Insect Sex Attractants; XIV[1]. All-*trans*-alkenol Acetates via Sodium-Liquid Ammonia Reduction[2]

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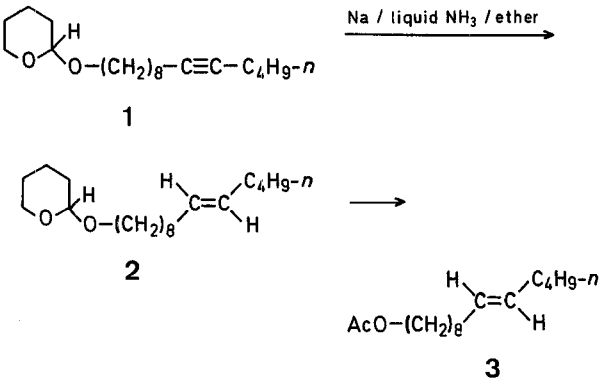
Alkenol acetate sex attractants having the *trans* configuration have already been isolated from 8 species of lepidopterous insects[3]. If field and laboratory tests with these chemicals are to result in meaningful data, the geometric purity of the *trans* double bond must be extremely high; otherwise, masking or synergism may lead to faulty conclusions. Examples of masking of the effect of *trans* compounds by the *cis* isomers are known[4].

Olefinic compounds having the *trans* configuration are usually generated by

(a) reduction of alkynes with metallic sodium in liquid ammonia[5],
(b) ring scission of 2-alkyl-3-chlorotetrahydropyrans[6], or
(c) elaidinization of a *cis*-olefinic compound with nitrous acid[7].

Of these three methods, only method (a) results in no detectable trace of *cis* isomer[8]. This method has been used successfully for the preparation of *E*-1-acetoxydodec-5-ene[9] and *E,E*-1-acetoxytrideca-5,9-diene[10]. We wish to report upon the difficulties involved in the preparation of a *trans*-alkenol acetate with a C-chain longer than C_{13} and to offer helpful suggestions for the success of this useful reaction. The reduction is carried out with the *O*-tetrahydropyran-2-yl derivative (**1**) of the alkynol. The resultant *O*-protected *trans*-olefinic compound **2** is hydrolyzed and *O*-acetylated to give the desired *trans*-alkenol acetate **3**.



The results summarized in the Table show that the reaction conditions A, which were employed successfully for the preparation of *E*-1-acetoxydodec-5-ene, were not satisfactory for the preparation of the higher homolog, *E*-1-acetoxytetradec-9-ene. The ratio of *trans* product to starting alkyne was 1.21:1. By increasing the amount of liquid ammonia ~2.5 times (conditions B), we increased the ratio of *trans* product to starting alkyne to 8.55:1. A 2-fold increase in ethyl ether in conditions C over conditions B did not increase the amount of *trans* product over starting alkyne. Further addition of sodium to the crude reduction product in liquid ammonia did not result in any further reduction of the small amount of unreduced alkyne. The use of other solvents for solubility was not investigated in this study.

This evidence seems to indicate that a problem in solubility develops as the chain length of the starting alkyne increases. An increase in the amount of liquid ammonia in relation to starting product is therefore advisable for reducing higher molecular weight homologs.

No *cis*-impurity was detectable by capillary G. L. C. of *E*-1-acetoxytetradec-9-ene prepared using conditions A, B, or C. Thus, the reduction of an acetylenic bond with sodium in liquid ammonia is extremely useful for the synthesis of all-*trans*-alkenol acetates if the reactants are used in the correct proportions.

Preparation of *trans*-Enyl Tetrahydropyranyl Ethers (2); General Procedure:

The procedure[9,10] for the liquid ammonia reduction of the starting *O*-tetrahydropyranyl-protected alkynol was carried out with 2-(tetradec-9-ynyloxy)-tetrahydropyran[11] (**1**) using the proportions of reactants given in the Table for conditions A, B, and C. After work-up, the crude reaction mixture was analyzed by G.L.C. on a column (1.52 m × 0.317 cm) of 5% Carbowax 20 M TPA ® on 60/80 mesh base-washed Chromosorb W ® at 170° and 23 ml N_2/min. Reduction in good yield of similar hexadecynyl derivatives has also been achieved in liquid ammonia with excess diethyl ether[12].

Preparation of *trans*-Enyl Acetates (3):

In each case, the *E*-2-(tetradec-9-enyl)-tetrahydropyran (**2**) obtained from the reduction was hydrolyzed and acetylated[11], and the isomeric content of the resultant *E*-1-acetoxytetradec-9-ene (**3**) was determined by capillary G.L.C.[13].

Table. Comparison of Reactant Proportions in the Sodium/Liquid Ammonia Reduction of 2-(Tetradec-9-ynyl)-tetrahydropyran **(1)** to *E*-2-(Tetradec-9-enyl)-tetrahydropyran **(2)**

Conditions	Alkyne **1** (mol)	Sodium (g-atom)	Liquid NH_3 (ml)	Ether (ml)	Ratio of *trans*-**2**:**1**
A	0.038	0.18	400	20	1.21:1
B	0.045	0.21	1000	50	8.55:1
C	0.038	0.18	1000	100	8.55:1

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[2] Mention of a commercial or proprietary product in this paper does not constitute an endorsement of this product by the USDA.

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