The dark-colored mixture was, after cooling, chromatographed over silica gel using CH_2Cl_2 as an eluting agent. By this procedure 2.6 g (0.016 mol, 82%) of XX was obtained, mp 77-79°. After five recrystallizations from CCl_4-hexane (3:5), we obtained 1.8 g of white crystals, mp 84° (lit.[32] mp 85°).

The thermal rearrangements of 1,2-dicarboxymethyl-4-methyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptene-2,3 to 4-methylnaphthyl-1,2-dicarboxylic acid dimethyl ester (IV → XXI) and 1,2-dicarboxymethyl-3,4-dimethyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptene-2,3 to 3,4-dimethylnaphthyl-1,2-dicarboxylic acid dimethyl ester (V → XXII) were carried out by the same procedure, yields 75%.

Thermal Rearrangement of 1-Carboxymethyl-5,6-benzo[3.0.2]-bicyclo-7-thiaheptene-2,3 (VI → XXIII) to α-Naphthylcarboxylic Acid Methyl Ester.—VI (1 g, 0.0045 mol) was in its pure form heated up in a Woods metal bath thermostated at 240° for 20 min. After 5-10 sec the mixture started to change color and the smell of sulfur was observable. The dark mixture was chromatographed over silica gel using CCl_4 as an eluting agent, yielding 0.65 g (77%) of pure methyl α-naphthoate: ir 1131 and 1276 (CO) and 1720 cm^{-1} (C=O); nmr δ 3.99 (s, OCH_3) and 7.3-8.1 (m, aromatic H).

The thermal rearrangement of 3-methyl-1-carboxymethyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptene-2,3 (VII → XXIV) to 3-methylnaphthyl-1-carboxylic acid methyl ester was carried out in the same way: yields 70%; nmr δ 2.44 (s, CH_3), 3.93 (s, OCH_3), and 7.1-8.0 (m, aromatic H).

Thermal Rearrangement of 1-Phenyl-2-carboxymethyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptene-2,3 (X → XXVI) to 1-Phenyl-2-naphthoic Acid Methyl Ester.—X (1 g, 0.0032 mol) was heated in a Woods metal bath thermostated at 240° for 10 min. After 5-10 sec the mixture became dark. The reaction was cooled and the mixture was chromatographed over silica gel using $HCCl_3$ as eluting agent to 0.72 g (81%) of pure 1-phenyl-2-naphthoic acid methyl ester. If very pure substance is required, one may purify this further by preparative vpc (column SE-30, oven temperature 260°), nmr δ 3.50 (s, OCH_3) and 7.0-7.9 (m, aromatic H).

The thermal rearrangement of 1-phenyl-2-carboxymethyl-3-methyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptene-2-3 (XI → XXV) to 1-phenyl-3-methyl-2-naphthoic acid methyl ester was carried out in the same way: yields 80%; nmr δ 2.50 (s, CH_3), 3.5 (s, OCH_3), and 7.0-7.9 (aromatic H).

Registry No.—I, 31739-28-3; III, 24014-47-9; IV, 24014-46-8; V, 24014-48-0; VI, 31739-32-9; VII, 31739-33-0; X, 31739-34-1; XI, 31739-35-2; XIII, 31739-36-3; XV, 31739-37-4; XVI, 31739-38-5; XVII, 31739-39-6; XVIII, 31739-40-9; XXIX, 31739-41-0; XX, 10060-32-9; XXIII, 2459-24-7; XXIV, 31739-44-3; XXV, 31739-45-4; XXVI, 31790-95-1; dimethyl acetylenedicarboxylate, 762-42-5; benzo[*b*]thiophene, 95-15-8; methyl propiolate, 922-67-8; 2-methylbenzo[*b*]thiophene, 1195-14-8; phenylpropiolic acid methyl ester, 4891-38-7; diphenylacetylene, 501-65-5; 2-phenylacetylene, 31739-46-5; dichloromaleic anhydride, 1122-17-4.

Acknowledgment.—The authors gratefully acknowledge the Eli Lilly Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The high resolution mass spectra reported were run at the University of Illinois mass spectroscopy center. We gratefully acknowledge the assistance of Professor J. C. Martin in this regard. One of the authors (J. H. D.) thanks the University of Groningen (Netherlands) for a travel fellowship.

Effects of Micelles on the Efficiency of Photoinduced Substitution Reactions and Fluorescence Quenching[1,2]

RICHARD R. HAUTALA AND ROBERT L. LETSINGER*

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received April 1, 1971

The reactions of cyanide ion with photoexcited aromatic nitro compounds (4-nitrophenyl alkyl ethers, 1-nitronaphthalene, and 4-methoxy-1-nitronaphthalene) were examined in aqueous solutions containing micelles derived from hexadecyltrimethylammonium halide, sodium dodecyl sulfate, and mixtures of hexadecyltrimethylammonium halide and quaternary nitrogen detergents of the type $(CH_3)_3N^+(CH_2)_mOC_6H_4O(CH_2)_nCH_3$ (m = 4, 10; n = 0, 3, 7, 9). It was found that hexadecyltrimethylammonium chloride enhances the quantum yield of the reaction of 4-methoxy-1-nitronaphthalene by a factor of about 6800 and has little effect on the reaction of the 4-nitrophenyl alkyl ethers and that sodium dodecyl sulfate strongly inhibits the reactions of cyanide with nitroaromatics solubilized by the detergent. The results are rationalized on the basis of the effect of the micelles on both the local concentration of reactants and the character of the excited state of the nitroaromatic. Studies with the mixed micelles revealed that the efficiency of interaction of two organic groups (4-methoxy-1-nitronaphthalene and ROC_6H_4OR') can be altered by changing the relative position of these groups in the micelles. Thus, both the effectiveness of ROC_6H_4OR' as a quencher of the photoinduced reaction of the nitroaromatic with cyanide and the extent of quenching of fluorescence from ROC_6H_4OR' by the nitroaromatic were found to depend upon the position of the aromatic ring in the detergent (*i.e.*, on m and n) when the conditions favored micelle formation.

