The zwitterionic complex is not a useful catalyst for the hydroformylation of simple monosubstituted olefins such as 1-heptene, since the branched/linear aldehyde ratio is near unity. However, if the substituent is bulky (e.g., 3,3-dimethyl-1-hexene), then regiospecific hydroformylation occurs leading to the linear aldehyde as the *only* product. In contrast, vinyl ethers (phenyl vinyl ether, vinyl 2-naphthyl ether, vinyl p-*tert*-butylphenyl ether, vinyl 3,4-dimethylphenyl ether) do undergo hydroformylation affording the branched-chain product in quite high regioselectivity.

While vinyl acetate undergoes hydroformylation with **1** to give principally the branched-chain aldehyde, isomeric methyl acrylate shows modest selectivity for the linear product. Unlike other 1,1-disubstituted olefins (above), methyl methacrylate affords aldehydes in low regioselectivity. The hydroformylation of allylic compounds (allylbenzene, allyl phenyl ether, *N*-methyl-*N*-phenylallylamine), while facile, are reactions of low regioselectivity. Finally, the carbon–carbon double bond of 2-cyclohexen-1-one is reduced under the usual hydroformylation conditions.

In conclusion, zwitterionic rhodium complexes display exceptionally high regioselectivity in the hydroformylation of vinylarenes and vinyl ethers to branched-chain aldehydes, while aliphatic or aromatic, 1,1-disubstituted olefins afford linear aldehydes in a regiospecific process. These reactions occur under remarkably mild conditions and are simple in both execution and workup.

Note Added in Proof. Rhodium complexes of trehalose-derived ligands (*not* zwitterionic) catalyze the hydroformylation of styrene in high regioselectivity. Unfortunately the naproxen precursor did not react in a regiospecific manner [95/5:b/l], and the ibuprofen precursor was not examined. We are indebted to Dr. John Brown for bringing this work to our attention [Brown, J. M.; Cook, S. J.; Khan, R. *Tetrahedron* **1986**, *42*, 5105].

Acknowledgment. We are grateful to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research. We are indebted to Karen Totland for experiments carried out with *p*-isobutylstyrene as reactant. We also are grateful to Johnson Matthey for providing a loan of rhodium chloride.

Novel Photorearrangements of Bridgehead-Substituted Dibenzobarrelene Derivatives in Solution and the Solid State

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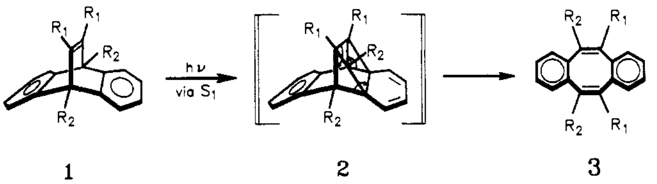
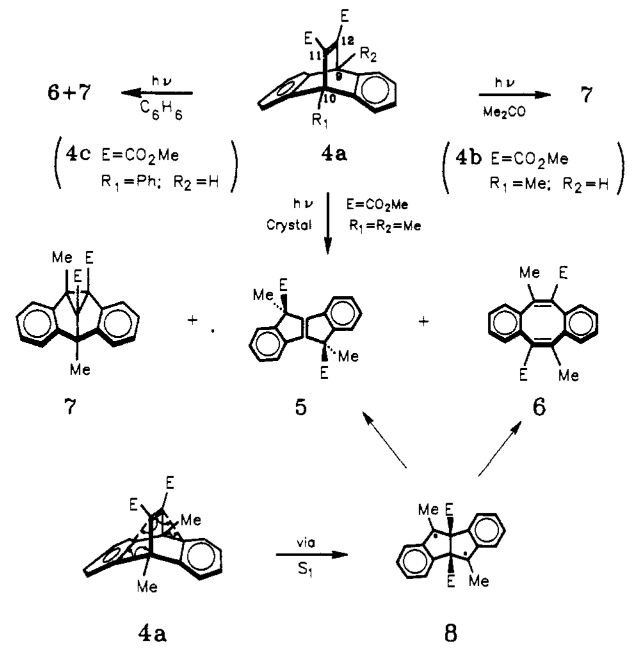
On the basis of an extrapolation from well-established benzo- and naphthobarrelene mechanisms,[1a-d] it has been assumed that the mechanism by which the analogous *di*benzobarrelene compounds rearrange photochemically to cyclooctatetraene (COT) derivatives involves initial intramolecular [2 + 2] cycloaddition through the singlet excited state followed by thermal reorganization of the resulting cage compound. This mechanism, outlined in Scheme I for the general dibenzobarrelene case, predicts the formation of dibenzocyclooctatetraenes with the substitutent pattern of structure **3**. We report in this communication that, for some bridgehead-substituted dibenzobarrelene derivatives, an alternative COT mechanism is followed, one that gives rise to a different labeling pattern in the derived dibenzocyclooctatetraenes.

