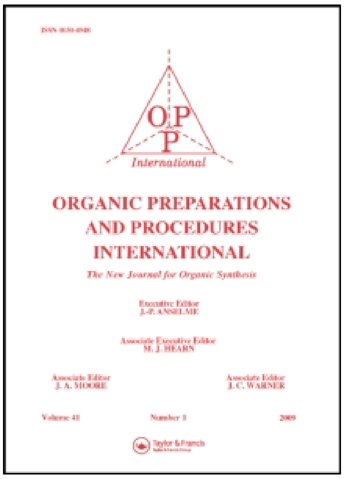

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# OXIDATION OF ALCOHOLS USING TRIPHOSGENE

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# OXIDATION OF ALCOHOLS USING TRIPHOSGENE

*Submitted by*
(11/15/91)

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The preferred method for the oxidization of primary alcohols to aldehydes is the Swern oxidation (DMSO and oxalyl chloride).[1] Recently Palomo and coworkers[2] utilized triphosgene-dimethyl sulfoxide (DMSO) to oxidize a limited number of heterocyclic primary and secondary alcohols to carbonyl compounds. The use of triphosgene [phosgene substitute from Aldrich[3]] as a DMSO activator has several advantages over oxalyl chloride. It is a solid that can be weighed accurately and is less susceptible to hydrolysis. Furthermore, the oxidation of β-phenylethanols with triphosgene-DMSO gave better yields compared to oxalyl chloride-DMSO or TFAA-DMSO methods[1a]. Our results complement and confirm those previously reported.[1]

Triphosgene was added to DMSO at -78°; no evolution of carbon dioxide was observed until after the addition of the alcohol, suggesting perhaps the formation of a mixture of reactive intermediates **1** and **2** (at RT DMSO reacts exothermally with triphosgene with the evolution of $CO_2$). To this mixture was added a variety of primary and secondary alcohols in the presence of triethylamine to give the corresponding aldehyde or ketone.

$$[Me_2\overset{+}{S}OCO_2CCl_3]\ Cl^- \qquad\qquad [Me_2\overset{+}{S}OCOCl]\ Cl^-$$

**1** **2**

## EXPERIMENTAL SECTION

All products were analyzed by NMR (Chemagnetic 200MHz and Varian EM-390MHz) and GC (Analytical Instruments, Capillary Column DB-17) for purity and they were compared with authentic samples obtained from Aldrich Chem. Co. and San Diego State University, except 2-(*p*-anisyl)-ethanal[4] and 3-methyl-2-heptanone.[5] Mass spectra were obtained on a Finnigan 3000 at 70 ev. Infrared Spectra were recorded on a Perkin Elmer FT-IR 1750 spectrophotometer.

**General Procedure**.- To a solution of triphosgene (0.29 g, 0.97 mmol)[3] in dry methylene chloride (40 mL) at -78° was added anhydrous DMSO (0.5 mL, 7.06 mmol) dropwise with stirring. After 5 min, 2-(*p*-anisyl)ethanol (0.403 g, 2.63 mmol) in dry methylene chloride (10 mL) was added dropwise. The mixture was stirred at -78° for an additional 15 min., then triethylamine (2.0 mL, 14.28 mmol) was added and the reaction allowed to come to RT (~10 min.). The reaction mixture was quenched with water (50 mL) and the organic phase was washed with dil. HCl (5%, 50 mL), followed by $NaHCO_3$ (5%, 50 mL), saturated NaCl and water. The final organic layer was dried over $Na_2SO_4$, subjected to flash chromatography (15 g silica gel) and the solvent removed at reduced pressure to give the aldehyde in 79% yield.

