(CHO, $J = 1$ Hz), 1.02 ($CH_3$ doublet, $J = 7$ Hz), 1.00 ($CH_3$ doublet, $J = 7$ Hz), and 0.97 ppm ($CH_3$ doublet, $J = 6$ Hz).

*Anal.* Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.7; H, 11.15.

**B. Moffatt Reagent.**[7]—A solution of 598 mg of alcohol **4**, 285 mg of pyridinium trifluoroacetate, and 1.44 g of dicyclohexylcarbodiimide in 4.6 ml of benzene and 4.6 ml of dimethyl sulfoxide was stirred at room temperature for 12 hr. Ethyl acetate (25 ml) followed by 1 g of oxalic acid in 8 ml of methanol was added and after 0.5 hr of stirring the product was isolated with hexane and distilled affording 608 mg of aldehyde **5** contaminated with a small amount of dicyclohexylurea.

**Oxidation of Aldehyde 5. Ketones 6 and 7.**—A mixture of 465 mg of aldehyde **5** and 200 mg of powdered KOH in 20 ml of *tert*-BuOH was vigorously stirred under an oxygen atmosphere for 0.5 hr.[8] The product was isolated with hexane and distilled affording 213 mg (48%) of a nearly 1:1 mixture of ketones **6** and **7**:[12,13] bp 107° (bath temperature) (0.1 mm); $\lambda_{\max}^{\text{film}}$ 5.88, 8.61 $\mu$m; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 2.06 ($CH_3CO$), 2.05 ($CH_3CO$), 1.17–0.84 ppm ($CH_3$ doublets). Replicate C and H analyses on a purified sample of this mixture showed successively decreasing carbon percentages indicative of rapid oxygen uptake.

**Oxidation of Ketones 6 and 7. Esters 8 and 9.**—A solution of NaOBr was prepared from 1.36 g of NaOH in 11.8 ml of water, 1.41 g of bromine, and 7.7 ml of dioxane. This cold (0°) solution was added with stirring to 510 mg of ketone mixture **6** and **7** in 35.5 ml of dioxane and 10.5 ml of water at 0°. After 3 hr a solution of 0.56 g of sodium sulfite in 5.6 ml of water was added. The solution was poured into 15 ml of 10% NaOH and washed with ether. The aqueous phase was acidified with dilute sulfuric acid and the product was isolated with ether affording the crude acid which was directly esterified with ethereal diazomethane to give 157 mg (29%) of an 85:15 mixture[14] of esters **8** and **9**: bp 110° (bath temperature) (0.05 mm); $\lambda_{\max}^{\text{film}}$ 5.78, 7.00, and 8.60 $\mu$m; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 3.56 ($CH_3O$), 1.02 ($CH_3$ doublet, $J = 7$ Hz), and 0.97 ppm ($CH_3$ doublet, $J = 7$ Hz).

Equilibration in refluxing methanolic sodium methoxide (0.4 *M*) afforded a 50:50 mixture. The equilibrium mixture of these esters was separated *via* preparative gas chromatography[15] ($t_R$ of **8**:**9** = 1.1).

**Ester 8:** $\lambda_{\max}^{\text{film}}$ 5.78, 6.92, 7.00, 8.59, and 9.75 $\mu$m; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 3.56 ($OCH_3$), 1.02 ($CH_3$ doublet, $J = 7$ Hz), and 0.96 ppm ($CH_3$ doublet, $J = 7$ Hz).

*Anal.* Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.8; H, 10.1.

**Ester 9:** $\lambda_{\max}^{\text{film}}$ 5.77, 6.92, 7.00, 8.62, and 9.63 $\mu$m; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 3.56 ($OCH_3$), 1.00 ($CH_3$ doublet, $J = 7$ Hz), and 0.94 ppm ($CH_3$ doublet, $J = 6$ Hz).

*Anal.* Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.4; H, 10.1.

**Guaiol (1) and Epiguaiol (10). A. From Ketones 6 and 7.**—To a stirred solution of 1.10 g of ketones **6** and **7** (1:1 mixture) in 50 ml of ether was added 10 ml of 1.6 *M* ethereal methyllithium. After 1 hr, 2 ml of water was carefully added and the product was isolated with ether. Low temperature crystallization from hexane yielded 342 mg of guaiol (**1**): mp 82–85°; $\lambda_{\max}^{\text{KBr}}$ 3.00, 7.37, 8.69, 8.70, 10.03, 10.41, 10.80, 10.97, 11.36, and 12.18 $\mu$m; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.18 ($CH_3$), 0.98 ($CH_3$ doublet, $J = 7.5$ Hz), and 0.96 ppm ($CH_3$ doublet, $J = 7$ Hz).

