMR signals (in italics) corresponding to the methyl groups (R^1) at the bridgehead position adjacent to the phenyl-substituted oxetane carbon (Table III). Their chemical shifts showed characteristic differences of about 0.6 ppm, with the methyl group of the diastereomer *exo*-**a** always

Table III. Chemical Shifts (^{1}H NMR, δ in ppm, $CDCl_3$, 250 MHz) of R^1 and R^2 in the Paternò–Büchi Adducts



a **b**

				endo-**a**		*exo*-**a**		*endo*-**b**		*exo*-**b**	
no.	X	R^1	R^2	R^2	R^2	R^1	R^2	R^1	R^2	R^1	R^2
1	CH_2	H	H	3.34	5.40	2.99	5.32				
2	CH_2	CH_3	H	*1.35*	4.86	*0.68*	4.70	1.60	2.83	1.48	2.55
3	CH_2	CH_3	CH_3	*1.21*	1.46	*0.57*	1.32				
4	$(CH_2)_2$	H	H	2.93	4.99	2.81	5.41				
5	$(CH_2)_2$	CH_3	H	*1.45*	4.57	*0.78*	4.57	1.44	2.76	1.26	2.59
6	$(CH_2)_2$	CH_3	CH_3	*1.22*	1.49	*0.66*	1.29				
7	O	H	H	5.05	5.51	5.50	4.64				
8	O	CH_3	H	*1.52*	5.10	*0.88*	4.99				

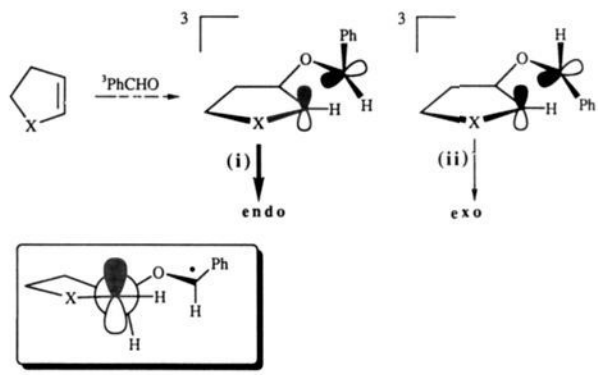
at higher fields (anisotropic effect of the phenyl group). For the 1,2-dimethylcyclobutene case[6] where exclusive exo attack has been observed, these correlations were confirmed also by means of NOE experiments. The diastereomeric mixture of the regioisomeric oxetanes **a** and **b** could be separated in most cases into the individual diastereomers. Whenever this was possible, substantial decomposition of the endo diastereomeric products could be observed during chromatography and/or distillation. This is especially crucial for the 2,3-dihydrofuran and 5-methyl-2,3-dihydrofuran cases.

Discussion

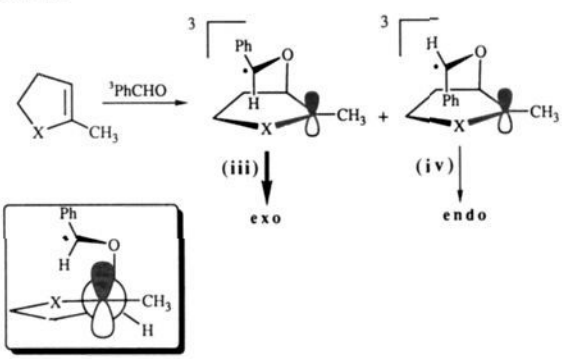
The results show that for the regiochemical outcome of the reaction, preorientation of the substrates is more important than the difference in biradical stability. This is in good agreement with a series of results concerning the regioselectivity of Paternò–Büchi reactions[12] and with spectroscopic indications for exciplex intermediates,[13] especially luminescence from the carbonyl radical anion.[13d] The exciplex-like preorientation is more pronounced for more highly polarizable cyclic enol ethers such as **7** and **8**, than for the simple trisubstituted cycloalkenes **2** and **5**. The existence of exciplex intermediates in Paternò–Büchi reactions is still an open question, but in many cases its assumption is helpful in explaining regioselectivity phenomena that are not consistent with expected radical stabilities. The same is true for the corresponding [2 + 2] photocycloaddition reactions of cyclic enones and electron-rich olefins. In these cases, the observation of concentration effects on regioselectivity (which was never observed in our experiments) accounts for preorientation complexes in the ground as well as in the excited state.[14]

From the data in Table I one clear trend is obvious: methyl groups at either position 1 or 2 on the cycloalkene moiety, as well as methyl groups at both positions, lower the amount of *endo*-oxetane in the diastereomeric oxetane mixture compared to the unsubstituted case. For the pronounced endo selectivity in the reaction between aromatic aldehydes[15,16] and unsubstituted cycloalkenes, we consider the two biradical conformers i and ii to

Scheme II



Scheme III



be responsible, with the alkyloxy substituent localized in a pseudoequatorial position and conformer i being more populated because of fewer steric interactions.

The angle between the p orbitals at the radical centers is approximately 90° for maximum spin orbit coupling[17] and rate-determining ISC to the singlet manifold. This conformational influence on ISC rates has also been convincingly demonstrated in the oxygen-trapping reaction of cyclic triplet 1,*n*-biradicals.[18] If R^1 corresponds to methyl, these conformers are no longer the only ones to be considered. The increasing gauche interactions with the β-alkyloxy substituent (see the Newman projections in

(12) (a) Yang, N. C.; Eisenhardt, W. *J. Am. Chem. Soc.* **1971**, *93*, 1277. (b) Carless, H. A. J.; Maitra, A. K.; Trivedi, H. S. *J. Chem. Soc., Chem. Commun.* **1979**, 984. (c) Carless, H. A. J. *Tetrahedron Lett.* **1973**, 3173. (d) Schroeter, S. H.; Orlando, C. M. *J. Org. Chem.* **1969**, *34*, 1181. (e) Schore, N. E.; Turro, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 2482.

