

## Photochemical Hydrogen Abstraction from Cymenes

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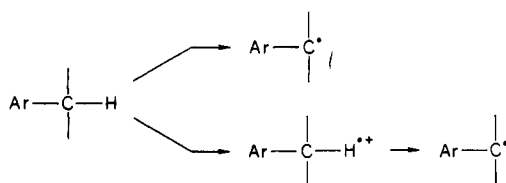
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The three isomeric cymenes are examined in photochemical reactions involving hydrogen transfer with 1,4-naphthalenedicarbonitrile (NDN),  $\alpha,\alpha,\alpha$ -trifluoroacetophenone (TFA), and benzophenone (BP). Selectivity for attack at primary vs tertiary position (P/T) and quantum yield are determined. The reactions are rationalized as involving loose perpendicular complexes yielding a low P/T ratio in the products (with BP  $n\pi$  triplet), a face-to-face charge transfer complex yielding a high P/T (with TFA  $\pi\pi^*$  triplet and also NDN singlet, but only as far as the benzylnaphthalenes 1 and 2 are concerned), and a tighter charge transfer complex yielding again a low P/T in the formation of the dibenzomethanocyclooctenes 3, the main products from NDN. The energetic limit of such a directing effect of the conformation of the intermediate complex onto photochemical reactivity is evidenced by the different results obtained with *o*-cymene.

## Introduction

The distinction between homolytic abstraction and two-step electron and proton abstraction is a subject of current interest. Alkyl aromatics have been thoroughly investigated in this respect, also in view of the practical importance of side-chain functionalization.<sup>1-6</sup>



One of the arguments considered is the intramolecular (primary vs tertiary) selectivity in *p*-cymene, following an

observation by Onopchenko et al.<sup>4</sup> that radical attack is faster at the tertiary position, while in the case of electron-transfer deprotonation from the tertiary carbon is disfavored since the predominant conformation has the isopropyl group perpendicular to the aromatic ring, and thus the incipient tertiary radical receives no stabilization. As it has been recently pointed out,<sup>5</sup> this argument is not complete since benzylic stabilization of the tertiary radical and interaction of the methyl groups with the ortho hydrogens are opposed whatever is the mechanism, but the fact remains that the primary vs tertiary selectivity is different with reagents acting via electron transfer<sup>2m,v,x,3a</sup> or by hydrogen abstraction (e.g.  $\text{ROO}^{\cdot 2w}$ ).

As far as photochemical reactions are concerned, Wagner reported several years ago that  $\alpha,\alpha,\alpha$ -trifluoroacetophenone reacts with alkylbenzenes via electron transfer<sup>6a,b</sup> and inter alia found that with *p*-cymene attack at the primary position is predominant.<sup>6c,d</sup> The same group recently reported a systematic study of the reaction of *p*-cymene with substituted acetophenones, benzophenones, and trifluoroacetophenones,<sup>5</sup> and the authors found that the results were best rationalized on the basis of the preferential conformation of the intermediate complex (perpendicular or parallel), in turn related to the type of triplet involved ( $n\pi^*$ ,  $\pi\pi^*$ ), besides to the degree of charge transfer. This rationalization is certainly appealing and well explains the trend observed in the three series of ketones studied.

The importance of understanding the role of charge transfer and complex formation in bimolecular photochemical reactions and our long-standing interest in the photochemistry of aromatics<sup>7b,8</sup> suggested the extension of the scope of that investigation in three ways, viz. by considering (i) singlet excited besides triplet acceptors; (ii) reactions in which  $\Delta G$  for electron transfer is largely negative (whereas with the above-mentioned ketones electron transfer is endergonic or at most slightly exergonic); (iii) reactions with all three isomeric cymenes in the idea that different steric requirements of the donors, in particular with *o*-cymene, would give new evidence about the role of conformational factors. Thus, we presently report a product study of the photochemical reaction between a singlet excited acceptor, 1,4-naphthalenedicarbonitrile, and two triplet acceptors, benzophenone and  $\alpha,\alpha,\alpha$ -trifluoroacetophenone, with the three isomeric cymenes, as well as quantitative steady-state measurements, and attempt to

