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 (2.5×10^{-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

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.

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.

(9) C. A. Bunton, E. J. Fendler, L. Sepulveda, and K-U. Yang, *J. Amer. Chem. Soc.*, **90**, 5512 (1968).

(10) D. G. Herries, W. Bishop, and F. M. Richards, *J. Phys. Chem.*, **68**, 1842 (1964); R. B. Dunlap and E. M. Cordes, *J. Amer. Chem. Soc.*, **90**, 4395 (1968); L. R. Romsted and E. M. Cordes, *ibid.*, **90**, 4404 (1968).

(11) C. A. Bunton and L. Robinson, *ibid.*, **90**, 5972 (1968).

(12) L. Sepulveda and F. MacRitchie, *J. Colloid Interface Sci.*, **28**, 19 (1968).

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 5×10^{-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 0.28×10^{-4} *M*, and in the detergent-rich phase it was 3.03×10^{-4} *M*.

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

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

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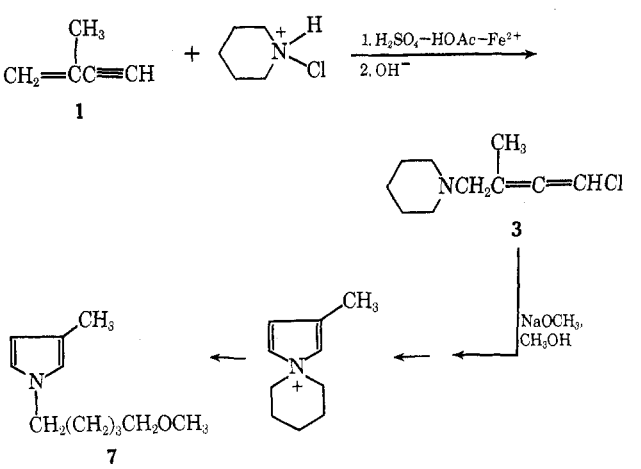
As part of a general survey of radical additions to conjugated enynes,[1] we have briefly examined the addition of *N*-chloropiperidine in acidic solution to 2-methyl-1-buten-3-yne (**1**), 1-penten-3-yne (**2**), and



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 ($R_2\dot{N}H$) as the chain-carrying species. Although the polar character of the

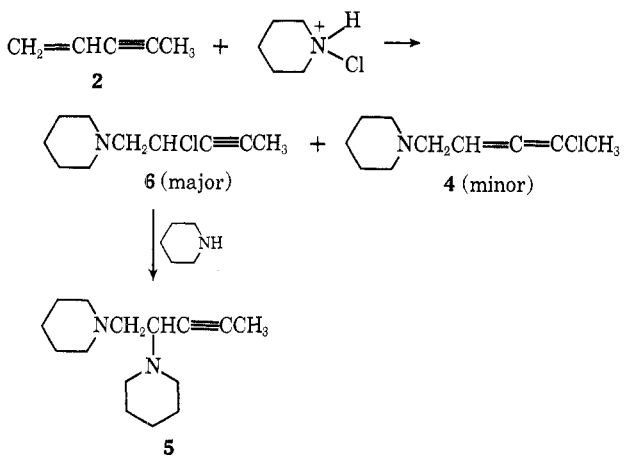
(1) M. L. Poutsma and P. A. Ibarbia, *J. Org. Chem.*, **35**, 4038 (1970).

(2) R. S. Neale, *ibid.*, **32**, 3263 (1967).

reaction medium (4 M sulfuric acid in acetic acid), the method of mixing reactants (enyne:$R_2\overset{+}{N}HCl$ < 1 during most of the reaction), and the work-up procedure are such as not to allow us to be absolutely certain that the isolated products are those of kinetic control, the nature of the products is of some synthetic interest.