(13) (a) Kochevar, I. E.; Wagner, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 3859. (b) Caldwell, R. A.; Sovocool, G. W.; Gajewski, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 2549. (c) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45. (d) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6255.

(14) Examples in: Baldwin, S. B. *Org. Photochem.*; Padwa, A., Ed.; **1981**, *5*, 123.

(15) A highly stereoselective photocycloaddition between acetophenone and an acyclic olefin has been reported: Fleming, S. A.; Jones, R. W. *J. Heterocycl. Chem.* **1990**, *27*, 1167.

(16) *endo*-Phenyl selective Paternò–Büchi reactions with chiral phenylglyoxalates: (a) Buschmann, H.; Scharf, H.-D.; Hoffmann, N.; Plath, M. W.; Runsink, J. *J. Am. Chem. Soc.* **1989**, *111*, 5367. (b) Nehrings, A.; Scharf, H.-D.; Runsink, J. *Angew. Chem.* **1985**, *97*, 882. (c) Pelzer, R.; Scharf, H.-D.; Buschmann, H.; Runsink, J. *Chem. Ber.* **1989**, *122*, 1187.

(17) (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) Salem, L. *Pure Appl. Chem.* **1973**, *33*, 317. (c) Shaik, S. S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 18. (d) Shaik, S. S.; Epiotis, N. D. *J. Am. Chem Soc.* **1980**, *102*, 122. (e) de Kanter, F. J. J.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759. (f) Carlacci, L.; Doubleday, C., Jr.; Furlani, T. R.; King, H. F.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 5323. (g) Doubleday, C., Jr.; Turro, N. J.; Wang, J.-F. *Acc. Chem. Res.* **1989**, *22*, 199.

(18) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165.

Scheme III) lead to a certain concentration of the conformers iii and iv, again with iii being preferred because of fewer steric interactions. However, this conformer gives rise to the formation of the exo diastereomer via ISC and subsequent ring closure. Therefore, the inversion in stereoselectivity comparing **1** (61% endo) and **2a** (84% exo) can be rationalized. A methyl group at position 2 of the cycloalkene causes an intermediate situation between the favorable conformations i and iii, and therefore an averaged endo/exo ratio (49% endo for **2b**) is observed. The same arguments fit for the cyclohexene derivatives **5** and **6**; here however, more conformational flexibility leads to less pronounced effects.

From these data it becomes clear that the stereoselectivity of triplet [2 + 2] photocycloaddition reactions is controlled by reactive 1,4-biradical conformations of appropiate orbital alignment for rapid ISC. Two points should be emphasized. First, all 1,4-biradical conformations that are assumed to exhibit favorable geometry for rapid ISC must not be real minima on the triplet potential energy surface. They can be interpreted as transient points through which stable 1,4-biradicals (or even exciplexes) have to pass in order to invert the spin and overcome the spin barrier for bond formation. In this sense, they are crossover points between triplet and singlet potential energy surfaces. Second, spin–orbit coupling, which is assumed to be the most important contribution for determining the ISC rate, is strongly distance dependent (inversely proportional to the third power of R, the distance between the radical centers).[17] Steric effects, therefore, are expected to be exceedingly important in these "tight geometries".

Experimental Section

General Aspects. Instrumentation was as follows: Infrared (IR) spectra, Perkin-Elmer 1420; ^{1}H NMR spectra, Bruker WM 400 (400 MHz), Bruker AC 250 (250 MHz), TMS (δ 0.00) as internal standard; ^{13}C NMR spectra, Bruker AC 250 (63 MHz), $CDCl_3$ (δ 77.0) as internal standard; mass spectra (MS), 8200 Finnigan MAT; HRMS MAT 90 Finnigan; thin-layer chromatography (TLC) was performed with Poligram SIL/G/UV 254 (Machery and Nagel); column chromatography with silica gel (60–220 μm), eluent 90:10 petroleum ether/ethyl acetate (by vol); radial chromatography was performed with a Harrison Research Chromatotron and silica gel plates (2 mm). Combustion analyses were obtained in house. A high-pressure mercury lamp TQ 150 was used for the irradiations. Irradiations were performed in an 80-mL Pyrex vessel. Reagents and solvents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. 1,2-Dimethylcyclopentene and 1,2-dimethylcyclohexene were synthesized according to literature procedure.[19]

General Irradiation Procedure. Benzaldehyde was irradiated with a 2–30-fold excess of olefin in 60 mL of benzene at 4–6 °C in a Pyrex vessel. Before and during the reaction the mixture was deoxygenated by bubbling a stream of nitrogen through the solution. Consumption of the aldehyde was monitored by TLC. Upon consumption of the aldehyde, the solvent and excess olefin were removed by rotoevaporation at ca. 25 °C (20 Torr). The product distribution was determined by 250/400 MHz ^{1}H NMR spectroscopy immediately after the removal of the solvent. The crude product mixture was separated by radial or column chromatography with a mixture of petroleum ether/ethyl acetate (15:1 to 5:1). *meso*- and D,L-1,2-diphenylglycol, which could be isolated in all cases as byproducts (cf. Table III) either by crystallization from petroleum ether/ethyl acetate or as final fractions of the column chromatography, are described in the literature.[20]

(1) **Irradiation of Benzaldehyde with Cyclopentene (1).** From 1.00 g (9.52 mmol) of benzaldehyde and 19.0 g (280 mmol) of cyclopentene after irradiation for 24 h was obtained 1.50 g (90%) of crude reaction mixture as a colorless oil. The following products were isolated and described in the order of their eluation by chromatography.

