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Medium-Dependent Type Selectivity in Photoreactions of a Crown Ether-Annelated Dibenzobarrelene Derivative

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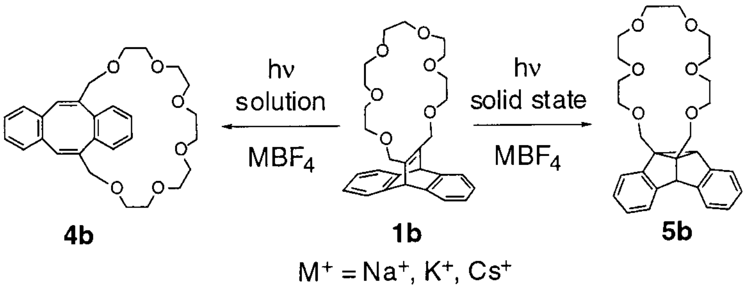
ABSTRACT



A concept for modifying the photochemical properties of a dibenzobarrelene derivative by the combination of supramolecular assembly and solid-state photochemistry is presented. The irradiation of dibenzobarrelene 1b and alkali metal complexes thereof (1:1) in acetonitrile or benzene solution leads preferentially to the dibenzocyclooctatetraene 4b as the photoproduct. In contrast, the dibenzosemibullvalene 5b is formed as the main photoproduct in the solid state because of a strong cation effect.

Photoreactions in the solid state exhibit remarkable differences compared to those in solution and provide insight into the geometric requirements of well-established photoreactions.[1] Despite the progress in this field, the control of the multiplicity in solid-state photoreactions is still a difficult task. Scheffer and co-workers solved this problem with the "ionic auxiliary" concept.[2] In this approach, the chromophore is linked to a sensitizer or a heavy atom, and solid-state irradiation of these salts results in an increase in the triplet photoproduct. Herein, we present a new concept in which the photochemical properties of a chromophore are modified by a alkali metal ion that is associated through a crown ether complex. The modification of *photophysical* properties of crown ether-linked chromophores by complexation of cations is well investigated,[3] and selective photocycloadditions have been achieved with the help of supramolecular assemblies of crown ethers;[4] but apparently there exist no reports on the modification of type selectivity[5] of *photochemical* reactions by crown ether complexation. To realize this

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[1] (a) *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991. (b) Ito, Y. *Synthesis* **1998**, 1. (c) Keating, A. E.; Garcia-Garibay, M. A. In *Inorganic and Organic Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1998; p 195.

[2] (a) Gamlin, J. G.; Jones, R.; Leibovitch, M.; Patrick, B.; Scheffer, J. R.; Trotter, J. *Acc. Chem. Res.* **1996**, *29*, 203. (b) Borecka, B.; Gudmundsdottir, A. D.; Olovsson, G.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1994**, *116*, 10322. (c) Ihmels, H.; Patrick, B. O.; Scheffer, J. R.; Trotter, J. *Tetrahedron* **1999**, *55*, 2171. (d) Janz, K. M.; Scheffer, J. R. *Tetrahedron Lett.* **1999**, *40*, 8725.

[3] (a) *Chemosensors of Ion and Molecular Recognition*; Desvergne, J.-P., Czarnik, A. W., Eds.; Kluwer Academic Press: Dordrecht, The Netherlands, 1997; Vol. 492. (b) *Fluorescent Chemosensors for Ion and Molecule Recognition*; A. W. Czarnik, Ed.; ACS Symposium Series 538; American Chemical Society: Washington, DC, 1993.

[4] (a) Marquis, D.; Desvergne, J.-P.; Bouas-Laurent, H. *J. Org. Chem.* **1995**, *60*, 7984. (b) Desvergne, J.-P.; Fages, F.; Bouas-Laurent, H.; Marsau, P. *Pure Appl. Chem.* **1992**, *64*, 1231. (c) Armirsakis, D. G.; Garcia-Garibay, M.; A.; Rowan, S. J.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4179. (d) Kokubo, K.; Kakimoto, H.; Oshima, T. *J. Am. Chem. Soc.* **2002**, *124*, 6548.

