

of a coupling between the olefinic protons. $^1J(\text{C}6/7\text{-H}6/7)$ increases on bonding to iron whereas it decreases on bonding to lithium in **2b**,⁵ which means that charge transfer to and rehybridization at C6/7 do not dominate the coupling.

The isolation of **4** shows that even if the π -system of Cp anions is broken down into olefinic and allylic systems bonding to transition metals is still possible. "Opening" Cp ligands once as realized in metal-pentadienyl chemistry¹⁴ is not the ultimate perturbation that π -complexes tolerate.

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Supplementary Material Available: NMR data⁵ of **1**, **2a**, and **3** and complete tables of atomic coordinates and displacement parameters for **4** (7 pages); listing of observed and calculated structure factors for **4** (8 pages). Ordering information is given on any current masthead page.

(14) Recent contributions: (a) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1988**, *6*, 2612. (b) Bleeke, J. R.; Rauscher, D. J.; Moore, D. A. *Ibid.* **1988**, *6*, 2614.

Modification of Photochemical Reactivity by Zeolites: Norrish Type I and Type II Reactions of Benzoin Derivatives

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Selectivity in organic phototransformations continues to be one of the main topics of current interest.¹ Of the various approaches use of constrained and ordered media has shown considerable promise.² By the utilization of the cage effect³ and conformational control we illustrate below that one can induce molecules included in zeolites to follow reaction pathways that are improbable in isotropic solvents.

The photochemical behavior of benzoin alkyl ethers (**1a**) and alkyl deoxy benzoin (**2a**) in solution are fairly well understood.^{4,5} In benzene, the former prefers the Norrish type II pathway while the latter gives the Norrish type I products in high yields (Scheme I). Photolyses of alkyl benzoin ethers and alkyl deoxy benzoin in zeolites⁶ show a dramatic difference in behavior when compared to that in benzene (Table I). Results on benzoin methyl ether and propyl deoxy benzoin in faujasite zeolite (M-X type)⁷ alone

[†] Contribution No. 4643.

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(5) Heine, H. G.; Hartmann, W.; Kory, D. R.; Magya, J. G.; Hoyle, C. E.; McVey, J. K.; Lewis, F. D. *J. Org. Chem.* **1974**, *39*, 691. Lewis, F. D.; Hoyle, C. E.; Magyar, J. G.; Heine, H. G.; Hartmann, W. *J. Org. Chem.* **1975**, *40*, 488. Dasaratha Reddy, G.; Ramamurthy, V. *J. Org. Chem.* **1987**, *52*, 5521.

(6) Benzoin ethers and deoxy benzoin were included in zeolites by stirring known amounts of the guest and the host in trimethylpentane for 10 h. The complex was filtered and washed with ether under dry nitrogen atmosphere. Known amounts of the complex was degassed (10^{-4} Torr) and irradiated under sealed conditions. Products were extracted by stirring the irradiated complex in 10 mL of ether for 12 h. For comparison the products were also extracted by dissolving the zeolite with HCl. Material balance was ~90% in all cases. Amounts of the guest included were estimated by elemental analysis of the zeolite and by GC analysis of the reextracted material.

Scheme I

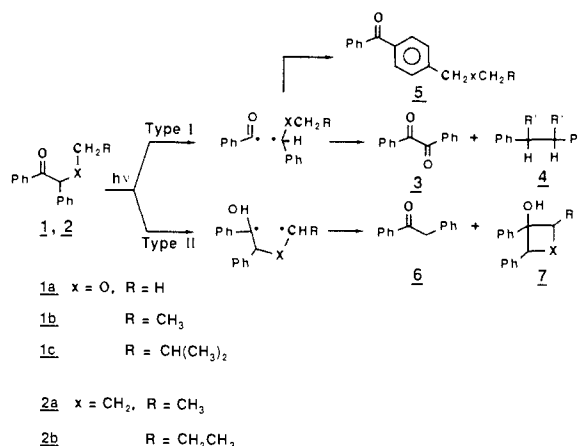


Table I. Product Distribution upon Photolysis of Benzoin Methyl Ether and Propyl Deoxy Benzoin in Zeolites

