# Enol Acetates, Enol Ethers, and Amines by Mercuration of Acetylenes

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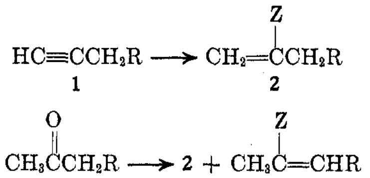
An improvement on the catalytic mercuration of terminal acetylenes to form enol acetates was developed, and solvomercuration–demercuration of terminal acetylenes was investigated and shown to be a useful method for the preparation of methyl enol ethers and, in lower yields, ethyl enol ethers and aziridine enamines. All enol derivatives prepared by these reactions were shown to be isomerically pure. 1-Octyne (**1a**) was converted into 2-acetoxy-1-octene (**2a**) by treatment with catalytic amounts of mercuric acetate and boron trifluoride etherate in acetic anhydride. Similarly, the tosylate (**1b**) of 3-butyn-1-ol was converted into enol acetate **2b**. The enol ethers **2c** and **2d** were prepared by treating 1-octyne with mercuric acetate in methanol and ethanol, respectively, followed by demercuration with alkaline sodium borohydride. Although the use of aziridine in a similar reaction gave the enamine **2e**, the use of pyrrolidine resulted in the formation of the saturated amine **8**.

In connection with another project, we needed synthetic methods for the preparation of enol acetates, enol ethers, and enamines having a terminal double bond (**2**). Enol derivatives are commonly prepared from the corresponding ketone (**3**).[1,2] However, as unsymmetrical ketones generally give a mixture of double bond isomers (**2** and **4**), we have investigated the solvomercuration reactions of terminal acetylenes as a route to these enol derivatives.

Although the preparation of vinyl derivatives from acetylene itself has been of some commercial importance,[3–5] the use of higher acetylenes is not common. Enol esters have been prepared on a laboratory scale from acetylenes and carboxylic acids in the presence of a catalytic amount of a mercury salt and a strong acid.[6–11,13] Although solvomercuration–demercuration



$$HC{\equiv}CCH_2R \longrightarrow CH_2{=}\overset{Z}{C}CH_2R$$

1 → 2

$$CH_3\overset{O}{\overset{\|}{C}}CH_2R \longrightarrow 2 + CH_3\overset{Z}{C}{=}CHR$$

3 → 4

**a**, R = $C_5H_{11}$; Z = OAc
**b**, R = $CH_2OTs$; Z = OAc
**c**, R = $C_5H_{11}$; Z = OMe
**d**, R = $C_5H_{11}$; Z = OEt
**e**, R = $C_5H_{11}$; Z = $N(CH_2)_2$

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(1) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972.

(2) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

(3) (a) J. A. Nieuwland and R. R. Vogt, "The Chemistry of Acetylene," Reinhold, New York, N. Y., 1945; (b) J. W. Reppe, "Acetylene Chemistry," Charles A. Meyer, New York, N. Y., 1949; (c) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold, New York, N. Y., 1949; (d) S. A. Miller, "Acetylene Its Properties, Manufacture, and Uses," Vol. II, Academic Press, New York, N. Y., 1966; (e) T. F. Rutledge, "Acetylenes and Allenes," Reinhold, New York, N. Y., 1969.

(4) (a) W. Reppe, *Justus Liebigs Ann. Chem.*, **601**, 81 (1956); (b) C. W. Kruse and R. F. Kleinschmidt, *J. Amer. Chem. Soc.*, **83**, 213 (1961).

(5) I. A. Chekulaeva and L. V. Kondrat'eva, *Russ. Chem. Rev.*, **34**, 669 (1965).

(6) (a) G. F. Hennion and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **56**, 1802 (1934); (b) G. F. Hennion, D. B. Killian, T. H. Vaughn, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **56**, 1130 (1934); (c) G. F. Hennion, R. R. Vogt, and J. A. Nieuwland, *J. Org. Chem.*, **1**, 159 (1936); (d) E. A. Bried and G. F. Hennion, *J. Amer. Chem. Soc.*, **60**, 1717 (1938).

(7) H. Lemaire and H. J. Lucas, *J. Amer. Chem. Soc.*, **77**, 939 (1955).

(8) R. H. Wiley, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 853.

(9) (a) A. I. Bol'shukhin and V. L. Zhitorchuk, *Zh. Obshch. Khim.*, **25**, 1459 (1955); *Chem. Abstr.*, **50**, 4832 (1956); (b) A. I. Bol'shukhin and A. G. Egorov, *Zh. Obshch. Khim.*, **26**, 1121 (1956); *Chem. Abstr.*, **50**, 16665 (1956); (c) A. G. Egorov, *Uch. Zap., Leningrad. Gos. Pedagog. Inst. im. A. I. Gertsena*, **179**, 211 (1958); *Chem. Abstr.*, **55**, 3421 (1961).

(10) H. C. Haas, N. W. Schuler, and R. L. MacDonald, *J. Polym. Sci., Part A-1*, **7**, 3440 (1969).

(11) The intermediate organomercury compounds were isolated and characterized in some cases where the mercury salt was used in equivalent amounts and the strong acid was omitted.[12] The organomercury compounds resulting from the addition of hydrogen chloride to acetylene have also been characterized.[12,ab]

(12) (a) A. N. Nesmeyanov, "Selected Works in Organic Chemistry," Pergamon Press, Elmsford, N. Y., 1963; (b) A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957); (c) G. Drefahl, G. Heublein, and A. Wintzer, *Angew. Chem.*, **70**, 166 (1958); see however G. Drefahl and S. Schaaf, *Chem. Ber.*, **90**, 148 (1957).

