Insertion Reactions of Nortricyclene with Ethyl Diazoacetate

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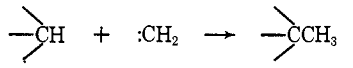
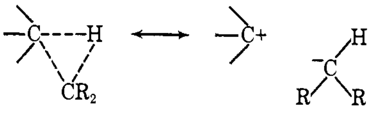
Abstract: Photolysis of ethyl diazoacetate in the presence of nortricyclene (**2**) led to a mixture of esters **3** and **4**. The diminished reactivity of the bridgehead CH bond supports a charge-separated mechanism. No insertion on the C–C bond of the three-membered ring was observed.

One of the more intriguing reaction types in organic chemistry is the insertion reaction of carbenes (*e.g.*, eq 1). The experiments of Doering and Knox[1] have yielded valuable information about the nature of the transition state of this "no-mechanism" reaction. In particular, it appears that charge separation is a useful hypothesis in the rationalization of the selectivity of various substituted carbenes toward primary, secondary, and tertiary carbon–hydrogen bonds.


(1)

Resonance forms of the type symbolized by **1** are expedient not only in providing a simple explanation of the relative reactivity of CH bonds, *i.e.*, primary < secondary < tertiary, but also in rationalizing the selectivity sequence: $(CH_3O_2C)_2C: > CH_3O_2CCH: \gg :CH_2$.[1]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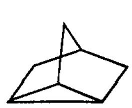
It was of interest to examine the validity of these generalizations in other systems in which predictions concerning the ease of charge separation could be made. Specifically, the relative reactivity of a proton affixed to a bridgehead was to be evaluated. Diminution of the normal tertiary reactivity would lend support to a polarized transition state owing to the known difficulty in developing positive charge at bridgehead positions.[2]

For several reasons, it was decided to examine the reaction of ethyl diazoacetate with nortricyclene (**2**). Ethyl diazoacetate was chosen as the carbene precursor owing to the anticipated ease of product identification, although the selectivity would be modest at best (tertiary/secondary ≡ 1.3[1]). Owing to symmetry, nortricyclene as a substrate is appealing since it has but three nonequivalent CH bonds. Additionally, the possibility of carbene insertion into the strained carbon–carbon bond of the three-membered ring[3] was not an unreasonable alternative reaction pathway of interest.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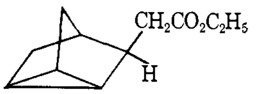
Results and Discussion

A complex mixture of products was obtained upon irradiation of ethyl diazoacetate in nortricyclene. Owing to the relatively minor amounts of some of the constituents, it was decided to synthesize the products of major interest for the purposes of identification. Accordingly, we undertook preparation of esters **3**, **4**, and **5**.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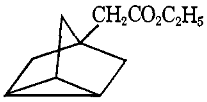
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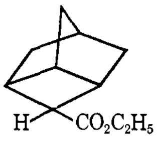
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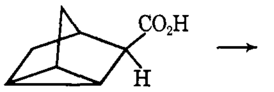
Ester **3** was readily available by homologation of 3-nortricyclenecarboxylic acid (**6**) *via* the Arndt–Eistert sequence.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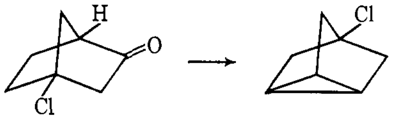
The availability of ester **4** depended on development of synthetic entries into the hitherto unknown 4-substituted nortricyclene system. 4-Chloronortricyclene (**8**) proved to be accessible *via* decomposition of the lithium salt of the *p*-tosylhydrazone[4] of 4-chloronorcamphor[5] (**7**). The appearance of typical nortricyclene absorptions in the infrared spectrum at $12.5\ \mu$[6] and the presence of two singlets of relative area 2:1 at 1.6 and 1.2 ppm[7] substantiated the structure of **8**. Metalation


7 **8**

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(1) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **83**, 1989 (1961).

(2) R. C. Fort and P. von R. Schleyer, "Advances in Alicyclic Chemistry," Vol. I, H. Hart and G. Karabatsos, Ed., Academic Press Inc., New York, N. Y., 1966, Chapter 5.

(3) One such insertion into a C–C bond has been reported by K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish [*Tetrahedron*, **21**, 2729 (1965)]. A 1% yield of bicyclo[1.1.1]pentane was reportedly formed from photolysis of diazomethane in bicyclo[1.1.0]butane.

(4) G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Am. Chem. Soc.*, **87**, 935 (1965).