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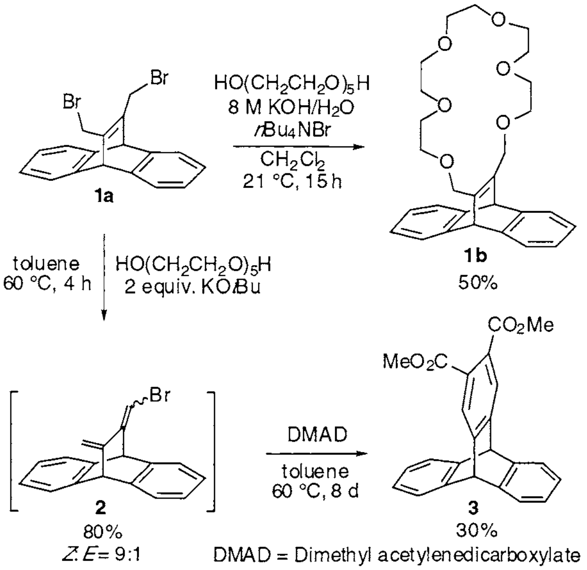
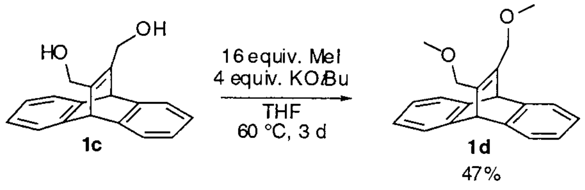
approach, we chose the dibenzobarrelene **1b**,[6] which is annelated with a crown ether. The dibenzobarrelene is an ideal chromophore for our studies because it exhibits a well-known dual-channel photoreactivity.[7] These compounds react from the first excited singlet state to give dibenzocyclooctatetraenes, whereas triplet sensitization leads to the dibenzosemibullvalenes through the di-π-methane rearrangement.[8]

The dibenzobarrelene derivative **1b** could not be obtained by the standard procedure commonly used for the synthesis of areno-20-crown-6 derivatives.[9] Thus, the reaction of the known dibromomethyl dibenzobarrelene **1a**[10] with pentaethylene glycol in the presence of potassium *tert*-butylate gave the bromodienes (*E*)-**2** and (*Z*)-**2** by a 1,4-elimination (Scheme 1). The dienes **2** are persistent at room temperature for several days, but they could not be isolated by column chromatography. Their structure was elucidated by comparison with similar bromodienes[11] and by trapping these intermediates with dimethyl acetylenedicarboxylate (DMAD) to give the known triptycene derivative **3**.[12] Finally, phase-transfer catalysis served as the key to the synthesis of the crown ether **1b**, which was obtained in 50% yield as a pale yellow oil by the reaction of **1a** with KOH/pentaethylene glycol (Scheme 1). The di(methoxymethyl)-substituted dibenzobarrelene **1d** was also synthesized as a reference compound by the etherification of the diol **1c**[9] with methyl iodide (Scheme 2).

Scheme 1. Synthesis of Crown Ether **1b**



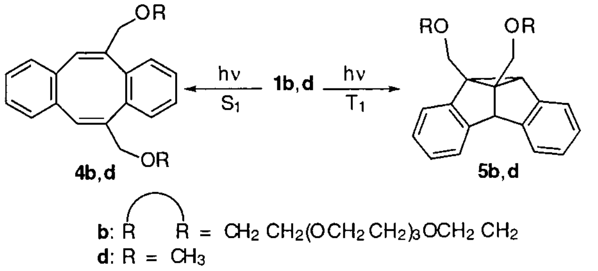
Scheme 2. Synthesis of Dibenzobarrelene Derivative **1d**