(13) Acetals and ketals have been prepared from acetylenes and alcohols by this method,[6b,c,14–16] and the synthesis of several enol ethers[3d,14i,17] and an enamine[18a] has been claimed. Several claims for the preparation of enol ethers in the early patent literature are questionable owing to the instability of enol ethers in strong acid. The yields were often poor and the products were accompanied by acetals;[3d] some of the reactions were later repeated and disputed.[3b,c,14j] Reactions of acetylenes with amines have yielded products for which enamines were postulated as intermediates.[3a,e,5,18] There is a recent report of the formation of a ketene acetal from ethoxyacetylene.[19] A few specialized examples are known of the formation of enol derivatives from certain acetylenes in the absence of mercury salt catalysis.[3–5,20,24–28]

(14) (a) J. S. Reichert, J. H. Bailey, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **45**, 1552 (1923); (b) H. S. Hill and H. Hibbert, *ibid.*, **45**, 3108 (1923); (c) J. A. Nieuwland, R. R. Vogt, and W. L. Foohey, *ibid.*, **52**, 1018 (1930); (d) H. D. Hinton and J. A. Nieuwland, *ibid.*, **52**, 2892 (1930); (e) D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *ibid.*, **56**, 1384 (1934); (f) G. F. Hennion and J. A. Nieuwland, *ibid.*, **57**, 2006 (1935); (g) D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *ibid.*, **58**, 80 (1936); (h) *ibid.*, **58**, 1658 (1936); (i) G. F. Hennion and W. S. Murray, *ibid.*, **64**, 1220 (1942); (j) G. F. Hennion and F. P. Kupiecki, *J. Org. Chem.*, **18**, 1601 (1953).

(15) (a) S. Tamaru and Y. Tanaka, *J. Chem. Soc. Jap.*, **56**, 486 (1935); *Chem. Abstr.*, **29**, 4733 (1935); (b) A. Contardi and B. Ciocca, *Ric. Sci.*, (2) **7**, II, 610 (1936); *Chem. Abstr.*, **32**, 9039 (1938).

(16) D. D. Coffman, U. S. Patent 2,387,495 (1945); *Chem. Abstr.*, **40**, 1870 (1946); D. D. Coffman, G. H. Kalb, and A. B. Ness, *J. Org. Chem.*, **13**, 223 (1948).

(17) (a) Plausons Forschungsinstitut G. M. B. H., German Patent 338,281 (1923); *Chem. Abstr.*, **17**, 1804 (1923); (b) T. Henshall, British Patent 616, 853 (1949); *Chem. Abstr.*, **43**, 5414 (1949).

(18) (a) J. A. Loritsch and R. R. Vogt, *J. Amer. Chem. Soc.*, **61**, 1462 (1939); (b) H. B. Kagan, A. Marquet, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1079 (1960), and references cited therein.

(19) H. H. Wasserman, J. U. Piper, and E. V. Dehmlow, *J. Org. Chem.*, **38**, 1451 (1973).

(20) Some intramolecular reactions to give cyclic enol derivatives are known.[3e] Acetylenes conjugated with an activating group (such as trifluoromethyl or carbonyl) form addition products readily without metal catalysis. Examples are given in ref 3e, 5, and 21–23.

(21) A. L. Henne, J. V. Schmitz, and W. G. Finnegan, *J. Amer. Chem. Soc.*, **72**, 4195 (1950); A. L. Henne and M. Nager, *ibid.*, **74**, 650 (1952).

(22) A. G. Evans, E. D. Owen, and B. D. Phillips, *J. Chem. Soc.*, 5021 (1964).

(23) (a) J. E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965); (b) R. Huisgen, B. Giese, and H. Huber, *Tetrahedron Lett.*, 1883 (1967); (c) B. Giese and R. Huisgen, *ibid.*, 1889 (1967).

(24) For an example of enol ester formation catalyzed by zinc salts, see E. S. Rothman, S. S. Hecht, P. E. Pfeffer, and L. S. Silbert, *J. Org. Chem.*, **37**, 3551 (1972).

(25) P. E. Peterson and J. E. Duddey, *J. Amer. Chem. Soc.*, **85**, 2865 (1963); P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966).

(26) Moureu, *C. R. Acad. Sci.*, **138**, 288 (1904).

(27) M. D. Gauthier, *Ann. Chim. Phys.*, **16**, 289 (1909); *Chem. Abstr.*, **3**, 1873 (1909). See also ref 14j.

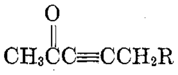
(28) (a) A. Favorsky, *J. Russ. Chem. Soc.*, 414 (1887); *J. Chem. Soc.*, **54**, 798 (1888); (b) A. Favorsky, *J. Prakt. Chem.*, (2) **37**, 382 (1888); (c) *ibid.*, (2) **37**, 531 (1888); (d) *ibid.*, (2) **44**, 208 (1891). See also D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **57**, 544 (1935).

reactions of olefins have been intensively studied in recent years,[1,29–35] the use of these reactions to prepare enol derivatives from acetylenes has not been been investigated.