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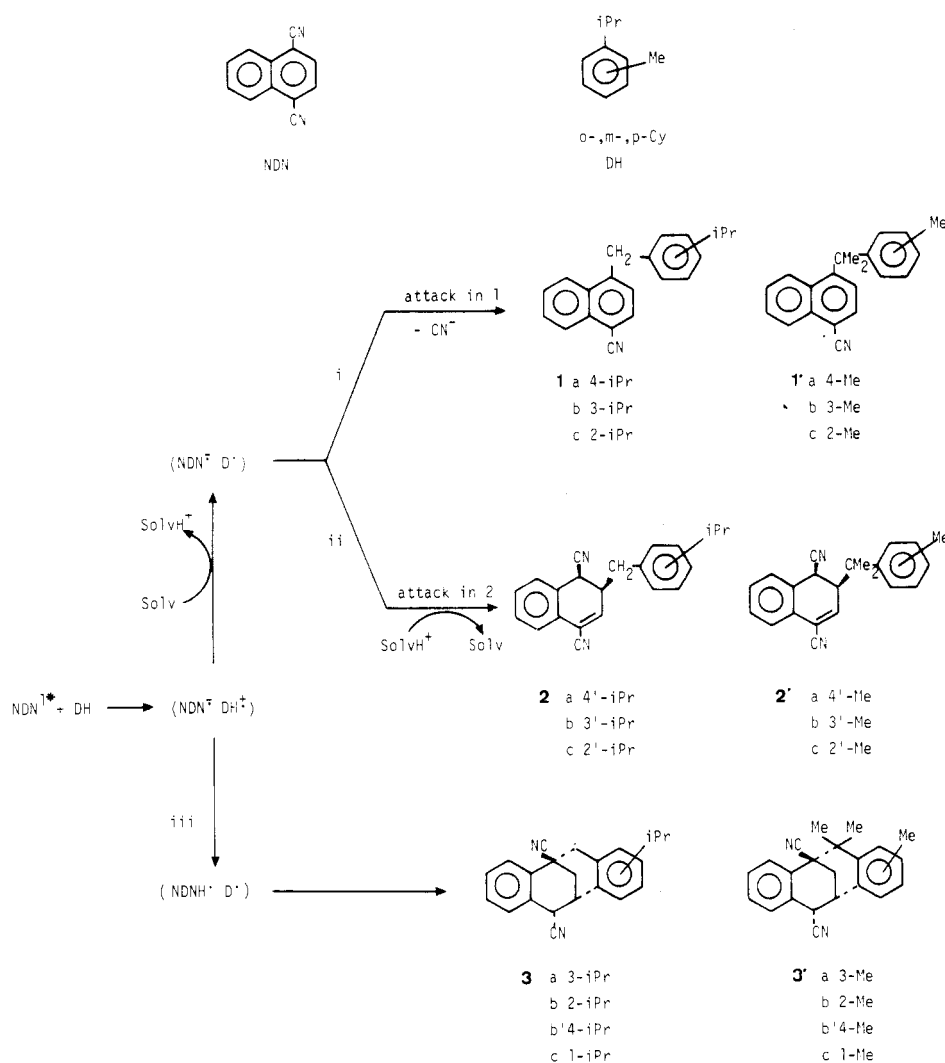
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Scheme I



obtain mechanistic information from these data.

### Results

**Reaction with NDN.** Much work of electron-poor aromatics, in most cases nitriles, with alkyl aromatics has been reported in recent years.<sup>7</sup> 1,4-Naphthalenedicarbonitrile (NDN) was chosen for the present investigation since it was hoped that its reactivity could give more information. Indeed, previous studies<sup>8</sup> on the reaction of NDN with various alkylbenzenes, including toluene and cumene, showed that three different types of products are formed through different pathways. The reaction is in every case initiated by electron transfer to singlet excited NDN, as shown by the requirement of a polar medium and the correspondence between fluorescence-quenching plots and reaction quantum yield. Then the radical cation undergoes deprotonation in either of two ways. In the first one proton transfer to the medium leads to the radical anion-neutral radical (NDN<sup>•-</sup> D<sup>•+</sup>) complex (see Scheme I) and then attack of the benzyl radical in position 1 followed by cyanide loss yields the benzylidene derivatives **1** (path i) or alternatively attack in position 2 and stereoselective reprotonation yields the 2-benzylidene derivatives **2** (path ii). In the other way, the proton is directly transferred to the radical anion and in cage recombination of the two radicals leads the dibenzomethanocyclooctene derivatives **3** (path iii).