This paper reports results of a study of the effect of detergents on the course of some photochemical reactions of aromatic nitro compounds. The experiments were designed to test the extent to which rates of photoinduced bimolecular reactions might be influenced and controlled by exploiting local organizing and environmental effects of micelles.

That ionic detergents may appreciably alter rates of reaction of nucleophiles with organic substances in the ground state is well known.[3] For example, the rate of alkaline hydrolysis of 4-nitrophenyl esters of long-chain aliphatic acids is increased 8-18-fold by quaternary am-

---

[1] This research was supported by a grant from the National Science Foundation (GP-5 715).

[2] Part IX in the series on photoinduced substitution reactions. For part VIII, see K. E. Steller and R. L. Letsinger, *J. Org. Chem.*, **35**, 308 (1970).

[3] J. Baumrucker, M. Calzadilla, M. Centeno, G. Lehrmann, P. Lindquist, D. Dunham, M. Price, B. Sears, and E. H. Cordes, *J. Phys. Chem.*, **74**, 1152 (1970); C. A. Bunton and L. Robinson, *J. Org. Chem.*, **34**, 773, 780 (1969); **35**, 733 (1970); *J. Amer. Chem. Soc.*, **91**, 6072 (1969); **92**, 356 (1970); *J. Phys. Chem.*, **74**, 1062 (1970). For a review of the earlier literature, see E. H. Cordes, *Accounts Chem. Res.*, **2**, 329 (1969).

monium detergents[4] and is severely retarded by sodium dodecyl sulfate.[5] Utilization of detergent solutions as media for bimolecular photochemical reactions appeared attractive since micelle solutions transparent in the ultraviolet region could be prepared, the reactions could be initiated and terminated at will after the components have been thermally equilibrated, and micelles might in principle affect photochemical reactions by altering the properties of the excited states of the substrates as well as by changing the local concentration of the reactants.

Results

Reactions with Cyanide.—The reaction of cyanide ion with photoexcited nitroaromatics was selected to test the effect of detergents on a photochemical reaction involving an anion and a neutral organic species. Initial experiments were carried out with 4-nitroanisole which, on irradiation in aqueous solution in absence of detergents, reacts readily with cyanide ion and oxygen to give 2-cyano-4-nitroanisole and with hydroxide ion to give a mixture of 4-nitrophenoxide and 4-methoxyphenoxide.[6] The data in Table I show that neither hexadecyltrimethylammonium chloride (HDTCl) nor sodium dodecyl sulfate (SDS) at 0.01 *M* concentration has an appreciable effect on the quantum yield for disappearance of 4-nitroanisole in these photoreactions, the value being within a factor of two of that in the detergent-free solution in each case. This result corresponds to the absence of a significant effect of detergents on the rate of alkaline hydrolysis of 4-nitrophenyl acetate[5] and may be rationalized by the assumption that 4-nitroanisole resides and reacts preponderantly in the aqueous medium outside the micelles.

TABLE I

QUANTUM YIELDS FOR REACTIONS OF 4-$ROC_6H_5NO_2$ IN WATER

R	Detergent (0.01 *M*)	Nucleophile (0.01 *M*)	Φ
CH_3			0.0002
CH_3		OH^-	0.026
CH_3	HDTCl	OH^-	0.020
CH_3	SDS	OH^-	0.026
$C_{10}H_{21}$	HDTCl	OH^-	0.024
$C_{10}H_{21}$	SDS	OH^-	∼0.0003
CH_3		CN^-	0.32
CH_3	HDTCl	CN^-	0.18
$C_{10}H_{21}$	HDTCl	CN^-	0.21

Decyl 4-nitrophenyl ether was selected as a representative substrate possessing both the 4-nitrophenoxy chromophore and an apolar chain sufficiently long to ensure incorporation of the substrate in the micelles. It was prepared and found to be essentially insoluble in water (Table II) but readily solubilized by aqueous solutions of HDTCl and SDS. In contrast to 4-nitroanisole, no photoreaction was observed between decyl 4-nitrophenyl ether and cyanide ion in 0.01 *M* aqueous SDS (Table I). The inhibitory effect of the anionic detergent on the reaction of cyanide ion is in accord with expectations based on studies of effects of detergents on reactions of neutral molecules with hydroxide ion[5] and provides evidence that the substrate is indeed closely associated with the micelles in this sytem. On the other hand, the efficiency of the photoreaction of decyl 4-nitrophenyl ether with cyanide in the aqueous HDTCl medium was about the same as that of cyanide with 4-nitroanisole in either water or aqueous HDTCl (Table I); that is, incorporation of the nitrophenoxy chromophore in the positively charged micelles did not lead to enhancement in the efficiency of reaction with an anionic nucleophile.

TABLE II

PROPERTIES OF NITROAROMATICS

	Solubility[a] in H_2O × 10^4 (*M*)	λ_{max}, nm		
		H_2O	Detergent[b]	CH_3CN[c]
4-Nitroanisole	6.5	316	315	308
Decyl 4-nitrophenyl ether	∼0.024		315	309
1-Nitronaphthalene	2.3	343	338	334
4-Methoxy-1-nitronaphthalene	0.44	380	370	365

[a] Determined spectrometrically from uv absorption spectra of saturated solutions. [b] 0.01 *M* hexadecyltrimethylammonium chloride in H_2O. [c] 90% CH_3CN–10% H_2O.

Attention was then turned to the naphthalene derivatives, 1-nitronaphthalene and 4-methoxy-1-nitronaphthalene, which absorb at considerably longer wavelengths than the nitrophenyl ethers. Control experiments showed both compounds to be relatively stable when irradiated in water or aqueous organic or aqueous detergent solutions, the quantum yield for disappearance of the nitroaromatic being of the order of 2×10^{-3} for 1-nitronaphthalene and 2×10^{-4} for 5-methoxy-1-nitronaphthalene.