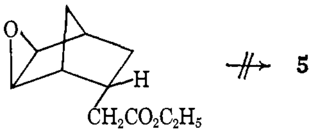
(5) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3998 (1961).

(6) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

(7) Nortricyclene shows three singlets at 1.2, 1.0, and 1.9 ppm in the area ratios of 6:3:1.

of **8** with lithium dispersion, followed by carboxylation and homologation, yielded ethyl 4-nortricyclylacetate (**4**) without complication.

Initial efforts to prepare 4-substituted derivatives of tricyclo[3.2.1.$0^{3,6}$]octane were patterned after the original synthesis of this system.[8] Treatment of the epoxy ester **9** with sodium hydride failed to yield significant amounts of material with the expected volatility. In a closely related sequence, the esters **10** underwent cyclization on treatment with potassium *t*-butoxide. Small amounts of olefinic products were removed by potassium permanganate treatment, and the residue consisted of a 3:1 mixture of tricyclic esters with the required elemental composition. Degradation of **5** to the known hydrocarbon[8] tricyclo[3.2.1.$0^{3,6}$]octane (**13**) *via* the Hunsdieker reaction and reduction of the bromide **12** (eq 2) established the structure of **5** beyond doubt. None of the isomeric hydrocarbon, tricyclo[3.3.0.$0^{3,7}$]-octane, was detected.[9]



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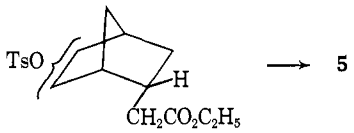

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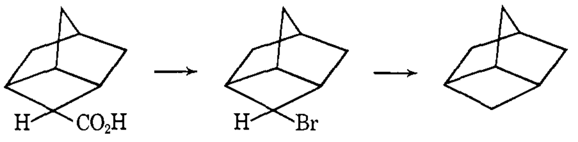


11 **12** **13**

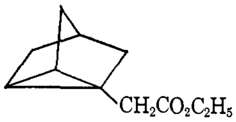
The relative amounts of esters **3** and **4** produced in the insertion reaction could now be evaluated. The observed ratio was found to be 14.8:1. The significance of this ratio can be best appreciated by a comparison with the "expected" ratio, calculated assuming normal reactivity of both types of hydrogens. This treatment yields a value of 4.6:1 for the predicted ratio of **3**:**4** taking into account both the statistical and the selectivity factors. These data suggest that either the methylene carbon-hydrogen bonds are unusually reactive or the bridgehead bond is unusually unreactive. A decision in favor of the latter alternative was made on the basis of the results of a competition experiment carried out with a mixture of nortricyclene and cyclohexane.

It was found that, in fact, the methylene groups of nortricyclene were less reactive than the methylene groups of cyclohexane by a factor of 0.67.

Clearly, the bridgehead C-H bond is unusually unreactive in nortricyclene. Steric considerations would lead one to expect at least no more hindrance to approach at this center than the corresponding bond in isobutane. The angular distortions in this system probably allow greater accessibility of this bond than in aliphatic counterparts.

An electronic rationale is favored, therefore, and the original arguments of Doering and Knox[1] seem well suited for this purpose.[10]

Although no insertion into the C-C bonds was observed, a third product was observed. It is presumed that this material has structure **14** (see Experimental Section). Insertion on the C-H bonds of the cyclopropyl ring would be expected to be even more unfavorable than insertion at the bridgehead owing to the well-known instability of cyclopropyl cations. Although there are three equivalent cyclopropyl C-H bonds, insertion at the bridgehead was evidently more favorable as seen from the ratio of **4**:**14** (*ca.* 1:2.8).



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Experimental Section

Analyses are by Micro-Tech Labs, Skokie, Ill. Infrared spectra were determined on a Perkin-Elmer Model 21 or a Beckman Model 5A spectrometer in carbon tetrachloride or as noted. Nuclear magnetic resonance spectra were obtained from a Varian Model A-60 spectrometer in carbon tetrachloride unless otherwise noted. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Gas chromatograms were determined on an Aerograph Model A 90-P instrument and a Barber-Colman Model 5000 instrument in the case of capillary chromatograms. Melting points were determined on a Mel-Temp apparatus and are uncorrected.