The reaction of the three isomeric cymenes (*o*-Cy, *m*-Cy, *p*-Cy) with NDN takes place as expected. In polar solvents

**Table I. Percent Yield of Photoproducts from the Irradiation of Various Acceptors in the Presence of Cymenes in Acetonitrile**

acceptor	<i>p</i> -Cy (% yield)	<i>m</i> -Cy (% yield)	<i>o</i> -Cy (% yield)	
NDN <sup>a</sup>	<b>1a</b> (9)	<b>1b</b> (8)	<b>1c</b> (15)	
	<b>1'a</b> (3)	<b>1'b</b> (3)	<b>2c</b> (23)	
	<b>2a</b> (12)	<b>2b</b> (10)	<b>3c</b> (27)	
	<b>2'a</b> (4.5)	<b>2'b</b> (3)		
	<b>3a</b> (10)	<b>3b</b> } (14.5) <sup>b</sup>		
	<b>3'a</b> (43)	<b>3'b'</b> }		
		<b>3'b</b> (14)		
		<b>3'b'</b> (15)		
	TFA	<b>4a</b> (16)	<b>4b</b> (8)	<b>4c</b> (7)
		<b>5a</b> (7.5)	<b>5b</b> (6)	<b>7c</b> (43)
<b>6a</b> (0.1)		<b>6b</b> (1.5)	<b>11</b> (35)	
<b>7a</b> (43)		<b>7b</b> (22)		
<b>9a</b> (9)		<b>9b</b> (8)		
<b>11</b> (39)		<b>11</b> (38)		
BP		<b>4a</b> (2)	<b>4b</b> (5)	<b>4c-6c</b> (low)
	<b>5a</b> (8)	<b>5b</b> (4)	<b>8c</b> (13)	
	<b>6a</b> (16)	<b>6b</b> (11)	<b>10c</b> (4)	
	<b>8a</b> (12)	<b>8b</b> (7)	<b>12</b> (35)	
	<b>10a</b> (35)	<b>10b</b> (22)		
	<b>12</b> (33)	<b>12</b> (33)		

<sup>a</sup> A minor product obtained in most cases is 1,2-dihydro-1,4-naphthalenedicarbonitrile. <sup>b</sup> Mixture of the two, one isomer (reasonably **3b**) greatly predominating.

attack both at the primary and at the tertiary position is competitively observed (unprimed and primed numbers in Scheme I and Table I), except in the case of *o*-Cy, which yields only products arising from the attack at the methyl