Reaction of enyne **1** and N-chloropiperidine proceeded smoothly with use of a catalytic amount of ferrous ion to give as the only isolable basic product a 1,4 adduct, 1-chloro-3-methyl-4-piperidino-1,2-butadiene (**3**), in 70–75% yield. Similar structures lacking the 3-alkyl group, *i.e*, 1-bromo-4-dialkylamino-1,2-butadienes, have been prepared previously by treatment of the bromination product of vinylacetylene (largely $BrCH_2CH{=}C{=}CHBr$) with secondary amines.[3]

Parallel reaction with enyne **2** gave 60–65% crude basic product whose spectral properties and distillation range indicated a complex mixture. The most and least volatile components were each isolated by distillation in 85–90% purity. Spectral and analytical data allowed their assignment as the 1,4 adduct, 4-chloro-1-piperidino-2,3-pentadiene (**4**) (low yield) and 4,5-bispiperidino-2-pentyne (**5**). Fractions of intermediate boiling point showed spectral evidence for hydroxyl and acetoxy groups in addition to piperidino groups. Therefore, on the hypothesis that the initial product was largely the 1,2 adduct, 4-chloro-5-piperidino-2-pentyne (**6**), which largely solvolyzed during basification and work-up, the reaction was repeated except that excess piperidine was added after reaction but before basification. Under these conditions diamine **5** was indeed isolated in 47% yield along with again a small amount of allene **4**.



Reaction with vinylacetylene gave only 30% crude basic product which largely decomposed on attempted distillation in contrast to the adducts from **1** and **2**. Nmr evidence tentatively suggests that the basic product was >50% the 1,4 adduct, 1-chloro-4-piperidino-1,2-butadiene, but this product could not be purified. Reaction with 2-penten-4-yne also gave only a moderate amount of basic product which was not successfully purified or identified.

In the context of our previous discussion[1] concerning the factors affecting orientation in radical addition to enynes,[4] the conversion of enyne **1** to allene **3** is unusual in that an allenic product is the *major* product from an atom transfer reaction to a propargylic radical.[5] However, since it has not been rigorously demonstrated that the isolated products are those of kinetic control, mechanistic conclusions should be drawn with caution. It is nevertheless true that an added electrostatic factor is operative in the present system which would be expected to favor 1,4 over 1,2 addition; *i.e.*, approach of the positively charged atom transfer agent ($R_2\overset{+}{N}HCl$) at the site farthest removed from the positively charged substituent in the intermediate propargylic radical [$C_5H_{10}\overset{+}{N}HCH_2\dot{C}(CH_3)C{=}CH$] should be favored from coulombic considerations.

Treatment of adduct **3** with sodium methoxide in refluxing methanol led to formation in moderate yield of 1-(5′-methoxypentyl)-3-methylpyrrole (**7**); the assignment as a 1,3-dialkylpyrrole was unambiguous based on the uv and nmr spectral behavior in strong acid compared to nonpolar solvents.[6,7] This initially surprising rearrangement has analogy in the conversion of 1-bromo-4-dialkylamino-1,2-butadienes[3] to pyrroles by treatment with excess amine, a reaction which proceeds *via* an intermediate propargylic amine [$C{\equiv}CC(NR_2)CNR_2$];[8] similarly, acetylenic aminohydrins [$C{\equiv}CC(OH)CNR_2$] can be converted to pyrroles.[9]

Experimental Section

All ir and nmr spectra were taken in carbon tetrachloride unless otherwise specified. Preparation of the enynes has been described.[1] A typical preparation of N-chloropiperidine follows.[2] A solution of 17.0 g (0.20 mol) of piperidine in 100 ml of ether was stirred for 1 hr with a suspension of 28.4 g (0.21 mol) of N-chlorosuccinimide. The mixture was washed with water and with 2.5 N sulfuric acid, dried, and evaporated to leave 19.0 g (0.16 mol) of crude chloramine which was dissolved in a cooled mixture of 75 ml of sulfuric acid and 260 ml of acetic acid for subsequent use.