Reaction of Ethyl Diazoacetate with Nortricyclene (2). A solution of 0.057 g (0.5 mmole) of ethyl diazoacetate and 0.807 g (8.6 mmoles) of nortricyclene in two drops of pentane was irradiated with a sunlamp, type RS (275 w), for 4 hr. Nitrogen evolution had essentially ceased at this point. Analysis of the resulting mixture by gas chromatography (150 ft × 0.01 in. Apiezon L, 130°) revealed three major products in the ratios 15.0:5.3:78.6 (**14**:**4**:**3**). The same values ±0.5% were obtained in a second experiment.

Preparative gas chromatography on a 15-ft Carbowax column at 160° yielded sufficient amounts of **3**, **4**, and **14** for spectral purposes. The nmr and infrared spectrum of **3** matched those of the sample prepared below. The nmr spectrum of **4** coincided with that obtained for this compound from the route described below. The infrared spectrum of the compound assigned structure **14** showed a carbonyl absorption at 5.82 μ and a strong band at 9.72 μ. The nmr spectrum showed the ethyl quartet at 4.1 ppm and a singlet at 2.4 ppm which was assigned to the methylene group adjacent to the carbonyl function. Complex absorption extended from 2.2 to 1.0 ppm.

Reaction of Ethyl Diazoacetate with Cyclohexane and Nortricyclene. A mixture of 5.0 g (0.053 mole) of nortricyclene, 2.2 g (0.0265 mole) of cyclohexane, and 1.7 g (0.0158 mole) of ethyl diazoacetate was irradiated with the sunlamp for 18 hr. A stream of running water flowing over the reaction flask was used for cooling. Most of the cyclohexane was removed by distillation, and the resulting mixture was analyzed by gas chromatography. The area ratio of the ethyl cyclohexylacetate:ethyl 3-nortricyclylacetate peak was 2.4:1. The molar ratio was calculated to be 60:40, respectively, based on comparisons with relative areas of a weighed mixture of the two. The identity of ethyl cyclohexylacetate was established by comparison of nmr and infrared spectra of a collected sample with those of an authentic sample.[1]

4-Chloronorcamphor Tosylhydrazone. A solution of 37.2 g (0.20 mole) of tosylhydrazine in 100 ml of hot glacial acetic acid was added in portions to a solution of 60 g (0.41 mole) of crude 4-

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(8) R. R. Sauers and R. A. Parent, *J. Org. Chem.*, **28**, 605 (1963); R. R. Sauers, R. A. Parent, and S. B. Damle, *J. Am. Chem. Soc.*, **88**, 2257 (1966).

(9) P. K. Freeman, V. N. M. Rao, and G. E. Bigam, *Chem. Commun.*, **21**, 511 (1965).

(10) Similar conclusions were reached by M. R. Willcott, III, Ph.D. Thesis, Yale University, 1963.

chloronorcamphor (7)[11] in 50 ml of glacial acetic acid. There was obtained a crystalline precipitate on standing overnight at room temperature. The product was removed by filtration and washed with water. Recrystallization from ethanol–water gave 40 g (70%) of 4-chloronorcamphor tosylhydrazone, mp 176–178°.

Anal. Calcd for $C_{14}H_{17}O_2SCl$: C, 53.75; H, 5.44; N, 8.93. Found: C, 53.73; H, 5.45; N, 8.90.

4-Chloronortricyclene (8). A solution of 35 ml of 1.6 *N* *n*-butyllithium in hexane (*ca.* 0.056 mole) was injected through a serum cap over 5 min into a stirred slurry of the tosylhydrazone (15.65 g, 0.055 mole) in 200 ml of dry tetrahydrofuran. A nitrogen atmosphere was maintained throughout, and the temperature was kept at 0–5° during the addition and for 0.5 hr afterward. Stirring at room temperature for 0.5 hr was followed by evaporation of the solvent on a rotary evaporator at 40° (0.5 mm). The salt was then pyrolyzed by gradually raising the temperature to 175–225° whereupon 4-chloronortricyclene distilled from the flask. The vapors were condensed in a Dry Ice trap and distilled to give 4.0 g (62%) of 4-chloronortricyclene, bp 142–144°, n^{25}D 1.4814.

Anal. Calcd for C_7H_9Cl: C, 65.37; H, 7.00; Cl, 27.62. Found: C, 65.10; H, 7.19; Cl, 27.47.

The nmr spectrum displayed two singlets of relative area 2:1 at 1.6 and 1.2 ppm, respectively. Selected infrared bands appeared at 3.29 (w), 8.03 (s), and 9.95 (s) μ.

