inclusion, the variation in the fluorescence intensity was monitored. Stock solutions of 1.1×10^{-2} M of 1 and 5 were prepared in methanol. Small portions (30 μL) of the stock solution were added to 10-mL standard flasks containing varying amounts of β-cyclodextrin solution (4–8 mL of 10^{-3} M stock solution). These solutions were made up to 10 mL and magnetically stirred well for 24 h. Fluorescence emission spectra ($\lambda_{excitation}$ = 310 nm) were recorded and emission intensity at 390 nm was used for the stability constant calculations. A plot of [guest]/ΔI vs. 1/[host] was linear with the slope and intercept being equal to $1/K_d\Delta I$ and $1/\Delta I$, respectively (ΔI = increment of the fluorescence intensity of guest molecule on addition of cyclodextrin). The value of K_d was obtained from these linear plots. K_d values for dibenzyl ketone and α-ethyldibenzyl ketones were 8.6×10^{-4} and 1.4×10^{-4}, respectively.

Photolysis. (a) Homogeneous Solution. Preparative-scale irradiations of 1–7 in benzene and methanol were carried out in Pyrex vessels at room temperature by using a 450-W medium pressure mercury arc lamp. The samples were deaerated before irradiation by passing dry nitrogen gas for 30 min. After about 40% conversion (12 h), the solvent was evaporated and the products were separated by repetitive column and preparative thin layer chromatography (silica gel, hexane/chloroform). The products were identified on the basis of their spectral properties. The products formed from 3–7 were the diphenylalkanes AA, AB, and BB, cyclobutanols, and dibenzyl ketone and from 1 and 2 decarbonylated coupling products were the only products. Since the spectral data for products derived from 1–7 were closely similar, the spectral data of products from α-propyldibenzyl ketone alone are presented below as an example.

1,2-Diphenylpentane: IR (neat) cm^{-1} 2980, 2920, 1600, 1490, 1450, 1260; ^1H NMR ($CDCl_3$) 0.78 (t, 3 H), 0.85–1.33 (m, 6 H), 2.75–2.86 (m, 3 H), 7.0–7.38 (m, 10 H).

1-Phenyl-4′-butylacetophenone: IR (neat) cm^{-1} 3020, 2940, 1680, 1600, 1220; ^1H NMR ($CDCl_3$) 0.93 (t, 3 H), 1.25–1.42 (m, 4 H), 2.65 (t, 2 H), 4.26 (s, 2 H), 7.0–7.36 (m, 7 H), 7.94 (d, 2 H).

1-Benzyl-2-phenyl-4-methylcyclobutanol (two isomers): IR (neat) cm^{-1} 3520–3200 (b), 2940, 1600, 1500, 1460, 1060; ^1H NMR ($CDCl_3$) (i) 0.84 (d, 3 H), 1.25–1.44 (m, 3 H), 2.92 (s, 2 H), 3.41 (dd, 1 H), 7.14–7.44 (m, 10 H); (ii) 1.21 (d, 3 H), 1.98–2.4 (m, 3 H), 2.58 (s, 2 H), 3.6 (dd, 1 H), 7.14–7.44 (m, 10 H).

The small-scale analytical irradiations were carried out either in NMR tubes or in small Pyrex test tubes. Conversions were kept below ~15% and the products were analyzed by GC. The product distribution was calculated on the basis of the area of the peak corresponding to each product on the GC trace. No correction for detector response was made.

(b) Solid Cyclodextrin Complexes. Photolysis of microcrystalline complexes was carried out by using a Hanovia 450-W medium pressure mercury arc lamp. Samples were degassed, sealed, and irradiated for 24 h. In order to obtain a uniform exposure, the sample tubes were rotated periodically. The irradiated cyclodextrin complexes were dissolved in warm water and extracted with chloroform. The products were analysed by GC and ^1H NMR.

(c) Cyclodextrin Complexes in Aqueous Solution. Aqueous solutions of the complexes prepared by dissolving the microcrystalline complex (50 mg) and an excess of β-cyclodextrin in 250 mL of water were irradiated in Pyrex tubes, using a 450-W medium pressure mercury arc lamp after purging with dry nitrogen for about 45 min. After irradiation (3 h) the products were extracted by using warm chloroform and analyzed by GC.

Experiments with varying ratios of host/guest were also carried out as above. Irradiations under an oxygen atmosphere were carried out by photolyzing as described above while oxygen was continuously bubbled through the solution. Photolysis of dibenzyl ketone complex in the presence of excess cupric chloride (3 M) was conducted in Pyrex vessels using a 450-W medium pressure mercury lamp with a potassium chromate solution filter.

Registry No. 1, 102-04-5; 1·β-cyclodextrin complex, 99765-87-4; 2, 13363-25-2; 3, 6363-21-9; 3·β-cyclodextrin complex, 110826-48-7; 4, 110826-44-3; 5, 110826-45-4; 6, 110826-46-5; 7, 110826-47-6; β-cyclodextrin, 7585-39-9; 1,2-diphenylpentane, 110826-49-8; 1-phenyl-4′-butylacetophenone, 69383-34-2; 1-benzyl-2-phenyl-4-methylcyclobutanol, 110826-50-1.

Modification of Photochemical Reactivity by Cyclodextrin Complexation: Alteration of Photochemical Behavior via Restriction of Translational and Rotational Motions. Alkyldeoxybenzoins

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The photochemical behavior of alkyldeoxybenzoins has been investigated in isotropic organic solvents, in aqueous cyclodextrin solutions, and when they are bound to cyclodextrin in the solid state. Norrish type I and type II reactions occur in these media and the product distributions resulting from these primary processes are dependent on the medium. While in organic solvents the type I and the type II products are obtained in equal amounts, in the aqueous cyclodextrin solution the type II products are formed in large excess. In the solid state the type II products constitute more than 90% of the product distribution. Ratios of products resulting via elimination and cyclization from the type II 1,4-diradical are also altered by the host cyclodextrin. Conformational and super-cage effects have been invoked to rationalize the dramatic alteration of the photobehavior of alkyldeoxybenzoins by the cyclodextrin.

