<u>N,N'-Bis[2-(3-methyl-3-nitrosoureido)ethyl]-N,N,N',N'-tetramethylethylenediammonium Di-</u> <u>tosylate (X).</u> A solution of 0.86 g (15 mmoles) of methyl isocyanate in 8 ml of dry MeCN was cooled to 0°C and 0.88 g (5 mmoles) of (XI) in 8 ml MeCN was added with stirring. After 1 h 5.6 g (30 mmoles) of methyl tosylate was added and the mixture was refluxed for 8 h. The reaction mixture was diluted with ether and the resulting oil was dissolved in 30 ml MeCN and 10 ml DMFA. The resulting solution was treated at -10° C with gaseous N₂O₃; a precipitate formed. When the reaction mixture had turned blue, the nitrogen oxides were evaporated under vacuum and the resulting precipitate was filtered and washed with MeCN. Yield, 2.1 g (57%).

<u>N,N'-Bis{2-[3-(2-chloroethyl)ureido]ethyl}-N,N'-dimethylethylenediamine (XII)</u>. A solution of 0.8 g (7.6 mmoles) of chloroethyl isocyanate in 4 ml of dry MeCN was treated with 0.44 g (2.5 mmoles) of (XI) in 4 ml of dry MeCN at -5° C with stirring. After 1 h the resulting precipitate was filtered and washed with MeCN. Yield 0.7 g (72%).

CONCLUSIONS

A method has been developed for the synthesis of new nitrosoalkylureas based on bisquaternary ethylenediammonium salts.

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OXIDATION OF HOMOALLYL ALCOHOLS

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The oxidation of diallylcarbinol (II) is the most convenient method for the synthesis of diallyl ketone (I). However, there is no information at all on the oxidation of bis(homoal-lyl)-type alcohols, and in some examples of oxidation of homoallyl alcohols unsatisfactory results were obtained.

We studied the oxidation of homoallyl alcohols both by standard methods usually used for oxidation of unsaturated alcohols and by some new original modifications of known methods.

The specific effect of two β,γ double bonds on the oxidation process of the alcohol was shown.

Thus, in the oxidation of (II) and allylpropenylcarbonol (III) by chromic acid under standard conditions [1] to ~100% conversion (GLC), there were significant overconsumption of the reagent (3-4 equivalents) and large losses of the product. Under these same conditions, propargylpropenylcarbinol (IV) was oxidized with degradation. With aqueous chromic acid, sat-isfactory yields of ketone (I) were obtained by two-phase oxidation in a medium of methylene chloride or ether (Table 1, No. 1a). Other standard methods for oxidation of alcohols based on Cr^{6+} , with pyridinium chloride chromate (PCC) and pyridinium dichromate (PDC), also gave unsatisfactory results for alcohols (II)-(IV) (see Table 1, Nos. 4a and 6a and b). In addition, a polymeric by-product was always obtained which was apparently formed via radical intermediates of oxidation by intermediate-valence chromium (Cr^{4+}) compounds (cf. [1]). Examples are known for suppression of the undesirable participation of such active oxidizing agents by a radical path with the addition of catalysts of the disproportionation $Cr^{4+} \rightarrow Cr^{3+} + Cr^{4-}$ of

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 614-616, March, 1986. Original article submitted September 11, 1984. Ce^{4+} type and cooxidizing agents [1]. In our case, this method did not block polymerization, although it did lead to some improvement of the yield of ketone (I) (see Table 1, Nos. 1b and 3).

It is of interest that in an attempt to increase the conversion by using a significant excess of the chromium mixture, the yield of the ketone decreased until its complete disappearance. An increase of the reaction time also led to a decrease of the yield on the basis of the reacted alcohol (see Table 1, Nos. 6a and b). Apparently, parallel oxidation, degradation, and polymerization reactions occurred in these cases.

From the data of Table 1, it is evident that the "reoxidation" and polymerization processes were not directly related to the excess acidity of the reagents based on Cr^{6+} because the use of milder weakly acidic (see Table 1, Nos. 2 and 3) and neutral reagents (Nos. 4d and 6a) did not give favorable results. This was also true of the strongly acidic complex $CrO_3 \cdot C_5H_5N \cdot {}^1/_2H_2SO_4$ (PSC) (see Table 1, No. 5), described for the first time in this paper. The activation of PCC and PDC by molecular sieves [2] also gave no perceptible effect.

It should be emphasized that all the above-mentioned known and proposed modifications of the oxidation methods were checked beforehand and the case of cyclohexanol with invariably quite satisfactory results (75-100% according to GLC).

We were able to achieve an improvement of the results by carrying out the oxidation reaction in the $PCC-H_2O$ system with CH_2Cl_2 (moist PCC, see Table 1, Nos. 4b and c).

