OXIDATION OF POLYUNSATURATED ETHERS AND ESTERS BY MOLECULAR OXYGEN CATALYZED BY PALLADIUM SALTS

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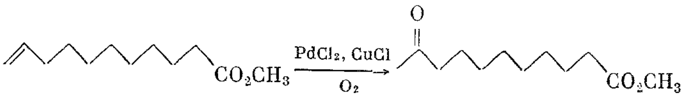
The oxidation of simple olefins by molecular oxygen in the presence of palladium salts to the corresponding carbonyl compounds [1-3] has been well elucidated. Recently, the possibility of using olefins with more complex structure in this reaction has been demonstrated [4-12] by employing the $PdCl_2$—CuCl catalyst system in DMF. However, there is virtually no information on the use of this method for the oxidation of oxygen-containing functional unsaturated compounds containing several double bonds with different extents of substitution.

Hence, it was of interest to study the oxidation of polyunsaturated ethers and esters using O_2 by the action of Pd(II) salts in order to obtain unsaturated ketoethers and ketoesters of given structure which are difficult to prepare. In order to select the optimal conditions for the introduction of the carbonyl group into unsaturated compounds, we studied the oxidation of the methyl ester of 10-undecen-1-oic acid (I) by O_2 in the presence of $PdCl_2$—CuCl and the effect of the ratio of the catalyst components and the reaction conditions on the yield of the methyl ester of 10-oxoundecan-1-oic acid (II).

The nature of the solvent has a marked effect on the yield of (II). The best results are obtained by carrying out the reaction in THF. Acetonitrile, sulfolane, nitromethane, and HMPTA completely inhibit the reaction (Table 1), probably as a result of the formation of rather strong complexes with Cu or Pd salts which have low reactivity in this reaction.



(I) (II)

A decrease in the amount of catalyst to the ratio Pd:Cu:(I) = 1:10:20 has virtually no effect on the yield of (II) (Table 2). A further decrease in the catalyst concentration leads to a marked decrease in the yield of (II).

The oxidation of (I) to yield (II) by O_2 on the $PdCl_2$—CuCl catalyst system in DMF proceeds quantitatively at 60°C over 1 h or at 20°C over 10 h.

The oxidation of (I) to ketoester (II) is accelerated by quaternary ammonium salts which are ordinarily used as interphase transfer catalysts [13, 14]. The catalytic effect is significant for the Pd:R_4NCl ratio of 1:3. If the corresponding bromides are used instead of the tetraalkylammonium chlorides, the yield of ketoester (II) is somewhat reduced. The complete inhibition of the oxidation of (I) is found upon the introduction of quaternary ammonium iodides.

The activating effect of R_4NCl salts is more pronounced in DMF than in the oxidation in THF solution. The reaction does not proceed at all in dioxane (Table 3).

In addition to (I), we oxidized the methyl esters of 2E,5E,10-undecatrie-1-oic (III) and 1,6E(Z),13E,18-nonadecapentaen-10-carboxylic acids (V). The oxidation of (III) gives only the methyl ester of 10-oxo-2E,5E-undecadien-1-oic acid, while (V) yields a mixture of 2-oxo-10-methoxycarbonyl-6E,10E(Z),13E,18-nondecatetraene (VI) and 2,18-dioxo-10-methoxycarbonyl-6E,10E(Z),13E-nonadecatriene (VII) with ∿95% overall yield. The selectivity relative to diketoester (VII) may be raised to 82% if the oxidation of (V) is carried out at higher temperature

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TABLE 1. Effect of the Nature of the Solvent on the Yield of (II) in the Oxidation of (I) by O_2 in the Presence of $PdCl_2$–CuCl*

Solvent	Yield of (II), % †	Solvent	Yield of (II), % †
Tetrahydrofuran	90	Ethylacetate	2
Dimethylformamide	73	Acetonitrile	–
Dioxane	48	Sulpholan	–
Ethylene glycol	34	Nitromethane	–
Dimethylsulfoxide	12	HMPTA	–
Diethylene glycol	7		

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*The reaction was carried out at 20°C for 6 h with molar ratio (I): $CuCl:PdCl_2$ = 10:10:1.

†The yield of ketoester (II) was close to quantitative.