The clue that led to this discovery came from the isolation of an unusual and unexpected photoproduct in the *solid-state* irradiation of the dibenzobarrelene derivative **4a** (Scheme II).[2]

Scheme I



Scheme II



Photolysis of crystals of **4a** to low (≈5%) conversions afforded mainly (85%) the novel diester **5**, whose structure and stereochemistry were proved by X-ray crystallography;[3] small amounts of a COT derivative as well as the di-π-methane[4] photoproduct **7** were also formed. The structure of this latter material was assigned on the basis of its spectral data. Unsensitized *solution-phase* irradiation of **4a** gave approximately equal amounts of COT and **7**, and acetone-sensitized photolysis of **4a** gave **7** exclusively. Appropriate control experiments established that product interconversion was not occurring under the photolysis conditions.

It seems likely that the mechanism by which diester **5** is formed involves sequential carbomethoxy group migration in the bisbenzylic biradical **8** (Scheme II). This mechanism nicely rationalizes the stereochemistry of **5**, and such migrations, while rare, do have literature precedent.[5] The probable intermediacy of biradical **8** suggested that it might also be involved in COT formation through Grob-type fragmentation. This predicts the formation of a COT with C_2 symmetry rather than the C_s symmetry predicted by the mechanism of Scheme I. For this reason, a single-crystal X-ray diffraction study of COT **6** was undertaken.[3] The results of this study unambiguously establish that **6** has the unexpected, Grob fragmentation labeling pattern shown in Scheme II.[6]

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(1) (a) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 6096. (b) Zimmerman, H. E.; Bender, C. O. *J. Am. Chem. Soc.* **1970**, *92*, 4366. (c) Bender, C. O.; Shugarman, S. S. *J. Chem. Soc., Chem. Commun.* **1974**, 934. (d) Bender, C. O.; Brooks, D. W. *Can. J. Chem.* **1975**, *53*, 1684.

(2) Compounds **4a–c** were synthesized by Diels–Alder addition of dimethyl acetylenedicarboxylate to the appropriately 9-substituted or 9,10-disubstituted anthracene derivative. The structures of adducts **4a–c** were verified by X-ray crystallography.[3] The solution-phase photochemistry of compounds **4b** and **4c** has been reported, without, however, any mention being made of COT formation. (a) Iwamura, M.; Takuka, H.; Iwamura, H. *Tetrahedron Lett.* **1980**, *21*, 4865. (b) Paddick, R. G.; Richards, K. E.; Wright, G. J. *Aust. J. Chem.* **1976**, *29*, 1005.

(3) Full details on the crystal and molecular structures of compounds **4a–c**, **5**, and **6**, as well as the COTs from **4b** and **4c**, will be published separately.

(4) For a review on the di-π-methane photorearrangement, see: Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, Chapter 16.

(5) Wollowitz, S.; Halpern, J. *J. Am. Chem. Soc.* **1984**, *106*, 8319 and references cited therein.

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To test the generality of these results, the photochemistry of the trisubstituted dibenzobarrelenes **4b** (E = CO$_2$Me; R$_1$ = Me; R$_2$ = H) and **4c** (E = CO$_2$Me; R$_1$ = Ph; R$_2$ = H) was investigated. In each case, both in the solid state and in solution, the COT formed was that derived from Grob fragmentation rather than $2\pi + 2\pi$ photocycloaddition. In neither case, however, was a photoproduct analogous to diester **5** isolated. The structures of both COTs were determined by X-ray crystallography.[3] This corrects an earlier publication from our group in which the COT from **4b** was assumed to have the $2\pi + 2\pi$ derived structure.[7,8] One might ask whether *all* dibenzobarrelenes give Grob fragmentation COTs. They do not. X-ray data indicate that the COT from 9-isopropyl 11-methyl 9,10-dihydro-9,10-ethenoanthracene-9,11-dicarboxylate is of the $2\pi + 2\pi$ type.[9]

The origin of biradical **8** presents an interesting mechanistic problem. Most likely of singlet multiplicity (since neither of the photoproducts thought to be derived from it are formed in the triplet-sensitized reaction), its formation involves, at least formally, a type of "tri-π-methane" interaction of both aromatic rings with the aliphatic double bond.[10] The simplest mechanism among several that will be discussed in a full paper involves direct (although probably not concerted[11]) rearrangement of **4a** to **8** (mechanistic arrows, Scheme II). The reluctance of **4a** to engage in $2\pi + 2\pi$ photocycloaddition can be attributed reasonably to steric factors. This, coupled with the additional stability afforded biradical **8** by the methyl substituents, plausibly rationalizes the unexpected singlet-state behavior of **4a**; similar arguments apply in the case of dibenzobarrelene derivatives **4b** and **4c**.[12] Current research is concerned with further elaborating the structural and environmental factors responsible for the novel photoreactivity.

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Registry No. 4a, 1100-93-2; **4b**, 58802-07-6; **4c**, 77452-72-3; **5**, 125903-02-8; **6**, 125903-03-9; **7**, 125903-01-7.