Addition of N-Chloropiperidine to 2-Methyl-1-buten-3-yne (1).—To a stirred solution of the chloramine (0.16 mol) in sulfuric acid–acetic acid was added dropwise 11.2 g (0.17 mol) of enyne **1**. A few crystals of ferrous ammonium sulfate were added after *ca.* 1 g of **1** had been introduced; from that point on, external cooling was needed to maintain a temperature of <30°. After addition of **1** was complete, the mixture was stirred 30 min before it was poured into 600 ml of water and 200 g of ice. Extraction with pentane gave 0.7 g of neutral product. The aqueous solution was carefully neutralized with 12 M sodium hydroxide solution. Extraction with ether gave, after drying and evaporation, 21.7 g of crude basic adduct (73%). Distillation through an 18-in. spinning-band column gave 12.7 g of adduct **3**: bp 50–51° (0.1 mm); $n^{22}D$ 1.5093; ir 1960 cm^{-1} (C=C=C); nmr δ 5.92 (m, =CHCl), 2.88 (d, $J \sim 1.7$ Hz, $R_2NCH_2C{=}$), 2.35 (br m, CH_2NCH_2), 1.97 (d, $J \sim 2$ Hz, $CH_3C{=}$), and 1.48 ppm (br m, ring CH_2). Ir and nmr spectral comparison showed that distillation had achieved negligible purification and that the crude adduct was >95% pure. Adduct **3** was analyzed as its cyrstalline picrate, mp 91–92° (95% ethanol).

(3) M. V. Mavrov, E. S. Voskanyan, and V. P. Kucherov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2646 (1967)

(4) If 4,3 ($CH_2{=}CRCCl{=}CRNR_2$) or 4,1 adducts ($ClCH_2CR{=}C{=}CRNR_2$) had formed, they would have been expected to hydrolyze during work-up to α,β-unsaturated aldehydes in analogy to the behavior of the adducts from acetylenes (ref 2). No spectral evidence for aldehydic material in the neutral products was obtained.

(5) R. M. Fantazier and M. L. Poutsma, *J. Amer. Chem. Soc.*, **90**, 5490 (1968).

(6) R. L. Hinman and S. Theodoropulos, *J. Org. Chem.*, **28**, 3052 (1963).

(7) Y. Chiang and E. B. Whipple, *J. Amer. Chem. Soc.*, **85**, 2763 (1963).

(8) E. S. Voskanyan, M. V. Mavrov, and V. F. Kucherov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1736 (1968).

(9) F. Y. Perveev and V. M. Demidova, *J. Gen. Chem. USSR*, **34**, 3220 (1964).

Anal. Calcd for $C_{16}H_{19}ClN_4O_7$: C, 46.33; H, 4.62; Cl, 8.58; N, 13.51. Found: C, 46.01; H, 4.82; Cl, 8.73; N, 13.27.

Reaction of Adduct 3 with Sodium Methoxide.—Allene **3** (7.41 g, 40.1 mmol) was added to a solution prepared from 1.80 g (78.3 mg-atoms) of sodium in 60 ml of methanol; the mixture was held at reflux 17 hr. The mixture was flooded with water and extracted with ether. The ether extracts were washed with 0.5 *N* sulfuric acid, dried, and evaporated to leave 2.79 g of crude product. Distillation gave 2.48 g (34%) of **7**: bp 78–79° (0.1 mm); uv (heptane) λ_{max} 222 nm (ϵ 5800);[6] uv (5 *M* H_2SO_4) λ_{max} 266 nm (ϵ 3900);[7,10] nmr δ 6.3 and 5.8 (m, pattern analogous to that of 1-*n*-propyl-3-methyl pyrrole[11]), 3.68 (t, J = 6.5 Hz, NCH_2), 3.27 (t, J = 6.5 Hz, OCH_2), 3.22 (s, OCH_3), 2.03 (s, ring CH_3), and 1.8–1.1 ppm (m, $-(CH_2)_3-$); nmr (H_2SO_4) consistent with protonation at the 2 position[7] δ 8.52 (br s, C^5 H), 6.71 (br s, C^4 H), 4.80 (br s, C^2 H_2), 4.35 (t, $J \sim 7$ Hz, $=\overset{+}{N}CH_2$), 4.05 (s, OCH_3), 4.02 (t, $J \sim 7$ Hz, OCH_2), 2.40 (br s, ring CH_3), and 2.35–1.0 ppm (br m, $-(CH_2)_3-$); mass spectrum (70 eV) *m/e* (rel intensity) 181 (85), 166 (60), 95 (100), and 94 (75).[12]