The continuing strive of chemists for selectivity in chemical reactions has led to the alteration of chemical properties through host–guest complexation.[1] The chemistry of cyclodextrins has occupied a central interest in host–guest phenomenon for the last 2 decades.[2] The facility with which cyclodextrins form inclusion compounds

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Table I. Product Distribution during Photolysis of α-Ethyldeoxybenzoin[a,b]

medium	benzaldehyde	3,4-diphenylhexane	benzil	deoxybenzoin	cyclobutanol(s)
benzene	19.8	49.0	10.0	13.0	7.7
methanol	12.9	46.3	8.0	23.8	8.0
neat crystals (mp 57–58 °C)[c]	no reaction				
β-CD–solid complex[c,d]	6.0			72.5	20.8
β-CD + ketone[c] (mechanical mixture)	no reaction				
β-CD solution (1:1)[e]	19.2	24.1	1.0	20.2	36.1
β-CD solution (5:1)[e]	12.1	25.4	1.0	25.3	37.0
β-CD solution (5 °C)	13.5	15.0	1.3	16.7	53.3
β-CD solution (55 °C)	22.5	24.4	1.0	23.0	30.0

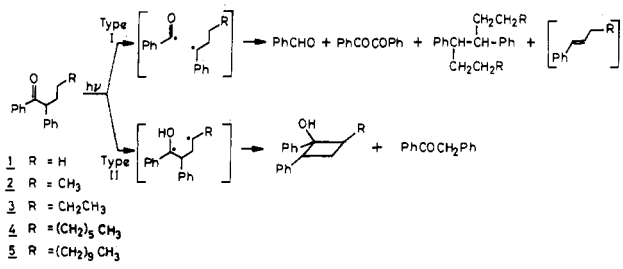
[a] Products were analyzed by GC; error limit ±5%. [b] All solution irradiations were carried out after passing nitrogen through the solution for 45 min. [c] Degassed and irradiated in sealed tubes. [d] Host/guest ratio 1.41; mp of the complex 212–214 °C. [e] Dissociation constant of β-cyclodextrin–ketone complex in water, $K_d = 5.76 \times 10^{-3}$ M; numbers in parentheses indicate the molar ratio of the host and the guest in solution.

with a great variety of organic compounds to modify one or more reactions is well-known. Specificity and selectivity are some of the important characteristics of the cyclodextrin catalysis.[3] However, a detailed analysis on the origin of the specificity and selectivity has been scant, mainly because of poor information on the structures of the inclusion complexes of cyclodextrin.

Recently, the authors reported two examples where β-cyclodextrin causes a reaction to proceed along one of the two competing pathways. A remarkable effect was observed on the photoreactivity of benzoin alkyl ethers[4] and α-alkyldibenzyl ketones[5] upon cyclodextrin complexation. Benzoin alkyl ethers are known to undergo Norrish type I reaction as the major photoprocess in organic solvents. The competing type II hydrogen abstraction process, though feasible in these substrates, is not observed at all in organic solvents. Quite interestingly, the solid β-cyclodextrin complexes of the benzoin alkyl ethers, upon irradiation, were found to yield only the type II products in quantitative yields. The photolysis of the aqueous solutions of the above complexes afforded a mixture of the type I and the type II products. On the contrary, α-alkyldibenzyl ketones, upon photolysis in isotropic solvents, give rise to products derived from both the type I and the type II processes. However, cyclodextrin complexation completely arrests the formation of the type II products and yields, most surprisingly, a rearranged product derived via the type I pathway. The substantial difference in photoreactivity of benzoin alkyl ethers and α-alkyldibenzyl ketones in cyclodextrin (compared to isotropic medium) was attributed to a combination of the "cage effect" and "conformational control" afforded by the cyclodextrin cavity. The contrasting influence of the cyclodextrin cavity on the photobehavior of benzoin alkyl ethers (encourages the type II reaction) and α-alkyldibenzyl ketones (facilitates the type I process) was traced to the differences in the geometries of the guests in the cavity of cyclodextrin. Thus, the studies on the above two series have provided significant information on the tendency of the guest to adopt a preferred orientation in a sterically restricted situation.

The work on alkyldeoxybenzoins reported below represents our continued interest in understanding the features controlling the photobehavior of organic molecules included in the cyclodextrin cavity.[6] The photochemistry

Scheme I



of alkyldeoxybenzoins of the type presented here has not been reported. However, their photobehavior can be easily predicted on the basis of analogous systems.[7] The α-cleavage and the γ-hydrogen abstraction are expected (Scheme I). It was our interest to investigate the effect of the cyclodextrin on the photobehavior of alkyldeoxybenzoins and to analyze the results in light of the known effects on benzoin alkyl ethers and α-alkyldibenzyl ketones. We hoped that the above study would yield information which when collectively viewed would enable us to predict beforehand the expected cavity effects on analogous systems and on similar reactions. Such information is crucial for utilizing cyclodextrin to control and modify the photochemical behavior of a large number of organic compounds.

Results

α-Alkyldeoxybenzoins 1–5 investigated here undergo Norrish type I and type II reactions upon irradiation either in benzene or in methanol. Cyclobutanols and deoxybenzoin were obtained as the products of cyclization and elimination processes, respectively, of the primary 1,4-diradical resulting via the γ-hydrogen abstraction process. The relative yield of the type II products is much higher in the case of 2–5 when compared to that in 1. This is consistent with the expected higher rate of secondary hydrogen abstraction in 2–5. Products resulting via the α-cleavage included benzaldehyde, benzil, and diphenylalkanes. Solution results are unexceptional and are

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Table II. Product Distribution during Photolysis of α-Propyldeoxybenzoin[a,b]

medium	benzaldehyde	4,5-diphenyloctane	benzil	deoxybenzoin	cyclobutanol(s)
benzene	11.2	16.6	6.3	37.4	27.9
methanol	7.5	11.6	5.3	39.7	35.7
water	22.6	14.7	6.1	25.3	31.1
β-CD–solid complex[c,d]	6.5			72.0	21.5
β-CD solution (1:1)[e]	19.8	2.9	5.6	17.3	53.6
β-CD solution (5:1)[e]	18.2	2.7	2.1	25.0	48.9
β-CD solution (5 °C)	14.7	1.0	4.3	6.5	73.2
β-CD solution (55 °C)	22.1	1.7	2.9	33.2	40.0

[a] Products were analyzed by GC; error limit ±5%. [b] All solution irradiations were carried out after purging with nitrogen for 45 min. [c] Degassed and irradiated in sealed tubes. [d] Host/guest ratio 1.48; mp of the complex 225–226 °C. [e] Dissociation constant of β-cyclodextrin–ketone complex in water, $K_d = 4.3 \times 10^{-3}$ M; numbers in parentheses indicate the molar ratio of the host and the guest in solution.