For our purposes, we anticipated that the use of catalytic amounts of mercury salts in the presence of acid catalysts would be suitable for the preparation of enol acetates. For the preparation of the more acid-sensitive enol ethers and enamines, we decided to investigate the solvomercuration–demercuration of acetylenes.

## Results

**Enol Acetates.**—The enol acetate of 3-hexanone has previously been prepared from 3-hexyne using mercuric acetate and boron trifluoride etherate in acetic acid.[7] When we applied this procedure to 1-octyne (**1a**), 2-octanone was the only product obtained. The same result was observed when acetic acid distilled from $P_2O_5$, or mixtures of acetic acid and acetic anhydride, were used as solvent. However, when acetic anhydride was used as the solvent, a good yield of the enol acetate **2a** was obtained, along with smaller amounts of 2-octanone (**3a**) and a product shown to be 3-decyn-2-one (**5a**)[36] by independent synthesis.



$CH_3\overset{\overset{O}{\|}}{C}C{\equiv}CCH_2R$

**5a**, R = $C_5H_{11}$
**b**, R = $CH_2OTs$

To check whether double bond isomers were formed, an authentic mixture of the isomeric enol acetates (**2a** and **4a**) of 2-octanone was prepared by quenching the potassium enolate in acetic anhydride. Comparison of the vpc and nmr spectra demonstrated that the acetoxymercuration product contained no detectable amount of the internal double bond isomers (**4a**).

Using the same mercuration procedure (with acetic anhydride), the tosylate (**1b**) of 3-butyn-1-ol was converted into the terminal enol acetate **2b**.

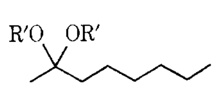
**Alkoxymercuration–Demercuration.**—We found that 1-octyne could be readily converted into the methyl enol ether **2c** by treatment with 1 equiv of mercuric acetate in methanol for 15 min, followed by reductive demercuration with sodium borohydride in aqueous sodium hydroxide. The product (formed in 65% yield) contained a small amount of the dimethyl ketal **6a** as the only impurity.

The use of other mercury salts was investigated in this reaction. Mercuric chloride gave a mixture of 2-octanol, 2-octanone, and the ketal **6a**. Mercuric nitrate and trifluoroacetate similarly gave little or no enol ether.

To determine the isomeric purity of the enol ether formed, a mixture of enol ethers (**2c** and **4c**) was prepared by cracking the dimethyl ketal **6a** of 2-octanone. No detectable amount of the internal double bond isomers was found in the methoxymercuration product.

The ethyl enol ether **2d** was prepared in an analogous manner from the reaction of ethanol with mercuric acetate and 1-octyne. The yield of enol ether (36%) was somewhat lower, and a considerable amount of white, crystalline material, which proved to be di-1-octynylmercury (**7**),[37] was also formed. The isomeric purity of the ethyl enol ether was established as before, by comparison with a mixture of enol ethers (**2d** and **4d**) prepared from the diethyl ketal **6b**.

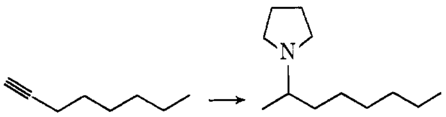
Attempts to prepare a *tert*-butyl enol ether from 1-octyne and mercuric acetate in *tert*-butyl alcohol led to di-1-octynylmercury as the only characterized product.



**6a**, R' = Me
**b**, R' = Et

$Hg[C{\equiv}C(CH_2)_5CH_3]_2$
**7**

**Aminomercuration–Demercuration.**—The reaction of 1-octyne with mercuric chloride in pyrrolidine, followed by alkaline sodium borohydride, produced a small amount of 2-octanol and a good yield of an acid-soluble product having ir and nmr spectra inconsistent with the desired enamine structure. The same compound was also obtained when mercuric acetate was used in place of mercuric chloride. The product was shown to be the saturated amine **8** by comparison with a sample prepared independently from pyrrolidine and 2-bromooctane.



**1a** **8**

Because of the possibility that the saturated amine was being produced by reduction of an intermediate iminium salt,[38] aminomercuration of 1-octyne with aziridine was attempted, since an iminium salt in this case would be much less favorable. Using mercuric acetate with short reaction times, the aziridine enamine **2e** was formed in 17.5% yield as the only volatile product. The structure of the enamine **2e** was established by its spectral and analytical data, and by hydrolysis to 2-octanone.

When the reaction of 1-octyne with mercuric acetate in aziridine was allowed to proceed for several hours, the yield of enamine dropped and a second volatile product was formed. Although never isolated pure, the ir and nmr spectra of the new compound, and its facile hydrolysis to 2-octanone, support the imine struc-

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[29] Reviews: J. Chatt, *Chem. Rev.*, **48**, 7 (1951); N. S. Zerfirov, *Russ. Chem. Rev.*, **34**, 527 (1965); W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

[30] D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, **93**, 6902 (1971), and references cited therein.

[31] (a) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967); (b) H. C. Brown and M.-H. Rei, *ibid.*, **91**, 5646 (1969); (c) H. C. Brown and J. T. Kurek, *ibid.*, **91**, 5647 (1969); (d) H. C. Brown and P. J. Geoghegan, Jr., *J. Org. Chem.*, **35**, 1844 (1970).

[32] (a) F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966); (b) G. M. Whitesides and J. San Filippo, Jr., *ibid.*, **92**, 6611 (1970).