4-Nortricyclenecarboxylic Acid. To a refluxing mixture of *ca.* 3.0 g (0.22 g-atom) of lithium dispersion[12] and 25 ml of dry cyclohexane was added 5.14 g (0.04 mole) of 4-chloronortricyclene in 15 ml of cyclohexane. The addition required 0.5 hr, and the resulting mixture was heated at reflux for an additional 5 hr. The cooled mixture was poured over crushed Dry Ice and allowed to stand for several hours. The mixture was then cautiously treated with water followed by dilute hydrochloric acid. The liberated acid was extracted into methylene chloride which was washed with water and dried. Evaporation of the extract yielded 4.5 g of crude acid which was purified by crystallization from methylene chloride–pentane. White needles, mp 156–158°, were obtained in 67% (3.7 g) yield.

Anal. Calcd for $C_8H_{10}O_2$: C, 69.56; H, 7.24. Found: C, 69.33; H, 7.35.

The infrared spectrum (Nujol) of this product showed carbonyl absorption at 5.90 μ and the typical broad absorption for the hydroxyl group centered at 3.0 μ. The nmr spectrum ($CHCl_3$) displayed singlets at 1.6 (6 H), 1.2 (3 H), and 11.3 (1 H) ppm.

Ethyl 4-Nortricyclylacetate (4). A mixture of 3.2 g (0.023 mole) of the acid was heated at reflux for 3 hr with 20 ml of thionyl chloride. The excess thionyl chloride was removed *in vacuo*, and the residue was distilled to give 2.6 g (72%) of 4-nortricyclenecarbonyl chloride, bp 47° (4 mm).

To a cold solution containing approximately 6 g of diazomethane and 1.6 g of triethylamine in 500 ml of dry ether was added 2.5 g (0.016 mole) of the acid chloride over a period of 15 min. The resulting mixture was stirred for 2 hr at 0° and overnight at room temperature. Excess diazomethane was removed by passing a stream of nitrogen through the solution. The amine hydrochloride was removed by filtration, and the ether was evaporated to yield a yellow oil.

The crude diazo ketone in 10 ml of ethanol was added dropwise to a refluxing mixture of 1.5 g of silver oxide in 20 ml of ethanol. A second 1.5-g portion of silver oxide was added portionwise during the addition of the diazo ketone. The additions required 0.5 hr and reflux was continued for a 2-hr period beyond. The cooled solution was filtered and diluted with 200 ml of water. The product was extracted into pentane which was washed with sodium bicarbonate solution and water and dried over magnesium sulfate. The pentane was evaporated, and the residue was distilled to give 1.78 g (62%) of ester **4**, bp 64–66° (1.5 mm).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.24; H, 8.94. Found: C, 73.43; H, 9.07.

The infrared spectrum showed bands at 3.30 (m) and 5.78 (s) μ. The nmr spectrum displayed a quartet (2 H) at 4.0, a singlet (2 H) at 2.4, and two singlets at 1.3 and 1.1superimposed on a triplet at *ca.* 1.2 ppm (12 H).

Ethyl 3-Nortricyclylacetate (3). 3-Nortricyclenecarbonyl chloride, bp 49–50° (4 mm), was prepared in 83% yield by heating 3-nortricyclenecarboxylic acid (7.0 g) with 25 ml of thionyl chloride for 3 hr followed by distillation. The acid chloride (3.9 g) was converted to the diazo ketone by the procedure mentioned. Treatment with silver oxide gave 2.7 g (60%) of the desired ester **3**, bp 80–81° (2.5 mm).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.24; H, 8.94. Found: C, 73.41; H, 9.11.

The infrared spectrum showed bands at 3.23 (m), 5.75 (s), 9.72 (s), and 12.52 (s) μ. The nmr spectrum showed a quartet (2 H) at 4.1 and complex absorption (14 H) between 2.2 and 0.9 ppm.

Ethyl Tricyclo[3.2.1.$0^{3,6}$]octane-4-carboxylate. A mixture of 5-norbornene-2-acetic acids was converted to ethyl esters,[13] bp 68–70° (0.25 mm), *via* the acid chlorides. Hydroboration of the mixture was effected by addition of 15 ml of 1 *M* BH_3 in tetrahydrofuran to a solution of 7.2 g (0.04 mole) of esters in 10 ml of tetrahydrofuran at 0–5°. The addition time was 1 hr. After stirring for 2 hr at 0° and 1 hr at 25°, the mixture was treated with 5 ml of 30% hydrogen peroxide and 13 ml of 1 *M* sodium hydroxide solution at 5–15°. After an additional 2-hr stirring at 5°, excess water was added, and the mixture was extracted with ether. The dried extracts were distilled to give 5.6 g (71%) of mixed hydroxy esters, bp 107–108° (0.2 mm). The infrared spectrum of the mixture showed hydroxyl and carbonyl absorption at 2.97 and 5.84 μ, respectively.