When 1-nitronaphthalene was irradiated in an aqueous solution containing cyanide ion, the maximum at 343 nm decreased and a new maximum developed at 300 nm, the position for λ_{max} for 1-cyanonaphthalene. That replacement of the nitro group by the cyano group occurred was confirmed by isolation of 1-cyanonaphthalene. Data for quantum yields for disappearance of 1-nitronaphthalene for reactions in water and in aqueous detergent solutions are presented in Table III. A plot of $1/\Phi$ *vs.* $1/[CN^-]$ for the reaction in water yields a straight line (intercept = 2.6); accordingly, this reaction, like that of cyanide with photoexcited 4-nitroanisole,[6] conforms to a scheme in which cyanide ion attacks the photoexcited nitroaromatic in a bimolecular process. Hexadecyltrimethylammonium chloride

TABLE III

REACTION OF 1-NITRONAPHTHALENE WITH CYANIDE

Detergent (*M*)	KCN, mol/l.	Φ[a]
	0.004	0.06
	0.008	0.10
	0.020	0.17
	0.040	0.26
	0.010	0.10[b]
HDTCl (0.001)	0.004	0.06
HDTCl (0.008)	0.004	0.14
HDTCl (0.010)	0.004	0.11
HDTCl (0.020)	0.010	0.07
SDS (0.010)	0.004	0.035

[a] In H_2O. [b] In H_2O–CH_3CN (80:20).

---

[4] L. R. Romsted and E. H. Cordes, *J. Amer. Chem. Soc.*, **90**, 4404 (1968).

[5] M. T. A. Behm, J. G. Fullington, R. Noel, and E. H. Cordes, *ibid.*, **87**, 266 (1965).

[6] R. L. Letsinger and J. H. McCain, *ibid.*, **91**, 6425 (1969).

(0.01 *M*) increased the efficiency of the photochemical reaction by a factor of ~2-fold at [CN$^-$] = 0.004 *M*, whereas sodium dodecyl sulfate retarded the reaction.

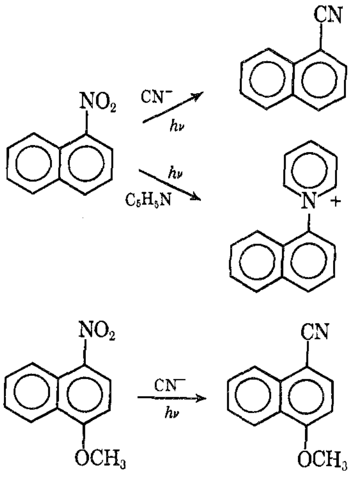
Cyanide ion in aqueous solution also displaced nitrite from photoexcited 4-methoxy-1-nitronaphthalene, yielding 4-methoxy-1-napthonitrile; however, the reactivity of the photoexcited species was very low. Even at a cyanide concentration of 0.8 *M* the quantum yield for disappearance of 4-methoxy-1-nitronaphthalene was only 0.0017 (Table IV). When the photoreaction was carried out in the presence of hexadecyltrimethylammonium chloride, a remarkable enhancement in quantum yield was observed. For reaction in an aqueous solution 0.01 *M* in KCN and 0.01 *M* in HDTCl, the quantum yield for disappearance of 4-methoxy-1-nitronaphthalene was 0.13, which corresponds to a 6800-fold enhancement relative to the quantum yield ($\Phi = 1.9 \times 10^{-5}$) for a reaction conducted in the absence of detergent.[7] From a preparative scale reaction conducted in the detergent medium, 4-methoxy-1-naphthonitrile was isolated as the sole material extractable with ether after precipitation of the detergent with a cation exchange resin. It may be noted that no photinduced reaction with cyanide was observed when the anionic detergent SDS, was used to solubilize the nitroaromatic.

TABLE IV

REACTION OF 4-METHOXY-1-NITRONAPHTHALENE WITH CYANIDE

Detergent (0.01 *M*)	KCN, mol/l.	Φ^a
	0	0.00015
	0.02	0.00020
	0.10	0.00035
	0.20	0.00048
	0.40	0.0009
	0.80	0.0017
HDTCl	0.004	0.068
HDTCl	0.006	0.091
HDTCl	0.010	0.130
HDTCl	0.020	0.168
SDS	0	0.00015
SDS	0.004	0.00015

[a] Quantum yield for disappearance of nitroaromatic at 375 nm. The solvent was water for solutions containing HDTCl and SDS and was water–*tert*-butyl alcohol (80:20) for detergent-free solutions.



Solvent Effects.—To assist in the interpretation of these results, an investigation of the effects of solvents on the efficiency of the photoinduced reactions of nitroaromatics with cyanide ion was undertaken. Preliminary studies, which have been published,[8] showed that a shift from 90% water–10% acetonitrile to 90% acetonitrile–10% water reduced the efficiency of reaction of potassium cyanide (0.01 *M*) with 4-nitroanisole by a factor of 50, had little effect on the reaction with 1-nitronaphthalene, and greatly enhanced the reaction with 4-methoxy-1-nitronaphthalene. Additional data on 4-methoxy-1-nitronaphthalene presented in Table V confirm the conclusion that solvents of low polarity favor the photochemical reaction of this nitroaromatic with cyanide ion. Indeed, the quantum yields in aqueous 90% acetonitrile, dioxane, or *tert*-butyl alcohol are comparable to those in the cationic detergent solution, and these organic solvents serve as good media for preparative scale reactions.

TABLE V

EFFECTS OF SOLVENTS ON PHOTOREACTIONS OF 4-METHOXY-1-NITRONAPHTHALENE WITH CYANIDE

Organic component^a of solvent (%)	[KCN], mol/l.	Φ
tert-Butyl alcohol (40)	0.01	0.0007
tert-Butyl alcohol (90)	0.01	0.038
Dioxane (80)	0.01	0.032
Dioxane (90)	0	0.002
	0.004	0.057
	0.006	0.074
	0.010	0.12
Acetonitrile (90)	0	0.0004
	0.004	0.0092
	0.010	0.021
	0.020	0.036
Acetonitrile (95)	0	0.0004
	0.0004	0.021
	0.006	0.029
	0.010	0.047

[a] The other component was water.

Aside from the influence of solvents on the character of the excited state of the nitroaromatic,[8] one would expect a shift to a less polar solvent to retard a reaction of a neutral organic substrate with an electrically neutral nucleophile as a consequence of the charge separation that develops in the transition state. In agreement with this expectation, photoexcited 1-nitronaphthalene was found to react readily with pyridine in a medium predominately water (80:20 water–*tert*-butyl alcohol) to give the 1-naphthylpyridinium ion, which was obtained in 89% yield as a picrate. When the solvent was 90:10 acetonitrile–water, the efficiency was only $^1/_{25}$th of that for the more polar medium.