The ability of the crown ether **1b** to complex cations was exemplarily shown by the titration of $NaBF_4$, KBF_4, and $CsBF_4$ to **1b** in acetonitrile-d_6. The titration was monitored by ^{1}H NMR spectroscopy, as the bridgehead protons and the allylic hydrogen atoms exhibit significant downfield shifts on cation addition ($\Delta\delta = 0.05-0.15$). The titration data were used to determine the association constants of the crown ether complexes with the EQNMR program.[13] The cesium ion ($K_a = 2.3 \times 10^4$ M^{-1}) and the potassium ion ($K_a = 9.4 \times 10^3$ M^{-1}) exhibit similar affinity to **1b** and bind more strongly to the crown ether than the sodium ion ($K_a = 3 \times 10^2$ M^{-1}).[14] By contrast, the addition of $NaBF_4$ or KBF_4 did not change the ^{1}H NMR spectrum of the dibenzobarrelene **1d**, i.e., this compound does not complex significantly sodium or potassium ions.

The direct irradiation of dibenzobarrelenes **1b** and **1d** in acetonitrile or benzene solution gave the dibenzocyclooctatetraenes **4b** and **4d** in 79 and 85% yields, respectively, whereas the dibenzosemibullvalenes **5b** and **5d** were isolated in 64 and 57% yields, respectively, after irradiation of **1b** and **1d** in the presence of acetone as a triplet sensitizer (Scheme 3). The structural assignments of cyclooctatetraene **4b** and dibenzosemibullvalene **5b** are based on their ^{1}H and ^{13}C NMR spectroscopic and mass spectrometric data of the isolated materials (cf. Supporting Information). The photo-

Scheme 3. Photoreactions of Dibenzobarrelenes **1b** and **1d**[a]



[a] Key. S_1: $\lambda > 210$ nm, CH_3CN, 21 °C, 80 min. T_1: $\lambda > 310$ nm; CH_3CN/acetone; 21 °C, 80 min.

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(6) For a crown ether-annelated trypticene, see: Gakh, A. A.; Sachleben, R. A.; Bryan, J. C.; Moyer, B. A. *Tetrahedron Lett.* **1995**, *45*, 8163.

(7) Scheffer, J. R.; Trotter, J.; Gudmundsdottir, A. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P. S., Eds.; CRC Press: Boca Raton, FL, 1995; p 204.

(8) Zimmerman, H. E. *Organic Photochemistry* **1991**, *11*, 1. One of the referees pointed out that under special circumstances, the di-π-methane rearrangement may also take place from the singlet excited state of dibenzobarrelenes. Although this may be the case, we maintain the proposition of a di-π-methane rearrangement from the triplet excited state of dibenzobarrelene derivatives, since there is no precedent for the singlet pathway.

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(11) Cossu, S.; Cuomo, G.; De Lucchi, O.; Maggini, M.; Valle, G. *J. Org. Chem.* **1996**, *61*, 153.

(12) Butler, D. N.; Snow, R. A. *Can. J. Chem.* **1975**, *53*, 256.

products **4d** and **5d** were isolated as spectroscopically pure compounds (as determined by ^{1}H NMR) by alumina chromatography; however, further attempts to crystallize them led to decomposition. The irradiation of complexes of **1b** with sodium, potassium, or cesium tetrafluoroborate (1 molar equiv) in acetonitrile solution also gave the cyclooctatetraene **4b** as the main product (Table 1). In each reaction, small amounts (<5%) of the semibullvalene **5b** were detected, which could not be quantified within the error limits of the ^{1}H NMR spectroscopic analysis. In contrast, irradiation of **1b** in the presence of 5 equiv of KBF_4 gave a mixture of photoproducts **4b** and **5b** (49:51). Upon irradiation of **1d**, which does not bind alkali ions, in the presence of 5 equiv of KBF_4, even more triplet product was formed (**5d**:**4d** = 75:25), so it may be concluded that the semibullvalene formation results from an external cation effect. The smaller extent of semibullvalene formation in the case of **1b** may be explained by the steric hinderence of the chromophore by the crown ether moiety compared to the methoxy groups in **1d**.