Table III. Product Distribution during Photolysis of α-Butyldeoxybenzoin[a,b]

medium	benzaldehyde	5,6-diphenyldecane	benzil	deoxybenzoin	cyclobutanol(s)
benzene	13.5	21.8	7.6	32.7	24.0
methanol	12.1	13.4	9.5	38.0	26.7
neat crystals[c] (mp 73–74 °C)	no reaction				
β-CD complex,[c,d]	5.7			80.1	13.2
β-CD + ketone[c] (mechanical mixture)	no reaction				
β-CD solution (1:1)[e]	18.4	6.1	1.0	33.5	46.7
β-CD solution (5:1)[e]	23.9	3.1	1.0	34.8	38.0
β-CD solution (5 °C)	20.7	1.7	1.0	14.1	63.9
β-CD solution (55 °C)	19.0	1.0	1.0	24.0	56.8

[a] Products were analyzed by GC; error limit ±5%. [b] All solution irradiations were carried out after purging with nitrogen for 45 min. [c] Degassed and irradiated in sealed tubes. [d] Host/guest ratio 1.49, mp 198–200 °C. [e] Dissociation constant of β-cyclodextrin–ketone complex in water, $K_d = 9.8 \times 10^{-4}$ M; numbers in parentheses indicate the molar ratio of the host and the guest in solution.

Table IV. Product Distribution upon Photolysis of α-Octyldeoxybenzoin and α-Dodecyldeoxybenzoin[a,b]

medium	benzaldehyde	diphenylalkane	benzil	deoxybenzoin	cyclobutanol
	(i) α-Octyldeoxybenzoin (4)				
benzene	33.0	14.4	2.2	42.0	8.3
methanol	25.2	18.0	2.5	48.6	5.7
β-cyclodextrin solution (1:1)	11.6	11.1	4.6	48.8	23.7
β-cyclodextrin solution (5:1)	10.8	9.8	4.3	47.3	27.6
β-cyclodextrin–solid complex[c]	3.0	2.5	2.0	69.9	18.5
	(ii) α-Dodecyldeoxybenzoin (5)				
benzene	39.3	13.4	3.5	30.1	13.6
methanol	27.5	17.5	3.7	40.8	10.7
β-cyclodextrin solution (1:1)	22.1	10.0	2.5	46.2	19.0
β-cyclodextrin solution (5:1)	22.8	13.0	5.4	32.6	26.0
β-cyclodextrin–solid complex[c]	4.0	1.5	1.5	74.4	19.0

[a] Products analyzed by GC; error limit ±5%. [b] All solution irradiations were carried out under a nitrogen atmosphere. [c] Degassed and irradiated in sealed tubes.

analogous to the literature reports on related systems.[7] Based on the established photobehavior of α-methyldeoxybenzoin and related molecules,[8] we assume that **1–5** also react exclusively from the lowest $n\pi^*$ triplet state. The rate of the α-cleavage is expected to be in the range of 2–3 $\times 10^7$ s^{-1} and that of the γ-hydrogen abstraction in the range of 1–10 $\times 10^7$ s^{-1} (**1**, 1 $\times 10^7$ s^{-1}; **2–5**, 1 $\times 10^8$ s^{-1}). Photolyses of aqueous solutions of the β-cyclodextrin complexes as well as those of the solid complexes of **1–5** were conducted. Results of the above photolyses are summarized in Tables I–IV.

Before pursuing the photolysis of the cyclodextrin complexes of **1–5**, it was essential to establish the presence of inclusion complexes both in the aqueous solution and in the solid state. The existence of an inclusion complex in the aqueous solution was conceived on the basis of ^1H NMR studies and on the basis of the measurement of dissociation constants using UV–vis absorption measurements. Evidence for the formation of complexes in the solid state came from the X-ray powder photographs and the estimation of host–guest ratios.

Addition of α-alkyldeoxybenzoins **1–5** to saturated aqueous solutions of β-cyclodextrin precipitated a white solid which was soluble in an excess of water. The X-ray powder photographs of the precipitated white solid differed considerably from that of the guests **1–5** and the host β-cyclodextrin, recorded individually. This supported the inclusion of the guest α-alkyldeoxybenzoins into the cavity of cyclodextrin. Furthermore, the molar ratio of the guest to the host was calculated by estimating the amount of the ketone extracted from a known amount of the solid complex. The molar ratios of ketone to β-cyclodextrin for all the solid complexes were ~1:1 (Tables I–IV), suggesting that one molecule of cyclodextrin includes only one molecule of the guest in the solid state.

The 270-MHz ^1H NMR spectra of the aqueous solutions of β-cyclodextrin and solutions containing various ratios of the host to the guest (**1–3**) were recorded. The chemical shifts of β-cyclodextrin protons in the presence and in the absence of the guests were utilized for drawing conclusions regarding the complexation.[9] In all three ketones investigated, inclusion of the guest in the cavity of the β-cy-

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clodextrin is evident from the upfield shifts of the inner protons (H_3, H_5, and H_6) and from the absence of a change in the chemical shifts of the outer protons (H_1, H_2, and H_4) of cyclodextrin.[10] Similar observation has earlier been made upon inclusion of aryl alkyl ketones,[6a] benzoin alkyl ethers,[4] and α-alkyldibenzyl ketones.[5] The results of ^1H NMR studies unequivocally support the inclusion of the guest α-alkyldeoxybenzoins in the cavity of the cyclodextrin in the aqueous solution. However, a firm conclusion regarding the structure of the inclusion complex could not be forwarded on the basis of ^1H NMR results.

Further support for the inclusion phenomena in the aqueous solution was obtained through electronic absorption studies of **1–3**. Aqueous solutions of **1–3** experienced an increase in spectral intensity but no discernible change of the spectral shape upon addition of β-cyclodextrin. The dissociation constants of the β-cyclodextrin complexes of **1–3** were determined in water by using the approach of Benesi and Hilderbrand.[11] The poor solubility of **4** and **5** in water did not allow us to estimate the K_d of their complexes. It is of interest to note that the stability of the complexes is fairly high in aqueous solution and it increases with the length of the alkyl chain (Tables I–III). Such a behavior has been reported earlier in other systems.[6a,12]