[33] (a) J. J. Perie and A. Lattes, *Bull. Soc. Chim. Fr.*, 583 (1970), and references cited therein; (b) A. Dobrev, J. J. Perie, and A. Lattes, *Tetrahedron Lett.*, 4013 (1972), and references cited therein; (c) V. G. Aranda, J. B. Mur, G. Asensio, and M. Yus, *ibid.*, 3621 (1972), and references cited therein; (d) H. K. Hall, Jr., J. P. Schaefer, and R. J. Spanggord, *J. Org. Chem.*, **37**, 3069 (1972), and references cited therein.

[34] C. H. Heathcock, *Angew. Chem., Int. Ed. Engl.*, **8**, 134 (1969).

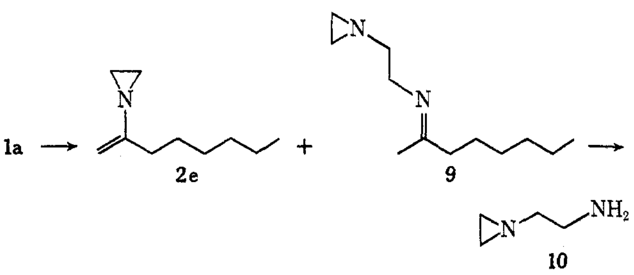
[35] D. H. Ballard and A. J. Bloodworth, *J. Chem. Soc. C*, 945 (1971).

[36] R. B. Davis and D. H. Scheiber, *J. Amer. Chem. Soc.*, **78**, 1675 (1956).

[37] (a) G. Eglinton and W. McCrae, *J. Chem. Soc.*, 2295 (1963); (b) T. H. Vaughn, *J. Amer. Chem. Soc.*, **55**, 3453 (1933).

[38] See, for example, R. D. Bach and D. K. Mitra, *Chem. Commun.*, 1433 (1971).

ture **9** for the product.[39] When a solution of **9** in carbon tetrachloride or benzene was stirred with deuterium oxide for 3 hr, the nmr spectrum of the organic layer showed mainly peaks corresponding to 2-octanone, while the nmr spectrum of the aqueous layer showed a symmetric pair of multiplets at $\delta$ 1.33 and 1.73 and a symmetric pair of multiplets at $\delta$ 2.32 and 2.78. The chemical shifts agree very well with those reported for 1-(2-aminoethyl)aziridine (**10**).[41]



**2e** **9** **10**

## Discussion

As discussed earlier, there are several reports of the synthesis of enol acetates from acetylenes and acetic acid in the presence of a mercuric salt and a strong acid. Most of these reports appeared before modern spectroscopic techniques, particularly nmr, became available, and the possibility of double bond isomerization could not be studied. In many of the reported procedures, a significant quantity of ketone was isolated along with the enol acetate.

The mercuric acetate–boron trifluoride etherate–acetic anhydride procedure appears to be a useful synthetic method for the preparation of terminal enol acetates. Double bond isomerization is not a problem, and in the acidic reaction conditions the mercury catalyst is continually regenerated, so that a full equivalent is not necessary.

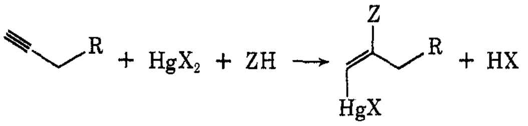
The mercury salt–strong acid catalyzed reactions would not be expected to be useful for the preparation of enol ethers and enamines from terminal acetylenes, since the double bonds would be more easily isomerized than those of enol acetates. We did not investigate this approach to enol ethers or enamines.[42]

The solvomercuration–demercuration approach promises to be a useful method for the preparation of methyl enol ethers from terminal acetylenes. With higher alcohols, the formation of the dialkynylmercury becomes a major competing reaction,[43] although a modest yield of the ethyl enol ether could be obtained.

We have so far been unsuccessful in preparing pyrrolidine enamines by this approach, presumably owing to the ease of formation of an iminium salt intermediate (for example, by addition of a proton or mercury ion to the initial aminomercuration adduct) which is easily reduced to a saturated amine. The use of aziridine rather than pyrrolidine effectively prevents the formation of an iminium salt because of the strain involved in generating an sp$^2$ center in a three-membered ring,[44] and the enamine can be isolated.

Aziridine enamines are relatively rare. The only previous examples of aziridine enamines of simple ketones are those of cycloheptanone and cyclooctanone.[40,45] The reluctance of the nitrogen atom in the three-membered ring to adopt the planar geometry necessary for maximum orbital overlap with the double bond manifests itself in the downfield chemical shift of the vinyl hydrogens[48] of the enamine **2e**.[49] The chemical shift of enamines has in turn been correlated with their reactivity toward electrophiles;[53] thus one would expect that the aziridine enamines would be comparatively unreactive (with respect to reactions at the carbon atom).

In the solvomercuration reactions, 1 equiv of acid is generated, as shown below. The initial adduct contains a double bond which could in principle undergo



protonation or further mercuration. In the alkoxymercuration reactions, this process, followed by reaction with alcohol, may be responsible for the formation of the small quantities of ketal **6** obtained after reduction. In the aminomercuration reactions with pyrrolidine, this process would lead to a relatively stable iminium salt[38] which is probably the precursor of the saturated amine **8**. It is conceivable that this process, followed by deprotonation, could lead to a product with an isomerized double bond (**4**); under our conditions, this does not appear to be a problem.