Table 1. Irradiation ($\lambda > 210$ nm) of the Dibenzobarrelene Derivatives **1b** and **1d** in the Presence of 1 equiv of Alkali Tetrafluoroborates, MX, in Different Media

compd	medium[a]	MX	conversion [%][b]	product distribution [%] 4	5
1b	CH_3CN	$NaBF_4$	>95	>95	<5
1b	C_6H_6	$NaBF_4$	>95	>95	<5
1b	CH_3CN	KBF_4	>95	>95	<5
1b	CH_3CN	KBF_4[c]	79	49	51
1b	C_6H_6	KBF_4	>95	>95	<5
1b	CH_3CN	$CsBF_4$	>95[d]	>95	<5
1d	CH_3CN	KBF_4[c]	95	25	75
1b	solid[e]	$LiBF_4$	<5		
1b	solid[e]	$NaBF_4$	13	<5	>95
1b	solid[e]	KBF_4	47	17	83
1b	solid[e]	$CsBF_4$	20	<5	>95
1d	solid[e]		8	75	25
1d	solid[e]	$NaBF_4$	6	58	42
1d	solid[e]	KBF_4	8	61	39

[a] Irradiation times for photoreactions in solution and solid state were 80 min and 11 h, respectively. [b] Determined by ^{1}H NMR spectroscopic analysis of the reaction mixture; estimated error is ±5% of the given value. [c] KBF_4 (5 molar equiv). [d] ca. 10% of unidentified byproducts formed. [e] Obtained by slow evaporation of acetonitrile solutions to dryness.

The crown ether **1b** is an oil at room temperature; thus, its solid-state reactivity could not be investigated. Also, the complexes of **1b** with alkali metal ions could not be obtained in crystalline form. However, Pedersen showed that crown ether complexes are readily available as solids upon slow evaporation of their solutions to dryness.[15] Thus, solid samples of complexes of **1b** with $LiBF_4$, $NaBF_4$, KBF_4, and $CsBF_4$ were obtained by this method and irradiated in the solid state (Table 1). The lithium complex is photoinert; however, the solid-state photoreactions of the sodium, potassium, and cesium complexes gave the dibenzosemibullvalene **5b** as the main product in each case. Whereas **1b**-$NaBF_4$ and **1b**-$CsBF_4$ gave **5b** almost exclusively, the irradiation of **1b**-KBF_4 yielded also small amounts (17%) of the dibenzocyclooctatetraene **4b**. Solid−solid mixtures of **1d** with $NaBF_4$ or KBF_4, which were obtained by the same method, were also irradiated. In both cases, significant amounts (42 and 39%, respectively) of the dibenzosemibullvalene **5d** were formed, whereas the dibenzocyclooctatetraene **4d** is still the main photoproduct. Nevertheless, even irradiation of crystals of **1d** obtained by the evaporation of an acetonitrile solution to dryness resulted in significant amounts (25%) of triplet product **5d**, along with the singlet product **4d** (Table 1). The dibenzobarrelene **1d**, which was crystallized from dichloromethane/hexane, is photoinert in the crystalline state.

Since it was shown that the crown ether associates with sodium and potassium ions in solution and, thus, the metal ion should be located close to the chromophore within the complex, it is remarkable that no cation effect was observed in solution. Although this observation cannot be explained unambiguously on the basis of the experiments, we carefully propose that upon irradiation, the complexes pass through excited states in which positive polarization accumulates close to the binding sites. This leads to a significant destabilization of the excited complex because of electrostatic repulsion and subsequent “photoejection”[16] of the cation before photorearrangement takes place. Presumably, the photoreaction of the remaining uncomplexed **1b** proceeds faster than reformation of the complex, so that a cation cannot be effective. Also, as an alternative, it may be assumed that the ion is separated from the chromophore by solvation; however, if this were the case, even an excess of cations would not lead to the observed external cation effect.