***endo*-6-Phenyl-7-oxabicyclo[3.2.0]heptane (*endo*-1a)**: ^{1}H NMR ($CDCl_3$) δ 1.25–2.38 (m, 6 H), 3.34 (m, J = 7.3 Hz, 1 H), 5.40 (dd, J = 4.4, 4.0 Hz, 1 H), 5.92 (d, J = 7.3 Hz, 1 H), 7.20–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.7 (t), 24.9 (t), 34.3 (t), 43.2 (d), 81.0 (d), 85.3 (d), 124.3 (d), 126.5 (d), 128.8 (d), 139.9 (s).

***exo*-6-Phenyl-7-oxabicyclo[3.2.0]heptane (*exo*-1a)**: ^{1}H NMR ($CDCl_3$) δ 1.25–2.38 (m, 6 H), 2.99 (m, J = 5.0 Hz, 1 H), 5.07 (d, J = 4.1 Hz, 1 H), 5.32 (dd, J = 4.1, 5.0 Hz, 1 H), 7.20–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.0 (t), 30.6 (t), 34.8 (t), 47.2 (d), 85.4 (d), 86.0 (d), 125.0 (d), 128.5 (d), 129.5 (d), 143.5 (s); IR (CCl_4, endo/exo) 2960, 2875, 1500, 1450, 1260, 1220, 1005, 985 cm^{-1}; MS (m/z, endo/exo) 174 (M^+), 130, 107, 105, 79, 50; HRMS calcd for $C_{12}H_{14}O$ 174.1045, found 174.1046.

Cyclopent-2-enylphenylmethanol (1c, *R*S/*R*R** Mixture). First diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.19 (br s, 1 H, OH), 1.48–1.92 (m, 2 H), 2.10–2.35 (m, 2 H), 3.04 (m, 1 H), 4.42 (d, J = 6.6 Hz, 1 H), 5.32 (dd, J = 2.2, 5.7 Hz, 1 H), 5.77 (dd, J = 2.2, 5.7 Hz, 1 H), 7.15–7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.1 (t), 32.3 (t), 54.0 (d), 77.8 (d), 126.3 (d), 127.4 (d), 128.3 (d), 131.3 (d), 133.7 (d), 143.9 (s). **Second diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.99 (br s, 1 H, OH), 1.48–1.92 (m, 2 H), 2.10–2.35 (m, 2 H), 3.04 (m, J = 2.2 Hz, 1 H), 4.47 (d, J = 6.6 Hz, 1 H), 5.68 (dd, J = 2.2, 5.7 Hz, 1 H), 5.82 (dd, J = 2.2, 5.7 Hz, 1 H), 7.15–7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 26.5 (t), 32.3 (t), 53.5 (d), 76.6 (d), 126.2 (d), 127.4 (d), 128.3 (d), 130.6 (d), 133.9 (d), 143.5 (s); IR (CCl_4, mixture) 3620, 3060, 2960, 1600, 1490, 1310, 1090, 1018 cm^{-1}; MS (m/z, mixture) 174 (M^+), 130, 107, 79, 77, 67; HRMS calcd for $C_{12}H_{14}O$ 174.1045, found 174.1047.

(2) **Irradiation of Benzaldehyde with 1-Methylcyclopentene (2).** From 2.51 g (23.6 mmol) of benzaldehyde and 3.90 g (47.5 mmol) of 1-methylcyclopentene after irradiation for 24 h was obtained 4.00 g (90%) of crude reaction mixture as a colorless oil.

***exo*-7-Phenyl-1-methyl-6-oxabicyclo[3.2.0]heptane (*exo*-2a)**: ^{1}H NMR ($CDCl_3$) δ 0.68 (s, 3 H), 0.91–2.37 (m, 6 H), 4.70 (d, J = 3.5 Hz, 1 H), 5.17 (s, 1 H), 7.10–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.6 (q), 25.0 (t), 34.8 (t), 39.2 (t), 49.6 (s), 89.0 (d), 91.1 (d), 125.5 (d), 128.2 (d), 127.2 (d), 141.3 (s).

***endo*-7-Phenyl-1-methyl-6-oxabicyclo[3.2.0]heptane (*endo*-2a)**: ^{1}H NMR ($CDCl_3$) δ 0.91–2.37 (m, 6 H), 1.35 (s, 3 H), 4.86 (d, J = 3.4 Hz, 1 H), 5.52 s, 1 H), 7.10–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.1 (q), 25.7 (t), 33.9 (t), 33.9 (t), 50.6 (s), 88.0 (d), 90.8 (d), 124.3 (d), 126.8 (d), 128.0 (d), 140.0 (s).

***exo*-7-Phenyl-5-methyl-6-oxabicyclo[3.2.0]heptane (*exo*-2b)**: ^{1}H NMR ($CDCl_3$) δ 0.91–2.37 (m, 6 H), 1.48 (s, 3 H), 2.55 (dd, J = 2.5, 4.3 Hz, 1 H), 4.99 (d, J = 4.3 Hz, 1 H), 7.10–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.0 (q), 25.7 (t), 31.2 (t), 40.1 (t), 51.1 (d), 81.7 (d), 92.0 (s), 124.7 (d), 127.1 (d), 128.4 (d), 144.3 (s).

***endo*-7-Phenyl-5-methyl-6-oxabicyclo[3.2.0]heptane (*endo*-2b)**: ^{1}H NMR ($CDCl_3$) δ 0.91–2.37 (m, 6 H), 1.60 (s, 3 H), 2.83 (m, J = 7.2 Hz, 1 H), 5.78 (d, J = 7.2 Hz, 1 H), 7.10–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 23.9 (q), 26.6 (t), 27.3 (t), 39.7 (t), 47.3 (d), 77.8 (d), 92.4 (s), 124.7 (d), 126.5 (d), 128.0 (d), 140.0 (s); IR (CCl_4, mixture) 3085, 2920, 1625, 1515, 1475, 1015 cm^{-1}; MS (m/z, regioisomer mixture) 188 (M^+), 173, 144, 107, 82, 67, 43; HRMS calcd for $C_{13}H_{16}O$ 188.1201, found 188.1194.