From the mother liquor was obtained an enriched sample (75%) of epiguaiol (**10**) which was purified by preparative gas chromatography[16] ($t_R$ of **1**:**10** = 0.92): $\lambda_{\max}^{\text{film}}$ 2.95, 6.85, 7.32, 8.82, 10.79, and 11.14 $\mu$m; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.19 ($CH_3$), 1.04 ($CH_3$ doublet, $J = 7$ Hz), and 1.03 ppm ($CH_3$ doublet, $J = 6$ Hz).

*Anal.* Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.9; H, 11.8.

**B. From Esters 8 and 9.**—A purified sample of ester **8** (10 mg) was treated with ethereal methyllithium (1.0 ml of 1.6 *M*) as described above affording 9.6 mg (96%) of guaiol (**1**) identified by spectral comparison.

A sample of ester **9** when similarly treated afforded epiguaiol (**10**) identified by spectral comparison with the aforementioned sample.

**Registry No.**—**1**, 489-86-1; **4** (11*R*), 30166-94-0; **4** (11*S*), 30166-99-5; **5** (11*R*), 30166-95-1; **5** (11*S*), 30167-00-1; **6**, 30246-75-4; **7**, 30246-76-5; **8**, 30166-96-2; **9**, 30166-97-3; **10**, 30166-98-4.

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[12] This ratio was determined by gas chromatographic analysis of the alcohols secured through addition of ethereal methyllithium to this mixture.

[13] A 22 ft × 1/8 in. column of 1% Carbowax 20M on 80–100 mesh CG, AW-DMCS, was used.

[14] A 15 ft × 1/8 in. column of 3% FFAP on Chromosorb G, 70–80 mesh AW-DMCS, was used for this analysis.

[15] A 15 ft × 3/8 in. column of 6% FFAP on 60–80 mesh Chromosorb G-NAW was used.

[16] A 15 ft × 0.25 in. column of 24% 1:4 KOH–Carbowax 20M on 60–80 mesh Chromosorb G was used for the separation.

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## Inhibition of the Hydrolysis of Bis-2,4-dinitrophenyl Phosphate by a Nonionic Detergent[1]

C. A. Bunton,*[2] A. Kamego, and L. Sepulveda

*Department of Chemistry, University of California, Santa Barbara, California 93106, and Faculty of Chemistry and Pharmacy, University of Chile, Santiago, Chile*

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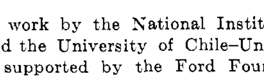
There are many examples of catalysis or inhibition by micellized detergents, and they generally follow the simple electrostatic rules put forward by Hartley to explain equilibrium effects (for reviews, see ref 3-5). In agreement with these rules, nonionic detergents generally have only small effects upon the rates of ionic reactions.[3-5] However, micellar effects depend very markedly upon hydrophobic interactions, and a few reactions between an ionic reagent and an uncharged substrate are inhibited by nonionic micelles,[6,7] probably because the substrate becomes buried in the interior of the micelle.

We unexpectedly observed that the reaction of hydroxide ion with bis-2,4-dinitrophenyl phosphate monoanion is strongly inhibited by Igepal,[8] and we suggested that despite its negative charge the ionic substrate is

$$(ArO)_2PO_2^- + OH^- \xrightarrow{k_1} ArO^- + ArOPO_3^{2-}$$

$$ArOPO_3^{2-} \xrightarrow{k_2} ArO^- + PO_3^- \longrightarrow HPO_4^{2-}$$



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incorporated strongly into the nonionic micelle and protected by it from hydroxide ion. (Igepal is a polyoxyethylene dinonylphenol with 24 ethylene oxide units).

The spontaneous hydrolysis of 2,4-dinitrophenyl phosphate dianion is unaffected by nonionic micelles of Igepal[9] and in their presence is much faster than the first step of the reaction, the attack of hydroxide ion upon the diaryl phosphate monoanion.

The aim of the present work was to find out whether other nonionic detergents had the same kinetic effect as Igepal and, if possible, to find evidence for incorporation of the substrate into the micelle. The general methods for demonstrating micellar incorporation, *e.g.*, column chromatography[10] or solubility,[11] were unsatisfactory, and we therefore fell back on the observation that mixtures of water and Triton X-114 separated into two phases with an increase in temperature.[12] (Triton X-114 is a polyoxyethylene octylphenol, with 7–8 ethylene oxide units.) Aqueous Igepal does not give this phase separation at a low temperature.

The detergent-rich phase contains 20% by weight of the detergent, whereas the water-rich phase contains only the critical micelle concentration of the detergent ($2.5 \times 10^{-4}$ *M*).[12] When bis-2,4-dinitrophenyl phosphate was dissolved in a 10% (by weight) aqueous solution of Triton X-114 and the temperature was raised to 40°, approximately 90% of the diaryl phosphate was found in the detergent-rich layer, indicating strong interactions between the phosphate monoanion and the detergent.