In conclusion, the mercuration of terminal acetylenes provides a useful synthetic method for isomerically pure enol acetates and methyl enol ethers with a terminal double bond and, in lower yields, ethyl enol ethers and aziridine enamines, all of which are difficult to prepare by other methods. The use of the solvomercuration–demercuration approach to the synthesis of other enol derivatives deserves more study.

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[39] Imines of this type are known. See ref 40.

[40] S. C. Kuo and W. H. Daly, *J. Org. Chem.*, **35**, 1861 (1970).

[41] H. P. Fritz and G. Hierl, *Z. Naturforsch., B*, **26**, 476 (1971).

[42] The preparation of an enamine from the reaction of *N*-ethylaniline and 1-heptyne with mercuric oxide and boron trifluoride etherate has been reported;[18a] we were unable to repeat this with *N*-methylaniline and 1-octyne.

[43] This could be an intermediate in the methoxymercuration reaction.

[44] This property of aziridine derivatives has been used for a synthesis of aldehydes. See ref 1, p 81.

[45] Aziridine enamines which are vinylogous amides have been prepared by the uncatalyzed addition of aziridine to acetylenecarboxylic esters[23] and to $\beta$-chlorocyclohexenones,[46] and a ketene *N,O*-acetal, 1-aziridinyl-1-trimethylsiloxyethylene, is known.[47]

[46] (a) H. W. Whitlock, Jr., and G. L. Smith, *Tetrahedron Lett.*, 1389 (1965); (b) G. L. Smith and H. W. Whitlock, Jr., *ibid.*, 2711 (1966).

[47] P. F. Hudrlik and D. Peterson, unpublished results.

[48] For a correlation between the chemical shift of the vinyl hydrogens of enamines and the degree of overlap of the lone pair electrons on nitrogen, see W. D. Gurowitz and M. A. Joseph, *J. Org. Chem.*, **32**, 3289 (1967).

[49] The chemical shift of the vinyl hydrogens of **2e** is lower than those for the reported terminal enamines from other methyl alkyl ketones with morpholine and diethylamine.[50] The products resulting from the addition of various secondary amines to dimethyl acetylenedicarboxylate also showed the aziridine compounds to occur at low fields in the nmr,[23a,51] and the vinyl hydrogens of 1-aziridinyl-1-trimethylsiloxyethylene[47] occur downfield from those of the dialkylamino analogs.[52] Aziridine enamines of cycloheptanone and cyclooctanone also absorb at low fields.[40]

[50] (a) R. Jacquier, C. Petrus, and F. Petrus, *Bull. Soc. Chim. Fr.*, 2845 (1966); (b) H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 4041 (1966); W. A. White and H. Weingarten, *ibid.*, **32**, 213 (1967).

[51] (a) E. Winterfeldt and H. Preuss, *Angew. Chem., Int. Ed. Engl.*, **4**, 689 (1965); (b) R. Huisgen, K. Herbig, A. Siegl, and H. Huber, *Chem. Ber.*, **99**, 2526 (1966).

[52] A. S. Kostyuk, Yu. I. Baukov, and I. F. Lutsenko, *J. Gen. Chem. USSR*, **40**, 598 (1970).

[53] M. E. Kuehne and T. Garbacik, *J. Org. Chem.*, **35**, 1555 (1970). See also A. I. Meyers and N. Nazarenko, *J. Amer. Chem. Soc.*, **94**, 3243 (1972).

## Experimental Section[54]

**Reagents.**—Acetic anhydride was distilled (bp 139–140°) before use. Methanol and ethanol were distilled from their magnesium alkoxides. Pyrrolidine was distilled from barium oxide. Aziridine[55] was distilled from potassium hydroxide.

All mercuration reactions were run under a nitrogen atmosphere, and transfers of liquids and solutions were done with syringes which had been filled with nitrogen. Organic extracts were dried with sodium sulfate followed by magnesium sulfate unless otherwise indicated.

**1-Octyne with Mercuric Acetate in Acetic Anhydride. 2-Acetoxy-1-octene (2a).**—To a solution[56] of 17 mg (0.053 mol) of $Hg(OAc)_2$ in 10 ml of acetic anhydride was added 0.02 ml of $BF_3 \cdot Et_2O$, followed by 0.50 ml (0.37 g, 3.4 mmol) of 1-octyne (**1a**) added dropwise. The solution, which turned yellow, was stirred at room temperature for 3 hr,[57] diluted with 10 ml of ether, and injected into an an ice-cooled solution of 18 g of KOH in 200 ml of water overlaid with ether. The layers were separated, and the ether layer was washed with brine, dried, concentrated,[58] and evaporatively distilled (0.1 mm, 70°), yielding 0.51 g (89%) of colorless liquid having ir and nmr compatible with the enol acetate structure [with extra small peaks at 4.51 (**5a**) and 5.83 μ (**3a**) in the ir]. Vpc analysis (SE-30)[54a,b] showed three peaks having relative areas of 14:79:7. The 14% peak had the same retention time as 2-octanone (**3a**); the other two products were purified by vpc collection (SE-30).[54b]

The minor product had ir and nmr spectra and vpc retention time (SE-30)[54b] identical with those of 3-decyn-2-one (**5a**)[36] obtained from 1-octynyllithium plus CuI and acetyl chloride (room temperature, 22 hr, 64% yield).[59]

The major product was identified as 2-acetoxy-1-octene (**2a**):[9b,c] ir ($CCl_4$) 5.71, 6.02 μ; nmr ($CCl_4$) δ 4.65 (m, 2 H), 2.36–1.97 including singlet at 2.05 (5.3 H), 1.63–0.8 (11 H); mass spectrum *m/e* 170 ($M^+$, small), 128, 110, 71, 58, 43.