TABLE. Oxidation of Alcohols

| | | Yield(%)[a] | | bp(°C/mm Hg) | |
|---|---|---|---|---|---|
| Alcohol | Product | A | B | Lit.[b] | Rep. |
| *n*-Heptanol | Heptanal | 82 | — | 153 | 50/20 |
| *n*-Octanol | Octanal | 91 | 95 | 171 | 65/20 |
| Geraniol | Geranial | 95 | 95 | 229 | 105/20 |
| Citronellol | Citronellal | 95 | 85 | 207 | 95/20 |
| *n*-Dodecanol | Dodecanal | 90 | 100 | 185/100 | 133/20 |
| 2-Phenyl-1-propanol | 2-Phenylpropanal | 75 | 38 | 93/12 | 105/20 |
| 2-(p-Anisyl)ethanol | 2-(p-Anisyl)ethanal | 79 | 27[c] | 123-4/12[d] | 130/20 |
| 2-Phenylethanol | 2-Phenylethanal | 51 | 23 | 195 | 86/20 |
| 4-Methoxybenzyl alcohol | 4-Anisaldehyde | 95 | — | 248 | 130/20 |
| Cinnamyl alcohol | Cinnamaldehyde | 95 | 97 | 248 | 130/20 |
| 3-Pentanol | 3-Pentanone | 90 | — | 102 | 100-102 |
| 2-Hexanol | 2-Hexanone | 92 | — | 127 | 125-127 |
| 3-Methylcyclohexanol | 3-Methylcyclohexanone | 92 | 100 | 169-170 | 65/20 |
| 2-Octanol | 2-Octanone | 95 | 98 | 173 | 70/20 |
| 3-Methyl-2-heptanol | 3-Methyl-2-heptanone | 78 | — | 155[e] | 58-60/20 |
| 5-Nonanol | 5-Nonanone | 68 | — | 186-187 | 78/20 |
| Benzoin | Benzil | 95 | 95 | mp. 94-95 | 95 |

a) Method A: Triphosgene-DMSO; method B: Oxalyl Chloride-DMSO b) Reference 7 unless otherwise noted c) Ref. 6. d) Ref. 8. e) Ref. 9.

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4. $^1$H NMR ($CDCl_3$): $\delta$ 9.71 (t, 1H, *J* = 2.4 Hz, H-C=O), 9.12 (d, 2H, *J* = 8.9 Hz, Ar), 6.99 (d, 2H, *J* = 8.9 Hz, Ar), 3.85 (s, 3H, $OCH_3$), 3.62 (d, 2H, *J* = 2.4 Hz) ppm. MS: m/e 150 ($M^+$). IR (liquid film): 1724 (C=O)$cm^{-1}$.

5. $^1$NMR ($CDCl_3$): $\delta$ 2.40 (dt, 1H, *J* = 7.3Hz), 2.20 (s, 3H, $CH_3$), 1.50- 1.20 (m, 6H), 1.05 (d, 3H, $CH_3$), 0.80 (t, 3H, $CH_3$). MS: m/e 128 ($M^+$). IR (liquid film): 1713 (C=O)$cm^{-1}$.

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# A STUDY ON CYANOACETIC ACID HYDRAZIDE

*Submitted by*
(03/12/92)

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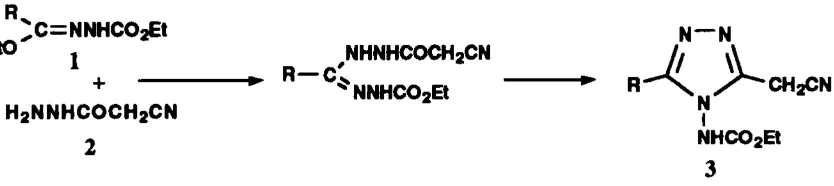
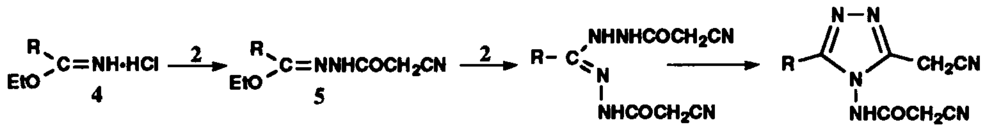
The reaction of various ester ethoxycarbonylhydrazones with amines and hydrazines has been reported.[1-5] The present study describes the treatment of some ester ethoxycarbonylhydrazones (**1**) with cyanoacetic acid hydrazide. Although the reaction of ester ethoxycarbonylhydrazone with amines or hydrazine generally led to the formation of 3,4-disubstituted-4,5-dihydro-1,2,4-triazol-5-ones, this type of compound was not obtained in this study. Instead, 3-alkyl-4-carbethoxyamino-5-cyanomethyl-4H-1,2,4-triazoles (**3**) were isolated.



a) R = $CH_3$ b) R = $CH_3CH_2$ c) R = $n$-$C_3H_7$ d) R = $C_6H_5CH_2$ e) 4-$ClC_6H_4CH_2$

The formation of ester hydrazone derivatives **5** or 2,5-disubstituted-1,3,4-oxadiazoles from the reaction of alkyl imidate hydrochlorides (**4**) with carboxylic acid hydrazides has also been



a) R = $CH_3$ b) R = $C_6H_5CH_2$

**6**