Photolysis in cyclodextrin media revealed a significant difference in behavior. For the ketones investigated here, the effect of the cyclodextrin cavity was more pronounced in the solid complexes than in aqueous solutions. No products other than those derived from the type I and the type II reactions were isolated. Importantly, no products derived from the abstraction of cyclodextrin protons by ketones were obtained. Perusal of Tables I–IV reveals that the relative yield of the type I products is decreased in the presence of the β-cyclodextrin in the aqueous solution. Further, the formation of benzil is greatly suppressed with respect to isotropic solvent medium. Ratios of products derived from the type II 1,4-diradical via cyclization and elimination are significantly altered by the cyclodextrin cavity in comparison to organic solvents. Cyclodextrin complexation reduces the yield of the elimination product (alternatively enhances the cyclization product). The following results suggest that the above changes are indeed due to cyclodextrin complexation: (a) Photolysis of **2** in water (sparingly soluble) gave a product distribution similar to that in benzene and methanol. However, addition of cyclodextrin altered the product ratios (Table II). (b) Addition of more than 1 equiv of cyclodextrin did not produce any significant variation in the product distribution. This indicated that the complex formed is essentially an 1:1 adduct (similar to solid complexes) and the observed product distribution is mainly due to the complexed material. (c) Most importantly, the elimination to cyclization ratio (derived via the type II process) was temperature-dependent in **1–3** in the presence of excess cyclodextrin; lower temperature favors cyclization. However, no such

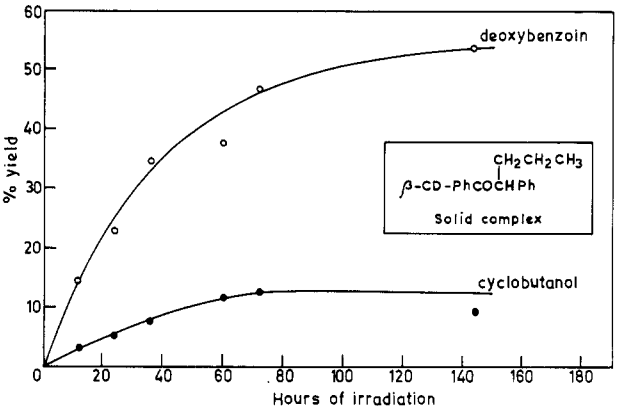

Figure 1.

significant variation was found with respect to temperature in organic solvents. This clearly establishes that it is the cyclodextrin cavity that influences the temperature-dependent rotational process that is involved in the elimination and the cyclization of the type II 1,4-diradical.

The most significant alteration in the photobehavior of **1–5** was found in the photolysis of the cyclodextrin complexes in the solid state. Irradiation of the solid complexes yielded mainly the type II products; among the type I products only benzaldehyde was obtained in yields less than 10%. This is remarkable, considering that in an aqueous solution the type I products were obtained in significant yields. Among the type II products that are obtained in more than 90% yield, the elimination product deoxybenzoin was the major (Tables I–IV). The importance of the cyclodextrin cavity in bringing about this remarkable change in the photobehavior of **1–5** is revealed by the following observations: (a) When microcrystalline compounds of **1** and **3** were irradiated, no change was observed even after a week. (b) Irradiation of a mechanical mixture of **1–3** and β-cyclodextrin did not produce any photoreaction.

The above reactions of cyclodextrin complexes, both in the aqueous solution and in the solid state, can be taken to very high conversions. A plot of the product distribution vs. duration of irradiation in the case of a solid complex shown in Figure 1 illustrates that the ratio of elimination to cyclization products is independent of the conversion and that the reaction proceeds smoothly to a minimum of 60% conversion. Above this conversion, the competitive absorption by the product deoxybenzoin slows down the reaction. While the photoconversion is efficient in the aqueous solution (30 min for 20% conversion), that in the solid state is quite low (4 h for 10% conversion). This is most likely due to poor absorption by the microcrystalline solid complexes.

Discussion

The observed photochemical behavior of alkyldeoxybenzoins in isotropic solvents followed a predictable pattern and therefore a detailed mechanistic study was not of immediate interest. Examination of Tables I–IV allows us to make the following significant conclusions: (a) Ketones **1–5**, upon photolysis in isotropic solvent, yield products derived via the type I and the type II processes. (b) Most remarkably, the photolysis of the solid cyclodextrin complexes results in the type II products in near quantitative yields; the type I products were obtained only as minor products. (c) The photolysis of the cyclodextrin complexes in the aqueous solution gave products derived from both the type I and the type II reactions; however, the relative yield of the type II products was higher than

(10) ^1H NMR chemical shifts (Hz) of β-cyclodextrin protons and its complexes with **1–3** are provided

	H-1	H-2	H-3	H-4	H-5	H-6
β-cyclodextrin	1363.0	976.2	1066.5	962.7	1034.9	1042.7
β-cyclodextrin–1	1359.9	968.9	1049.0	958.0	1012.2	1041.2
β-cyclodextrin–2	1359.8	969.8	1055.6	958.1	1013.6	1041.5
β-cyclodextrin–3	1359.5	970.3	1060.2	960.3	1025.8	1040.6

here.

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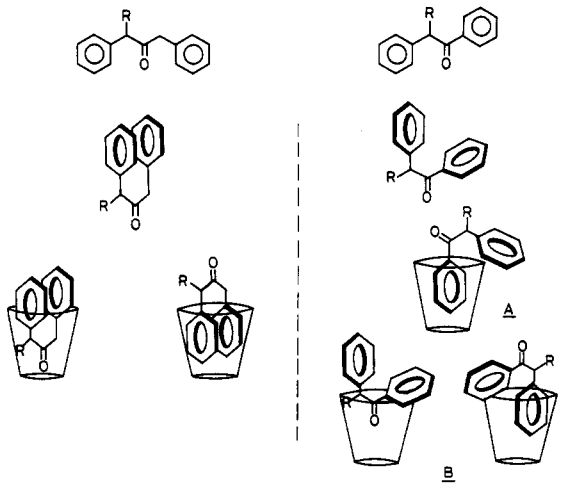
Scheme II



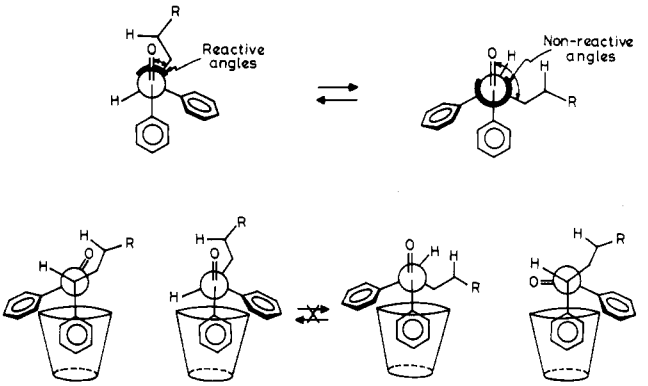
in isotropic solvents and smaller than in the solid complexes. (d) In addition to the influence of the host on the type I and the type II partitioning of the excited ketone, it also has a significant effect on the reactions of the type II 1,4-diradical. In aqueous solution, cyclodextrin favors cyclization while in the solid state it facilitates elimination.