*Anal.* Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.24; H, 10.79.

An authentic mixture of the isomeric enol acetates of 2-octanone (**2a** and **4a**) was made by quenching the enolate (prepared by adding the ketone to a solution of triphenylmethylpotassium in dimethoxyethane) in acetic anhydride.[2] The enol acetates were separated from the triphenylmethane by evaporative distillation (0.1 mm, 60°). The distillate had ir (film) 5.7, 5.83 (small, **3a**), 6.0 μ; nmr ($CCl_4$) δ 4.90 (broad t, $J = 7$ Hz), 4.65 (m), 2.05 (s), 1.83 (broad s). Vpc analysis (SE-30)[54b] indicated a ketone–enol acetates peak area ratio of 20:80. The partially resolved mixture of three enol acetates[60] had an approximate peak area ratio (in order of increasing retention times) of 35:55:10. The major product from the acetoxymercuration was identical in retention time and on coinjection with the major enol acetate peak from the authentic mixture. No peaks due to the other enol acetate isomers could be detected in the vpc (or the nmr) of the acetoxymercuration product.

**Tosylate of 3-Butyn-1-ol with Mercuric Acetate in Acetic Anhydride. 3-Acetoxy-3-buten-1-ol Tosylate (2b).**—The tosylate (**1b**) of 3-butyn-1-ol[61] (0.19 g) was treated with 2.5 ml of a mercuric acetate solution [prepared by dissolving 17 mg of $Hg(OAc)_2$ in 10 ml of acetic anhydride and adding 0.02 ml of $BF_3 \cdot Et_2O$] for 3 hr. After work-up (as for **2a**), 0.21 g of a light yellow oil was obtained: ir (film) 4.51 (small, impurity of **5b?**), 5.71, 5.99 μ; nmr ($CCl_4$) δ 7.8–7.15 (4 H, aromatic), 4.77 (d, $J = 2$ Hz) and 4.70 (m) (1.8 H, vinyl H), 4.07 (t, 2.1 H, $J = 6$ Hz, $CH_2O$), 2.67–2.36 (m, $C{=}CCH_2$) and 2.42 (broad s, $ArCH_3$) (5.1 H total), 2.18 (small s, impurity of **5b?**), 2.0 (s, 2.9 H, $CH_3CO$).

A portion of the product was chromatographed on Florisil (benzene–methylene chloride), giving a colorless oil having the same ir and nmr spectra as before chromatography. The mass spectrum showed *m/e* 284 ($M^+$, very small), 242, 224 (small), 172, 155, 112, 91, 70, 43.

**1-Octyne with Mercuric Acetate in Methanol. 2-Methoxy-1-octene (2c).**—A mixture of 1.09 g (3.4 mmol) of $Hg(OAc)_2$ and 8 ml of methanol was stirred for 5 min, then cooled in ice, and 0.5 ml (0.37 g, 3.4 mmol) of 1-octyne was added dropwise. The ice bath was removed and the mixture was stirred for 15 min.[57] After cooling in ice again, 8 ml of pentane was added followed immediately by 140 mg of $NaBH_4$ in 3.4 ml of 3 *M* NaOH. Sodium chloride was added to saturate, the ice bath was removed, and the mixture was stirred for 15 min.[62] The pentane was separated and the remainder was extracted twice more with pentane. The combined pentane extracts were dried, concentrated,[58] and evaporatively distilled (0.1 mm, 70°) yielding 0.31 g (65%) of colorless liquid, ir (film) 6.05 μ. The nmr spectrum ($CCl_4$) indicated the product to be the terminal enol ether **2c** containing 9% of the dimethyl ketal **6a**. No other peaks were present; in particular, no peaks due to the double bond isomer(s) of the enol ether **4c** were detectable. Vpc (SE-30)[54a,b] showed two peaks assigned to the enol ether and ketal.[63]

The enol ether was purified by vpc collection (SE-30):[54b] ir ($CCl_4$) 6.05 μ; nmr ($CCl_4$) δ 3.76 (s, 2 H), 3.49 (s, 3 H), 2.25–0.7 (13.4 H); mass spectrum *m/e* 142 ($M^+$), 85, 72.

The analytical sample was prepared by vpc collection (Carbowax).[54c] *Anal.* Calcd for $C_9H_{18}O$: C, 75.99; H, 12.96. Found: C, 75.64; H, 13.16.

To prepare an authentic mixture of the isomeric methyl enol ethers of 2-octanone (**2c** and **4c**), the ketone was converted to the dimethyl ketal **6a** with trimethyl orthoformate.[64] A sample of the ketal free from ketone was obtained by percolation through Florisil in hexane: ir no carbonyl or hydroxyl; nmr ($CCl_4$) δ 3.08 (s, 6 H), 1.6–0.8 including s at 1.17 (16 H). This ketal was heated with a crystal of *p*-toluenesulfonic acid monohydrate in a distillation apparatus under nitrogen (175°, 30 min), and the residue was evaporatively distilled (0.1 mm, 40°), giving the mixture of enol ethers **2c** and **4c**: ir (film) 5.83 (small, **3a**), 6.01, 6.05 μ; nmr ($CCl_4$) δ 4.25 (broad t, $J = 7$ Hz, vinyl H of **4c**), 3.76 (s, vinyl H of **2c**), 3.49 (s, $CH_3O$ of **2c**), 3.43 (s, $CH_3O$ of **4c**), 3.08 (small s, $CH_3O$ of **6a**), 2.25–0.7 including s at 1.70 (vinyl methyl of **4c**). The ratio of more substituted to less substituted double bond was approximately 1:1 and the percentage of ketal was less than 5% by the nmr integration.

