7. B. M. Mikhailov and Yu. N. Bubnov, Organoboron Compounds in Organic Synthesis [in Russian], Nauka, Moscow (1977), p. 55.
8. F. Bohlmann, R. Zeisberg, and E. Klein, Org. Magn. Reson., 7, 426 (1975).
9. N. Ya. Grigor'eva, E. P. Prokof'ev, and A. V. Semenovskii, Dokl. Akad. Nauk SSSR, 245, 366 (1979).

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# CATALYTIC CONVERSIONS OF $C_3$-CYCLIC OLEFINS IN THE PRESENCE OF METAL COMPLEXES.

## 2. INFLUENCE OF THE LIGAND ENVIRONMENT OF NICKEL ON THE ACTIVITY AND SELECTIVITY OF METAL COMPLEXES IN DI- and TRIMERIZATION OF METHYLENECYCLOPROPANE

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Several features of the catalytic di- and trimerization of methylenecyclopropane (MCP) in the presence of $(Ph_3P)_2Ni(MCP)$ (Kt-1) have already been established [1]. In particular, 2-methyl-4-methylenehexa-1,5-diene (I) is found among the dimers. According to [1, 3], Kt-1 is assumed to be the primary intermediate from which a series of nickel aliphatic alkanes is formed, precursors of MCP dimers and trimers. The formation of (I) from MCP on phosphine-modified complexes had not been observed previously. In such a case, it is not clear whether it is possible to consider Kt-1 as the primary intermediate for various phosphine complexes of Ni(0). There is also no information in the literature on the effect of the valence state of the metal in the initial complex on the course of the reaction.

In the present work, we have studied catalytic conversions of MCP in the presence of Ni complexes with differing ligand environments and oxidation states of the central atom. A point of particular interest was to clarify to what extent the observed features of the catalytic conversion of MCP in the presence of Kt-1 are of a general character for Ni complexes containing triphenylphosphine as one of the ligands.

We have also tested, under the same conditions, the catalytic systems $(Ni(COD)_2$ (Kt-2), Kt-2—$PPh_3$, and Kt-2—Dipy (COD = cyclooctadiene).

It can be seen from the results, set out in Tables 1 and 2, that the activity of the catalysts and the selectivity of the reactions are strongly dependent on the ligand environment of the Ni. Furthermore, when using Kt-2 the chief products are oligomers and dimers (II) and (III) (dispiro[2.1.2.1]octane and methylene spiro[4.2]heptane, respectively) in addition to trimers (IV) and (V) [Eq. (1)]. Replacing one of the COD molecules in the coordination sphere of the Ni by DQ (DQ = duroquinone) leads to complete deactivation of the complex.

Adding Dipy to Kt-2 suppresses the catalytic conversion of MCP, only a stoichiometric reaction of MCP with $Ni(COD)_2$ in 1:1 ratio being observed (the yield of dimer amounts to 1 mole/mole Ni).

However, in the presence of Ni(0) complexes containing $PPh_3$, prepared previously or *in situ* (complexes 4-6, 8, Table 1), the catalytic conversion of MCP proceeds similarly to that observed in the presence of Kt-1.

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TABLE 1. Catalytic Conversions of MCP on Nickel Complexes $[MCP]_0$ = 1.38 mole/liter, T = 60°C, benzene, t = 7 h

| Complex No. | Complex | $[Ni]_0$, mmole/liter | Activity mole MCP / mole Ni · h | Selectivity, % | | |
|---|---|---|---|---|---|---|
| | | | | dimers | trimers | oligomers |
| 1 | $Ni(COD)_2$ | 3,4 | 2,2 | 33 | 20 | 47 |
| 2 | Ni(COD)(DQ) | 2,5 | 0 | – | – | – |
| 3 | $Ni(COD)_2$+Dipy (1 : 1) | 7,7 | 1* | 1* | – | – |
| 4 | $Ni(COD)_2+PPh_3$ (1 : 2) | 4,7 | 14 | 27 | 38 | 35 |
| 5 | $Ni(PPh_3)_2(C_2H_4)$ | 3,4 | 28 | 20 | 72 | 8 |
| 6 | $Ni(PPh_3)_2(CO)_2$ | 2,5 | 3,2** | – | 100 | 0 |
| 7 | $Ni(PPh_3)_2(MCP)$ | 2,4 | 48 | 22 | 72 | 6 |
| 8 | $Ni(PPh_3)_4$ | 1,7 | 23 | 31 | 69 | 0 |

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*Reaction is stoichiometric with formation of 100% dimer (III).