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(6) It might at first sight seem that COT **6** could be formed through photoisomerization of an initially formed $2\pi + 2\pi$ derived COT. For example, Stiles and Burckhardt (Stiles, M.; Burckhardt, U. *J. Am. Chem. Soc.* **1964**, *86*, 3396) and Salisbury (Salisbury, L. E. *J. Org. Chem.* **1978**, *43*, 4987) have shown that 5,6-disubstituted COTs rearrange to their 5,11 isomers via "crossed" [2 + 2] photocycloaddition followed by thermal ring opening in the opposite sense. This mechanism, when applied to the hypothetical $2\pi + 2\pi$ COT from **4a**, returns the starting material. A second concern that can be dismissed with a little thought is the possibility that di-π-methane photoproduct **7** could be confused with the hypothetical product resulting from coupling of biradical **8**. The ^{1}H NMR spectrum of **7**, however, which shows two nonequivalent methyl ester resonances at δ 3.76 and 3.88 and two additional nonequivalent methyl singlets at δ 1.90 and 1.98, clearly rules out this possibility. As added evidence, crystallography shows that the di-π-methane photoproduct from dibenzobarrelene derivative **4c** has the expected structure: Trotter, J.; Pokkuluri, P. R., unpublished results.

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(8) Other workers have assigned $2\pi + 2\pi$ structures to COTs derived from bridgehead-substituted dibenzobarrelene derivatives. See, for example, ref 2b. See also: Kumar, C. V.; Murty, B. A. R. C.; Lahiri, S.; Chackachery, E.; Scaiano, J. C.; George, M. V. *J. Org. Chem.* **1984**, *49*, 4923. Pratapan, S.; Ashok, K.; Cyr, D. R.; Das, P. K.; George, M. V. *J. Org. Chem.* **1987**, *52*, 5512.

(9) Pokkuluri, P. R.; Scheffer, J. R.; Trotter, J. Unpublished results.

(10) The "tri-π-methane" terminology is borrowed from Zimmerman, who coined it some time ago and used it recently in describing the unusual solid-state photorearrangement of an aliphatic trivinylmethane derivative to a substituted vinylcyclopentene. See: Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 7974.

(11) In considering possible mechanisms for the di-π-methane photorearrangement of barrelene, Zimmerman et al. (Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932) concluded, on the basis of extended Hückel calculations, that concerted double bridging has a relatively high activation barrier compared to the corresponding stepwise process.

(12) The reason why **4a** affords the diester migration product **5** when photolyzed in the solid state, whereas **4b** and **4c** do not, is not clear at the present time. We tentatively ascribe this to crystal packing effects that are unique to **4a**.

In Situ Scanning Tunneling Microscopy of Adsorbates on Electrode Surfaces: Images of the $(\sqrt{3}\times\sqrt{3})R30°$-Iodine Adlattice on Platinum(111)

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In the study of electrified interfaces, it is extremely difficult to acquire information concerning the detailed structure of the interfacial region. Two promising methods for in situ characterization of electrode surfaces are scanning tunneling microscopy (STM)[1] and atomic force microscopy (AFM).[1,2] Application of STM to the study of metal surfaces in situ has been limited to the observation of gross-scale (1 nm to 1 μm) morphological features as illustrated by several studies of the effect of surface pretreatments on the roughness of platinum electrodes.[3,4] Other studies of this type have looked at electrodeposition processes[5-10] and stainless steel.[11] Improved resolution leading to the observation of monoatomic steps has been achieved by only a few researchers using either single crystals or evaporated films.[12,13]

In this communication, we report further improvement in the resolution attainable with an STM operating in situ. We have imaged the $(\sqrt{3}\times\sqrt{3})R30°$-I adlattice on a Pt(111) single crystal in aqueous 0.1 M HClO$_4$. This suggests that STM has a bright future as a tool for studying fundamental processes at electrode surfaces. We have also managed to find conditions that allowed imaging the Pt(111) substrate lattice in ambient laboratory air. The Pt(111) substrate lattice image aids in interpretation of the in situ images.

Iodine dosing of a platinum(111) surface in ultrahigh vacuum (UHV) produces two ordered adlattices.[14] At a fractional surface coverage of 0.33, the iodine orders into a $(\sqrt{3}\times\sqrt{3})R30°$ lattice with one iodine atom per surface unit cell. At a fractional coverage of 0.43, the iodine orders into a $(\sqrt{7}\times\sqrt{7})R19.1°$ unit cell containing three iodine atoms. The $(\sqrt{7}\times\sqrt{7})R19.1°$ phase can be prepared by a convenient gas-phase dosing procedure that does not require the use of UHV.[15,16] The procedure involves annealing the single-crystal surface in a hydrogen flame followed by cooling in a glass dosing cell containing iodine crystals and being purged with N$_2$. In previous research, we were able to use STM to image the $(\sqrt{7}\times\sqrt{7})R19.1°$ phase of iodine in the ambient laboratory atmosphere.[17]

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