The suppression of the solid-state photoreaction because of strong steric constraints in the crystal lattice has been documented, also for some dibenzobarrelene derivatives.[2c,17] Accordingly, we deduce that the dibenzobarrelene **1d**, which was crystallized from dichloromethane/hexane, and the lithium complex of **1a** are also photoinert because their solid-state arrangement limits molecular movement. Interestingly, the mixtures of **1d** with $NaBF_4$ or KBF_4 react in the solid state. This may indicate that **1d** crystallizes in a different, photoreactive solid-state arrangement upon evaporation in the presence of the salts; however, it cannot be excluded that under these conditions, the photoreaction takes place only at defect sites, in amorphous phases, or on the surface of the solid.

In the solid-state photoreactions of the complexes of **1b**, the cation effect of the complexed ion is significant. A similar effect was also observed in the solid-state photoreaction of

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(13) Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.

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(17) Fu, T. Y.; Gamlin, J. N.; Olovsson, G.; Scheffer, J. R.; Trotter, J.; Young, Dean, T. Y. *Tetrahedron Lett.* **1995**, *36*, 2025.

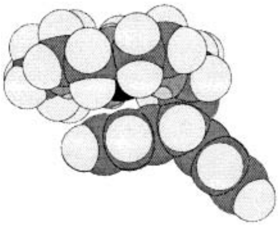

Figure 1. Minimum-energy conformation of dibenzobarrelene **1b** complexed to a potassium ion (deduced from force-field calculations MMFF94).

dibenzobarrelene **1d** in the presence of sodium and potassium ions; however, the semibullvalene **5d** is also formed in the absence of cations, as has been also observed on solid-state irradiation of the parent dibenzobarrelene,[18] so the net cation effect is relatively small. Since it was shown that **1d** does not complex metal ions in solution, we conclude that there is no effective complexation in the solid state either. Thus, the cation effect may result from the statistically determined close vicinity of the chromophore and the cation in the solid–solid mixture. A similar effect was shown by Scheffer et al. who observed triplet sensitization in the solid-state photoreaction of the parent dibenzobarrelene in the presence of triplet energy sensitizers.[19] Alternatively, weak π-cation interactions between the ion and **1d**, which may lead to a cation effect, cannot be excluded. Most notably, the comparison between **1b** and **1d** showed that the crown ether functionality is a necessary structural feature for achieving a highly efficient cation effect.

The heavier potassium ion exhibits a less pronounced effect compared to the "lighter" sodium ion, although the potassium ion binds more strongly to the crown ether than the sodium ion. The reason for this unexpected behavior may be found in the structure of the complex. Unfortunately, we were not able to grow single crystals of the crown ether complexes, so that information about their structure in the solid state is not available. But even simple force-field calculations reveal that the crown ether unit is oriented coplanar to one of the dibenzobarrelene benzene rings, so that cation–π interactions[19] may take place (Figure 1).

Thus, the determined binding constant may be a combination of the association of the cation with the crown ether *and* with the π system. According to Ramamurthy and Scheffer,[20] such a cation–π interaction perturbs the excited state of the dibenzobarrelene derivatives to promote efficient intersystem crossing ("light-cation effect"). Since sodium ions bind significantly stronger to π systems than potassium ions (e.g., in the gas phase, Na^+/benzene = 28.0 kcal/mol and K^+/benzene = 19.2 kcal/mol),[19] it may be assumed that this is also the case in the complexes of **1b**, which leads to a more efficient cation effect from the sodium ion compared to the potassium ion.

Our results clearly show that a cation effect operates in the solid-state photoreaction of complexes of dibenzobarrelene **1b** with alkali metal ions and induces a di-π-methane rearrangement, whereas in solution such an effect is absent and dibenzocyclooctatetraene formation takes place. Thus, we have achieved a successful combination of supramolecular assembly and solid-state photochemistry, which leads to a medium-dependent type selectivity. This strategy may be readily extended to the use of sodium or potassium salts of chiral carboxylates for the asymmetric induction in the formation of the chiral dibenzosemibullvalene **5b**, a worthwhile endeavor for investigation.

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Supporting Information Available: Experimental procedures, synthesis, and physical data of compounds **1b**,**d**, **2**, **3**, **4 b**,**d**, and **5b**,**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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