**Induction period 7 h; in remaining cases, <1 h.

TABLE 2. Distribution of the Products of the Conversion of MCP in the Presence of Ni(0) Complexes

| Complex No* | Composition, % | | | | | |
|---|---|---|---|---|---|---|
| | dimers | | | trimers | | unidentified trimers |
| | (I) | (II) | (III) | (IV) | (V) | |
| 1 | – | 57 | 43 | – | – | – |
| 2 | – | – | – | – | – | – |
| 3 | – | 60 | 40 | – | – | – |
| 4 | 24 | Traces | 76 | 30 | 61 | 9 |
| 5 | 13 | Traces | 87 | 30 | 61 | 9 |
| 6 | – | – | – | 28 | 69 | 3 |
| 7 | 17 | Traces | 83 | 37 | 59 | 4 |
| 8 | 25 | Traces | 75 | 31 | 67 | 2 |

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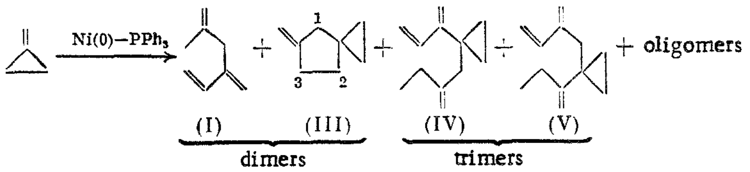
*See Table 1.

TABLE 3. Influence of Experimental Conditions on the Composition of Oligomerization Products of MCP on $Ni(COD)_2$–$PPh_3$

| P/N | $[Ni]_0 \cdot 10^3$ | $[MCP]_0$ | T, °C | t, h | Conversion, % | Selectivity, % | | | Dimer composition, % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | mole/liter | | | | | $\sum C_8$ | $\sum C_{12}$ | $\sum C_{16+}$ | I | II | III |
| 1 | 22,8 | 11,5 | 40 | 9 | 60 | 19 | 63 | 18 | 2 | 2 | 96 |
| 2 | 4,6 | 0,85 | 60 | 5 | 38 | 41 | 58 | 1 | 24 | Traces | 76 |



(1)

Traces of (II) were observed under the conditions used in the study; the main products were (I), (III)-(V). Such a distribution of the products of the catalytic conversion of MCP is also found when the system Kt-2–$PPh_3$ is used. These results are not in agreement with those of [2], according to which only (II) and (III) were observed among the dimers, this evidently being associated with the differences in the experimental conditions. The results given in Table 3 support such a hypothesis: The selectivity varies considerably with change in conditions. A similar effect has been observed previously in the case of Kt-1, which lends additional support to the formation of Kt-1 as the primary intermediate in the catalytic conversion of MCP on Kt-2–$PPh_3$.

The considerable induction period which is characteristic of conversions of MCP on $Ni(CO)_2(PPh_3)_2$ is another indication of the formation of an active intermediate by replacement of CO, as has been described previously for a heterogenized analog of the complex under discussion [4].

In addition to the examinatin of Ni(0) complexes (Table 1), we also studied the catalytic activity of several Ni(I) and Ni(II) complexes: $Ni(PPh_3)_3Br$, $[Ni(PPh_3)_3Cl]_2$, $Ni(PCy_3)_2\cdot(Cl)(H)$, $(Ph_3PCH_3)_2(NiI_4)$ (Cy = cyclohexyl). No conversion of MCP was observed in the presence of these complexes. The absence of activity in $Ni(PCy_3)_2(Cl)(H)$, which is a model of an active particle according to a degenerate polymerization mechanism, casts doubt on whether MCP reacts by this mechanism.

Thus, since an identical set of reaction products is obtained in the presence of different Ni(0) triphenylphosphine complexes one can assume that the mechanisms of the catalytic conversions of MCP are similar. In particular, it seems that di- and trimerization of MCP on such catalysts proceeds with the formation of Kt-1 as an intermediate complex. This conclusion is further supported by the data presented (Tables 1 and 2) for the course of the reaction in the presence of the assumed [2, 3] primary intermediates.