TABLE 2. Effect of Content of the Catalyst Components on the Yield of (II)*

Mole ratio of (I): $CuCl:PdCl_2$			Yield of (II), %
10	10	1	73
10	8	0,8	72
10	5	0,5	71
10	1	0,1	15

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*The solvent was DMF–H_2O. The reaction was carried out at 20°C for 6 h.

TABLE 3. Effect of the Structure of Quaternary Ammonium Salts on the Yield of Ketoester (II)*

R_4NHal	Yield of ketoester (II)		R_4NHal	Yield of ketoester (II)	
	DMF solvent	THF solvent		DMF solvent	THF solvent
$(C_2H_5)_4NCl$	95	87	$(CH_3)_4NBr$	66	56
$C_6H_5CH_2N(C_2H_5)_3Cl$	80	66	$(C_2H_5)_4NBr$	57	46
$(C_4H_9)_4NBr$	77	62	$(C_2H_5)_4HI$	–	–
$C_4H_9N(C_2H_5)_3Br$	69	59	$CH_3N(C_2H_5)_3I$	–	–
			–	73	90

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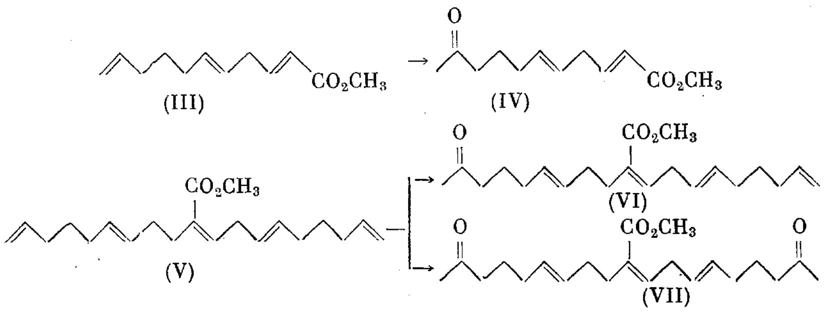
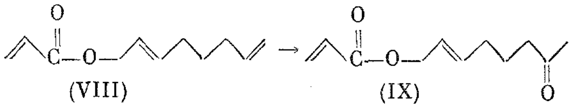
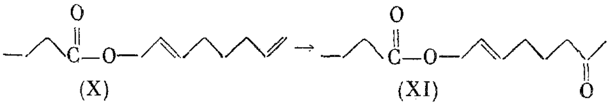
*The reaction was carried out at 20°C for 6 h with molar ratio (I):$CuCl:PdCl_2$ = 10:10:1.



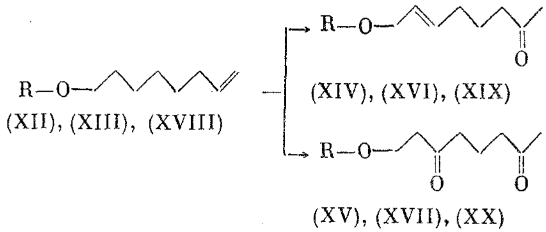
The oxidation of octadienyl esters of 3-oxo-4-oxa-1,6E,11-dodecatriene (VIII) and 4-oxo-5-oxa-7E,12-tridecadiene (X) proceeds selectively at the terminal double bonds which leads to 90% yields of the corresponding carbonyl compounds, 3,11-dioxo-4-oxa-1,6E-dodecadiene (IX) and 4,12-dioxo-5-oxa-7E-tridecene (XI).


(VIII) (IX)


(X) (XI)

On the other hand, 8-methoxy-1,6E-octadiene (XII) and 8-phenoxy-1,6E-octadiene (XIII) react with O_2 at both the terminal and internal double bond conjugated with the alkoxy group and are converted to mixture of mono- and diketoesters, 8-methoxy-2-oxo-6E-octene (XVI) and 2,6-dioxo-8-methoxyoctane (XV) or 2-oxo-8-phenoxy-6E-octene (XVI) and 2,6-dioxo-8-phenoxyoctane (XVII), respectively. Apparently, the allylic disubstituted double bond in (XII) and (XIII) has high reactivity comparable to that of the terminal vinyl group and thus undergoes oxidation along with the vinyl group to form (XV) and (XVII). The ratio of ketoesters (XIV) and (XVI) and of (XV) and (XVII) may be controlled by alteration of the reaction time.

