2. A synergistic effect of quaternary ammonium salts was found in the oxidation by molecular O_2 leading to an increase in the yield of carbonyl compounds.

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SYNTHESIS OF 1,1-DICHLORO-4-METHYL-1,3-PENTADIENE

FROM 1,1,1,3-TETRACHLORO-3-ALKOXYPROPANES

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1,1-Dichloro-4-methyl-1,3-pentadiene (I) is a starting compound for the synthesis of 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanoic (permetrinic) acid which is used for the preparation of pyrethroid insecticides. Many methods are known for the synthesis of diene (I) and have been summarized by Arlt et al. [1].

We have carried out the synthesis of diene (I) from available 1,1,1,3-tetrachloro-3-alkoxypropanes which are the products of the radical addition of CC1. to vinyl alkyl ethers [2]. Thus, 1,1,1,3-tetrachloro-3-butoxypropane (II) yields diene (I) according to the scheme.



According to our previous work [3], heating of ether (II) yields β , β -dichloroacrolein (III) which reacts smoothly with isopropylmagnesium chloride in ether to give 1,1-dichloro-3-hy-droxy-4-methyl-1-pentene (IV). The elimination of water from alcohol (IV) by the action of acid catalysts leads to the diene [4, 5].

The synthesis of diene (I) from 1,1,1,3-tetrachloro-3-ethoxypropane (V) was carried out by the following two methods.

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$$(V) \rightarrow (VI) \xrightarrow{i-\Pr MgCl} (VII) \longrightarrow (VII) \xrightarrow{HX} (VIII a, b)$$
$$\underbrace{\text{Br}(a), \ Cl(b).} \xrightarrow{(VIII a, b)} (VII) \xrightarrow{HX} (VIII a, b)$$

Heating of ether (V) according to our previous work [2] yields 1,1,3-trichloro-3-ethoxy-1propene (VI) and the action of isopropylmagnesium chloride on (VI) in ether yields 1,1-dichloro-3-ethoxy-4-methyl-1-pentene (VII). Passage of dry HBr through ether (VII) at 20°C leads to 1,1-dichloro-3-bromo-4-methylpentene (VIIIa). The action of dry HCl on (VII) in the presence of catalytic amounts of ZnCl₂ gives 1,1,3-trichloro-4-methyl-1-pentene (VIIIb). In this case, 1,1,1,3-tetrachloro-4-methylpentane (IX) is also formed in small amounts due to the addition of HCl to the CCl₂=CH group. Heating of (VIIIa) or a mixture of (VIIIb) and (IX) with a catalytic amount of SnCl₄ smoothly gave diene (I). The second method is significantly simpler and involves the elimination of ethanol from ether (VII) by the action of catalytic amounts of SnCl₄ or ZnCl₂ at 140-150°C and atmospheric pressure.

EXPERIMENTAL

The compounds prepared were analyzed by gas-liquid chromatography on an LKhM-8MD chromatograph with helium gas carrier on a 2000×3 -mm steel column packed with 15% SKTFT-50X on Chromatone N-AW-DMCS at 120-140°C. Ethers (II) and (V) were prepared according to our previous work [2]. Aldehyde (III) was prepared from ether (II) by our previous procedure [3] and ether (VI) was prepared from ether (V) as in our earlier work [2].

1,1-Dichloro-3-hydroxy-4-methyl-1-pentene (IV). A sample of 25 g (III) in 20 ml ether was added gradually to a solution of i-PrMgCl (prepared from 21 g i-PrCl) in 70 ml ether with stirring and cooling from -5° to 0° C. After completion of the addition, the mixture was heated at reflux for 10 min, cooled and decomposed with dilute HCl. The ethereal solution was dried with MgSO₄. The ether was removed and the residue was distilled in vacuum to yield 24.4 g (72%) (IV) with bp 87-88°C (12 mm). Found: C, 42.81; H, 6.12; Cl, 41.69%. Calculated for C₆H₁₀Cl₂O: C, 42.60; H, 5.91; Cl, 42.01%.

<u>1,1-Dichloro-3-ethoxy-4-methyl-1-pentene</u> (VII). A sample of 33 g (VI) was added dropwise with stirring to a solution of i-PrMgCl (from 2l g i-PrCl) in 70 ml ether at -10°C. After completion of the addition, the mixture was heated for 0.5 h, cooled and decomposed with dilute HCl. The ethereal solution was dried over Na₂SO₄. The ether was removed and the residue was distilled in vacuum to yield 23 g (69%) (VII) with bp 75-77°C (14 mm), $n_{\rm D}^{20}$ 1.4493. Found: C, 49.07; H, 7.07%. Calculated for C₈H₄Cl₂O: C, 48.75; H, 7.16%.