Quenching by ROC_6H_4OR'.—Having found that the photoinduced reaction of 4-methoxy-1-nitronaphthalene with cyanide ion in aqueous media was greatly facilitated by the detergent HDTCl, we next inquired into the possibility of modifying the reactivity of the nitroaromatic by means of aromatic fragments

---

[7] The value for the homogeneous solution was interpolated from the data in Table IV after subtracting the quantum yield for decomposition of 4-methoxy-1-nitronaphthalene in the absence of cyanide. Because of the low solubility of 4-methoxy-1-nitronaphthalene in water, water–*tert*-butyl alcohol (80:20) was used as a solvent for the homogeneous solutions. Control experiments conducted with very low concentrations of the nitroaromatic in water showed that Φ for reaction in the mixed solvent represents an upper limit for the reaction in pure water.

[8] R. L. Letsinger and R. R. Hautala, *Tetrahedron Lett.*, 4205 (1969).

aligned in the micelles. For this purpose detergents I–IV, possessing 1,4-dioxybenzene moieties four to ten carbon atoms removed from the quaternary nitrogen, were synthesized and were used to solubilize 4-methoxy-1-nitronaphthalene. It was of interest to see if the dioxybenzene fragments would inhibit the reaction of the nitroaromatic with cyanide and whether the extent of inhibition would depende upon the position of the inhibitory group in the micelles. The selection of this particular aromatic function was based on the previous observation that 1,4-dimethoxybenzene inhibits the photoreaction of 4-nitroanisole with cyanide, apparently *via* formation of a complex between the dimethoxybenzene and the excited nitroaromatic.[2]

I, $(CH_3)_3\overset{+}{N}(CH_2)_{10}OC_6H_4OCH_3\ Br^-$

II, $(CH_3)_3\overset{+}{N}(CH_2)_{10}OC_6H_4O(CH_2)_3CH_3\ Br^-$

III, $(CH_3)_3\overset{+}{N}(CH_2)_{10}OC_6H_4O(CH_2)_7CH_3\ Br^-$

IV, $(CH_3)_3\overset{+}{N}(CH_2)_4OC_6H_4O(CH_2)_9CH_3\ Br^-$

To minimize intrinsic differences in the ability of the modifier detergents to form micelles, hexadecyltrimethylammonium bromide was used as a support detergent to form mixed micelles.[9] Irradiation was carried out with the monochromator set at 375 nm in order to ensure that the light was absorbed by 4-methoxy-1-nitronaphthalene rather than by the dioxybenzene groups. The data in Table VI show that the detergents possessing dialkoxybenzene groups do function as inhibitors of the photochemical reaction and, further, that the extent of inhibition depends upon the position of the dialkoxybenzene moiety in the apolar chain of the detergent. Detergent IV is the most effective. At a concentration of 5 × 10^{-4} M it reduces the efficiency of the photoinduced substitution reaction of 4-methoxy-1-nitronaphthalene by a factor of 9.7. As the relative concentration of this detergent is increased the quenching factor increases, reaching 50 when the quencher detergent is present at 2 × 10^{-3} M. Detergent I is the least active and II and III are of intermediate activity. For comparison it may be noted that $\Phi_0/\Phi = 1.5$ for quenching of the reaction of 4-methoxy-1-nitronaphthalene with cyanide by 1,4-dimethoxybenzene at 5 × 10^{-4} M in homogeneous solution (95% acetonitrile–5% water).

TABLE VI

EFFECT OF QUENCHER DETERGENTS ON REACTION OF 4-METHOXY-1-NITRONAPHTHALENE (10^{-4} M) WITH CYANIDE (10^{-2} M)

Quencher detergent	Molarity × 10^3	HDTBr molarity × 10^3	Φ_0/Φ
None		2.0	1.0
I	0.5	1.5	1.5
II	0.5	1.5	5.3
III	0.5	1.5	5.6
IV	0.5	1.5	9.7
IV	1.0	1.0	24.0
IV	2.0	0	50.0

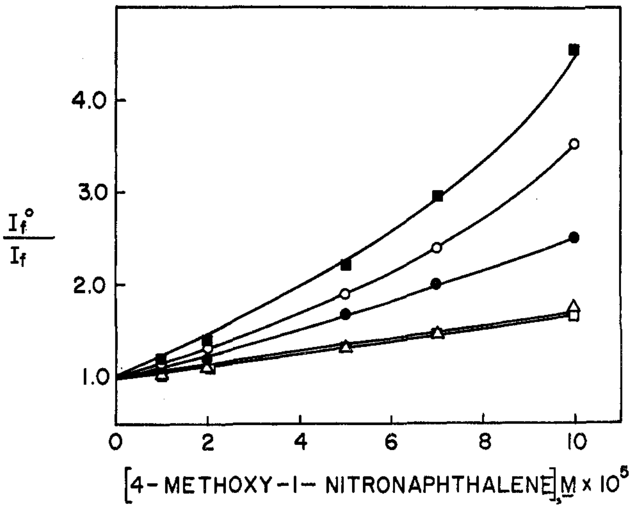


Figure 1.—Quenching of fluorescence from ROC_6H_4OR' in detergents I (□), II (●), III (■), and IV (○) by 4-methoxy-1-nitronaphthalene in 2 × 10^{-3} M hexadecyltrimethylammonium bromide in water and quenching of fluorescence from 1,4-dimethoxybenzene by 4-methoxy-1-nitronaphthalene in methanol (△).

Fluorescence Quenching.—Previous work has shown that a nitroaromatic will quench the fluorescence of a 1,4-dialkoxybenzene in homogeneous solution.[2] Accordingly, detergents I–IV may be used to study another question; namely, to what extent does micellar organization influence the interaction of organic fragments as measured by fluorescence quenching? For this study solutions were prepared that contained hexadecyltrimethylammonium bromide as the primary detergent (2 × 10^{-3} M), one of the quencher detergents (compounds I–IV, 1 × 10^{-4} M), and 4-methoxy-1-nitronaphthalene (at concentrations ranging from 0 to 10^{-4} M). The solutions were then irradiated at 290 nm to excite the dialkoxybenzene groups, and the fluorescence from these groups was measured.