Addition of *N*-Chloropiperidine to 1-Penten-3-yne (2).—Reaction of 14.6 g (0.122 mol) of the crude chloramine and 8.0 g (0.121 mol) of enyne **2** gave, after the usual work-up, 0.32 g of neutral product and 14.0 g of basic product. Distillation of the latter gave several arbitrary fractions, bp 83–110° (0.5 mm), totalling 9.14 g. The first (0.2 g) had spectral properties consistent with adduct **4**: ir 1965 cm^{-1} (C=C=C); nmr δ 5.4 (m, CH=), 2.98 (d, J = 6.5 Hz, NCH_2), 2.4 (m, CH_2NCH_2), 2.08 (d, J = 2.5 Hz, $=CClCH_3$), and 1.5 ppm (m, $-(CH_2)_3-$); the nmr spectrum suggested ~85% purity. The final fraction (4.0 g) had an nmr spectrum consistent with bisamine **5**: δ 3.35 (m, area 1, NCHC≡), 2.24 (m, area 10, NCH_2), 1.82 (d, J = 2 Hz, area 3, $\equiv CCH_3$), and 1.5 ppm (m, area 12, $-(CH_2)_3-$). The nmr spectra of intermediate fractions showed a singlet at δ 2.00 (ir 1740 cm^{-1}, CH_3CO_2, ?), a cluster of bands at δ 1.8 ($\equiv CCH_3$ in a family of similar compounds, ?), and at least two broad multiplets at δ 3.9 and 4.2 ppm (CHXC≡, ?).

A parallel reaction was carried out with 17.9 g (0.15 mol) of the chloramine and 11.2 g (0.17 mol) of **2**. After reaction was complete, piperidine (12.75 g, 0.15 mol) was added with cooling; work-up gave 0.28 g of neutral product and 25.9 g of basic product. Distillation gave, after removal of piperidine at ~20 mm, (1) 1.7 g, bp 58–59° (0.05 mm), (2) 1.5 g, bp 70–95° (0.05 mm), and (3) 14.5 g, bp 95–102° (0.05 mm), $n^{22}D$ 1.5040. The nmr spectrum of 1 showed it to contain ~60% (6% yield) adduct **4** plus several minor components. Treatment of 0.31 g of 1 with picric acid in ethanol gave, after addition of water, 0.42 g of picrate, mp 129–133°; two crystallizations from ethanol–water gave 0.26 g, mp 139–140°.

Anal. Calcd for $C_{16}H_{19}ClN_4O_7$: C, 46.33; H, 4.62; Cl, 8.58; N, 13.51. Found: C, 45.84; H, 4.75; Cl, 9.01; N, 13.39.

The nmr spectrum of **3** showed it to be pure **5**. A very insoluble bispicrate formed in 97% yield and could be crystallized from a large volume of ethanol, mp 200° dec.

Anal. Calcd for $C_{27}H_{32}N_8O_{14}$: C, 46.82; H, 4.66; N, 16.18. Found: C, 46.55; H, 5.05; N, 15.75.

Addition of *N*-Chloropiperidine to Vinylacetylene.—Reaction between 13.7 g (0.11 mol) of the crude chloramine and 6.4 g (0.12 mol) of vinylacetylene, introduced as a gas in a stream of nitrogen into the reaction solution topped by a Dry Ice filled condenser, gave 1.2 g of neutral product and 5.8 g of basic product which quickly became deeply colored. Short-path distillation gave only 0.9 g, bp 68–71° (0.3 mm). The nmr spectrum showed the following reasonable bands for 1-chloro-4-piperidino-1,2-butadiene but they accounted for only 65% of the integrated area: δ 6.2–5.4 (m, CH=C=CHCl), 3.05 (d, d, J = 7 and 2 Hz, NCH_2), 2.4 (m, CH_2NCH_2), and 1.5 ppm (m, $-(CH_2)_3-$). The nmr spectrum of the original basic residue suggested that it was at least 50% this same product, but purification could not be achieved.