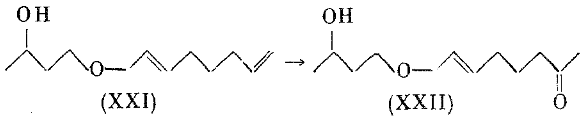
The oxidation of 9,12-dioxa-1,6E-tetradecadiene (XVIII) predominantly leads to 2,6-dioxo-9,12-dioxatetradecane (XX). In addition to diketone (XX), 2-oxo-9,12-dioxa-6E-octene (XIX) is also formed. The fraction of (XIX) in the reaction mixture does not exceed 20%.

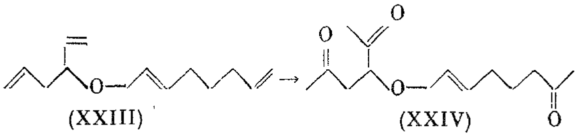

(XII), (XIII), (XVIII)
(XIV), (XVI), (XIX)
(XV), (XVII), (XX)

R = CH_3 (XII), (XIV), (XV); R = C_6H_5 (XIII), (XVI), (XVII); R = C_2H_5—O—C_2H_4 (XVIII), (XIX), (XX).

The IR spectra of (XIV)-(XVII), (XIX), and (XX) have a strong band at 1715 cm^{-1} which is characteristic of the carbonyl group. However, the spectra of diketones (XV), (XVII), and (XX) lack the band related to the disubstituted double bond at 985 cm^{-1}. The oxidation of the double bond in the γ-position to the alkoxy group in (XII), (XIII), and (XVIII) is indicated by transformation of the OCH_2 group proton signal ($\delta \sim 3.75$ ppm) in the PMR spectra from a doublet with J = 3 Hz to a multiplet upon the conversion of (XII), (XIII), and (XVIII) into diketones (XV), (XVII), and (XX), which is related to presence of a methylene group adjacent to the OCH_2 group.

The oxidation of 8-(3-hydroxybutoxy)-1,6E-octadiene (XXI) to 2-oxo-8-(3-hydroxybutoxy)-6E-octene (XXII) occurs rather readily at 40°C in 5 h. The yield of (XXII) was not less than 98%. Unsaturated ethers 4-vinyl-5-oxa-1,7E,12-tridecatriene (XXIII) and 2,5-divinyltetrahydropyran (XXV) which contain several vinyl groups are converted at 70°C over 10 h into 2,12-dioxo-5-oxa-4-methylcarbonyl-7E-tridecene (XXIV) and 2,5-diacyltetrahydropyran (XXVI), respectively.


(XXI) (XXII)


(XXIII) (XXIV)

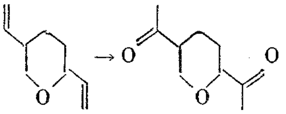

(XXV) (XXVI)

TABLE 4. Effect of the Oxidation Reaction Conditions on the Ketoester and Ketoether Yields

Starting compound	Yield, %	Reaction conditions*		Reaction products, yield, %
		°C	time, h	
(I)	73	20	6	(II)
	100	60	1	
	100	20	10	
(III)	84	20	6	(IV)
(V)		40	10	(VI) 60, (VII) 40
	95	70	6	(VI) 18, (VII) 82
(VIII)	70	50	6	(IX)
	77	70	14	
(X)	90	50	6	(XI)
(XII)	77	50	6	(XIV) 41, (XV) 59
(XIII)	85	60	6	(XIV) 70, (XVII) 30
		60	11	(XIV) 22, (XVII) 78
(XVIII)	100	50	6	(XIX) 20, (XX) 80
(XXI)	98	40	6	(XXII)
(XXIII)	31	40	10	(XXIV)
	100	70	10	
(XXV)	70	20	12	(XXVI)
	100	60	7	

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*The solvent was THF-H_2O; the ether-CuCl-$PdCl_2$ mole ratio was 10:10:1.

EXPERIMENTAL

The unsaturated esters and ethers were prepared according to Vostrikova [13] and our previous work [14]. The products were analyzed on a Chrom-4 chromatograph with flame ionization detector, 1.2-m column packed with SE-30 using helium gas carrier. The PMR spectra were obtained on a Tesla BS-487 spectrometer for $CDCl_3$ solutions using HMDS as internal standard. The IR spectra were taken on a UR-20 spectrophotometer neat or in vaseline oil. The mass spectra were taken on a MKh-13-06 mass spectrometer with 70 eV ionizing electron energy and 200°C ionization chamber temperature.