From among other milder reagents for oxidation of bis(homoally1) alcohols, we tested sodium hypochlorite in CH_2Cl_2 in the presence of a phase-transfer catalyst (PTC) and in glacial acetic acid [4], nickel peroxide [5], active MnO_2 [1], and $KMnO_4$ catalyzed by a molecular sieve [1] and Cu^{2+} salts [6], which did not give satisfactory results. Onium reagents based on DMSO have been widely used in recent years for oxidation of unsaturated alcohols [1, 3]. For alcohol (II), the best results from among the previously studied electrophiles (E) were shown by $SOCl_2$ and $(COCl)_2$ for an alcohol:DMSO:E molar ratio of 1:2:1 (see Table 1, Nos. 7a and b). From among the previously untested electrophiles, we tested several new ones: TiCl_4, Me_3SiCl, PBr_3. Alcohol (II) was oxidized most completely by DMSO and "activated" PBr_3 (see Table 1, No. 7c). In the presence of DMSO [7] and H_2O_2 [8], the oxidation of (II) catalyzed by Mo⁶⁺ gave no favorable results, nor did the purely catalytic dehydrogenation method of [9].

EXPERIMENTAL

The GLC analysis was carried out with a Boikhrom-1 instrument, with a glass capillary, 0.25×50 m, XE-60, at 100°C with N₂ at 1.5 atm. The internal standard was C₁₃H₂₈. The CH₂Cl₂ was treated with CrO₃. Freshly redistilled DMSO was used over CaH₂. The PMR spectrum was recorded on a Tesla BS-497 or Varian DA-60H instrument.

<u>1,6-Heptadien-4-ol (II)</u>. This dienol was obtained according to [10], bp 43°C (7 mm). PMR spectrum (CCl₄, δ , ppm): 1.92 singlet (OH), 2.02-2.23 multiplet (-CHC=C), 3.41-3.69 multiplet (CHOH), 4.87-5.13 multiplet (-C=CH₂), 5.54-5.98 multiplet (-C=CH-).

<u>1,5-Heptadien-4-ol (III)</u>. This dienol was obtained from crotonaldehyde according to [10] in 48.5% yield, bp 47°C (7 mm). PMR spectrum (CC1₄, δ , ppm): 1.57-1.73 multiplet (CH₃), 2.04-2.28 multiplet (CH₂), 2.38 singlet (OH), 3.83-4.11 multiplet (CHOH), 4.89-5.15 multiplet (C=CH₂), 5.38-5.57 multiplet (CH=CH), 5.25-5.95 multiplet (CH=CH₂).

<u>5-Hepten-1-yn-4-ol</u> (IV). To 4.5 g (0.185 g-atom) of Mg in 200 ml of abs. Et₂O under Ar at <16°C was added 15 ml (0.2 mole) of CH=CCH₂Br in 2.5 h. The beginning of the reaction was initiated with mercuric chloride. The whole was stirred for 1 h more, 15 ml (0.185 mole) of crotonaldehyde was added (at <25°C), and the whole was stirred for 0.5 h more. Then 30 ml of conc. HCl in 70 ml of H₂O was added with cooling. The organic layer was separated, and the aqueous layer was washed with 2×20 ml of Et₂O. The combined ether fraction was dried with K₂CO₃, and the ether was distilled in a rotor-type evaporator. The distillation gave 12.1 g of alcohol (III) in 59.4% yield, bp 55°C (8 mm). PMR spectrum (CC1₄, δ , ppm): 1.60-1.75 multiplet (CH₃), 1.75-1.88 triplet (=CH), 1.97 singlet (OH), 2.16-2.36 quartet (CH₂), 3.85-4.24 multiplet (CHOH), 5.40-5.70 multiplet (CH=CH).

Oxidation of Alcohol (II) by PCC in situ. To 5.75 ml (11.5 mmoles) of 2 M HCl was added with intense stirring and cooling 1.15 g (11.5 mmoles) of CrO_3 , and then 0.927 ml (11.5 mmoles) of pyridine was added carefully dropwise. A yellow-orange precipitate was formed during cooling of the mixture (~5°C). A solution of 0.5 ml (3.84 mmoles) of alcohol (I) and 0.5 ml