**1-Octyne with Mercuric Acetate in Ethanol. 2-Ethoxy-1-octene (2d).**—1-Octyne (0.5 ml, 0.37 g, 3.4 mmol) was treated with 1.09 g (3.4 mmol) of $Hg(OAc)_2$ in 8 ml of ethanol for 15 min[57] according to the procedure used for the methyl enol ether **2c**. After work-up, when most of the pentane solvent was removed by distillation, white crystals precipitated and were filtered off and dried. The crystals (0.20 g) had spectra and melting point compatible with di-1-octynylmercury (**7**): ir ($CCl_4$) 4.64 μ; nmr ($CCl_4$) δ 2.5–2.1 (4 H), 1.8–0.7 (22 H); mp 81.5–82.5° (lit. mp 82–83°,[37a] 80.4–80.7°[37b]).

The mother liquor was concentrated and evaporatively distilled (0.1 mm, 60°) producing 0.19 g (36%) of colorless liquid and 0.16 g of crystalline pot residue. The distilled product had ir (film) 6.05 μ; nmr ($CCl_4$) δ 3.73 (s), 3.67 (q, $J = 7$ Hz), 3.39 (small q partially covered by previous q, $J = 7$ Hz, impurity of **6b**), 2.24–0.7. The integration indicated that about 6% of the diethyl ketal **6b** was present.[63] No peaks attributable to the double bond isomer(s) of the enol ether (**4d**) were detectable. The mass spectrum showed *m/e* 156 ($M^+$), 99, 71.

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[54] Melting points were determined on a Fisher-Johns hot stage melting point apparatus. Infrared spectra were determined with a Perkin-Elmer Model 137 spectrometer. Nmr spectra were taken on a Varian T-60 spectrometer, using TMS as an internal standard, unless otherwise noted. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-7 instrument. Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. Vpc analyses were done on a Varian Aerograph Model 90-P3 gas chromatograph, using one of the following columns: (a) 10% SE-30 on Chromosorb W, 10 ft × 0.25 in.; (b) 5% SE-30 on Chromosorb W, 5 ft × 0.25 in.; (c) 20% Carbowax 20M on Chromosorb W, 10 ft × 0.25 in.

[55] The toxicity of aziridine is discussed in J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley-Interscience, New York, N. Y., 1970.

[56] The components were stirred for 1 hr at room temperature (under nitrogen) to effect solution.

[57] A similar reaction with an internal standard present suggested that this was approximately the optimum time.

[58] Ir and nmr spectra were taken of the crude product before distillation to ascertain that the products were present in the reaction mixture and were not formed during distillation.

[59] J. F. Normant and M. Bourgain, *Tetrahedron Lett.*, 2659 (1970).

[60] H. Nakata and A. Tatematsu, *Org. Mass Spectrom.*, **4**, 211 (1970).

[61] G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950).

[62] This *in situ* demercuration procedure is essentially that of Brown.[31]

[63] The vpc peak area ratios in duplicate runs were not always strictly reproducible, suggesting that the compounds were not completely stable to our vpc conditions; therefore vpc has not been used for quantitative determinations of product composition for this reaction.

[64] The procedure is analogous to that of House[2] for the preparation of diethyl ketals with triethyl orthoformate.

A sample was prepared for analysis by vpc collection (SE-30).[54b] *Anal.* Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.71; H, 13.18.

An authentic mixture of the ethyl enol ether isomers **2d** and **4d** of 2-octanone was prepared by the procedure[2] used for the methyl enol ethers **2c** and **4c**. The diethyl ketal **6b**[65] was made from triethyl orthoformate and 2-octanone and purified by percolation through Florisil: ir, no carbonyl or hydroxyl; nmr ($CCl_4$) δ 3.39 (q, $J = 7$ Hz, 3.3 H), 1.65–0.7 (22 H). The ketal was converted to the enol ethers by heating with *p*-toluenesulfonic acid as before, and the residue was evaporatively distilled (0.1 mm, 40°), giving the mixture of enol ethers **2d** and **4d**: ir (film) 5.83 (small, **3a**) 6.02, 6.05 μ; nmr ($CCl_4$) δ 4.25 (broad t, $J = 7$ Hz, vinyl H of **4d**), 3.73 (s, vinyl H of **2d**), 3.9–3.2 (appears to be three overlapping quartets, centered at 3.39, 3.62, and 3.68), 2.25–0.7 including broad s at 1.70 (vinyl methyl of **4d**).