(2-Methylcyclopent-2-enyl)phenylmethanol (2d, *R*S/*R*R** Mixture). First diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.68 (d, J = 2.0 Hz, 3 H, CH_3), 1.27–1.87 (m, 2 H), 2.02–2.29 (m, 3 H), 2.87 (m, 1 H), 4.89 (d, J = 3.1 Hz, 1 H), 5.52 (m, 1 H), 7.15–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.0 (q), 23.4 (t), 31.1 (t), 56.1 (d), 72.6 (d), 126.9 (d), 127.6 (d), 128.2 (d), 129.1 (d), 142.4 (s), 143.5 (s). **Second diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.66 (d, J = 2.0 Hz, 3 H, CH_3), 1.28–1.87 (m, 2 H), 2.02–2.29 (m, 3 H), 2.91 (m, 1 H), 4.64 (d, J = 5.8 Hz, 1 H), 5.36 (m, 1 H), 7.15–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.0 (q), 27.8 (t), 30.8 (t), 55.2 (d), 76.6 (d), 126.3 (d), 127.2 (d), 127.3 (d), 128.2 (d), 142.4 (s), 143.5 (s); IR (CCl_4, mixture) 3690, 2990, 1605, 1475, 1205, 1020 cm^{-1}.

(1-Methylcyclopent-2-enyl)phenylmethanol (2e, *R*S/*R*R** Mixture). First diastereomer**: ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 3 H), 1.28–1.87 (m, 2 H), 2.02–2.29 (m, 3 H), 4.44 (s, 1 H), 5.40 (dt, J = 2.1, 3.5 Hz, 1 H), 5.72 (m, 1 H), 7.15–7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 23.9 (q), 32.2 (t), 34.5 (t), 53.7 (s), 80.8 (d), 125.8 (d), 126.2 (d), 128.6 (d), 132.2 (d), 134.4 (d), 139.5 (s). **Second diastereomer**: ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 3 H), 1.28–1.87 (m, 2 H), 2.02–2.29 (m, 3 H), 4.49 (s, 1 H), 5.52 (m, 1 H), 5.72 (m, 1 H), 7.15–7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 22.8 (q), 32.0 (t), 32.3 (t), 54.7 (d), 79.8 (d), 125.8 (d), 126.2 (d), 128.5 (d), 131.9 (d), 135.6 (d), 140.6 (s).

(3-Methylcyclopent-2-enyl)phenylmethanol (2c, *R*S/*R*R** Mixture). First diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.67 (s, 3 H), 1.51–2.28 (m, 5 H), 3.00 (m, 1 H), 4.39 (d, J = 6.5 Hz, 1 H), 5.25 (m, 1 H), 7.18–7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 16.9 (q), 27.3 (t), 36.6 (t), 53.7 (d), 77.1 (d), 123.9 (d), 126.6 (d), 127.3 (d), 128.0 (d), 143.6 (s), 144.3 (s). **Second diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.63 (s, 3 H), 1.51–2.28 (m, 5 H), 3.00 (m, 1 H), 4.46 (d, J = 6.2 Hz, 1 H), 4.92 (m, 1 H), 7.18–7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 16.8 (q), 25.9 (t), 36.6 (t), 54.0 (d), 76.7 (d), 125.0 (d), 126.2 (d), 127.3 (d), 128.0 (d), 143.9 (s), 144.1 (s); IR (CCl_4, mixture) 3700, 3640, 3000, 1635, 1485, 1100 cm^{-1}; MS (m/z, mixture) 188 (M^+), 170, 120, 107, 105, 81, 77, 67, 53.

(19) Bartlett, P. D.; Barley, A. *J. Am. Chem Soc.* **1938**, *60*, 2416.
(20) Neudeck, H.; Schlögl, K. *Monatsh. Chem.* **1975**, *106*, 229.

(3) **Irradiation of Benzaldehyde with 1,2-Dimethylcyclopentene (3).** From 2.00 g (18.8 mmol) of benzaldehyde and 1.92 g (20.0 mmol) of 1,2-dimethylcyclopentene after irradiation for 24 h was obtained 3.58 g (91%) of crude reaction mixture as a colorless oil.

***exo*-7-Phenyl-1,5-dimethyl-6-oxabicyclo[3.2.0]heptane (*exo*-3a)**: ^{1}H NMR ($CDCl_3$) δ 0.57 (s, 3 H), 1.32 (s, 3 H), 0.66–2.22 (m, 6 H), 5.17 (s, 1 H), 7.10–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 16.8 (q), 22.0 (q), 23.0 (t), 40.3 (t), 40.6 (t), 49.6 (s), 86.3 (d), 93.4 (s), 125.2 (d), 126.9 (d), 128.1 (d), 141.8 (s).

***endo*-7-Phenyl-1,5-dimethyl-6-oxabicyclo[3.2.0]heptane (*endo*-3a)**: ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 3 H), 1.46 (s, 3 H), 0.60–2.22 (m, 6 H), 5.40 (s, 1 H), 7.10–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.6 (q), 21.5 (q), 23.6 (t), 35.1 (t), 39.7 (t), 49.6 (s), 85.6 (d), 93.4 (s), 124.4 (d), 126.6 (d), 128.0 (d), 140.0 (s); IR (CCl_4, endo/exo) 3060, 2995, 2900, 1640, 1510, 1460, 1395, 1220 cm^{-1}; MS (*m/z*, endo/exo) 202 (M^+), 144, 129, 105, 96, 81, 67, 43. Anal. ($C_{14}H_{18}O$) calcd: C, 83.04; H, 8.90. Found: C, 82.56; H, 9.00.