To delineate the role of the cyclodextrin cavity in altering the photobehavior of the included guests, it is essential to know the exact structure of the complex. Of the various available structural tools, the X-ray crystallographic analysis provides a complete picture. However, we have thus far not been successful[13] in fully solving the X-ray crystallographic structure of any inclusion complexes of cyclodextrin. This is due to either the inability to obtain suitable single crystals or due to the disorder present in the unit cell that complicates structure solution. Therefore, even in the present case one has to be satisfied with an intutive structure arrived at on the basis of ^{1}H NMR and the chemical behavior of the included guests.

In general one could visualize several types of structures for the cyclodextrin complexes of **1–5**. Of these, one class involves inclusion of only one phenyl ring into the cavity (A, Scheme II) and the other inclusion of both the phenyl rings (B, Scheme II). In addition, the inclusion could occur either from the narrower or the wider opening of the cavity. While the entrance of **1–5** from either the narrower or the wider opening of the cyclodextrin cavity is not expected to have any significant consequence on the photochemical behavior, the product formation is expected to very much depend on the number of phenyl rings inside the cavity of the cyclodextrin.

Alkyldeoxybenzoins resemble benzoin alkyl ethers in their excited-state behavior. More importantly, the photobehavior of alkyldeoxybenzoins differs remarkably form that of α-alkyldibenzyl ketones. On this basis, we propose that the structure of the inclusion complexes between the cyclodextrin and the ketone **1–5** resembles that of benzoin alkyl ethers.[4] ^{1}H NMR spectral results are not inconsistent with this proposal.[10] It is important to note that due to structural restrictions the two phenyl rings of 1,2-diphenyl systems (e.g., alkyldeoxybenzoins and benzoin alkyl ethers) cannot achieve a parallel geometry such that both the phenyl rings can enter the cavity of cyclodextrin (Scheme II). On the other hand, 1,3-diphenyl systems (e.g., alkyldibenzyl ketones) can achieve the above parallel arrangement and thus an easy entry into the cavity of the cyclodextrin is possible. While the location (inside or outside of the cavity) of the two phenyl rings determines the extent of the type I reaction, the position of the alkyl side chain is expected to be important for the occurrence of the type II process. The formation of cyclobutanols and deoxybenzoin from **1–5** even upon inclusion in the cyclodextrin cavity, suggests that the alkyldeoxybenzoins are included by the cyclodextrin in a conformation suitable for γ-hydrogen abstraction.

Scheme III



In the following paragraphs, we will attempt to rationalize how the hydrophobic cavity of the cyclodextrin controls the chemical behavior of the excited alkyldeoxybenzoins and of the intermediates resulting from them. The influence of the cyclodextrin on the γ-hydrogen abstraction and on the elimination to cyclization ratio from the type II 1,4-diradical is presented first and this is followed by the effect on the type I α-cleavage process.

Through extensive studies on the structure–reactivity relationships in the crystalline state,[14] it has become evident that the γ-hydrogen abstraction follows a stringent geometrical criteria. As illustrated in Scheme III, two conformations for alkyldeoxybenzoins are possible in which the γ-hydrogens are present either within the allowed reactive or in the nonreactive regions. In isotropic solvents and in the absence of any encumberences, a free rotation would equilibrate the two conformers and thus facilitate the γ-hydrogen abstraction. On the other hand, cyclodextrin encapsulation would forbid an interconversion between the two conformers by restricting rotation about the central σ bond. Although an interconversion between the two forms can occur through "in–out" exchange in the aqueous solution, such an interconversion would not be expected in the solid state. Since the photolysis of the solid cyclodextrin complexes of **1–5** yields exclusively the γ-hydrogen abstraction products, we propose that the cyclodextrin prefers to include the alkyldeoxybenzoins in a conformation suitable for the type II process. Thus the photochemistry of the alkyldeoxybenzoins is an example of the use of cyclodextrin in controlling the conformation of the guest molecule and thus altering the nature of the excited-state chemistry.

The ratio of the cyclobutanols to deoxybenzoin, the products of cyclization and elimination from the type II 1,4-diradical, is also altered by the cyclodextrin. In the

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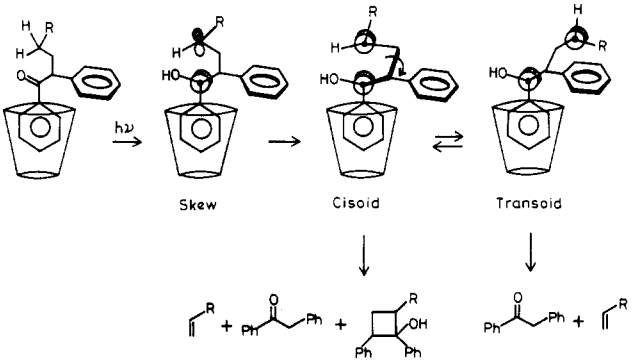
Scheme IV

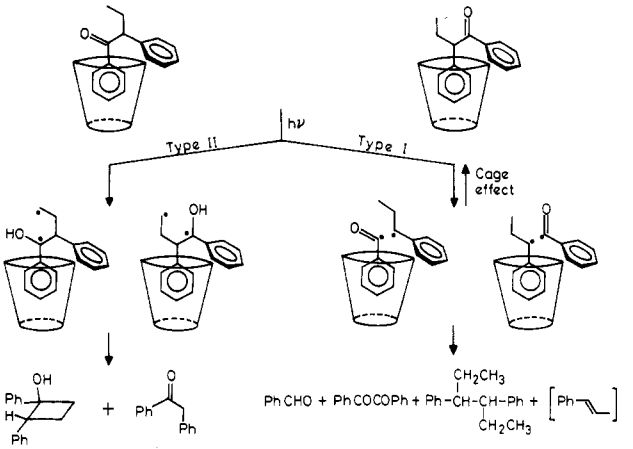


aqueous solution the cyclization is favored, whereas in the solid state, the elimination is encouraged. Consideration of the following features of the type II process are helpful in understanding the role of the cyclodextrin in altering the decay of the above 1,4-diradical: (a) The elimination to cyclization ratio is dependent on the equilibrium between and the rates of decay of the cisoid and the transoid 1,4-diradicals (Scheme IV). It is important to note that the transoid form can undergo only fragmentation, whereas the cisoid form can also cyclize to give the cyclobutanol. (b) The elimination to cyclization ratio is further controlled by orbital overlap requirements. It is widely accepted that the efficient cleavage requires a 1,4-diradical conformation in which both the singly occupied p orbitals can overlap significantly with the central σ bond being broken; failing this, cyclization occurs from a conformation involving small nonbonded interactions and only partial orbital overlap. (c) In a medium such as the solid state where rotational motions are restricted, decay via cleavage and elimination would occur directly from the skewed form. Under this condition the "less motion" pathway would be favored. From the skewed geometry, cleavage requires less motion than the cyclization.