**1-Octyne with Mercuric Chloride in Pyrrolidine. *N*-2-Octylpyrrolidine (8).**—To a solution of 1.84 g (6.8 mmol) of $HgCl_2$ in 16 ml of pyrrolidine was added 1.0 ml (0.74 g, 6.8 mmol) of 1-octyne dropwise. After stirring at room temperature for 3.5 hr, the reaction mixture was cooled in ice and 16 ml of pentane was added followed by a solution of 280 mg of $NaBH_4$ in 6.8 ml of 3 *M* NaOH. NaCl was added to saturate, the ice bath was removed, and the mixture was stirred for 15 min.[62] The pentane was separated and the remainder was extracted twice more with pentane. The combined pentane extracts were dried, concentrated,[58] and evaporatively distilled (0.1 mm, 70°) yielding 1.06 g (86%) of colorless liquid having ir and nmr spectra compatible with the saturated amine structure. Vpc analysis (SE-30 and Carbowax)[54a,c] showed two peaks, the smaller (10% of the peak area) having the same retention time as 2-octanol. The major product was purified by vpc collection (SE-30)[54a] and had ir, nmr, and vpc retention time identical with those obtained from the reaction product of 2-bromooctane and pyrrolidine (5.5 hr, 80–110°), nmr (benzene) δ 2.65–2.05 (5 H), 1.85–0.8 including doublet at 1.05 ($J = 6$ Hz) (20 H).

A sample was prepared for analysis by partitioning the aminomercuration product between ether and 1 *N* HCl. The aqueous layer was washed twice with ether and neutralized with NaOH. The neutralized solution was extracted with ether; the ether extract was dried, the solvent was removed, and the residue was evaporatively distilled (0.1 mm, 70°).

*Anal.* Calcd for $C_{12}H_{25}N$: C, 78.61; H, 13.75. Found: C, 78.82; H, 13.80.

**1-Octyne with Mercuric Acetate in Aziridine. 2-Aziridinyl-1-octene (2e).**—To an ice-cooled solution of 2.18 g (6.8 mmol) of $Hg(OAc)_2$ in 16 ml of aziridine was added 1.0 ml (0.74 g, 6.7 mmol) of 1-octyne dropwise. The ice bath was removed and the reaction solution was stirred for 20 min.[57] The solution was cooled in ice and 16 ml of pentane was added followed by a solution of 280 mg of $NaBH_4$ in 6.8 ml of 3 *M* NaOH. NaCl was added to saturate, the ice bath was removed, and the mixture was stirred at room temperature for 15 min.[62] The layers were separated and the aqueous layer was extracted twice with pentane. The combined pentane extracts were dried, concentrated,[58] and evaporatively distilled (0.1 mm, 80°), producing 0.18 g (17.5%) of a colorless distillate: ir (film) 5.83 (small, **3a**?), 6.15 μ; nmr (benzene) δ 4.28 (m, 1.5 H, vinyl H), 2.4–0.7 (17 H) including s at 1.52 (aziridine ring H) (in $CCl_4$ the vinyl protons occurred as a multiplet centered at δ 4.08); mass spectrum *m/e* 153 ($M^+$), 96, 55.

*Anal.* Calcd for $C_{10}H_{19}N$: C, 78.36; H, 12.50. Found: C, 77.96; H, 12.76.

The nmr sample ($CCl_4$) of the enamine was stirred for 5 min with an equal volume of 6 *N* HCl. After neutralization with NaOH, the layers were separated. The organic layer was washed with 1 *N* HCl and dried ($Na_2SO_4$). The nmr was identical with that of 2-octanone and the vpc (SE-30)[54b] showed only a large peak at the same retention time as that of 2-octanone.

**1-Octyne with Mercuric Acetate in Aziridine. Long Reaction Time.**—To an ice-cooled solution of 0.82 g (2.6 mmol) of $Hg(OAc)_2$ in 6 ml of aziridine was added 0.38 ml (0.28 g, 2.5 mmol) of 1-octyne dropwise. The ice bath was removed and the reaction solution was stirred for 4.25 hr. After work-up as before (see **2e**),[58] the crude product was evaporatively distilled in two fractions: (1) 0.1 mm, 64–80°, 0.20 g; (2) 0.1 mm, 80°, 0.19 g. Vpc analysis[63] (SE-30)[54a,b] indicated the first fraction to contain a considerable amount of enamine and the second to contain mostly higher retention time substance. The spectra of the second fraction showed ir (film) 5.83 (small, **3a** impurity), 6.02 μ; nmr ($CCl_4$)[66] δ 3.37 (broad t, $J = 7$ Hz), 2.9–0.7 with broad s at 1.80.

The nmr sample of the second fraction was stirred with $D_2O$ for 3 hr. The nmr[66] of the $CCl_4$ layer showed mainly peaks corresponding to 2-octanone while the spectrum[66] of the $D_2O$ layer (relative to DSS) showed only two mirror-image multiplets centered at δ 1.33 and 1.73 (area ratio 1:1) and two mirror image multiplets centered at δ 2.32 and 2.78 (area ratio 1:1).

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**Registry No.**—**1a**, 629-05-0; **1b**, 23418-85-1; **2a**, 26735-84-2; **2b**, 42367-31-7; **2c**, 42401-58-1; **2d**, 42367-32-8; **2e**, 42434-73-1; **7**, 42367-33-9; **8**, 42367-34-0; mercuric acetate, 1600-27-7; mercuric chloride, 7487-94-7.

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[65] H. E. Carswell and H. Adkins, *J. Amer. Chem. Soc.*, **50**, 235 (1928).

[66] Nmr spectra were taken on both JEOL MH-100 and Varian T-60 instruments.