(2,3-Dimethylcyclopent-2-enyl)phenylmethanol (3c, *R*S*/R*R Mixture). First diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.57 (s, 3 H), 1.63 (s, 3 H), 1.45–2.34 (m, 5 H), 3.00 (m, 1 H), 4.73 (d, J = 5.3 Hz, 1 H), 7.21–7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.3 (q), 14.4 (q), 26.0 (t), 37.1 (t), 57.3 (d), 77.5 (d), 126.5 (d), 127.4 (d), 128.2 (d), 131.2 (s), 136.1 (s), 143.8 (s). **Second diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 3 H), 1.66 (s, 3 H), 1.28–2.30 (m, 5 H), 2.83 (m, 1 H), 4.86 (d, J = 3.1 Hz, 1 H), 7.10–7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.2 (q), 14.7 (q), 21.7 (t), 37.3 (t), 58.1 (d), 73.0 (d), 126.2 (d), 127.5 (d), 128.1 (d), 130.4 (s), 136.8 (s), 144.2 (s); IR (CCl_4) 3690, 3090, 2990, 1520, 1480, 1410, 1010, 935 cm^{-1}; MS (*m/z*, mixture) 202 (M^+), 144, 129, 107, 96, 95, 81, 77, 67, 41.

2-(2-Methylcyclopentenyl)-1-phenylethanol (3f): ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 3 H), 0.92–1.06 (m, 2 H), 1.60–2.43 (m, 5 H), 2.59 (dd, J = 4.3, 8.8 Hz, 2 H), 4.77 (dd, J = 4.3, 8.8 Hz, 1 H), 7.21–7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.2 (q), 22.1 (t), 36.5 (t), 38.9 (t), 39.6 (t), 76.9 (d), 126.1 (d), 127.5 (d), 128.3 (d), 131.4 (s), 134.5 (s), 144.0 (s); IR (CCl_4) 3670, 3070, 2965, 1575, 1470, 1400, 1270, 1235, 1020, 995 cm^{-1}.

(1,2-Dimethylcyclopent-2-enyl)phenylmethanol (3e, *R*S*/R*R Mixture). First diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 3 H), 1.58 (s, 3 H), 1.22–1.90 (m, 3 H), 2.05–2.33 (m, 2 H), 4.53 (s, 1 H), 5.45 (m, 1 H), 7.11–7.29 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 12.5 (q), 23.1 (q), 29.9 (t), 34.7 (t), 55.6 (s), 78.9 (d), 127.1 (d), 127.7 (d), 128.0 (d), 128.3 (d), 142.8 (s), 143.9 (s). **Second diastereomer**: ^{1}H NMR ($CDCl_3$) δ 0.80 (s, 3 H), 1.68 (s, 3 H), 1.22–1.90 (m, 3 H), 2.05–2.33 (m, 2 H), 4.51 (s, 1 H), 5.15 (m, 1 H), 7.11–7.29 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 12.2 (q), 23.4 (q), 30.1 (t), 34.3 (t), 55.1 (s), 77.6 (d), 127.4 (d), 127.9 (d), 122 (d), 128.5 (d), 142.8 (s), 144.4 (s); IR (CCl_4, mixture) 3650, 3605, 3060, 2990, 1565, 1460, 1390, 1195, 920 cm^{-1}.

(4) **Irradiation of Benzaldehyde with Cyclohexene (4).** From 2.00 g (18.5 mmol) of benzaldehyde and 16.1 g (196 mmol) of cyclohexene after irradiation for 24 h was obtained 3.34 g (96%) of crude reaction mixture as a colorless oil.

***endo*-8-Phenyl-7-oxabicyclo[4.2.0]octane (*endo*-4a)**: ^{1}H NMR ($CDCl_3$) δ 0.90–1.96 (m, 8 H), 2.93 (m, 1 H), 4.99 (m, 1 H), 5.87 (d, J = 6.3 Hz, 1 H), 7.19–7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.1 (t), 20.2 (t), 21.2 (t), 29.0 (t), 37.4 (d), 75.7 (d), 81.6 (d), 125.2 (d), 126.8 (d), 128.0 (d), 140.2 (s).

***exo*-8-Phenyl-7-oxabicyclo[4.2.0]octane (*exo*-4a)**: ^{1}H NMR ($CDCl_3$) δ 0.90–1.96 (m, 8 H), 2.81 (m, 1 H), 4.91 (m, 1 H), 5.41 (d, J = 6.0 Hz, 1 H), 7.19–7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.0 (t), 20.1 (t), 24.7 (t), 29.3 (t), 40.8 (d), 76.7 (d), 85.6 (d), 125.0 (d), 127.4 (d), 128.4 (d), 143.4 (s); IR (CCl_4, endo/exo) 3020, 2900, 1605, 1500, 1455, 1345, 1150 cm^{-1}.

Cyclohex-2-enylphenylmethanol (4c, *R*S*/R*R Mixture). First diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.20–2.51 (m, 8 H), 4.53 (d, J = 6.6 Hz, 1 H), 5.35 (m, 1 H), 5.66 (m, 1 H), 5.84 (s br, 1 H), 7.15–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.6 (t), 25.3 (t), 26.3 (t), 42.9 (d), 77.3 (d), 126.4 (d), 127.4 (d), 128.1 (d), 129.6 (d), 129.7 (d), 142.6 (s). **Second diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.20–2.51 (m, 8 H), 4.41 (d, J = 7.1 Hz, 1 H), 5.54–5.89 (m, 2 H), 5.84 (s br, 1 H), 7.15–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.2 (t), 24.1 (t), 25.3 (t), 43.0 (d), 77.4 (d), 126.6 (d), 126.9 (d), 127.3 (d), 128.1 (d), 130.1 (d), 142.0 (s); IR (CCl_4, mixture) 3635, 3480, 3050, 2950, 1605, 1455, 1275, 915 cm^{-1}.