Scheme II

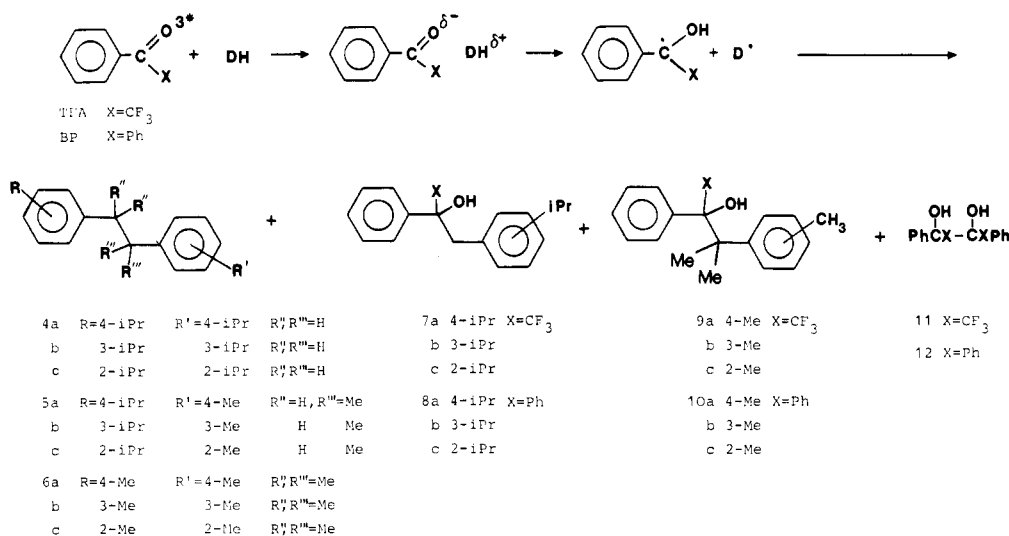


Table II. Primary vs Tertiary Reactivity of the Cymenes

acceptor	donor											
	<i>p</i> -Cy				<i>m</i> -Cy				<i>o</i> -Cy			
	<i>K<sub>sv</sub></i> , M <sup>-1</sup>	$\Phi_{rel}^a$	P/T	(product)	<i>K<sub>sv</sub></i> , M <sup>-1</sup>	$\Phi_{rel}^a$	P/T	(product)	<i>K<sub>sv</sub></i> , M <sup>-1</sup>	$\Phi_{rel}^a$	P/T	(product)
NDN	126	1	3	(1)	112	0.1	2.7	(1)	135	0.1	>10	(1)
			2.7	(2)			3.3	(2)			>10	(2)
			0.23	(3)			0.5	(3)			>10	(3)
TFA		1	4.7			1.1	2.8			0.39	>10	
BP		1	0.35			0.62	0.32			0.62	3.2	

<sup>a</sup> Relative to the value for *p*-Cy with each acceptor. The absolute value for the reaction of NDN with 0.02 M *p*-Cy is 0.29.

group. The isomeric adducts are separated by chromatography and easily identified through their spectroscopic properties (see the Experimental Section). In the case of *m*-Cy four adducts of type 3 are expected and indeed are formed (3b,b'; 3'b,b'). Though in this case preparative separation was not complete for two of the isomers, identification and quantitative determination could be achieved. The yields reported in Table I are overall yields at high ( $\geq 90\%$ ) conversion of the acceptor.

**Reaction with Ketones.** The ketones considered are trifluoroacetophenone (TFA) and benzophenone (BP). Their photochemical reaction with the cymenes (see Table I) yields benzyl and ketyl radicals, and these undergo statistical coupling to yield in each case three bibenzyls (products 4–6, Scheme II), two 1,2-diphenylethyl alcohols (7–10), and the respective pinacol (11 or 12, two stereoisomers in the former case). The products were again separated by chromatography and by VPC and identified through their spectroscopic properties (those arising from *p*-Cy were already known).<sup>5,6</sup>

**Quantitative Measurements.** Separate low-conversion experiments were carried out, and the product distribution was found to change but little from the high-conversion irradiation. Quantum yield for product formation was measured under these conditions. Stern-Volmer quenching constants for NDN fluorescence quenching, chemical quantum yields, and the primary vs tertiary ratio (P/T) observed for each type of compound obtained are reported in Table II.

## Discussion

The material balance in these reactions is very good, and the results show that the reactivity at the primary vs the tertiary position of cymenes in hydrogen abstraction reactions depends on the structure of the reagents, the P/T ratio spanning over a large interval (a factor of  $\sim 50$ ).

Since the photochemical reactions of both aromatic ketones and aromatic nitriles with alkylbenzenes, bibenzyls, and related donors have been extensively investigated and the mechanism well established,<sup>5-8</sup> nor do the reactions with the cymenes appear to differ from the general course observed with these donors, we are confident that the observed P/T ratios, in conjunction with the measured steady-state parameters, can be used to refine the available mechanistic picture.

As far as the photochemical reaction of *p*-Cy and *m*-Cy with ketones is concerned (in the former case we confirm previous reports<sup>5,6</sup>), the P/T ratio is low with BP (0.35, 0.32) and high with TFA (4.7, 2.8). In the reaction of NDN with the same donors the ratios for the formation of products 1 and 2 are only slightly lower than with TFA. Considering the redox characteristics, one notices that electron transfer is a fast process with NDN ( $\Delta G$  for electron transfer from *p*-Cy to NDN<sup>1\*</sup> is ca.  $-9$  kcal/mol)<sup>9</sup> and a slower process with TFA ( $\Delta G$  ca.  $+2.5$  kcal/mol for transfer from *p*-Cy to TFA<sup>3\*</sup>; on the other hand Wagner found<sup>5</sup> a similar P/T ratio for various substituted TFAs with a  $\Delta G$  0 to  $-2$  kcal/mol. The efficiency of electron transfer with the TFA's is enhanced by the long lifetime of the triplet state). On the contrary, electron transfer to BP<sup>3\*</sup> is slow ( $\Delta G$  ca. 13 kcal/mol).