Triton X-114 retards the attack of hydroxide ion upon bis-2,4-dinitrophenyl phosphate monoanion (Table I). This rate retardation is very similar to that observed with Igepal,[8] although slightly smaller, probably because of the shorter side chain of Triton. The loss of hydration of the relatively hydrophobic anionic phosphate ester in incorporation into a nonionic micelle is apparently more than offset by the hydrophobic binding of the nonpolar aryl groups with the micelle. Micelles of both Igepal and Triton X-114 appear to contain a considerable amount of water in their interiors[12] which could assist incorporation of the diaryl phosphate monoanion.

TABLE I
EFFECT OF TRITON X-114 UPON THE REACTION OF BIS-2,4-DINITROPHENYL PHOSPHATE WITH HYDROXIDE ION[a]

| $C_D$, *M* | $10^5K$, sec$^{-1}$ |
|---|---|
| | 3.0[b] |
| 0.005 | 0.54 |
| 0.010 | 0.43 |
| 0.025 | 0.32 |

[a] At 25.0° in 0.01 *M* NaOH. The concentration of Triton ($C_D$) is calculated on the assumption that it contains 7 ethylene oxide units. [b] Reference 8.

### Experimental Section

**Kinetics.**—The reaction was followed spectrophotometrically using a Cary 11 spectrophotometer with a water-jacketed cell at 25.0°. The preparation of the materials and the kinetic solutions has already been described.[8] Triton X-114 was used without purification, and we are indebted to Rohm and Haas for a sample of it. The first-order rate constants, $k_1$, for the attack of hydroxide ion upon bis-2,4-dinitrophenyl phosphate monoanion are in reciprocal seconds. Solutions containing less than $5 \times 10^{-3}$ *M* Triton were turbid and were not used for kinetic experiments. The rate constants were cleanly first order for 3 half-lives, indicating that the second step of the overall reaction, the hydrolysis of 2,4-dinitrophenyl phosphate dianion is much faster than the first step. (Igepal has little effect upon the hydrolysis of the dianion.[9])

**Phase Separation.**—Bis-2,4-dinitrophenyl phosphate (pyridinium salt, 5 mg) was dissolved in 50 ml of a 10 wt % aqueous solution of Triton X-114, and the mixture heated to 40°. Phase separation occurred,[12] portions (5 ml) of each phase were removed, and the diaryl phosphate was completely hydrolyzed. The concentration of 2,4-dinitrophenol, determined spectrophotometrically as phenoxide ion at 3580 Å in the water-rich phase was $0.28 \times 10^{-4}$ *M*, and in the detergent-rich phase it was $3.03 \times 10^{-4}$ *M*.

**Registry No.**—Bis-2,4-dinitrophenyl phosphate, 18962-97-5; hydroxide ion, 14280-30-9.

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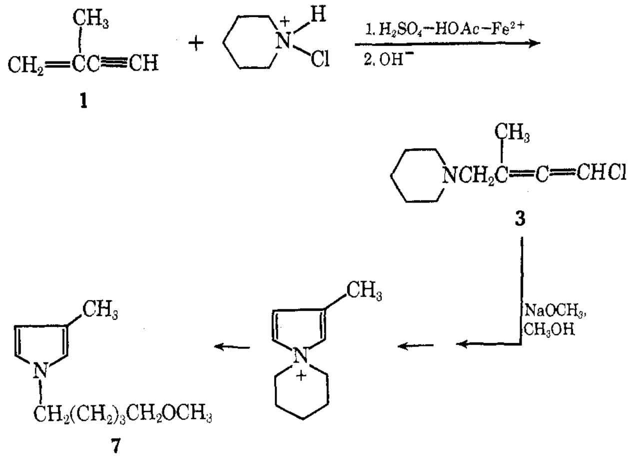
## Radical Addition of Protonated *N*-Chloropiperidine to Conjugated Enynes

MARVIN L. POUTSMA* AND PEDRO A. IBARBIA

*Union Carbide Research Institute,*
*Union Carbide Corporation, Tarrytown, New York 10591*

*Received February 8, 1971*

As part of a general survey of radical additions to conjugated enynes,[1] we have briefly examined the addition of *N*-chloropiperidine in acidic solution to 2-methyl-1-buten-3-yne (**1**), 1-penten-3-yne (**2**), and 1-buten-3-yne. Additions of *N*-chloramines in acidic media to olefins, allenes, and conjugated dienes have been studied extensively by Neale[2] and are believed to involve aminium cation radicals ($R_2\overset{+\cdot}{N}H$) as the chain-carrying species. Although the polar character of the



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