Registry No.—**3**, 30344-85-5; **3** picrate, 30344-86-6; **4**, 30344-87-7; **4** picrate, 30344-88-8; **5**, 30344-89-9; **5** picrate, 30344-90-2; **7**, 30344-91-3; 1-chloro-4-piperidino-1,2-butadiene, 30344-92-4; *N*-chloropiperidine, 2156-71-0.

(10) The group shifts in ref 7 predict λ_{max} 263 nm for an α-protonated 1,3-dialkylpyrrole.

(11) F. Y. Perveev, V. Y. Statsevich, and L. P. Gavryuchenkova, *J. Org. Chem. USSR*, **2**, 395 (1966).

(12) See A. M. Duffield, R. Beugelmans, H. Budzikiewicz, D. A. Lightner, D. H. Williams, and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 805 (1965), for discussion of the analogous *m/e* 81 and 80 in *N*-*n*-alkylpyrroles.

The Conversion of Vicinal Nitro Nitrates to Nitroalkanes with Sodium Borohydride

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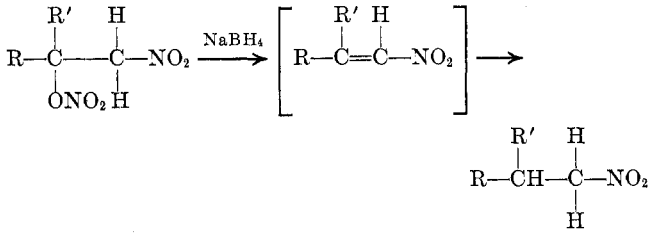
Available literature procedures for the conversion of 1-alkenes to terminal nitroalkanes[1-3] have certain limitations. The operation consists of first converting the olefin to dinitroalkanes, nitro alcohols, nitro nitrites, or mixtures of these compounds, treating the latter with base to form nitro olefins, and then catalytically hydrogenating the nitro olefins to nitroalkanes. The disadvantages are that (a) two separate steps are involved in converting the substituted nitro compounds to nitroalkanes, (b) nitro olefins often dimerize[4] or polymerize,[5] (c) catalytic reductions are sometimes inconvenient on a laboratory scale, and (d) care must be exercised that the nitro paraffins are not further reduced to amines in the last step.

The sodium borohydride reduction of β-nitro nitrates provides a route to nitroalkanes free from these disadvantages. 1-Nitro-2-alkyl nitrates are readily obtained in high yield from 1-alkenes, nitrogen oxides, and oxygen.[6] The sodium borohydride reduction step requires only simple mixing of reactants in ordinary glassware at room temperature. Sodium borohydride has been employed previously in the preparation of nitroalkanes from α-nitro ketones[7] and β-nitro hydroxy and chloro compounds.[8] The reaction presumably proceeds *via* the nitroalkene intermediate resulting from base-induced nitric acid elimination.



Rapid reduction of the nitroalkene intermediate apparently precludes side reactions such as dimerization and polymerization. By contrast, in the reduction of

(1) G. A. Bonetti, J. J. Gavigan, H. O. Hansen, and R. Rosenthal, U. S. Patent 3,240,823 (March 15, 1966).

(2) C. Michalski and G. A. Bonetti, U. S. Patent 3,297,769, (Jan 10, 1967).

(3) W. K. Seifert and L. L. Ferstandig, U. S. Patent 3,035,101 (May 15, 1962); W. K. Seifert, *J. Org. Chem.*, **28**, 265 (1963).

(4) A. I. Meyers and J. C. Sicar, *ibid.*, **32**, 4134 (1967).

(5) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

(6) (a) D. R. Lachowicz and K. L. Kreuz, U. S. Patent 3,282,983 (Nov 1, 1966). (b) D. R. Lachowicz, J. M. Larkin, and K. L. Kreuz, unpublished results; a less suitable procedure is described in the earlier work of N. Levy, C. W. Scaife, and A. E. Wilder-Smith, *J. Chem. Soc.*, 52 (1948).

(7) A. Hassner, J. M. Larkin, and J. E. Dowd, *J. Org. Chem.*, **33**, 1733 (1968).

(8) A. Hassner and C. H. Heathcock, *ibid.*, **29**, 1350 (1964).