(5) **Irradiation of Benzaldehyde with 1-Methylcyclohexene (5).** From 2.24 g (21.1 mmol) of benzaldehyde and 4.06 g (42.2 mmol) of 1-methylcyclohexene after irradiation for 24 h was obtained 3.75 g (88%) of crude reaction mixture as a colorless oil.

***exo*-8-Phenyl-1-methyl-7-oxabicyclo[4.2.0]octane (*exo*-5a)**: ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 3 H), 0.90–1.99 (m, 8 H), 4.55–4.59 (m, 1 H), 5.37 (s, 1 H), 7.18–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.8 (t), 20.1 (t), 21.6 (q), 28.2 (t), 35.0 (t), 41.1 (s), 84.5 (d), 88.9 (d), 125.7 (d), 127.9 (d), 128.7 (d), 141.2 (s).

***endo*-8-Phenyl-1-methyl-7-oxabicyclo[4.2.0]octane (*endo*-5a)**: ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 3 H), 0.90–1.99 (m, 8 H), 4.57 (m, 1 H), 5.43 (s, 1 H), 7.18–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.3 (t), 20.8 (t), 22.2 (t), 24.5 (q), 29.5 (t), 43.6 (s), 82.9 (d), 88.6 (d), 125.6 (d), 127.3 (d), 128.5 (d), 140.5 (s).

***exo*-8-Phenyl-6-methyl-7-oxabicyclo[4.2.0]octane (*exo*-5b)**: ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 3 H), 0.90–1.99 (m, 8 H), 2.59 (dt, J = 3.2, 8.0 Hz, 1 H), 5.36 (d, J = 8.0, Hz, 1 H), 7.18–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 29.6 (q), 49.2 (d), 79.4 (d), 81.4 (s), other signals not detectable.

***endo*-8-Phenyl-6-methyl-7-oxabicyclo[4.2.0]octane (*endo*-5b)**: ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 3 H), 0.90–1.99 (m, 8 H), 2.76 (dt, J = 7.6 Hz, 1 H), 5.90 (d, J = 7.6 Hz, 1 H), 7.18–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.1 (t), 20.8 (t), 28.4 (t), 28.9 (q), 36.0 (t), 42.7 (d), 79.8 (d), 81.9 (s), 125.4 (d), 127.1 (d), 128.5 (d), 141.3 (s); IR (CCl_4, regioisomer mixture) 3020, 2950, 1610, 1470, 1390, 1010, 970, 950 cm^{-1}; MS (*m/z*, regioisomer mixture) 202 (M^+), 184, 144, 129, 117, 105, 96, 81, 67; HRMS calcd for $C_{14}H_{18}O$ 202.1358, found 202.1352.

(2-Methylcyclohex-2-enyl)phenylmethanol (5d, *R*S*/R*R)**: ^{1}H NMR ($CDCl_3$) δ 1.06–1.96 (m, 7 H), 1.72 (s, 3 H), 2.27 (m, 1 H), 5.07 (d, J = 2.5 Hz, 1 H), 5.66 (m, 1 H), 7.12–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.9 (q), 21.9 (t), 22.1 (t), 25.5 (t), 46.3 (d), 72.8 (d), 125.8 (d), 126.8 (d), 128.1 (d), 128.9 (d), 133.2 (s), 143.1 (s).

(3-Methylcyclohex-2-enyl)phenylmethanol (5c, *RS*/R*R Mixture). First diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.21–1.94 (m, 6 H), 1.62 (s, 3 H), 2.30 (m, 1 H), 2.55 (br, 1 H), 4.22 (d, J = 6.9 Hz, 1 H), 5.42 (m, 1 H), 7.14–7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.1 (t), 24.0 (q), 24.7 (t), 25.6 (t), 42.7 (t), 77.3 (d), 120.9 (d), 125.9 (d), 126.7 (d), 127.7 (d), 133.9 (s), 142.8 (s). **Second diastereomer**: ^{1}H NMR ($CDCl_3$) δ 1.21–1.94 (m, 6 H), 1.57 (s, 3 H), 2.29 (m, 1 H), 2.55 (br, 1 H), 4.37 (d, J = 6.3 Hz, 1 H), 4.96 (m, 1 H), 7.14–7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.5 (t), 22.4 (t), 23.6 (q), 23.6 (t), 42.9 (d), 76.9 (d), 121.8 (d), 126.1 (d), 126.9 (d), 127.6 (d), 133.8 (s), 143.4 (s); IR (CCl_4, mixture) 3640, 3310, 2985, 1610, 1505, 1465, 1390, 1230, 1005 cm^{-1}.

(1-Methylcyclohex-2-enyl)phenylmethanol (5e, *R*S*/R*R Mixture). First diastereomer**: ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 3 H), 1.08–1.94 (m, 7 H), 4.42 (s, 1 H), 5.29 (s, 1 H), 5.75–5.85 (m, 1 H), 7.02–7.32 (m, 5 H). **Second diastereomer**: ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 3 H), 1.08–1.94 (m, 7 H), 4.40 (s, 1 H), 5.36 (s, 1 H), 5.75–5.85 (m, 1 H), 7.02–7.32 (m, 5 H).

(6) **Irradiation of Benzaldehyde with 1,2-Dimethylcyclohexene (6).** From 1.00 g (9.43 mmol) of benzaldehyde and 7.00 g (63.0 mmol) of 1,2-dimethylcyclohexene after irradiation for 24 h was obtained 1.83 g (90%) of crude reaction mixture as a colorless oil.