The mixture of alcohols was converted to *p*-toluenesulfonate esters by treatment with tosyl chloride in pyridine. From 11.88 g of alcohols there was obtained 20.3 g of crude tosylates.[10]

Cyclization was effected by treatment of 5.7 g (0.016 mole) of tosylates with 1.79 g (0.016 mole) of potassium *t*-butoxide in 200 ml of benzene at 25°. The mixture was stirred overnight after which the benzene was washed with water and dried over magnesium sulfate. Evaporation of the benzene gave 1.4 g of an oil, bp 75–120° (0.25 mm). From two other runs there was obtained 12 g of this material. This fraction was washed with hot potassium permanganate solution to remove unsaturates. Distillation gave 3.0 g (12%) of the tricyclic esters, bp 82–85° (0.2 mm). A second fraction boiling from 85 to 110° (0.2 mm) was essentially pure ester.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.24; H, 8.94. Found: C, 73.17; H, 8.97.

The infrared spectrum showed a carbonyl stretching band at 5.85 μ. The nmr spectrum displayed a quartet at 4.1, broad multiplets at 3.1 and 2.5, a sharp singlet at 2.2, and complex absorptions between 1.7 and 1.1 ppm. Capillary gas chromatography (150 ft × 0.01 in. Apiezon L, 140°) indicated two components in an area ratio of *ca.* 3:1.

4-Tricyclo[3.2.1.$0^{3,6}$]octanecarboxylic Acid (11). Hydrolysis of the ester (2.8 g) was effected by treatment with 1.7 g of potassium hydroxide in 50% aqueous ethanol for 7 hr at reflux. Evaporation of most of the ethanol was followed by acidification and ether extraction to yield 2.2 g (93%) of crude acid. After crystallization from pentane and sublimation the acid had mp 76–78°.

Anal. Calcd for $C_9H_{12}O_2$: C, 71.05; H, 7.89. Found: C, 71.16; H, 7.99.

The nmr spectrum ($CHCl_3$) showed a singlet at 11.9 (1 H), a crude triplet at 3.1 (1 H), broad singlet at 2.5 (3 H), sharp singlet at 2.3 (1 H), and broad singlets at 1.6 (4 H) and 1.3 (2 H) ppm.

4-Bromotricyclo[3.2.1.$0^{3,6}$]octane (12). The silver salt of the acid **11** was prepared by treatment of 2.0 g (0.013 mole) of acid in 20 ml of water with sufficient ammonium hydroxide to effect salt formation. The excess ammonia was removed by gentle heating, and the silver salt was precipitated by addition of a solution of 2.2 g (0.013 mole) of silver nitrate in 30 ml of water. The salt was collected on a filter and washed with water, ether, and alcohol. After drying overnight at 115°, the weight of salt was 3.0 g. This product was suspended in 50 ml of dry petroleum ether (bp 30–60°) and cooled to −10°. Bromine (2.0 g, 0.012 mole) in 10 ml of petroleum ether was added dropwise with stirring, and the resulting mixture was stirred at −10° for 1 hr. After an additional hour at 25° and one at reflux the mixture was filtered to remove the salts. Distillation gave 0.72 g (29%) of the bromide, bp 52° (2.2 mm).

Anal. Calcd for $C_8H_{11}Br$: C, 51.38; H, 5.88; Br, 42.73 Found: C, 51.52; H, 6.16; Br, 42.38.

Strong infrared absorptions appeared at 8.12, 8.48, 9.93, 11.0, 13.0, and 14.4 μ. The nmr spectrum showed a sharp singlet at 3.8, a broad singlet at 3.4, and complex absorption extending from 3.0 to 1.0 ppm. Based on the total integrated area, the two low-field peaks accounted each *ca.* 0.8 proton. It is not unlikely that a mixture of bromides was present.

Tricyclo[3.2.1.$0^{3,6}$]octane (13). To a stirred suspension of 0.50 g of sodium in 15 ml of liquid ammonia was added 0.60 g of bromide **12**. The mixture was allowed to warm to room temperature at

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(11) Prepared from 1-chloronorbornane by the method of J. Bredt and P. Pinten, *J. Prakt. Chem.*, **115**, 45 (1927). From 60 g of 1-chloronorbornane was obtained 60 g of crude 7.