There is little doubt that the reaction with the  $n\pi^*$  BP triplet involves a loose, perpendicular complex with limited

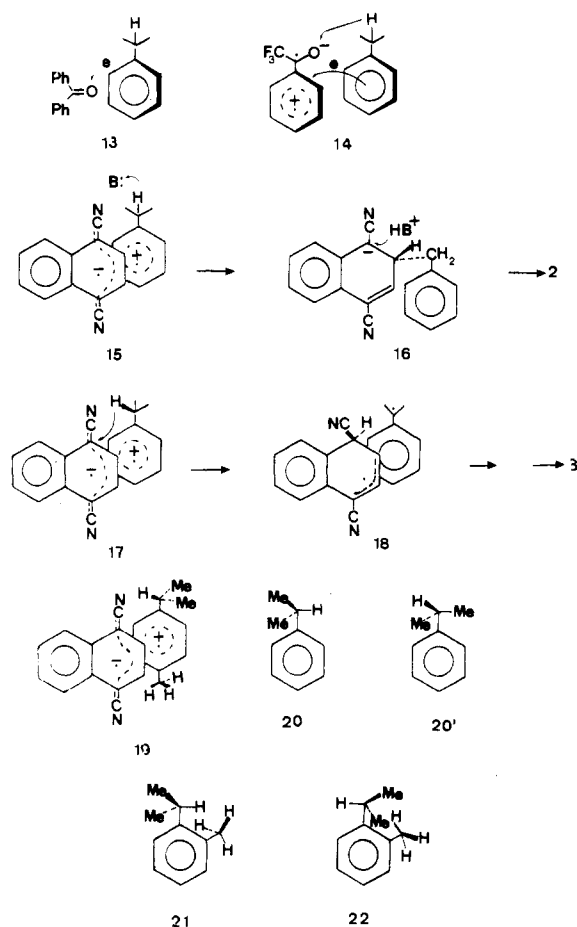
(9) Calculated according to the Weller equation (ref 10) and taking the following values:  $E_{red}^0$  NDN  $-1.28$  V vs SCE (ref 11), TFA  $-1.38$  V and BP  $-1.83$  V (ref 5);  $E_{ox}^0$  for *p*-Cy, the value for *p*-xylene (1.77 V) is taken (ref 12);  $E_{exc}$  NDN<sup>1\*</sup> 3.45 eV (ref 11), TFA<sup>3\*</sup> 3.03 eV and BP<sup>3\*</sup> 3.0 eV (ref 5).

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Scheme III



charge transfer character (the half-filled  $n$  orbital of the ketone points toward the donor, see structure 13, Scheme III).<sup>5,13</sup> Wagner finds only a small dependence of the P/T ratio on  $E_{red}$  for various BP's (as well as  $n\pi^*$  acetophenones),<sup>5</sup> and we find no difference between *p*-Cy and the less easily oxidized *m*-Cy. The reaction with the  $\pi\pi^*$  TFA triplet on the contrary involves a face-to-face complex<sup>13</sup> (see structure 14, Scheme III), with an important charge-transfer contribution, as evidenced, i.a., by the high rate of reaction observed.<sup>5</sup> Wagner rationalizes the high P/T ratio observed in this case on the basis of the better hyperconjugative stabilization of the positive charge by the methyl group in comparison with the isopropyl group.<sup>5</sup> Therefore, the complex having the methyl group near to the negative center of the acceptor radical anion is favored over the complex having the isopropyl group in that position, and thus prevails in the reaction. Indeed, Symons has reported<sup>14</sup> that hyperconjugation through the  $\sigma$  C-H bond is very important in the radical cations of alkyl aromatics (and, in ethylbenzene, the C-H bond is more important than the C-CH<sub>3</sub>).