medium	percentage of products				ratio of products	
	3, 4	5	6	7	5/ 6 + 7	3 + 4 + 5/ 6 + 7
(a) Benzoin Methyl Ether						
benzene	26, 66	0.2	1.1	7	0.03	12.2
Li-X (dry)	3	76	13	8	3.6	3.6
Li-X (wet)	18	40	19	23		
Na-X (dry)	4	72	10	14	2.9	3.1
Na-X (wet)	22	47	11	20		
K-X (dry)	24	44	14	18	1.5	2.2
Rb-X (dry)	15	46	17	22	1.1	1.5
Cs-X (dry)	31	34	15	20	0.9	1.9
(b) Propyl Deoxy Benzoin						
benzene	5, 19	54	22	0		0.3
Li-X (dry)		95	4	1	18.5	
Na-X (dry)		88	5	7	7.6	
K-X (dry)		51	35	14	1.1	
Rb-X (dry)		48	31	21	0.9	
Cs-X (dry)		32	42	26	0.5	

^a Product yields (relative) were measured at ~15% conversion by gas chromatography with *cis*-stilbene as the internal standard; error limit $\pm 5\%$. ^b Wet zeolite complexes were prepared by exposing the dry complex to atmospheric moisture; zeolites made wet prior to inclusion did not include benzoin methyl ether. ^c Extraction by dissolution of the zeolite framework with HCl gave the same products (and in the same yields) as those on ether extraction. Pinacol ether and other products were stable to acid. ^d Loading in all cases was about 2% by weight as estimated by carbon analysis and re-extraction. Loading variation carried out with NaX and NaY indicated that the product distribution is independent of the loading in the range 0.5-5% by weight. ^e ZSM-5, -8, and -11 did not include benzoin methyl ether and propyl deoxy benzoin.

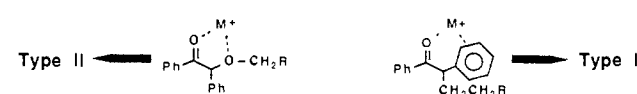


Figure 1.

are highlighted in Table I. Similar behavior was observed in M-Y zeolites. Identical behavior was found for other alkyl-substituted benzoin ethers (**1b,c**) and deoxy benzoin (**2b**).

With **1a** the amount of the type II products is considerably increased over that observed in benzene. Even more importantly, the rearrangement product, benzoylbenzyl alkyl ether (**5**), was

(7) Zeolites 13X (Na-X) and LZ-Y52 (Na-Y) were obtained from Linde. The cation of interest was exchanged into these powders by contacting the material with the appropriate nitrate solution at 90 °C. For each gram of zeolite, 10 mL of a 10% nitrate solution was used. This was repeated a number of times. The samples were then thoroughly washed with water and dried. Exchange loadings were typically between 40 and 90%. Prior to use the samples were heated in air at 1 deg/min to 500 °C and held at 500 °C for 7 h. The samples were removed at 100 °C and stored under anhydrous conditions.

major among the type I products.⁸ In contrast, **2a**, which generally gives type II products in benzene, gave the type I derived **5** as the major product in M-X zeolite. In both cases, the yield of the rearrangement product **5** was dependent upon the exchangeable cation. It is important to note that the inherent reactivity controlled product distribution has been dramatically altered by the zeolite cavity in both cases.