<u>1,1-Dichloro-3-bromo-4-methyl-1-pentene (VIIIa</u>). A slow stream of HBr was introduced to 6.6 g (VII) at 20°C until gas-liquid chromatography indicated the disappearance of the starting compound. Then, hexane and water were added. The hexane solution was washed with aq. NaHCO₃ and dried over Na₂SO₄. Vacuum distillation yielded 5.1 g (65%) (VIIIa) with bp 95-97°C (15 mm), $n_D^{2^\circ}$ 1.5110. Found: C, 31.74; H, 3.90%. Calculated for C₆H₉BrCl₂: C, 31.07; H, 3.91%.

<u>1,1,3-Trichloro-4-methyl-1-pentene</u> (VIIIb). A slow stream of dry HCl was added to a suspension of 0.5 g ZnCl₂ in 5 g (VII) at 20°C until the starting compound disappeared. After treatment of the reaction mixture as in the previous experiment, vacuum distillation yielded 3.1 g of a 9:1 mixture of (VIIIb) and (IX) (gas-liquid chromatographic analysis) with bp $81-83^{\circ}$ C (22 mm).

<u>l,l-Dichloro-4-methyl-1,3-pentadiene</u> (I). a) A mixture of 6.7 g (IV) and 0.1 g askanite in 10 ml toluene was heated for 2.5 h at 105-127 °C with the distillation of water. The solution was decanted from the precipitate, the solvent was removed, and residue was distilled to yield 4.2 g (70%) (I) with bp 72-73 °C (15 mm), $n_D^{2^\circ}$ 1.5190 [6].

b) A mixture of 6 g (VIIIa) and one drop of SnCl₄ was heated at reflux for 2 h and then distilled to yield 3.1 g (80%) (I) with bp 72-73°C (15 mm).

c) 5 g of a mixture of (VIIIb) and (IX) and one drop of $SnCl_4$ was heated at reflux for 2 h and then distilled to yield 2.5 g (I).

d) 12.5 g (VII) and 0.5 ml SnCl₄ was heated at 140-150°C with the distillation of ethanol to yield 7.5 g (77.4%) (I).

e) A suspension of 7 g (VII) and 0.3 g $ZnCl_2$ was heated for 2.5 h at 135-145°C with the distillation of ethanol. The liquid phase was removed and distilled to yield 3.5 g (65.5%) (I).

CONCLUSIONS

1. A method is proposed for the preparation of 1,1-dichloro-4-methyl-1,3-pentadiene from 1,1,1,3-tetrachloro-3-alkoxypropanes.

2. Heating of 1,1-dichloro-3-ethoxy-4-methyl-1-pentene with catalytic amounts of SnCl₄ or ZnCl₂ gives the elimination of ethanol and the formation of 1,1-dichloro-4-methyl-1,3-pentadiene.

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TWO-PHASE CATALYZED EXCHANGE OF SOME SUBSTITUENTS

IN THE $\alpha\text{-}\textsc{position}$ of acetates by the trichloromethyl group

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We have previously shown [1] that acylals of saturated, aromatic, and α,β -unsaturated aldehydes (Ia-h) react with chloroform in the presence of 50% aqueous NaOH and catalytic amounts of triethylbenzylammoniu chloride (TEBA) to give the acetates of α -trichloromethylsubstituted carbinols (IIa-h), and it was suggested that (II) were obtained as a result of the nucleophilic replacement of one of the acetate groups in (I) by the CCl₃ anion:

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 $\begin{array}{c} \operatorname{RCH}(\operatorname{OAc})_2 \xrightarrow{\operatorname{CHCl}_5, 50\%^{\bullet} \quad \operatorname{NaOH}} \operatorname{RCH}(\operatorname{CCl}_3)\operatorname{OAc} \\ (I) & (II) \\ \operatorname{R} = \operatorname{CH}_2(a), \ \operatorname{C}_3\operatorname{H}_7(b), \ \operatorname{Ph}(c), \ \operatorname{CH}_2 = \operatorname{CH}(d), \ \operatorname{CH}_3\operatorname{CH} = \operatorname{CH}(e), \ (\operatorname{CH}_3)_2\operatorname{C} = \operatorname{CH}(f), \ \operatorname{CCl}_2 = \operatorname{CH}(g), \\ \operatorname{PhCH} = \operatorname{CH}(b). \end{array}$

In continuation of this investigation, we have examined the reaction of $CHCl_3$ with the acylals of conjugated dienealdehydes using a two-phase catalytic system, and also with some α -substituted acetates RCHX(OAc) where X = Cl and CN. It was found that acylals of sorbal-dehyde (Ii), 5-phenylpenta-2,4-dienal (Ij) and 5,5-dichloropenta-2,4-dienal (Ik) react with CHCl₃ to form the corresponding acetates of α -trichloromethyl-substituted carbinols (II i-k), with no addition of dichlorocarbene to the double bonds of the diene system occurring.

 $\begin{array}{c} R^{1} & R^{1} \\ C = CH - CH = CH - CH(OAc)_{2} \rightarrow \\ R^{2} & (I) \\ R^{1} = H, \ R^{2} = CH_{3}(i); \ R' = H, \ R^{2} = Ph(j); \ R^{1} = R^{2} = Cl(k). \end{array}$

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