General Method for the Oxidation of Unsaturated Esters and Ethers by Oxygen in the Presence of Pd Complexes. A sample of 5 ml H_2O and 0.085 mole unsaturated ester or ether and, when necessary, the corresponding amount of R_4NHal to 1.5 g (0.0085 mole) $PdCl_2$ and 8.3 g (0.085 mole) CuCl in 50 ml of the corresponding solvent, and an oxygen stream was introduced into the reaction mass at a rate of 5 liter/h. The mixture was stirred for a given time at a given temperature. At the end of the reaction, the catalysate was diluted with $CHCl_3$, washed thrice with 100-ml portions of 5% HCl and then with water until the wash water was neutral. The organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was distilled in vacuum. The conditions for the oxidation reactions and the ketone yields are given in Table 4.

Methyl Ester of 10-Oxoundeca-1-oic Acid (II). Bp 120°C (1 mm), n_D^{20} 1.4445. IR spectrum (ν, cm^{-1}): 1710 (C=O), 1740 (CO_2CH_3). PMR spectrum (δ, ppm): 1.22 m (12H, CH_2), 1.95 s (3H, CH_3C=O), 2.01 m (4H, CH_2C=O), 3.5 s (3H, CH_3OCO-O). Found: C, 67.57; H, 10.49%. Calculated for $C_{12}H_{22}O_3$: C, 67.52; H, 10.28%. M^+ 214.

Methyl Ester of 10-Oxoundeca-2E,5E-dien-1-oic Acid (IV). Bp 135°C (1 mm), n_D^{20} 1.4881. IR spectrum (ν, cm^{-1}): 985, 3030 (trans-CH=CH), 1710 (C=O), 1720 (=CCO_2CH_3). PMR spectrum (δ, ppm): 1.5 s (2H, CH_2, 2.0 s (3H, O=CCH_3), 2.2 m (4H, =CCH_2, O=CCH_2), 2.7 m (2H, =CCH_2C=), 3.5 s (3H, O=$COCH_3$), 5.1-7.3 m (4H, CH=CH). Found: C, 68.57; H, 8.57%. Calculated for $C_{12}H_{18}O_3$: C, 68.68; H, 8.41%. M^+ 210.

2-Oxo-1-methoxycarbonyl-6E,10E(Z),13E,18-nonadecatetraene (VI). Bp 195°C (1 mm), n_D^{20} 1.4950. IR spectrum (ν, cm^{-1}): 920, 3085 (CH=CH_2), 980, 3030 (trans-CH=CH), 1720 (C=O), 1730 (CO_2CH_3). PMR spectrum (δ, ppm): 1.45 m (4H, CH_2), 2.0 s (3H, O=CCH_3), 2.2 m (10H, =$CHCH_2$), 2.4 m (2H, O=CCH_2), 3.6 d (3H, CH_3C=O), 4.8 t (2H, C=CH_2), 5.3-6.2 m (6H, CH, CH=CH). Found: C, 75.90; H, 9.63%. Calculated for $C_{21}H_{32}O_3$: C, 75.91; H, 9.62%. M^+ 332.

2,18-Dioxo-10-methoxycarbonyl-6E,10E(Z),13E-nonadecatriene (VII). Bp 205°C (1 mm), n_D^{20} 1.5010. IR spectrum (ν, cm^{-1}): 980, 3030 (trans-CH=CH), 1720 (C=O), 1735 (CO_2CH_3). PMR spectrum (δ, ppm): 1.4 m (4H, CH_2), 2.0 s (6H, O=CCH_3), 2.26 m (4H, CH_2C=O), 2.31 (10H,

$=CCH_2$), 3.6 d (3H, CH_3CO_2), 5.3-6.2 m (5H, CH=CH). Found: C, 72.41; H, 9.18%. Calculated for $C_{21}H_{32}O_4$: C, 72.43; H, 9.19%. M^+ 348.

3,11-Dioxo-4-oxa-1,6E-dodecadiene (IX). Bp 110°C (1 mm), n_D^{20} 1.4640. IR spectrum (ν, cm^{-1}): 820 (o-$CCH=CH_2$), 975 (trans-CH=CH), 1710 (C=O), 1720 ($=CCO_2$). PMR spectrum (δ, ppm): 1.6 m (2H, CH_2), 2.0 s (3H, $CH_3C=O$), 2.3 m (2H, $CH_2C=O$), 4.45 d (2H, $CO_2CH_2C=$), 5.7 m (2H, CH=CH), 6.08-6.21 (3H, $CO_2C=CH_2$). Found: C, 67.22; H, 8.15%. Calculated for $C_{11}H_{16}O_3$: C, 67.36; H, 8.15%. M^+ 196.