The enhancement of cyclization in the cavity of the cyclodextrin in the aqueous solution, we propose, reflects the rotational restriction brought on the transoid–cisoid diradical interconversion. Excitation of the alkyldeoxybenzoins trapped in the cyclodextrin cavity would result in a 1,4-diradical in which the two singly occupied p orbitals are perpendicular to each other (Scheme IV). Since one of the phenyl groups is locked inside the host cavity, the rotations required for further reaction has to occur on the alkyl side. The rotation about the central σ bond would result in the cisoid–transoid interconversion. We believe that such a rotation is inhibited by the cavity in the aqueous solution. Therefore, the secondary reaction essentially occurs form the cisoid conformation. However, in the absence of the cavity, the transoid form would be preferred and the observed product distribution in isotropic solvents would be dominated by the behavior of the transoid conformation. Therefore, the observed difference in product distribution between isotropic solvents and the aqueous cyclodextrin complex is essentially a reflection of the difference in the conformation of the precursor 1,4-diradical responsible for the products.

Such a restriction to the rotational interconversion between the transoid and the cisoid diradicals might indeed contribute to the temperature-dependent elimination to cyclization ratio in the aqueous solution. As illustrated in Tables I–III, cyclization is favored at low temperatures (5 °C) and elimination at higher temperatures (55 °C). It is tempting to attribute the variation in the product distribution to the temperature-dependent cisoid–transoid interconversion, though various other steps might also be

Scheme V



temperature-dependent. Since we did not observe any temperature dependence on the product distribution from **1–3**, in benzene and methanol the temperature dependence may not result from the reaction of ketone or diradical outside of β-cyclodextrin.

The photobehavior of the cyclodextrin complexes of **1–5** in the solid state is similar to that of a few aryl alkyl ketones in the crystalline phase;[14] i.e., elimination product is preferred. We attribute this to the stringent restriction imposed by the solid matrix on the rotational motions of the various single bonds in the 1,4-diradical. Elimination being the "less motion" pathway, the product resulting from that dominates the product mixture. The difference in product distribution resulting from the cyclodextrin complex in the solid state and in the aqueous solution phase is attributed to the difference in the nature of the restriction brought on the included reactive intermediate. In the aqueous phase, the included molecule has a certain amount of flexibility which does not exist in the solid phase due to the tight packing of the surrounding molecules of the complex. Hence, studies in the aqueous phase reveal the effect of the cavity alone, while those in the solid complexes show the effect of the cavity, as well as that of the rigid surroundings, on the guest molecule.

Perusal of Tables I–IV reveals that the type I product formation is suppressed to various degrees in the solid cyclodextrin complex and in the aqueous solution. On the basis of the recently observed effect on the cyclodextrin on the photobehavior of dibenzyl ketones and benzoin alkyl ethers, inhibition of the α-cleavage product formation in the solid state is expected indeed. As illustrated in Scheme V, the type I reaction does occur to yield the benzoyl–phenylalkyl radical pair but the radical pair generated undergoes geminate recombination. Thus the "super-cage effect" that operates in the solid complex channels all the reactant guest molecules into the type II products. However, in the aqueous solution the "super-cage effect" may not be expected to operate, if indeed the structure of the complex is as illustrated in Scheme V. In the proposed structure, a part of the molecule would be free to diffuse into the aqueous medium after the α-cleavage. Therefore, both the type I and the type II products are expected in the aqueous solution and only the type II products in the solid state. This is consistent with the observed behavior.[15]

(15) While there may be no report of conformation dependence of type I cleavage, surely benzyl radical delocation is necessary in the transition state. Thus restricted rotation about the C–Ph bond could inhibit α-cleavage. Therefore, stereoelectronic effect in addition to cage effect might also contribute to the low yield of the type I products in the solid state.

In conclusion, it can be stated that the study of the photobehavior of alkyldeoxybenzoins (complexed to cyclodextrin) has yielded information regarding the restriction on the rotational and translational motions of the guest molecules or intermediates derived therefrom. More encouragingly, their behavior closely resembles that of benzoin alkyl ethers, a closely analogous system, and differs significantly from alkyldibenzyl ketones, a system that is structurally different from alkyldeoxybenzoins. This suggests that one can predict the behavior of the guest molecules included in the cyclodextrin cavity on the basis of the well-established behavior of closely related systems. This indeed is a step forward in understanding, predicting, and controlling the reactivity of organic molecules included in a restricted environment.

Experimental Section

Materials. β-Cyclodextrin (Aldrich) was used as received. Doubly distilled water was used for all the experiments; all other solvents were distilled prior to use.

General Procedure for the Preparation of Ketones 1–5. To a 50-mL double-necked round-bottom flask fitted with a dropping funnel and reflux condenser were added sodium hydride (0.026 mol), the corresponding alkyl iodide (0.026 mol), and 20 mL of sodium-dried benzene. The contents were cooled to 5 °C in an ice bath and the deoxybenzoin (0.025 mol) dissolved in 15 mL of dry benzene was added dropwise over a period of 30 min. After the addition, the mixture was stirred for 12 h at room temperature and for two additional hours at reflux temperature. The reaction mixture was cooled and neutralized with dilute HCl, followed by extraction with diethyl ether. The crude product obtained after evaporation of the solvent was purified by column chromatography (silica gel/hexane–benzene 80:20). In general, the yields of the ketones varied between 70% and 90%.

1: mp 57–58 °C; UV (cyclohexane) λ_{max} (nm) 335 (ε 180), 240 (14 000); IR (Nujol) 1680, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (3 H, t), 2.0 (2 H, m), 4.3 (1 H, t), 7.05 (8 H, m), 7.70–7.90 (2 H, m).