We believe the preference for **5** among the type I products is a consequence of the restriction experienced by the geminal radical pair (Scheme I).⁹ Low yields of coupling products **3** and **4** in the product mixture in the case of **1a** and their absence in **2a** clearly indicate that the translational motion of the radical pair is restricted by the zeolite framework.¹⁰ Even more interesting is the fact that the rotational process required to produce the rearrangement product is greatly dependent upon the cavity free space. It is known that in proceeding from Li-X to Cs-X the degree of "lebensraum" or open void space is significantly reduced.¹¹ It is of interest to note that the relative yield of **5** decreases in the same order as the increase in the cation size. Such a space dependent rotational restriction is also evident when one compares the product distribution between the dry and the wet zeolites. Water decreases the void space by co-ordinating to the free cations present within the zeolite cavity.¹²

The behavior of benzoin alkyl ethers and alkyl deoxy benzoinz when viewed together provides important additional information. The zeolite cavity induces **1a** to yield products derived via the type II pathway, a minor pathway in benzene. On the other hand, zeolites do not cause **2a** to proceed via the type II pathway, which is favored in benzene. We attribute this to the ability of the cation present in the cavity to control the conformation of the included molecules (Figure 1). The presence of an alkoxy chain in **1a** most likely directs the chelation of the cation to a conformer that is favorable for the type II process. Similarly in **2a**, the phenyl ring directs the conformational preference in the cavity.¹³ Such a hypothesis is supported by the results on dealuminated zeolite-Y in which the Si to Al ratio is very high (>550).¹⁴ At very low levels of aluminum the cation concentration is also low. Therefore conformational control is expected to be minimal and indeed only the type I products, **3-5**, dominated the product mixture. Furthermore, the increase in the yield of benzil from Li-X to Cs-X (Table I) is also a reflection of the decreased interaction between the cation and the benzoyl radical.¹⁵ The increased yield of the type II products in **1a** in zeolite must also be the result of the cage effect as significant C¹³ enrichment (25%) of the oxetanol was observed.¹⁶

The results presented above illustrate the important role zeolites can play in selective phototransformations. Since zeolites of varied and tailor-made frameworks are readily prepared, the future for zeolites as a reaction medium appears bright.

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$(\mu\text{-NO})_2[\text{Co}(\eta^5\text{-C}_5\text{H}_5)]_2$ Is Not Paramagnetic

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A recent theoretical article, published in this journal, has suggested that the molecule, $\text{Cp}_2\text{Co}_2(\mu\text{-NO})_2$, is a ground-state triplet ($S = 1$) and therefore paramagnetic.¹ The only evidence in the literature relative to the magnetic properties of this molecule of idealized D_{2d} symmetry in the solid state² is the apparently normal ¹H NMR spectrum (for a diamagnetic molecule) that contains a single resonance at δ 4.77³ or 4.60,⁴ the temperature not being specified. In this brief paper we show that $\text{Cp}_2\text{Co}_2(\mu\text{-NO})_2$ is diamagnetic in the solid state (5–280 K) and in solution (C_6H_6 , 303–327 K) and conclude that the theoretical calculations of Demuyck, Mougenot, and Benard¹ predict the wrong result.

For a diamagnetic compound the magnetic susceptibility, χ , is negative and on the order of 10^{-6} (emu)(g⁻¹). For a paramagnetic compound χ is positive and on the order of 1–3 times greater than that of a diamagnetic compound. As can be seen from Table I, the only χ value that is negative is the value at 281 K at 5 kG. The other values of χ are positive though very small. The slightly positive values of χ could be due to trace metal or other paramagnetic impurities (cobalt metal is ferromagnetic with a magnetic moment of $1.7 \mu_B$)^{5c} or due to the TIP (temperature independent paramagnetism) term being positive, the TIP term for Co(II) can be as high as 10^{-4} emu mol⁻¹. Further, the molecule is diamagnetic as deduced by the Evans' method. Thus, 19.8 mg ml⁻¹ of $\text{Cp}_2\text{Co}_2(\mu\text{-NO})_2$ in C_6H_6 does not shift the ¹H NMR absorption of C_6H_6 (internal) relative to C_6H_6 (external) by a detectable amount at 32 °C and 54 °C. The resonance due to the equivalent protons of the C_5H_5 rings occurs at δ 4.54 at 32 °C and 54 °C with a line width at half height of 1.7 Hz.