As shown in Figure 1, the extent of quenching of fluorescence from the dialkoxybenzene groups does depend on the position of this group in the detergent molecules as well as on the concentration of the quencher, 4-methoxy-1-nitronaphthalene. Fluorescence quenching was most extensive in the case of III, in which the aromatic fragment is bounded by the longest apolar carbon chains, and was least in the case of I, in which the aromatic fragment resides at the end of the detergent molecule. Indeed, the extent of interaction of the nitroaromatic and dialkoxybenzene fragment measured by fluorescence quenching is no greater for the detergent system containing I than for solutions of 1,4-dimethoxybenzene and 4-methoxy-1-nitronaphthalene in homogeneous solution in methanol.

Organic solvents such as methanol are known to break up or "denature" micelles. Accordingly, if the variations in quenchability of fluorescence in the detergent solutions in fact stem from the micellar organization, the variations should disappear when sufficient methanol is added to afford solutions free of micelles. As a test of this point the experiments reported in Figure 1 were repeated with a solvent consisting of aqueous methanol (40% methanol) in place of water. For this set of experiments all detergents were found to behave identically and the plot of I_f^0/I_f *vs.* molarity of

---

[9] That mixed micelles are formed when different detergents of like charge are mixed has been demonstrated by H. Inoue and T. Nakagawa, *J. Phys. Chem.*, **70**, 1108 (1966).

4-methoxy-1-nitronaphthalene was superimposable on the curve for 1,4-dimethoxybenzene in Figure 1.

The ultraviolet spectra of dilute solutions of I–IV (1×10^{-4} *M*) in water exhibit a maximum at 287 nm. For comparable solutions that are also 4×10^{-3} *M* in HDTBr, λ_{max} shifts to longer wavelengths for II, III, and IV and is unchanged for I (see Table VII). These results suggest that I is not incorporated into the micelles of HDTBr, whereas the other detergents are. The low quenching efficiency for I can therefore be ascribed at least in part to the fact that most of this reagent resides in solution outside the micelles that contain the nitroaromatic. The difference in effectiveness of III and IV, however, appears to stem from differences in orientation of the dioxybenzene group within the micelles.

TABLE VII

Detergent	Formula[a]	Mp, °C	λ_{max}, nm[b]
I	$C_{20}H_{36}NO_2Br$	151–152	287
II	$C_{23}H_{42}NO_2Br \cdot {}^1/_2H_2O$	196–197	289
III	$C_{27}H_{50}NO_2Br$	213–214	290, 350 (sh)
IV	$C_{23}H_{42}NO_2Br \cdot {}^3/_4H_2O$	132–134	290, 350 (sh)

[a] Satisfactory analytical data were reported for I, II, III, and IV (H for IV was a little low: calcd H, 9.57; found H, 9.20). [b] For solutions 1×10^{-4} *M* in specified detergent and 4×10^{-3} *M* in HDTBr. In absence of HDTBr λ_{max} was 287 nm (ϵ 2250 ± 100) in all cases. For comparison, 1,4-dimethoxybenzene shows maxima at 286 nm in water and at 289, 291, and 300 nm in hexane.

Discussion

Three systems were employed to examine the effects of micelles on photochemical processes in aqueous media. These utilized (a) the reaction of two components (cyanide and an aromatic nitro compound) "organized" by a simple anionic or cationic detergent, (b) competitive reactions involving three components (cyanide, 4-methoxy-1-nitronaphthalene, and ROC_6H_4OR' in compounds I–IV) organized within cationic micelles, and (c) fluorescence quenching involving two aromatic substances (ROC_6H_4OR' in compounds I–IV and 4-methoxy-1-nitronaphthalene) arranged in cationic micelles.

A wide range in the effects of simple ionic detergents was found. Of special interest are the magnitudes of the effects of hexadecyltrimethylammonium chloride on the photoreactions. Enhancements in the quantum yield in the detergent media relative to water ranged from 6800 for 4-methoxy-1-nitronaphthalene to 2 for 1-nitronaphthalene to zero for the nitrophenyl ethers. Previous discussions of effects of micelles on reaction rates have emphasized the effect of the detergent on the local concentration of reactants. Thus some enhancement in rate of reaction of cyanide with a neutral molecule solubilized by a quaternary nitrogen detergent would be expected since anions should be concentrated at the surface of the micelles containing the aromatic. The 6800-fold enhancement observed for the reaction of 4-methoxy-1-nitronaphthalene, however, is far out of the range characteristically observed for micellar effects on ground-state reactions and indicates that some other factor must be important. We believe the additional factor to be the change in the local environment (from water to the less polar water–hydrocarbon medium within the micelles), which can influence the reactivity of the excited state of the nitroaromatic. This conclusion is based on the strong dependence on solvent observed for quantum yields of photoinduced aromatic substitution reactions in the homogeneous solutions.[8] A decrease in solvent polarity greatly favors the reaction of photoexcited 4-methoxy-1-nitronaphthalene with cyanide, has little effect on the corresponding reaction of 1-nitronaphthalene, and strongly retards the reaction of a 4-nitrophenyl alkyl ether. Accordingly, the concentration and medium factors augment each other in the case of 4-methoxy-1-nitronaphthalene, with the result that an unusually large enhancement is observed, and they counteract each other in the case of a 4-nitrophenyl alkyl ether, with the result that little change in effective rate is apparent. The small enhancement for 1-nitronaphthalene is in accord with the expectation that only the concentration factor is important in this case; however, it should be noted that a large enhancement here would not be possible since the quantum yield for the reference reaction in water is relatively high.

That reactions of photoexcited 4-nitrophenyl decyl ether, 1-nitronaphthalene, and 4-methoxy-1-nitronaphthalene with cyanide are very inefficient in the presence of sodium dodecyl sulfate may be ascribed to the effect of the detergent on the concentration of reactants, cyanide ion being effectively screened from the nitroaromatic solubilized in the micelles. In view of the relatively high solubility of 4-nitroanisole in water and the fact that sodium dodecyl sulfate has no effect on the photoinduced reaction of 4-nitroanisole with cyanide, it seems highly probable that little of the 4-nitroanisole is incorporated in the micelles and that most of the photochemical reaction in this case occurs in the aqueous medium outside the micelles.