4,12-Dioxo-5-oxa-7E-tridecene (XI). Bp 115°C (1 mm), n_D^{20} 1.450. IR spectrum (ν, cm^{-1}): 985, 3030 (trans-CH=CH), 1720 (C=O), 1740 (CO_2R). PMR spectrum (δ, ppm): 0.9 t (3H, CH_3C), 1.3-1.6 m (4H, CH_2), 2.0 s (3H, $CH_3C=O$), 2.03-2.4 m (6H, $=CCH_2$, $CH_2C=O$), 4.4 d (2H, CO_2, $CH_2C=$), 5.5 m (2H, CH=CH). Found: 67.67; H, 9.42%. Calculated for $C_{12}H_{20}O_3$: C, 67.94; H, 9.42%. M^+ 212.

8-Methoxy-2-oxo-6E-octene (XIV). Bp 95°C (1 mm), n_D^{20} 1.4410. IR spectrum (ν, cm^{-1}): 980, 3030 (trans-CH=CH), 1715 (C=O). PMR spectrum (δ, ppm): 1.5 m (2H, CH_2), 2.0 s (3H, $CH_3C=O$), 2.3 m (4H, $=CCH_2$, $CH_2C=O$), 3.2 s (3H, CH_3O), 3.75 d (2H, $OCH_2C=$), 5.5 m (2H, CH=CH). Found: C, 69.05; H, 10.20%. Calculated for $C_9H_{16}O_2$: C, 69.25; H, 10.25%. M^+ 156.

2-Dioxo-8-methoxyoctane (XV). Bp 105°C (1 mm), n_D^{20} 1.4470. IR spectrum (ν, cm^{-1}): 1718 (C=O). PMR spectrum (δ, ppm): 1.60 m (2H, CH_2), 2.0 s (3H, $CH_3C=O$), 2.2 m (6H, $CH_2C=O$), 3.2 s (3H, CH_3O), 3.5 m (2H, CH_2O). Found: C, 62.68; H, 9.20%. Calculated for $C_9H_{16}O_3$: C, 62.82; H, 9.29%. M^+ 172.

2-Oxo-8-phenoxy-6E-octene (XVI). Bp 170°C (2 mm), n_D^{20} 1.5160. IR spectrum (ν, cm^{-1}): 710, 770, 3010 (C_6H_5), 985, 3030 (trans-CH=CH), 1715 (C=O). PMR spectrum (δ, ppm): 1.5 m (2H, CH_2), 2.0 s (3H, $CH_3C=O$), 2.1 m (4H, $=CCH_2$, $CH_2C=O$), 4.05 d (2H, $OCH_2C=$), 5.4 m (2H, CH=CH), 6.4-6.7 (5H, C_6H_5). Found: C, 76.98; H, 8.16%. Calculated for $C_{14}H_{18}O_2$: C, 77.07; H, 8.25%. M^+ 218.

2,6-Dioxo-8-phenoxyoctane (XVII). Bp 52-53°C. IR spectrum (ν, cm^{-1}): 710, 770, 3010 C_6H_5), 1720 (C=O). PMR spectrum (δ, ppm): 1.55 m (2H, CH_2), 1.9 s (3H, $CH_3C=O$), 2.25-2.55 m (6H, $CH_2C=O$), 4.0 m (2H, OCH_2), 6.7 m (5H, C_6H_5). Found: C, 71.53; H, 7.86%. Calculated for $C_{14}H_{18}O_3$: C, 71.81; H, 7.68%. M^+ 234.

2-Oxo-9,12-dioxa-6E-octene (XIX). Bp 110°C (1 mm), n_D^{20} 1.3960. IR spectrum (ν, cm^{-1}): 980, 3020 (trans-CH=CH), 1720 (C=O). PMR spectrum (δ, ppm): 1.1 t (3H, CH_3C), 1.5 m (2H, CH_2), 2.03 s (3H, $CH_3C=O$), 2.45 m (2H, $CH_2C=O$), 3.46 m (6H, OCH_2), 3.9 d (2H, $=CCH_2O$), 5.5 m (2H, CH=CH). Found: C, 67.15; H, 10.20%. Calculated for $C_{12}H_{22}O_3$: C, 67.30; H, 10.27%. M^+ 214.