***exo*-8-Phenyl-1,6-dimethyl-7-oxabicyclo[4.2.0]octane (*exo*-6a)**: ^{1}H NMR ($CDCl_3$) δ 0.66 (s, 3 H), 1.29 (s, 3 H), 0.87–2.04 (m, 8 H), 5.51 (s, 1 H), 7.20–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.2 (t), 19.6 (t), 19.8 (q), 23.4 (q), 32.6 (t), 36.9 (t), 43.3 (s), 83.1 (s), 84.5 (d), 125.0 (d), 126.6 (d), 127.8 (d), 140.8 (s).

***endo*-8-Phenyl-1,6-dimethyl-7-oxabicyclo[4.2.0]octane (*endo*-6a)**: ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 3 H), 1.49 (s, 3 H), 0.87–2.04 (m, 8 H), 5.65 (s, 1 H), 7.20–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.9 (t), 21.4 (q), 21.4 (t), 23.8 (q), 29.8 (t), 34.9 (t), 43.8 (s), 84.0 (s), 86.7 (d), 124.8 (d), 126.7 (d), 127.8 (d), 140.5 (s); IR (CCl_4, endo/exo) 3080, 3000, 1625, 1520, 1010 cm^{-1}; MS (*m/z*, endo/exo) 216 (M^+), 158, 143, 110, 105, 95, 81, 67, 43. Anal. ($C_{15}H_{20}O$) Calcd: C, 83.29; H, 9.32. Found: C, 83.52, H. 9.30.

2-(2-Methylcyclohexenyl)-1-phenylethanol (6f): ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 3 H), 0.89–2.00 (m, 8 H), 2.22 (dd, J = 5.0, 13.4 Hz, 1 H), 2.43 (br s, 1 H), 2.65 (dd, J = 9.1, 13.4 Hz, 1 H), 4.77 (dd, J = 5.0, 9.1 Hz, 1 H), 7.21–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.5 (q), 23.2 (t), 23.4 (t), 29.9 (t), 32.1 (t), 44.1 (t), 72.5 (d), 125.8 (d), 127.1 (d), 128.1 (d), 130.9 (s), 144.4 (s), 144.6 (s); IR (CCl_4) 3690, 3530, 2985, 1625, 1515, 1475 cm^{-1}; MS (*m/z*) 216 (M^+), 201, 173, 129, 110, 79, 43. Anal. ($C_{15}H_{20}O$) Calcd: C, 83.29; H, 9.32. Found: C, 83.57; H, 9.86.

(7) **Irradiation of Benzaldehyde with 4,5-Dihydro-2-methylfuran (8).** From 1.00 g (9.43 mmol) of benzaldehyde and 4.61 g (54.8 mmol) of 4,5-dihydro-2-methylfuran after irradiation for 24 h was obtained 1.61 g (90%) of crude reaction mixture as a colorless oil.

***endo*-7-Phenyl-1-methyl-2,6-dioxabicyclo[3.2.0]heptane (*endo*-8a)**: ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 3 H), 1.68 (dddd, J = 4.2, 8.2, 11.2, 13.8 Hz, 1 H), 2.04 (dd, J = 5.3, 13.8 Hz, 1 H), 3.71 (ddd, J = 5.3, 8.8, 11.2 Hz, 1 H), 3.8 (dd, J = 8.2, 8.8 Hz, 1 H), 5.10 (d, J = 4.2 Hz, 1 H), 5.58 (s, 1 H), 7.17–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.4 (q), 33.0 (t), 69.1 (t), 77.2 (s), 89.1 (d), 89.6 (d), 124.3 (d), 127.0 (d), 128.1 (d), 137.8 (s).

exo-7-Phenyl-1-methyl-2,6-dioxabicyclo[3.2.0]heptane (exo-8a): ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 3 H), 1.80 (m, J = 4.0, 9.1 Hz, 1 H), 2.14 (m, J = 5.6, 13.7 Hz, 1 H), 4.29-4.36 (m, 2 H), 4.99 (d, J = 4.0 Hz, 1 H), 5.44 (s, 1 H), 7.19-7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.8 (q), 34.1 (t), 67.7 (t), 89.3 (d), 89.5 (s), 90.9 (d), 125.3 (d), 127.6 (d), 128.4 (d), 138.8 (s); IR (CCl_4, endo/exo) 3020, 2920, 1605, 1505, 1470, 1400, 1220, 1050, 825 cm^{-1}; MS (m/z, endo/exo) 190 (M^+), 134, 105, 91, 84, 77, 69, 43. Anal. ($C_{12}H_{14}O_2$) Calcd: C, 75.76; H, 7.42. Found: C, 75.20; H, 6.92.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (Projekt Gr 881/2-1 and 2-2), the Fonds der Chemischen Industrie, and the Universitätsbund Würzburg. We thank Prof. C. Doubleday, Jr. and Prof. S. S. Shaik for helpful and stimulating comments and encouragement.