No.	Reagent	Reaction conditions (modi- fication of the method)	Conversion, σ_{00}^{\prime}	Yield of ketone, %†	Lit, analog of method
1a b	$Cr^{6+} + H_2SO_4$	3-4 eq. 1,5-2h, 20° 3-4 eq. 1,5-2h, 20° (Ce ⁴⁺ - 10% per Cr ⁶⁺)	100 100	67 (40-50) ‡ 75	[1] [1]
с 2	Cr ⁶⁺ + (COOH)₂	1,4 eq., 0,5 h, 20° (cooxidation with (COOH) ₂) 3 eq, 10 h, 20°	69 58	28 (40,5) 30 (52)	[1] + +
э ía	$(Bu_3N \text{ or } Bu_4NBr)$ PCC	5 eq., $10-14$ ft, 20° PCC (dry) $- CH_2Cl_2(dry)$	72 65	58,7 (82) 15(23)	[1, 2]
b	(Py·nGi·GO ₃)	PCC $-H_2O - CH_2Cl_2$ 1,5 eq., 1,5-2 h, 20°	80	50 (62,5)	† +
d		$\begin{array}{c} FCC = H_2O = CH_2CI_2\\ 3 eq., \ 1,5=2 \ h, \ 20^{\circ}\\ PCC = H_2O = CH_2CI_2\\ \end{array}$	100 61	40 20 (33)	[<u>1</u>]
5	PSC	3 eq., 2 days 20° (buffer $CH_3COONa \cdot 3H_2O$) $PSC = H_2O - CH_2Cl_2$	75,5	45,5(60)	+
6a	$(Py \cdot \frac{1}{2}H_2SO_4 \cdot CrO_3)$ PDC (Py · 2CrO ₃)	$\begin{array}{cccc} & 5 & eq. & 2 & h, & 20 \\ PDC & - CH_2Cl_2(/dry) & , & Ar \\ 1.5 & eq. & 10-12 & h \\ \end{array}$	38	28 (74)	[1, 2]
7a	DMSO+electrophile	PDC $- CH_2Cl_2(buffer)Ar$ 1,5 eq., 24 h, 20° (I): DMSO: $(COCl)_2=1:2:1;$	50 83	25 (50) 33 (40)	[1, 2]
b		-60° (I): DMSO: SOCI ₂ =1:2:1; -60°	52	31 (60)	[3]
c		(I) : DMSO-PBr ₃ =1:2:2; -15° or -60° (I) : DMSO: PBr ₃ =1:2:1;	100 68	30 56,5(83)	† †
		-15°			ļ

TABLE 1. Conditions and Results of Oxidation of Alcohol (II)*

*If not stated otherwise, all the data are given according to GLC with an internal standard.

[†]The yield of the ketone on the basis of the reacted alcohol is given in parentheses.

‡Distilled product.

**Method proposed by us.

of the internal standard in 10 ml of CH_2Cl_2 prepared beforehand was added to a suspension of the PCC complex, and the whole was stirred for 1.5-2 h at 20°C or boiled with a reflux condenser with stirring for 1-1.5 h (monitoring by GLC). After cooling of the mixture, the organic layer was separated, and the aqueous layer was extracted with 2 × 5 ml of Et₂0. The combined organic layer and extracts were washed with H₂O and dried over H₂CO₃. The yield of ke-tone (I) was 40% with 100% conversion of the alcohol, bp 40°C (10 mm). PMR spectrum (CCl₄, δ , ppm): 2.97-3.20 multiplet (CH₂), 4.9-5.12 multiplet (C=CH₂), 5.4-6.2 multiplet (C=CH).

Oxidation of Alcohol (II) by PSC in situ. To 3 ml (55 mmoles) of conc. H_2SO_4 diluted with H_2O to 15 ml was added 10 g (0.1 mole) of CrO_3 . With cooling (~5°C), 8.1 ml (0.1 mole) of pyridine was added carefully dropwise. With cooling, a crystalline precipitate of PSC was formed. The oxidation of PSC was carried out similarly to that of PCC in situ according to run 5 of Table 1. The yield of ketone (I) was 45.5% with 75.5% conversion of the alcohol.

Oxidation of Alcohol (II) by DMSO/PBr₃. To 0.95 ml (10 mmoles) of PBr₃ in 10 ml of dry CH_2Cl_2 under Ar was added 1.42 ml (20 mmoles) of DMSO in 5 ml of dry CH_2Cl_2 with cooling (-15°C), and the whole was stirred for 10 min more. Then a mixture of 1.2 ml (10 mmoles) of alcohol (I) and 1 ml of the internal standard in 5 ml of dry CH_2Cl_2 prepared beforehand was added, the whole was stirred for 10 min more, and 5 ml (50 mmoles) of Et_3N was added at -15°C. After 30 min, the temperature was raised to ~20°C, and 10 ml of H_2O was added. The organic layer was separated, and the aqueous layer was extracted with 2 × 5 ml of Et_2O . The combined organic layer and extracts were washed with dilute HC1 and H_2O and dried with K_2CO_3 . The yield of ketone (I) was 56.5% with 68% conversion of the alcohol.

CONCLUSIONS

1. Parallel polymerization (10-20%) and oxidative-degradation (20-40%) reactions occur during oxidation of diallylcarbinol and related compounds to ketones.

2. The optimal oxidizing agents for diallylcarbinol are chromic acid in a two-phase system, moist PCC, and DMSO/PBr₃.

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