The experiments with the mixed micelles are of interest in that they demonstrate that three different types of reactants (an anion, a neutral molecule, and an aromatic fragment bearing a positive charge) can be assembled in a given micelle. Furthermore, the finding that the effectiveness of ROC_6H_4OR' in quenching the excited state of 4-methoxy-1-nitronaphthalene (as observed by inhibition of reaction of the nitroaromatic with cyanide) depends on the position of the dioxybenzene group in the hydrocarbon chain of the detergent indicates that photochemical reactions can be influenced or controlled by tailor-made molecules that affect the arrangement of groups within micelles. This conclusion is supported by the experiments that show that the quenching of fluorescence from ROC_6H_4OR' by interaction with 4-methoxy-1-nitronaphthalene is dependent on the position of the dioxybenzene group in the detergent molecule when micelles are present (*i.e.*, when the reaction is carried out in water) and is independent of the position of the dioxybenzene group in the detergent when the micellar structure is destroyed (*i.e.*, when the solution is "denatured" by addition of methanol). The differences in relative activity of III and IV as measured by quenching of the reaction of 4-methoxy-1-nitronaphthalene (Table VI) and by fluorescence quenching (Figure 1) probably reflect differences in the position of the functional groups in the micelles and differences in the geometrical requirements for the two types of interactions. Quenching of the photochemical reaction probably involves intimate molecular contact between the two interacting species, whereas fluorescence quenching can occur over relatively large distances.

Experimental Section

Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill., or by Miss Hilda Beck, Northwestern University. Melting points were taken on a Thomas hot-stage apparatus and are corrected. Ultraviolet, infrared, and nmr spectra were recorded on a Cary 11, a Baird AB-2, and a Varian A-60 spectrometer, respectively.

Fluorescence spectra were recorded on a Hitachi Perkin-Elmer spectrometer (MPF-2A) with an excitation wavelength of 290 nm (excitation slit set at 4 and emission slit at 12). The observed intensities were corrected for absorption by 4-methoxy-1-nitronaphthalene by use of eq 1, where I_f^{cor} is the corrected intensity, I_f is the observed intensity, A is the absorbance of a reaction solution containing the methoxynitronaphthalene, and A' is the absorbance of the reaction solution without the methoxynitronaphthalene.

$$I_f^{cor} = I_f\left[\frac{A'(1 - 10^{-A})}{A(1 - 10^{-A'})}\right] \qquad (1)$$

Quantum Yields.—Quantum yields were measured using a Bausch and Lomb monochromator (slits: 2 mm rear and 1 mm front) equipped with a 200-W Osram super pressure mercury arc. The wavelength of irradiation was near the absorption maximum of the nitroaromatic (Table II), a feature which minimizes any error in evaluating the quantity of light absorbed by the reactant. Quartz cuvettes equipped with Teflon microstirring bars were used as photolysis vessels. They were held in thermostated (25°) cell holders during irradiation and the extent of reaction was followed by the change in absorbance at the wavelength used for irradiation. In the course of the reaction, the absorbance fell to approximately one-third (for the nitrophenyl ethers) or one-fourth (for naphthalene derivatives) the initial value. The quantum yield, Φ, was evaluated by use of eq 2, where A and A_0 are absorbances at time t and t_0, respectively, ϵ is the molar extinction coefficient, and I is the incident intensity in einsteins/cm^{-2}/sec.[10] The incident intensity was determined before and after each photolysis by use of a ferrioxalate actinometer, and values for Φ were obtained from slopes of plots of the left hand portion of eq 2 against time. When the products of a reaction also absorbed at the wavelength of irradiation, it is necessary to correct the "raw" absorbance, A', which represents the sum of the absorbance of reactant and products. This correction was handled in the usual way by the relationship:[10] $A = A_0(A' - A_\infty)/(A_0 - A_\infty)$.

$$A_0 - A + \log\frac{1 - 10^{-A_0}}{1 + 10^{-A}} = \Phi\epsilon I(1000)(t - t_0) \qquad (2)$$

Decyl 4-Nitrophenyl Ether.—Sodium 4-nitrophenoxide (6.0 g, 37 mmol) and 1-bromodecane (5.0 ml, 25 mmol) were heated in refluxing dimethylformamide (50 ml) for 19 hr, whereupon the solution was cooled and poured onto ice. Filtration and recrystallization of the precipitate from ethanol–water afforded 4.35 g (87%) of decyl 4-nitrophenyl ether, which on recrystallization melted at 42.5–43°: λ_{max} 309 nm (ϵ 10,900) (in acetonitrile); nmr ($CDCl_3$) τ 1.86 (2 H, d, J = 9.0 Hz), 3.07 (2 H, d, J = 9.0 Hz), 5.90 (2 H, t), 8.0–9.05 (19 H, m).

Anal. Calcd for $C_{16}H_{25}NO_3$: C, 68.79; H, 9.02; N, 5.01. Found: C, 68.99; H, 8.97; N, 5.00.

The other nitroaromatics were obtained from commercial sources and were recrystallized before use. Hexadecyltrimethylammonium chloride was purified by the method of Duynstee and Grunwald.[11]

Quencher Detergents.—The quencher detergents were all prepared in the same manner in a two-step sequence from the appropriate 4-alkoxyphenol. The procedure is represented by the synthesis of *N*,*N*,*N*-trimethyl-*N*-[4-(4′-decyloxyphenoxy)-butyl]ammonium bromide.