2: UV (cyclohexane) λ_{max} 334 (ε 175), 325 (170), 241 (13 500); IR (neat) 1680, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (3 H, t), 1.0–1.60 (2 H, m), 1.60–2.30 (2 H, m), 4.45 (1 H, t), 7.0–7.45 (8 H, m), 7.70–7.95 (2 H, m).

3: mp 73–74 °C; UV (cyclohexane) λ_{max} 334 (ε 180), 336 (174), 241 (13 600); IR (Nujol) 1680, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (3 H, t), 1.0–2.2 (6 H, m), 4.35 (1 H, t), 7.05–7.40 (8 H, m), 7.70–7.90 (2 H, m).

4: mp 56–58 °C; UV (cyclohexane) λ_{max} 334 (ε 181), 326 (178), 241 (13 300); IR (Nujol) 1680, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (3 H, t), 1.2 (12 H, br s), 1.9 (2 H, m), 4.40 (1 H, t), 7.10–7.25 (8 H, m), 7.80–8.0 (2 H, m).

5: mp 74–75 °C; UV (cyclohexane) λ_{max} 335 (165), 326 (175), 241 (14 000); IR (Nujol) 1680, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (3 H, t), 1.20 (20 H, br s), 1.95 (2 H, m), 4.40 (1 H, t), 7.15–7.30 (8 H, m), 7.80–8.0 (2 H, m).

Preparation and Identification of Cyclodextrin Complexes. To a saturated solution of β-cyclodextrin in distilled water were added equimolar amounts of alkyldeoxybenzoins, and the solution was stirred for 24 h. The white precipitate that formed was filtered, washed with diethyl ether, and dried at 50 °C for 10 h. The solid complexes were identified by their X-ray diffractograms recorded with a Phillips X-ray powder diffractometer employing monochromated Cu Kα radiation. Powder patterns of the complexes are different from those of the guest ketones as well as of β-cyclodextrin. On this basis, it was concluded that inclusion complexes were formed between β-cyclodextrin and the corresponding ketone. The complex formation in aqueous solution was identified by ^1H NMR spectra in D_2O. Solutions of the 1:1 complexes were prepared by dissolving 2–3 mg of the β-cyclodextrin complex in 1 mL of D_2O and the spectra were recorded by using a Bruker WH 270 NMR spectrometer equipped with an ASPECT 2000 computing system. The spectral data are summarized in ref 10.

Photolysis and Identification of Products. The aqueous solution of the complex was prepared by the addition of a minimum amount of distilled water to the microcrystalline complex (100 mg of the complex dissolved in ~150 mL of distilled water), and the solution was warmed to 40 °C to obtain a transparent solution. The final concentration of the corresponding ketones is $\sim 10^{-4}$ M. These solutions were irradiated (>280 nm) for 45 min by using a Rayonet reactor fitted with RPR-3000 lamps in Pyrex tubes after purging with nitrogen for 45 min. After the irradiation, the products were extracted from the aqueous solution by using chloroform and were analyzed by gas chromatography (10% FFAP on charcoal or 5% SE-30 on Chromosorb P; 5 ft × $^1/_8$ in.). The peaks were identified by coinjection of authentic samples. Preparative-scale irradiations were carried out to identify the photoproducts. The spectral data of the cyclobutanols from compounds 1–4 are summarized below.

Cyclobutanols obtained from **1–4** were a mixture of stereoisomers and their spectral data are summarized below.

1,2-Diphenylcyclobutan-1-ol: IR (neat) 3600–3300, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (2 H, m), 2.50 (2 H, m), 3.95 (1 H, t), 7.15–7.50 (10 H, m).

1,2-Diphenyl-4-methylcyclobutan-1-ol: IR (neat) 3550–3250, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ (a) 1.13 (3 H, d), 2.10–2.50 (2 H, m), 3.95 (1 H, t), 7.2–7.6 (10 H, m); (b) 0.85 (3 H, d), 2.50–2.85 (2 H, m), 4.38 (1 H, t), 7.20–7.55 (10 H, m).

1,2-Diphenyl-4-ethylcyclobutan-1-ol: IR (neat) 3550–3250, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (3 H, t), 1.18 (2 H, m), 2.15 (2 H, m), 2.40 (1 H, m), 4.05 (1 H, t), 7.20–7.55 (10 H, m).

1,2-Diphenyl-4-butylcyclobutan-1-ol: IR (neat) 3550–3250, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (3 H, t), 1.22 (8 H, br s), 1.56 (2 H, m), 2.17 (1 H, m), 2.40 (1 H, m), 2.55 (1 H, m), 2.55 (1 H, m), 3.86 (1 H, t), 7.1–7.55 (10 H, m).

The cyclobutanol from **5** was identified by using GC based on its longer retention time. Photolysis of solid complexes was carried out by using a Hanovia 450-W medium pressure mercury arc lamp. Microcrystalline cyclodextrin complexes in Pyrex tubes were degassed under reduced pressure (10^{-4} mm), sealed, and irradiated (>280 nm) for 48 h. To obtain a uniform exposure to light the source, the sample tubes were rotated periodically. The photoproducts were extracted by using chloroform–water mixture and analyzed as described above.

Crystalline alkyldeoxybenzoins **1** and **3** were also irradiated under analogous conditions. The ketone **2** is a liquid; hence no reaction was carried out for a comparative run.

Irradiations of ketones **1–5** were also carried out in benzene and methanol. The procedure for the photolysis and analysis are similar to those of aqueous cyclodextrin complexes.

Measurement of Dissociation Constants (K_d). A stock solution (1.06×10^{-2} M) of β-cyclodextrin was prepared by dissolving 600 mg of β-cyclodextrin in 50 mL of distilled water. Ten-milliliter solutions containing varying amounts of β-cyclodextrin stock solution and a constant amount of the corresponding alkyldeoxybenzoin in methanol (1.5×10^{-3} M) were prepared in 10-mL standard flasks. The amount of methanol (0.1 mL) was constant in all the flasks. The final concentration of the ketone in the 10-mL solutions were in the order of $\sim 10^5$ M ([β-CD] ≫ [ketone]). Absorption spectra of these solutions were recorded on a Shimadzu UV-180 spectrometer and optical densities were monitered at 250 nm. A plot of $a_0b_0/\Delta OD$ vs. $(a_0 + b_0)$ was linear with the slope and intercept being equal to $1/\Delta\epsilon$ and $K_d/\Delta\epsilon$, respectively (a_0 and b_0 are the concentrations of β-cyclodextrin and ketone, respectively). The values of K_d were obtained from these linear plots on the basis of the Benesi–Hilderbrand method.[10] The dissociation constants obtained for the cyclodextrin complexes of **1–3** are as follows: **1**, 3.0×10^{-3} M; **2**, 4.3×10^{-3} M; and **3**, 9.6×10^{-4} M. The dissociation constants for the complexes of **4** and **5** were not obtained due to the poor solubility of the ketones in aqueous medium.