(8) The rearranged products were characterized by GCMS and PMR. Devanathan, S.; Ramamurthy, V. *J. Phys. Org. Chem.* **1988**, *1*, 91.

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(10) By independent experiments it was established that both **3** and **4** can enter and exit the zeolite. Furthermore it was shown that these are stable to acid extraction. Absence of pinacol ethers in zeolites also is a consequence of the fragmentation of the precursor radical to benzaldehyde when translational motion is restricted.

(11) Sefcik, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 2164. Onaka, M.; Isikawa, K.; Izumi, Y. *J. Inclusion Phenomena* **1984**, *2*, 359. Turro, N. J.; Zang, Z. *Tetrahedron Lett.* **1987**, 5637.

(12) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974; pp 412–415. Further experiments are underway to evaluate the effect of water on the product distribution.

(13) Similar chelation of the cation to the guest $\text{Ni}(\text{CO})_4$ has been reported recently: Bein, T.; McLain, S. J.; Corbin, D. R.; Farlee, R. F.; Moller, K.; Stucky, G. D.; Woolery, G.; Sayers, D. *J. Am. Chem. Soc.* **1988**, *110*, 1801. Carbonyl stretching frequency of **1a** (1694 cm⁻¹) in THF is also shifted by excess magnesium triflate (1681 cm⁻¹).

(14) Dealuminated zeolite Y was prepared according to the following: Grobet, P.; Jacobs, P. A.; Beyer, H. K. *Zeolites* **1986**, *6*, 47.

(15) Such an increase may not be due to the photolysis of the ketone adsorbed on the surface since the complexes were washed thoroughly with ether before processing for irradiation. No benzil or diphenyl alkanes were detected as products in the case of **2**. We believe that disproportionation occurs between benzoyl and benzyl radical pair to yield benzaldehyde and olefin, a reaction that is not possible in the case of **1**.

(16) Isotope enrichment was estimated by measuring the isotope distribution of the molecular ion peak of the oxetanol product. Oxetanol from benzene irradiation was taken as the standard. The isotope enrichment derives from the enrichment of the starting ketone and not due to the effect on the biradical precursor.

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(4) Weiner, W. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3922–3929.

(5) (a) Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities*; Clarendon Press: Oxford, 1932. (b) Bondreaux, E. A.; Mulay, L. N. *Theory and Application of Molecular Paramagnetism*; Wiley: New York, 1976. (c) Goodenough, J. B. *Magnetism and the Chemical Bond*; Wiley: New York, 1963.

(6) Magnetic susceptibility measurements were made on a SHE Model 905 superconducting magnetometer (SQUID). Sample containers were made from two tightly fitting KEL-F half-containers. In a typical experiment 78.01 mg of $\text{Cp}_2\text{Co}_2(\mu\text{-NO})_2$, which was freshly sublimed and ground to a fine powder before weighing, was placed into a KEL-F container inside of an argon-filled drybox. The two halves of the container were sealed with the aid of a small amount of silicone grease. After removal of the container from the drybox, the container was wired shut with nylon, microfilament thread and suspended in the sample chamber of the magnetometer by cotton thread. Samples were measured automatically at two fields and at temperatures between 5 and 280 K. Measurements were taken at 5 and 40 K with the following temperature intervals: 3 K from 6–21 K; 5 K from 25–50 K; 10 K from 50–100 K; 20 K from 100–280 K. Sample data were corrected for container (including grease) diamagnetism. In this case, a duplicate determination on a different chemical specimen gave the same result. An additional sublimation of the compound gave essentially the same χ_g values as those of the once sublimed compound though the value of χ_g for the crystallized specimen was 2 orders of magnitude higher than that of the sublimed specimen.