A methanolic solution of sodium methoxide, freshly prepared from 0.147 g (6.4 mmol) of sodium, was added to 1.60 g (6.4 mmol) of 4-(decyloxy)phenol (mp 71.5–72°) in anhydrous methanol. The solution was concentrated *in vacuo*, diluted with 50 ml of acetonitrile, and added dropwise over 2 hr to a refluxing solution of 1,4-dibromobutane (2.0 ml, 17 mmol) in 150 ml of acetonitrile. The solution was refluxed an additional 6 hr, cooled, and concentrated *in vacuo*. Ether and water were added to the mixture, and the resulting phases were extracted with 10% aqueous sodium hydroxide solution and ether. The ether layers were combined, dried over magnesium sulfate, and concentrated. Two recrystallizations from ethanol gave 1.37 g (57%) of the desired 1-bromo-4-(4′-decyloxyphenoxy) butane: mp 61–62°; nmr (CCl_4) τ 3.37 (4 H, s), 6.15 (4 H, t), 6.60 (2 H, t), 8.0–9.07 (23 H, m). To 0.70 g (18 mmol) of this ether in 30 ml of absolute ethanol was added through a Dry Ice–acetone condenser 7 ml (78 mmol) of trimethylamine. The solution was refluxed for 6 hr, concentrated *in vacuo*, and diluted with ether to precipitate the title compound (0.80 g, 99%). This material was dissolved in doubly distilled water, filtered through a fine-pore sintered-glass funnel, and lyophilized: mp 132–134°; nmr ($CDCl_3$) τ 3.16 (4 H, s), 6.11 (t) and 6.55 (s) (15 H total), 8.0–9.0 (m) with sharp signal at 8.7 and a distorted triplet at 9.09 (23 H total). The analyses for this compound and the related detergents in the series have been determined. All compounds in the series exhibited a maximum in the uv (water) at 287 nm with ϵ in the range of 2100–2360.

Preparative Photochemical Reactions. 4-Methoxy-1-naphthonitrile.—A Hanovia 450-W mercury lamp and immersion apparatus with a Pyrex filter sleeve were employed. The vessel, capacity 1100 ml, was equipped with a fritted-glass inlet for nitrogen and was cooled by a water condenser. For the reaction in aqueous acetronitrile, a solution containing 0.787 g of 4-methoxy-1-nitronaphthalene and 1.0 g of potassium cyanide in 740 ml of acetonitrile and 40 ml of water was irradiated for 90 min. The solution was then concentrated to 60 ml *in vacuo*, diluted to 160 ml with water, and extracted with three 200-ml portions of ether. The combined ether portions were dried, concentrated, and subjected to chromatography on a silica gel column (2.1 × 80 cm) with benzene–hexane (60:40) as solvent. In addition to 0.052 g of recovered 4-methoxy-1-nitronaphthalene there was obtained 0.458 g (70%) of 4-methoxy-1-naphthonitrile: mp 103–103.5° (lit.[12] mp 102.5, 104°); nmr τ 5.97 (3 H, s), 3.23 (1 H, d, J = 8.8 Hz), 2.23–2.53 (3 H, m), 2.19 (1 H, d, J = 8.8 Hz), 1.60–1.98 (2 H, m). This product also gave satisfactory analyses for C, H, and N.

For the reaction in the detergent solution, a solution was prepared from 0.203 g of 4-methoxy-1-nitronaphthalene, 0.651 g of potassium cyanide, and 3.96 g of hexadecyltrimethylammonium chloride in 1 l. of water. The mixture was photolyzed for 20 min in the immersion apparatus and then poured into a beaker and swirled with 60 g of Bio-Rex 70 resin (50–100 mesh, sodium form) to bind the detergent. The mixture was extracted with ether (500 ml) and worked up as before to give 0.098 g (54%) of 4-methoxy-1-naphthonitrile, mp 102.5–103° (mixture melting point undepressed).

Reaction of 1-Nitronaphthalene with Pyridine.—A solution containing 8.9 ml of pyridine and 47.6 mg (2.5 × 10^{-4} *M*) of 1-nitronaphthalene in 880 ml of water and 220 ml of *tert*-butyl alcohol was photolyzed in the Hanovia apparatus for 1 hr. It was then concentrated *in vacuo* at 40°, and a saturated aqueous solution of picric acid was added until no further precipitate appeared. The precipitate was collected and recrystallized from ethanol-acetone to give 82.1 mg (89%) of *N*-(1-naphthyl)-pyridinium picrate, mp 209–210°. A mixture melting point with a sample prepared independently from 1-napthylamine showed no depression.[13]

Anal. Calcd for $C_{21}H_{14}N_4O_7$: C, 58.07; H, 3.25; N, 12.90. Found: C, 58.02; H, 3.25; N, 12.84.

Reaction of 1-Nitronaphthalene with Cyanide.—A solution of 1-nitronaphthalene (50 ml, 5 × 10^{-4} *M*) and potassium cyanide

---

(10) R. R. Hautala, Doctoral Dissertation, Northwestern University, 1970. Other work in which descriptions of similar techniques for measuring quantum yields have appeared include A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); R. O. de Jongh, Ph.D. Dissertation, University of Leyden, 1965; Y. Otsuji, T. Kuroda, and E. Imoto, *Bull. Chem. Soc. Jap.*, **41**, 2173 (1968).

(11) E. F. Duynstee and E. Grunwald, *J. Amer. Chem. Soc.*, **81**, 4540, 4542 (1959).

(12) A. Fischer, M. A. Riddolls, and J. Vaughy, *J. Chem. Soc. B*, 106 (1966); E. Lorz and R. Baltzly, *J. Amer. Chem. Soc.*, **73**, 93 (1951).

(13) Prepared by the general method of A. F. Vompe and N. F. Turistsyama, *Zh. Obshch. Khim.*, **28**, 2864 (1958).

(0.01 *M*) in acetonitrile–water (95:5) was irradiated in a Pyrex vessel with a General Electric 1000-W photochemical lamp for 425 sec. The solution was then shaken with a mixture of 150 ml of dichloromethane and 100 ml of aqueous 2 *M* sodium chloride solution. The organic layer was separated, washed with additional salt solution, dried, concentrated, and subjected to gas chromatography on a Hewlett-Packard Model 720 gas chromatograph equipped with dual 10 ft × 0.25 in. columns of 4.5% silicone gum rubber (GE-SE-52) on Chromosorb G. Only two substances were obtained from the reaction mixture: 1-cyanonaphthalene (51%) and unreacted 1-nitronaphthalene (31%). These compounds were characterized by their retention times, by infrared spectra, and by mixture melting point with authentic samples.