Host/Guest Ratio. A known amount of white microcrystalline solid complex that was dried to constant weight, after being washed with cold water and ether, was redissolved in distilled water. The guest ketone(s) was extracted thoroughly with chloroform and the amount of ketone present in the complex was estimated by gas chromatography. Acenaphthalene was used as an internal standard. The molar ratios calculated for the compounds **1–5** are provided in Tables I–IV.

Acknowledgment. G.D.R. thanks the Council of Scientific and Industrial Research (CSIR), Government of India, for the award of a Senior Research Fellowship.

Registry No. 1, 16282-16-9; 2, 21383-02-8; 3, 2371-23-5; 4, 38821-25-9; 5, 110797-71-2; β-cyclodextrin, 7585-39-9; deoxybenzoin, 451-40-1; 1,2-diphenylcyclobutan-1-ol, 63776-27-2; 1,2-diphenyl-4-methylcyclobutan-1-ol, 110797-72-3; 1,2-diphenyl-4-ethylcyclobutan-1-ol, 110797-73-4; 1,2-diphenyl-4-butylcyclobutan-1-ol, 110797-74-5.

Cycloaddition and Copolymerization of Methyl Tricyanoethylenecarboxylate with Electron-Rich Olefins

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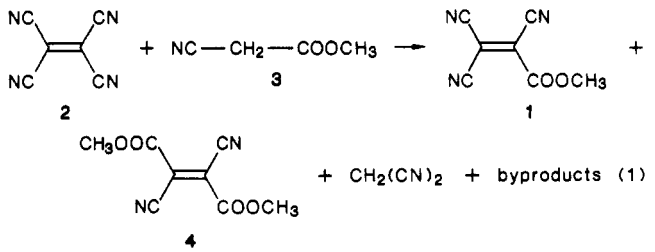
Methyl tricyanoethylenecarboxylate (1), an extremely electron-poor olefin, was synthesized by the exchange reaction of tetracyanoethylene and methyl cyanoacetate. The best yields for this reaction were obtained in the presence of pyridine. The cycloaddition reaction of 1 with electron-rich olefins such as *p*-methoxystyrene, *trans*-anethole, isobutyl vinyl ether, and ethyl *cis*-propenyl ether yielded cyclobutane and 3,4-dihydropyran adducts. The proposed mechanism involves a stepwise [2 + 2] reaction via a tetramethylene intermediate in competition with a [2 + 4] cycloaddition. The nature of the cycloadduct is determined by the orientation of the electrophilic olefin. Copolymerization of 1 with *p*-methoxystyrene under free-radical initiation gave an alternating copolymer.

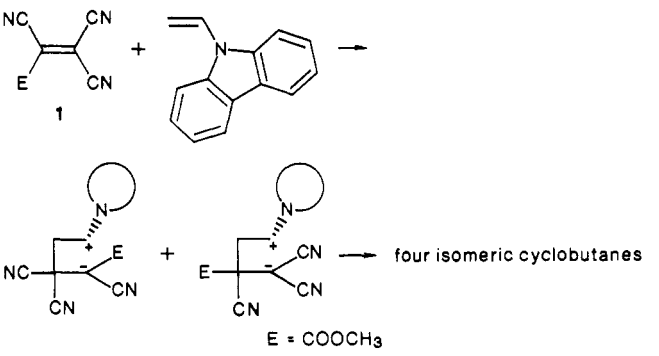
Methyl tricyanoethylenecarboxylate (1), an extremely electron-poor olefin, has been previously synthesized in this laboratory in 40% yield by the exchange reaction of TCNE (2) and methyl cyanoacetate (3) in acetic acid at 100 °C.[1]



Dimethyl dicyanofumarate (4) is formed if 1 undergoes a second exchange reaction with methyl cyanoacetate. The yields of this reaction vary a great deal from run to run and are rather low. In this study, the reaction will be studied in varying conditions in order to optimize the yield and reproducibility.

Methyl tricyanoethylenecarboxylate (1) has previously been compared to other tetrasubstituted electrophilic olefins in its reaction with *N*-vinylcarbazole.[1] In these reactions, the cyclobutane adducts are formed via a zwitterionic tetramethylene intermediate. Methyl tricyanoethylenecarboxylate was less electrophilic than TCNE, as could be deduced from cyclic voltammetry, from the λ_{max} value in the UV spectrum of the electron donor–acceptor (EDA) complex and from the rate of the cycloaddition reaction. Interestingly, the tetramethylene formation for this olefin with *N*-vinylcarbazole was not regiospecific, as witnessed by the formation of four isomeric cyclobutanes. This means that bond formation occurs at both the dicyano and the cyano carbomethoxy termini of the olefin, indicating that the electronic stabilization of the carbanion center by (CN, $COOCH_3$) is comparable to that by (CN, CN). The latter is preferred by a 60/40 ratio.

(1) Gotoh, T.; Padias, A. B.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4920.



The nonregiospecificity of 1 is unique among all the electrophilic olefins we have studied over the years. Therefore, we will systematically investigate the cycloaddition and polymerization reaction of 1 with other electron-rich olefins, such as *p*-methoxystyrene, vinyl ethers, and anethole.

Results

Synthesis of Electrophilic Olefin 1. Methyl tricyanoethylenecarboxylate (1) was synthesized by a retro–Michael exchange reaction of tetracyanoethylene (TCNE, 2) and methyl cyanoacetate (3, eq 1). The reaction has to be carefully controlled, because if the conditions are too harsh, a second exchange reaction takes place and dimethyl dicyanofumarate is formed. The reaction was studied in both basic and acidic conditions. A catalyst is required, as no exchange occurred in a blank experiment.

Figure 1 shows the yield of 1 as a function of time under various conditions. The yields are determined by NMR spectroscopy. Basic catalysts such as triethylamine and pyridine lead to the highest yields, while acidic catalysts such as acetic acid and boron trifluoride are much less effective. The isolated yield of the reaction with pyridine as catalyst is much better than that of triethylamine due to easier isolation.

Cycloaddition Reactions. The cycloaddition between 1 and *p*-methoxystyrene, *trans*-anethole, isobutyl vinyl

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