was in accord with previous work [5]. The addition of $MnCl_2$ and LiCl to $CuCl_2$ increased the yield of DMC twofold (20.7%) and barely changed with increase of CO pressure. However, the yield of MAc decreased under this condition. Increasing the temperature from 140° to 180° increased the yield of DMC to 89% and decreased the MA yield. In all experiments on the oxidative carbonylation of CH_3OH, the pressure decreased after 4 h. In the experiment conducted at 180°, pressure decrease was observed for 10 h. In the infrared spectrum of isolated DMC, absorption was detected at 800, 920, 1280, 1460, 1750, 2860, 2960, and 3010 cm^{-1}, corresponding to that reported [5]. In the NMR spectrum of DMC there was a signal at 3.74 ppm corresponding to the OCH_3 group.

CONCLUSIONS

1. The yield of methyl acrylate during oxidative carbonylation of ethylene in the presence of chlorides of palladium and copper sharply increased with the addition of LiCl and during the increase of the partial pressure of carbon monoxide in the gaseous mixture.

2. Highly effective as a catalyst, methanol served simultaneously as the reagent and formed methyl acrylate in yields approaching 73%.

3. In oxidative carbonylation of methanol, the system $MnCl_2$—$CuCl_2$—LiCl was highly active. At 180°, 40 atm carbon monoxide pressure, and 22.5 atm oxygen the yield of dimethyl carbonate approached 89%.

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NICKEL-COMPLEX-CATALYZED ADDITION OF METHANOL TO ESTERS OF α,β-UNSATURATED ACIDS

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Alcohols add to esters of α,β-unsaturated acids in the presence of strongly alkaline reagents and an excess of the alcohol [1, 2]. Information is lacking regarding the catalysis of these reactions by complexes of the transition metals.

We studied the addition of methanol to methyl acrylate (MA), methyl methacrylate (MMA), dimethyl maleate (DMM), and dimethyl fumarate (DMF) in the presence of nickel complexes. The methyl ester of β-methoxypropionic acid (I) was produced in approximately 100% yield when a 1:1 mixture of methanol and MA were reacted in a diethyl ether solution of $Ni(acac)_2$,

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TABLE 1

Activator	Solvent	Yield of the methyl ester of β-methoxypropionic acid, %	Activator	Solvent	Yield of the methyl ester of β-methoxypropionic acid, %
$(C_4H_9)_3P$	$(C_2H_5)_2$	98	$[C_2H_5O(CH_2)_2-O]_3P$	The same	15
$(PhO)_3P$	The same	74	$(C_2H_5)_3N$	»	34
$(C_2H_5O)_3P$	»	70	$(C_4H_9)_3P$	benzene	19
$(C_6H_5)_3Sb$	»	91	$(C_4H_9)_3P$	THF	40
$(C_6H_5)_3P$	»	64	$(C_4H_9)_3P$	Hexane	17
$(C_4H_9)_3B$	»	33	$(C_4H_9)_3P$	$(CH_3)_2SO$	73

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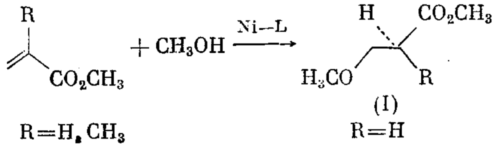
*Experimental conditions: 0.39 mole **Ni(acac)₂**, 0.39 mole activator, 0.78 mole $Al(C_2H_5)_3$, 0.39 mole NaOH, 5 ml solvent, 80°, 10 h.

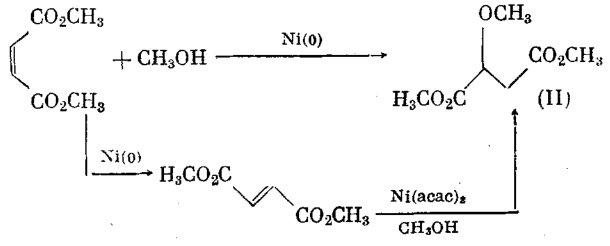
$P(C_4H_9)_3$, and $Al(C_2H_5)_3$ (1:1:2). The high yield is due to the addition to the catalyst of 0.5-1 mole of NaOH relative to the $Ni(acac)_2$. Ester (I) is also formed in the absence of NaOH but only in 20% yield. The yield does not exceed 30% on catalysis of the reaction by the above-mentioned quantity of NaOH without the $Ni(acac)_2$. Thus, the significant increase in yield on interaction of methanol with MA in the presence of the system $Ni(acac)_2$–$P(C_4H_9)_3$–$Al(C_2H_5)_3$–NaOH (1:1:2:1) can be attributed to the promoting influence of alkali on complexes of Ni.