It is further important to notice that due to the internal charge transfer character of the TFA  $\pi\pi^*$  triplet charge transfer involves the parallel rings, but the proton is transferred to the negatively polarized oxygen, thus to an atom not immediately adjacent to the interacting aromatic rings (see again structure 14). But this is exactly what, on the basis of previous experiments, we expect to happen

in the formation of products 1 and 2 from NDN. A charge-transfer, face-to-face complex is formed, and the benzylic proton is transferred to an external base (e.g. the solvent MeCN, or possibly even the CN group of the acceptor). The mechanism for product 2 is represented by the sequence 15  $\rightarrow$  16  $\rightarrow$  2 in Scheme III and is analogous for 1, except that rearomatization rather than re-protonation takes place. The similar conformation of the complex in the key step (proton transfer) with the TFA reaction is apparent and is experimentally supported by the similar P/T ratio observed with both acceptors.

Literature P/T values for the reaction of *p*-Cy with different oxidizers<sup>15</sup> vary from ca. 1 to very high,<sup>2m,v,x,3a</sup> and this is to be expected since different complexes are involved and the nature of the base to which the proton is transferred<sup>16</sup> as well as the intervening of secondary reactions and chain processes certainly play an important role,<sup>17</sup> but there is a definite trend for higher values than for homolytic hydrogen abstraction.<sup>18</sup>

The present results, adding for the first time a singlet excited acceptor and isomeric cymenes, strengthen the notion that transfer of a benzylic hydrogen is favored from the primary vs the tertiary position when charge transfer is significant, at least in tight complexes. On the contrary, in the loose BP complex 13 the half filled  $n_o$  orbital of the ketone freely explores the donor and ends up with the thermodynamically expected<sup>19</sup> product ratio just as in the purely homolytic process (though the complex is somewhat polarized also in this case, and this affects the reaction rate with different BP's<sup>5</sup>).

However, this is only half of what the NDN reaction reveals. Indeed, in sharp contrast with products 1 and 2, product 3 is formed with a low P/T ratio. This result might at first appear puzzling, since it is certain that all of these products arise from the same charge-transfer interaction with NDN<sup>1\*</sup>, but it is reconciled with the previous scheme when the mechanism of the reactions following electron transfer is taken into account. Thus, previous work<sup>8</sup> showed that, different from the case of products 1 and 2, formation of product 3 involves direct proton transfer to the aromatic ring (17  $\rightarrow$  18  $\rightarrow$  3, Scheme III). This demands a closer approach of the molecules, probably possible only in a singlet exciplex, and thus we are led to admit that two different face-to-face exciplexes are involved in the NDN/cymene reaction, a relatively loose and a more tight one. This hypothesis rationalizes the observed selectivity, since formation of the tight complex obviously requires that hindering by the alkyl substituents is minimized and thus favors structure 19, thereby at the same time selecting a conformation suitable for proton transfer from the isopropyl, not the methyl group. Notice also that in the more tight complex, the positive charge on the donor is further increased. The above-mentioned EPR studies<sup>14</sup> showed that at low temperature the radical cations of *p*-Cy and of cumene are

(15) Proton transfer from the cymenes radical cations is a thermodynamically favored process from both primary and tertiary position. For thermodynamic data on proton transfer from alkylbenzene radical cations see: Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132 and therein cited references.

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(17) The mechanism of some of these reactions is quite complex, and the P/T ratio as such might give little mechanistic information. This is probably the case for dicyanoanthracene sensitized photooxygenation (ref 3a), compare: Albini, A.; Sprei, Z. *Naturforsch.* **1986**, *41b*, 1286.

(18) An exception is the anodic oxidation in methanol, ref 3f.

(19) The difference in bond dissociation energy between PhCH<sub>2</sub>-H and PhCMe<sub>2</sub>-H is 2.8 kcal/mol, Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1982**, *104*, 5.