2,6-Dioxo-9,12-dioxaoctane (XX). Bp 115°C (1 mm), n_D^{20} 1.450. IR spectrum (ν, cm^{-1}): 1720 (C=O). PMR spectrum (δ, ppm): 1.1 t (3H, CH_3C), 1.5 m (2H, CH_2), 2.03 s (3H, $CH_3C=O$), 2.45 m (6H, $CH_2C=O$), 3.46 m (8H, OCH_2). Found: C, 62.43; H, 9.46%. Calculated for $C_{12}H_{22}O_4$: C, 62.63; H, 9.56%. M^+ 230.

2-Oxo-8-(3-hydroxybutoxy)-6E-octene (XXII). Bp 185°C (2 mm), n_D^{20} 1.4640. IR spectrum (ν, cm^{-1}): 980, 3030 (trans-CH=CH), 1715 (C=O). PMR spectrum (δ, ppm): 1.05 d (3H, CH_3C), 1.55 m (6H, CH_2), 2.0 s (3H, $CH_3C=O$), 2.35 m (2H, $=CCH_2$), 2.8 m (2H, $CH_2C=O$), 3.40 m (2H, CH_2O), 3.8 d (2H, $OCH_2C=$), 4.0 s (1H, OH), 5.5 m (2H, CH=CH). Found: C, 67.28; H, 10.25%. Calculated for $C_{12}H_{22}O_3$: C, 67.30; H, 10.27%. M^+ 214.

2,12-Dioxo-5-oxa-4-methylcarbonyl-7E-tridecene (XXIV). Bp 150°C (1 mm), n_D^{20} 1.4870. IR spectrum (ν, cm^{-1}): 980, 3030 (trans-CH=CH), 1720 (C=O). PMR spectrum (δ, ppm): 1.55 m (2H, CH_2), 2.0 s (3H, $CH_3C=O$), 2.3 m (7H, $CH_2C=$, $CH_2C=O$), 3.75 d (2H, $OCH_2C=$), 5.5 m (2H, CH=CH). Found: C, 66.20; H, 8.60%. Calculated for $C_{14}H_{22}O_4$: C, 66.16; H, 8.65%. M^+ 254.

2,5-Diacetyltetrahydropyran (XXVI). Bp 88°C (1 mm), n_D^{20} 1.3790. IR spectrum (ν, cm^{-1}): 1715 (C=O). PMR spectrum (δ, ppm): 1.6 m (4H, CH_2), 2.0 s (6H, $CH_3C=O$), 2.3 m (1H, CHC=O). 3.3-3.75 m (3H, OCH_2, OCHC=O). Found: C, 63.34; H, 8.11%. Calculated for $C_9H_{14}O$: C 63.54; H, 8.23%. M^+ 170.

CONCLUSIONS

1. A study was carried out on the oxidation of polyunsaturated ethers and esters by molecular oxygen catalyzed by the $PdCl_2$—CuCl system. A series of new mono-, di-, and triketoethers and triketoesters was obtained in high yield.

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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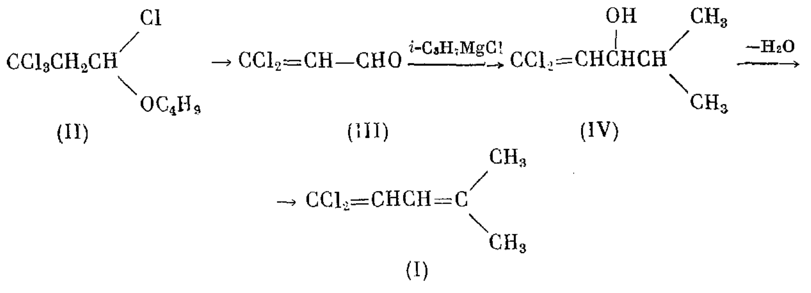
1,1-Dichloro-4-methyl-1,3-pentadiene (I) is a starting compound for the synthesis of 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanoic (permetrinic) acid which is used for the preparation of pyrethroid insecticides. Many methods are known for the synthesis of diene (I) and have been summarized by Arlt 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 CCl_4 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-hydroxy-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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