The yield of (I) is essentially unaffected by changes in the activator-to-$Ni(acac)_2$ ratio. The yield of (I) drops to 80%, and higher oligomers are formed only on fourfold increase in this ratio. As seen in Table 1, the yield of (I) increases with increase in electron-donating capacity of the activator in the series $(PhO)_3P$ > $(CH_2H_5O)_3P$ > $(C_6H_5)_3Sb$ > $(C_4H_9)_3P$. Formation of (I) is blocked if (β-ethoxyethyl) phosphite is used as the activator. It may be assumed that the β-position oxygen in that molecule is capable of coordinating with the nickel atom, making the approach and activation of the olefin difficult. This leads to a significant drop in the yield of (I).

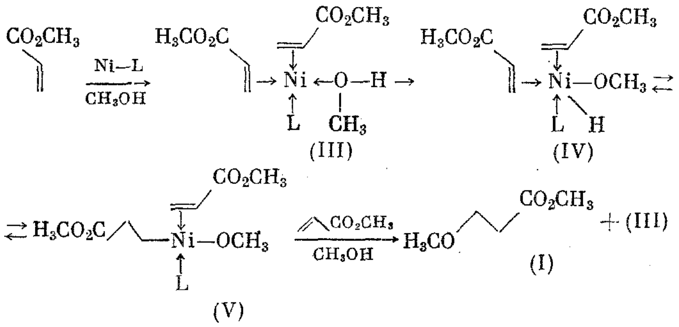
Unreacted monomer disappears completely from the reaction mixture. The diethyl ether can be successfully replaced by DMSO. The yield is dramatically reduced in hydrocarbon solvents.

All attempts to react MMA with methanol failed. DMF and DMM reacted with methanol in the presence of $Ni(acac)_2$–$(C_4H_9)_3P$–$Al(C_2H_5)_3$–NaOH (1:1:2:1) yielding the dimethyl ester of α-methoxysuccinic acid (II). The yield of (II) from DMF was significantly greater (∿90%) than for DMM. In the absence of methanol DMM isomerizes to DMF in up to 95% yield after 8-10 h in the system $Ni(acac)_2$–$P(C_4H_9)_3$–$Al(C_2H_5)_3$–NaOH (1:1:2:1). Based on these results it can be proposed that the addition of methanol proceeds via isomerization of DMM to DMF.

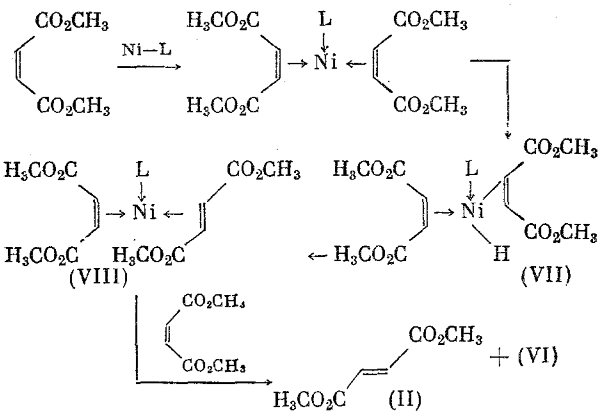


The formation of ester (I) and the isomerization of DMM to DMF under the influence of Ni complexes can be represented by the schemes:

SCHEME 1



SCHEME 2



In the first step of scheme 1 methanol and MA, reacting with the nickel complex, give (III). Oxidative addition of methanol leads to the hydrated complex (IV). Addition of the activated monomer at the Ni—H bond leads, probably, to the unstable σ complex (V), which converts to (I) and complex (III).

Esters of the α-methoxysuccinic acid are formed analogously. Isomerization of DMM to DMF can proceed by the proposed scheme 2 via hydrated complex (VII), in which the addition and subsequent removal of the hydrogen atom leads to the thermodynamically more stable trans isomer.

The activation of nickel complexes by NaOH in reactions of methanol with esters of α,β-unsaturated acids can be explained by the formation of coordinated complexes between nickel and OH^- in which the effective negative charge on the metal atom is increased.