Registry No.—I, 31657-32-6; II, 31657-33-7; III, 31657-34-8; IV, 31657-35-9; 1-nitronaphthalene, 86-57-7; cyanide, 57-12-5; 4-methoxy-1-nitronaphthalene, 4900-63-4; decyl 4-nitrophenyl ether, 31657-37-1; 4-nitroanisole, 100-17-4; pyridine, 110-86-1; *N*-(1-naphthyl)pyridinium picrate, 31657-38-2; 1-bromo-4-(4′-decyloxyphenoxy)butane, 31657-39-3.

Photochemical [2 + 2] Cycloaddition Reactions at Low Temperatures. Synthesis of Bridgehead Substituted Bicyclo[*n*.2.0]dicarboxylates from Maleic Acid Derivatives and Ethylene

DENNIS C. OWSLEY AND JORDAN J. BLOOMFIELD*

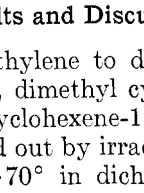
Central Research Department, Monsanto Company, St. Louis, Missouri 63166

Received July 1, 1971

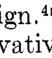
Irradiation through quartz at −65° or lower of ethylene saturated dichloromethane solutions of dimethyl cyclobutene-1,2-dicarboxylate, dimethyl cyclopentene-1,2-dicarboxylate, and cyclohexene-1,2-dicarboxylic anhydride produces the corresponding bicyclo [2.2.0], [3.2.0], and [4.2.0] derivatives in nearly quantitative yield in preparatively useful amounts with high quantum efficiency. Dimethyl cyclohexene-1,2-dicarboxylate does not add ethylene under a wide variety of experimental conditions. Maleic anhydride readily adds ethylene at low temperature in acetone to give a mixture of the maleic anhydride–acetone oxetane (21%) and cyclobutane-1,2-dicarboxylic anhydride (57%), while in an unreactive solvent the cyclobutane is the sole product (70%). Dimethyl acetylenedicarboxylate also reacts readily at low temperatures to add two molecules of ethylene to produce a 9:1 mixture (60–66% yield) of dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate and dimethyl bicyclopropyl-1,1′-dicarboxylate. Dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate is thermally converted to dimethyl *α,α*′-dimethyleneadipate with a half-life at 75° of about 53 min.

Photochemical [2 + 2] cycloaddition of olefins and/or acetylenes has provided an excellent route to a number of substituted cyclobutane and cyclobutene derivatives.[1-3] In most of the prior work, however, substituted olefins or acetylenes were the ground-state partners in the cycloadditions, giving substituted cyclobutanes or cyclobutenes. The use of ethylene[3] as the ground-state partner in [2 + 2] cycloadditions to give 1,2-disubstituted cyclobutanes has received much less attention. Furthermore, ethylene addition to a cyclic maleic acid derivative to give bridgehead dicarboxylate derivatives of bicyclo[*n*.2.0]alkanes has only recently been described.[4]

The use of low temperatures to carry out a variety of photochemical transformations can offer a number of distinct advantages. Among these are fewer undesirable side products which result from thermal reactions of the photoproduct, higher quantum yields, and greater solubility of gaseous reactants. We wish to report the results of some of our studies on the preparation of some 1,(*n* + 2)-bicyclo[*n*.2.0]alkanedicarboxylate derivatives **1**, where *n* = 2, 3, 4, by the photochemical cycloaddition of ethylene to the appropriate cyclic maleic acid derivatives, which show the advantages of low temperature preparative photochemistry.



1

where $R_1 = R_2 = OR', OH; R_1 =$ 

Results and Discussion

The additions of ethylene to dimethyl cyclobutene-1,2-dicarboxylate (**2**), dimethyl cyclopentene-1,2-dicarboxylate (**3**), and cyclohexene-1,2-dicarboxylic anhydride (**4**) were carried out by irradiation of solutions of each substrate at −70° in dichloromethane through quartz using a variable-temperature preparative photochemical reactor of our own design.[4a] Excellent yields of the bicyclo[*n*.2.0]alkane derivatives **5**–**7** were obtained in each case (eq 1–3). The use of low temperature and dichloromethane solvent to carry out these transformations is critical. For example, **2** gives a vari-

---

[1] Several reviews on these syntheses have appeared: (a) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968); (b) W. L. Dilling, *Chem. Rev.*, **69**, 845 (1969); (c) P. G. Bauslaugh, *Syn.*, 287 (1970); (d) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belg.*, **71**, 781 (1962).

[2] For syntheses of cyclobutanes and cyclobutenes from substituted olefins and acetylenes, *cf.* (a) E. J. Corey, J. D. Bass, R. Lemathieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (b) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *ibid.*, **88**, 1330 (1966); (c) G. O. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963); (d) R. Steinmetz, W. Hartmann, and G. O. Schenck, *ibid.*, **98**, 3854 (1965); (e) G. R. Evanega and D. L. Fabiny, *Tetrahedron Lett.*, 2241 (1968); (f) H. Yamazaki and R. J. Cretanovi, *J. Amer. Chem. Soc.*, **91**, 521 (1969); (g) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *ibid.*, **92**, 1399 (1970).

[3] For cyclobutane synthesis with ethylene, *cf.* (a) H.-D. Scharf and F. Korte, *Chem. Ber.*, **98**, 764 (1965); (b) *Angew. Chem., Int. Ed. Engl.*, **4**, 429 (1965); (c) Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966); (d) P. H. Nelson, J. W. Murphy, J. A. Edwards, and J. H. Fried, *J. Amer. Chem. Soc.*, **90**, 1307 (1968); (e) P. E. Eaton, Abstracts of Papers, 156th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; (f) P. E. Eaton and K. Nyi, *J. Amer. Chem. Soc.*, **93**, 2786 (1971); (g) W. C. Agosta and W. W. Lowrance, *Tetrahedron Lett.*, 3053 (1969).

[4] (a) D. C. Owsley and J. J. Bloomfield, *Org. Prep. Proced., Int.*, **3**, 61 (1971); (b) *J. Amer. Chem. Soc.*, **93**, 782 (1971).