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Table III. Selected <sup>1</sup>H NMR Values for the Photoproducts<sup>a</sup>

prod.	CH <sub>2</sub>	CMe <sub>2</sub>	Me	<i>i</i> -Pr			
1a	4.5			1.2, 2.75			
1b	4.4			1.15, 2.75			
1c	4.55			1.25, 3			
1'a		1.55	2.2				
1'b		1.5	2.25				
prod.	H-1	H-2	H-3	CH <sub>2</sub>	CMe <sub>2</sub>	Me	<i>i</i> -Pr
2a	3.9	2.8	6.8	2.9			1.25, 3.1
2b	3.8	2.9	6.75	2.8			1.2, 3.1
2c	3.95	3	6.8	2.95			1.25, 3
2'a	3.7	2.9	6.8		1.5, 1.6	2.4	
2'b	3.9	2.9	6.9		1.3, 1.5	2.2	
prod.	H-5	H-6	5,11-CH <sub>2</sub>	CH <sub>2</sub> <sup>b</sup>	CMe <sub>2</sub>	Me	<i>i</i> -Pr
3a	4.5	3.75	2.55, 3.05	2.4			1.25, 3.1
3b	4.5	3.6	2.9 <sup>b</sup>	2.55			1.2, 2.9
3c	4.55	3.7	3.4 <sup>b</sup>	2.6			1.05, 1.2, 2.9
3'a	4.5	3.55	2.4, 3		1.4, 1.55	2.25	
3'b	4.5	3.7	2.55, 3		1.45, 1.6	2.25	
3'b'	4.55	4.05	2.6, 3		1.6, 1.7	2.55	
prod.	CH <sub>2</sub>	CMe <sub>2</sub>	Me	<i>i</i> -Pr			
4a	2.95			1.3, 2.9			
4b	2.9			1.25, 3.25			
4c	3			1.25, 3.25			
5a	2.85	1.3	2.3	1.25, 2.9			
5b	2.85	1.3	2.25	1.1, 2.75			
6a		1.3	2.3				
6b		1.3	2.35				
7a	3.4			1.2, 2.9			
7b	3.4			1.05, 1.07, 2.6			
7c	3.55			1.05, 1.2, 3.1			
8a	3.65			1.15, 2.9			
8b	3.65			1.05, 2.75			
8c	3.75			1.05, 3.1			
9a		1.3	2.45				
9b		1.35, 1.55	2.3				
10a		1.55	2.3				
10b		1.5	2.2				
10c		1.3	2.15				

<sup>a</sup>  $\delta$  values in CDCl<sub>3</sub> solutions. <sup>b</sup> Center of the AB system.

initially formed in conformation 20, reflecting the geometry of the neutral molecule, but on annealing the conformation changes toward 20', and this supports the possibility that the isopropyl group takes the conformation shown in the radical ion pair 19. On the contrary, in the more loose  $\pi$  complexes, 14 and 15, since the proton is transferred at a longer distance, sterical hindering is less important and the better charge stabilization by the methyl group becomes the leading factor.

This dual mechanism also explains why TFA reacts more with toluene than with cumene,<sup>6</sup> whereas the contrary is true for the total NDN reaction.<sup>8</sup> Indeed, with NDN the ratio 3/(1 + 2) is higher with cumene, 4.5, than with toluene, 1.35, and thus the reactivity of complex 15 is lower with an isopropyl than with a methyl group, just as it happens with complex 14, but the contribution of the reaction via complex 19 becomes larger, since it reflects the greater reactivity of the isopropyl group when "frozen" in a conformation with the C-H bond parallel to the  $\pi$ -system.

A different situation arises with *o*-Cy; here all the products from NDN and TFA involve attack at the primary position, and only with BP does some attack at the tertiary position take place. This is understandable on the basis of the previously discussed mechanism. The barrier to rotation is now higher than with *p*- or *m*-Cy, and the least hindered conformations (21 and 22) play a determining role. Thus, even in the reaction with BP, involving a very loose, low-charge transfer complex of type 13, attack at the tertiary position is much less easy than with the

other isomers, and it becomes virtually impossible in charge-transfer complexes. The change in selectivity is accompanied by a drop of the quantum yield values, more apparent for reactions involving a larger charge transfer (see Table II). This is due to the steric hindrance exerted by the two ortho substituents, which makes close face-to-face approach difficult. Among the charge-transfer complexes formed by NDN, a close pair of type 17 is further disfavored in comparison to reaction via the less tight complex 15 (the yield ratio 3/(1 + 2) is only 0.71 with *o*-Cy, compared to 1.86 with *p*-Cy).

Notice that also with *m*-Cy there is some steric hindrance: in the NDN reaction the ratio 3/(1 + 2) is 1.81, similar with the *p*-Cy case, but the quantum yield drops by a factor of 10.