EXPERIMENTAL

The purity of all monomers was ≥ 99.8%. Mixtures of hydrocarbons were analyzed on a Chrom-4 chromatograph equipped with a 2-m column packed with silicone elastomer E-301. The carrier gas was nitrogen. Infrared spectra were taken on a UR-20 spectrophotometer. NMR spectra were obtained on a Tesla BS-480B instrument (CCl_4, internal standard HMDS). Mass spectra were obtained on an MKh-13-06 instrument at 50 eV.

General Procedure for Addition of Methanol to Esters of α,β-unsaturated Acids. To a solution of 0.39 mole $Ni(acac)_2$ and 0.39 mmole activator in 2 ml $(C_2H_5)_2O$ is added 0.78 mmole $Al(C_2H_5)_3$. The addition is made under argon at 0° and the solution is mixed for 30 min. The catalyst solution is then transferred to a 17-ml stainless-steel autoclave. To the solution is added 6 ml MA and 0.39 mmole NaOH in 3 ml methanol. The reaction mixture is then heated for 10 h at 80°. After cooling, the reaction mixture is diluted with 20 ml hexane and steam distilled. The distillate is separated and the water layer extracted with hexane. This extract is combined with the distillate and dried over $MgSO_4$. The solvent is then evaporated off and the residue analyzed by GLC.

Ester (I) was isolated by fractional distillation, bp 57°C (50 mm): n_D^{20} 1.4034 IR spectrum (ν, cm^{-1}); 1245, 1735 (CO_2CH_3) NMR spectrum (δ, ppm); 2.37 t (2H, CH_2); 3.20 s (3H, OCH_3); 3.50 t(2H, CH_2); 3.55 s (3H, CO_2CH_3), m/e 118.

On interaction of 14 g DMM with 3 g methanol in the presence of 0.156 g $Ni(acac)_2$, 0.123 g $(C_4H_9)_3P$, 0.139 g $Al(C_2H_5)_3$, and 0.024 g NaOH under conditions analogous to those described above, we obtain 12.6 g of (II) and 3.6 g of a mixture which, according to GLC analysis, contained DMM and DMF in an 8:2 ratio. (II) bp 125° (50 mm); n_D^{20} 1.4230 IR spectrum (ν, cm^{-1}): 1240, 1740 (CO_2CH_3). NMR spectrum (δ, ppm); 2.56 m (2H, CH_2); 32 s (3H, OCH_3); 3.6 s (6H, CO_2CH_3); 4.0 m (1H, C–H), m/e 176.

Under similar conditions 12 g of (II) were obtained from 10 g DMF and 2.1 g methanol.

Isomerization of Dimethyl Maleate to Dimethyl Fumarate. To a solution of catalyst prepared from 0.156 g $Ni(acac)_2$ are added 20 g DMM. The solution is heated 10 h at 80°. Following normal work-up procedures 19.8 g DMF were isolated. The product was identified by GLC, by comparison with known.

CONCLUSIONS

Nickel complexes, accompanied by phosphorus-containing ligands and alkali, catalyze addition of methanol to esters of acrylic, maleic, and fumaric acids.

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STEPWISE TELOMERIZATION OF 1-ALKENES WITH DIETHYL DIBROMOMALONATE: FORMATION OF SPIRODILACTONES

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Stepwise telomerization of haloolefins with a terminal carbon–halogen bond takes place at sufficiently reactive halogen atoms with the formation of adducts. The literature indicates, for example, the telomerization of alkenes with trichloroacetic acid [1, 2] and of vinyl chloride with methyl dibromoacetate [3]. Thus, we anticipated a stepwise telomerization on interaction of diethyl dibromomalonate (DBM) with 1-alkenes, considering that DBM appears significantly more active than methyl dibromoacetate [4].

The present work shows that with excess 1-alkene in the presence of either peroxide or a coordination initiator based on $Fe(CO)_5$, DBM reacts by stepwise telomerization, followed by radical lactonization. As assumed earlier [5], the reaction then terminates by a chain mechanism (Scheme 1). Homolytic addition takes place simultaneously with the formation of adducts (Scheme 2). Thus, reaction of DBM with 1-alkenes simultaneously generates two chain reactions resulting in the formation of adduct and of spirodilactone, respectively. The contribution of these two processes apparently is established by the structure of the alkene. Spirodilactones (II)-(IV) incorporate two monomeric units and thus correspond to a secondary telomer homolog.

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