Chemistry of Nitrenes Generated by the Photocleavage of Both Azides and a Five-Membered Heterocycle

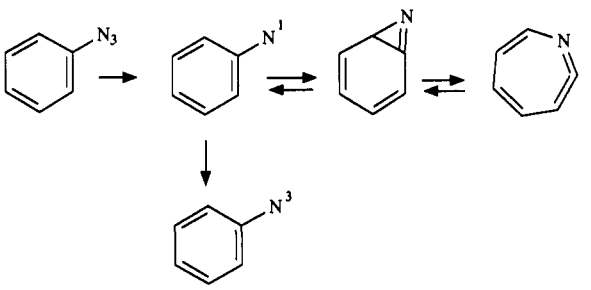
A. Albini, G. Bettinetti,* and G. Minoli

Contribution from the Department of Organic Chemistry, The University of Pavia, I-27100 Pavia, Italy. *Received October 16, 1990. Revised Manuscript Received May 2, 1991*

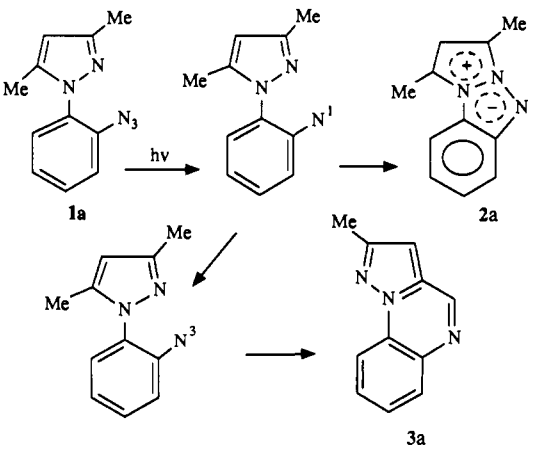
Abstract: Pyrazolo[1,2-*a*]benzotriazole and some of its derivatives (**2a-c**) are photochemically cleaved to form 2-(1-pyrazolyl)phenylnitrenes, which are also obtained through a more conventional path by photodecomposition of the pyrazolylphenyl azides (**1a-c**). Product studies and laser flash photolysis analysis of nitrenes from both sources show that there is competition between fast intramolecular reclosure to heterocycles **2** and rearrangement to dehydroazepines. The latter species are trapped by nucleophiles, or otherwise slowly rearrange back to the nitrenes (conformational factors affect these processes). The (quite unreactive) triplet nitrenes are identified spectroscopically and possibly are in equilibrium with the previous transients.

The study of the photodecomposition of aromatic azides has gradually revealed various chemical paths that require the involvement of different intermediates.[1-5] Thus the reactivities of singlet (e.g. electrophilic attack on aromatics) and triplet nitrene (e.g. coupling to yield azo derivatives) have been distinguished one from the other. In order to rationalize the addition of nucleophiles, it has been proposed that bond reorganization of the nitrene to a bicyclic azirine should precede the reaction.[6] Following this, matrix isolation[7] and flash photolytic investigation,[8] as well as preparative studies,[9,10] have supported the intervention of both azirines and dehydroazepines. Recent work on phenyl, 2-naphthyl, and pyrenyl azide suggests that these rearranged intermediates are actually in equilibrium with singlet nitrene[11] (Scheme I). We rationalized the photochemistry of some phenazinyl azides through a related scheme.[12]

Scheme I



Scheme II



The available evidence for the occurrence of these rearranged intermediates in solution has been mainly indirect (e.g. relatively

(1) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900.
(2) Smith, P. A. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: Orlando, 1984; Chapter 3.
(3) Scriven, E. F. V. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1981; Vol. 2, Chapter 1.
(4) Lwowski, W. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1981; Chapter 8.
(5) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 279.
(6) Huisgen, R.; Vossius, D.; Appl, M. *Chem. Ber.* **1958**, *91*, 1. Huisgen, R.; Appl, M. *Ibid.* **1958**, *91*, 12.
(7) (a) Chapman, O. L.; Le Roux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282 and 6245. (b) Chapman, O. L., Sheridan, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 3690. (c) Dunkin, I. R.; Thompson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1980**, 499. (d) Wentrup, C. Reference 2, Chapter 8. (e) Wentrup, C.; Winter, H. W. *J. Am. Chem. Soc.* **1980**, *102*, 6159. (f) Wentrup, C.; Thétaz, C.; Tagliaferri, E.; Lindner, H. J.; Kitscke, B.; Winter, H. W.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 566.
(8) (a) Sundberg, R. J.; Heintzelman, R. W. *J. Org. Chem.* **1974**, *39*, 2546. (b) De Graff, B. A.; Gillespie, D. W.; Sundberg, R. J. *J. Am. Chem. Soc.* **1974**, *95*, 7491. (c) Sumitani, M.; Nagakura, S.; Yoshihara, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2995. (d) Nielsen, P. E.; Buchard, O. *Photochem. Photobiol.* **1982**, *35*, 317.
(9) (a) Sundberg, R. J.; Suter, S. R.; Brenner, M. *J. Am. Chem. Soc.* **1972**, *94*, 513. (b) Carrol, S. E.; Nay, B.; Scriven, E. F. V.; Suschitzky, H. *Tetrahedron Lett.* **1977**, 943. (c) Rigaudy, J.; Igier, C.; Barcelo, J. *Tetrahedron Lett.* **1975**, 3845. (d) Rigaudy, J.; Igier, C.; Barcelo, J. *Tetrahedron Lett.* **1979**, 1837. (e) Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* **1968**, 6149. (f) von Doering, W. E.; Odum, R. A. *Tetrahedron* **1966**, *22*, 81.
(10) (a) Khan, Z. U.; Patel, D. I.; Smalley, R. K.; Scriven, E. F. V.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1983**, 4. (b) Sawanishi, H.; Hirai, T.; Tsuchiya, T. *Heterocycles* **1982**, *19*, 2071. (c) Bettinetti, G. F.; Fasani, E.; Minoli, G.; Pietra, S. *Gazz. Chim. Ital.* **1980**, *110*, 135. (d) Albini, A.; Bettinetti, G. F.; Fasani, E.; Pietra, S. *Gazz. Chim. Ital.* **1982**, *112*, 15.
(11) (a) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228 and 5234. (b) Leyva, E.; Platz, M.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 5783.
(12) Albini, A.; Bettinetti, G.; Minoli, G. *J. Org. Chem.* **1987**, *52*, 1245.

0002-7863/91/1513-6928$02.50/0