It appears to us that three conclusions are obtained from this work. First, the primary vs tertiary selectivity in the hydrogen abstraction from cymenes depends indeed on the degree of electron transfer to the acceptor. However, at least in photochemical reactions, this is more a property of the donor-acceptor complex than of the radical cation of the donor per se. Second, the intimate mechanism of the reaction must be taken into account: 14, 15, and 17 are all face-to-face  $\pi$  complexes, but since the proton is transferred to a different base in a different geometric arrangement the P/T ratio changes. Third, the present results stress again the potential of exciplexes in controlling photochemical processes. Stabilization of the exciplex (or tight radical ion pair) is the driving force that selects the conformation of the interacting molecules and leads to new

site selectivity, as well as stereoselective, chemical reactions. At the same time, the results with *o*-Cy show the energetic extent to which different conformations can be competitive during the short lifetime of charge transfer exciplexes. Thus, conformation 19 is dominant with *p*-Cy and *m*-Cy, but going to *o*-Cy, and thus enhancing by a few kilocalories/mole the energy of the conformation with the isopropyl C-H bond parallel to the  $\pi$ -system, makes the role of a similar structure insignificant.

### Experimental Section

NDN was prepared from 1,4-dibromonaphthalene and purified by alumina chromatography and recrystallization; BP, TFA, and *p*-Cy (distilled prior to use) were high purity commercial products. *m*-Cy and *o*-Cy were prepared and purified by conventional procedures.<sup>20</sup> Spectroscopic grade solvents were used as received. NMR spectra were obtained on Brüker 80 and 200 instruments, UV spectra on a Cary 19, IR spectra on a Perkin-Elmer 297, and mass spectra on a Du Pont DU2 instrument.

**Preparative Photochemical Reactions.** A solution of NDN (200 mg,  $8 \times 10^{-3}$  M) in 140 mL of acetonitrile was refluxed and then allowed to return to room temperature while being flushing with argon. *p*-Cy ( $0.68 \text{ g } 3.6 \times 10^{-2} \text{ M}$ ) was added, and the solution further purged and then irradiated by means of a 150-W high-pressure mercury arc lamp through Pyrex while the temperature was maintained at 17 °C until a sufficient conversion had been reached (ca. 20 h). Evaporation of the solvent, column chromatography over silica gel, eluting with cyclohexane and then with cyclohexane-ethyl acetate mixtures of increasing polarity, followed by preparative TLC of the main fractions with cyclohexane-ethyl acetate mixtures yielded the products reported in Table I (the order of elution is 1a, 1'a, 2a, 2'a, 3a, 3'a). The reaction was analogously carried out with the isomeric cymenes, with the results reported. The identification of the photoproducts is based on the elemental analysis as well as the comparison of the spectroscopic properties with those of the previously described NDN-

toluene and cumene adducts.<sup>8</sup> A selection of the significant NMR data is gathered in Table III (assignments supported by double-irradiation experiments). The other physical properties are as expected.<sup>8</sup> The reactions with the ketones were carried out on 140 mL of acetonitrile solutions containing 0.49 g of TFA (or 0.4 g of BP) ( $2 \times 10^{-2}$  M) and 1.12 g of the cymenes ( $6 \times 10^{-2}$  M) by irradiation in a multilamp apparatus fitted with six fluorescing lamps (15 W, center of emission 320 nm) at 30 °C. The products were separated by column chromatography as above and by VPC (in particular for the hydrocarbons 4-6).

**Quantitative Measurements.** Fluorescence spectra were measured by means of an Aminco-Bowman MPF spectrophotometer; 1-cm optical path cells were used after deoxygenation by means of five freeze-degas-thaw cycles. The photochemical reaction was effected on samples prepared in the same way with the 313-nm radiation (intensity ca.  $10^{-7}$  Einstein  $\text{min}^{-1} \text{cm}^{-2}$ ) obtained from a focalized Osram 200-W high-pressure mercury arc lamp by means of an interference filter ( $\Delta\lambda_{1/2} = 5 \text{ nm}$ ). Relative yields were also determined in degassed tubes inserted in a rotating merry-go-round in the multilamp apparatus described above. Consumption of the reagents and products formation were assayed by VPC and/or HPLC.

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