(12) Available as a 50% slurry in hexane.

(13) K. Alder and E. Windemuth, *Ber.*, 71, 1939 (1938).

which time 75 ml of pentane was added followed by dropwise addition of water. The pentane layer was separated and dried over magnesium sulfate. The pentane was evaporated to yield an oil. Essentially one peak was present on a gas chromatogram on a 15-ft Carbowax column at 90°. A 60-mg sample was collected and submitted to nmr analysis. The spectrum was identical with that of a sample prepared earlier.[8]

Acknowledgments. We wish to acknowledge the generous financial support of the National Institutes of Health (GM 8701). We are also indebted to Mrs. Nancy Crowder Roberts who initiated some of the experiments in this project. For a generous gift of nortricyclene, we are indebted to Mr. W. Washburn.

On the Chemistry of Reactions Proceeding inside Molecular Aggregates

F. M. Menger and Carolyn E. Portnoy

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322. *Received April 7, 1967*

Abstract: The rate constants for basic hydrolysis of *p*-nitrophenyl acetate, mono-*p*-nitrophenyl dodecanedioate, *p*-nitrophenyl octanoate, and benzoylcholine chloride (two neutral and two ionic substrates) were determined in surfactant solutions containing varying amounts of either laurate anion, *n*-dodecyltrimethylammonium cation, or *n*-dodecylpyridinium cation. Laurate inhibits hydrolysis of all four esters, *n*-dodecyltrimethylammonium cation enhances the rates, and *n*-dodecylpyridinium cation has very little effect. A kinetic scheme is proposed for the laurate system which involves partitioning of the substrates between the solution and the micellar phases. It is possible to evaluate both the substrate–micelle association constants (which are very large numbers and exceed those for many enzyme-specific substrate complexes) and the rate constants for adsorbed ester (which are within experimental error of zero). The kinetic data are discussed in terms of the complex structure of micelles.

The living cell contains a large number of particles composed of aggregates of molecules.[1] The particles associate to form subcellular bodies such as mitochondria and chloroplasts. Thus, life processes proceed mainly within complicated assemblages of molecules rather than in the free solution (where control of the reactions would be difficult). A knowledge of chemical behavior inside molecular aggregates is essential to the understanding of these highly organized biological processes. Consequently we have begun a study of the subject and present our initial results in this paper. The report concerns reactions occurring inside one particular type of biologically important aggregate,[2] the micelle. Micelles are formed in aqueous solutions by surfactants, which are compounds possessing a water-solubilizing moiety (often an ionic group) and a water-insoluble portion (a long hydrocarbon chain). Micelles are spherical aggregates, of 30 or more molecules, containing hydrocarbon interiors and ionic surfaces.[3]

Several examples have appeared recently of organic reactions whose rates are perturbed by the presence of small quantities of surfactant. The acid hydrolysis of benzylideneaniline to benzaldehyde and aniline is inhibited by cetyltrimethylammonium bromide.[4] Duynstee and Grunwald[5] showed that surfactants affect the rate of dye fading, and Kurz[6] found that acid-catalyzed hydrolysis of long-chain sodium alkyl sulfates is accelerated, and base-catalyzed hydrolysis inhibited, by micellation. Other reactions that have been studied in the presence of surfactants include the hydrolysis of Schiff bases[7] and esters,[8] the reaction of 1-fluoro-2,4-dinitrobenzene with amines,[9] and porphyrin–metal interaction.[10] Letsinger and Wagner[11] used cationic and anionic surfactants to regulate the rate of reaction of a polyuridylic acid derivative.

In this paper we elucidate the dependence of the rate constants for basic hydrolysis of four substrates A–D on the concentration of each of the three surfactants E–G. We selected ester hydrolysis for study because it can be followed spectrophotometrically at very low substrate concentrations where the structure of the micelles, formed by the surfactants, is not

Substrates	Surfactants
$CH_3COOC_6H_4NO_2$ A	$^{-}OOC(CH_2)_{10}CH_3$ E
$^{-}OOC(CH_2)_{10}COOC_6H_4NO_2$ B	$(CH_3)_3N^+(CH_2)_{11}CH_3$ F
$CH_3(CH_2)_6COOC_6H_4NO_2$ C	$C_5H_5N^+(CH_2)_{11}CH_3$ G
$(CH_3)_3N^+CH_2CH_2OOCC_6H_5$ D	

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