## EXPERIMENTAL

A Bruker M-250 spectrometer, working at 250 MHz, was used to obtain NMR spectra in $C_6D_6$ as solvent with $C_6H_6$ as internal standard, the chemical shifts being exprsesed as ppm from TMS. The accuracy of the chemical shifts was ±0.03 ppm and the $^{13}C-^{1}H$ spin–spin coupling interaction ±0.09. Hz Chromatography-mass spectrometry was effected on a Varian MAT-111 instrument.

A Biochrom-1 gas chromatograph was used for GLC analysis, this being provided with a flame-ionization detector and a glass capillary column 55 m × 0.25 mm using OV-101 as the stationary phase.

Methylene cyclopropane was prepared by the method of [1]. The complexes $Ni(COD)_2$, Ni(COD)(DQ), $Ni(PPh_3)_2(C_2H_4)$, $Ni(PPh_3)_2(CO)_2$, $(Ph_3P)_2Ni-$  and $Ni(PPh_3)_4$ were prepared by methods given in [5-10].

<u>Identification of the Di- and Trimers of MCP</u>. Benzene was distilled off from the mixture obtained by the catalytic conversion of MCP and then the dimer and trimer fractions were collected, monitored by GLC. The individual products of (I) were separated from the mixture of dimers by preparative GLC.

The mass spectrum and PMR spectrum of (I) were in agreement with those given in [1].

PMR spectrum of (III) (δ, ppm, J, Hz): 0.34 s (4H, cyclopropane), 4.92 m and 4.99 m (2H, $CH_2$=), 2.16 (2H, $H^1$), 2.0, 1.44 t (2H, $H^2$), 7.5, 2.40 t (2H, $H^3$), 7.5. Mass spectrum (m/z): 108 ($M^+$), 93, 91, 80, 79.

PMR spectrum of (IV) (δ, ppm, J, Hz): 0.69 m and 0.87 m (4H, cyclopropane), 1.22 t (3H, $CH_3$), 7.5, 2.25 q (2H, $CH_2CH_3$, 7.5, 5.0-5.7 m (6H, $CH_2$=), 2.52 s (2H, $CH_2$), 6.59 m (1H, CH), 10.5, and 17.5. Mass spectrum (m/z): 162 ($M^+$), 147, 133, 119, 105, 93.

PMR spectrum of (V) (δ, ppm, J, Hz): 0.69 m and 0.87 m (4H, cyclopropane), 1.21 t (3H, $CH_3$), 7.5, 2.25 q (2H, $CH_2CH_3$), 7.5, 5.0-5.7 m (6H, $CH_2$=), 2.40 s (2H, $CH_2$), 6.48 m (1H, CH), 10.5, and 17.5. The spectroscopic characteristics of (I)-(V) were found to be in good agreement with those of [1, 2].

## CONCLUSIONS

1. It has been shown that in the presence of ($\eta^2$-methylenecyclopropane)bis(triphenylphosphine)nickel (Kt-1) and of a series of triphenylphosphine Ni(0) complexes the catalytic conversion of methylenecyclopropane (MCP) proceeds with the formation of identical di- and trimerization products.

It is postulated that the mechanism of di- and trimerization of MCP on all Ni(0) phosphine complexes is similar, with the formation of Kt-1 as a general intermediate.

2. Complexes of Ni(I) and Ni(II) which have been studied were found to be inactive in MCP conversion.

## LITERATURE CITED

1. D. B. Furman, A. V. Kudryashev, L. S. Isaeva, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1231 (1987).

2. P. Binger, A. Brinkmann, and J. McMeeking, Justus Liebig's Ann. Chem., 1065 (1977).
3. P. Binger, M. Cetinkaya, M. J. Doyle, et al., Fund. Res. Homogeneous Catal., 3, 271 (1979).
4. D. B. Furman, N. V. Volchkov, and O. V. Bragin, 5th International Symposium on Heterogeneous Catalysis [in Russian], Varna, Bulgaria, Vol. 2 (1983), p. 249.
5. B. Bogdanovic, M. Kröner, and G. Wilke, Justus Liebig's Ann. Chem., 699, 1 (1966).
6. A. N. Nesmeyanov, L. S. Isaeva, L. N. Morozova, et al., J. Organomet. Chem., 172, 185 (1979).
7. J. Ashley-Smith, M. Green, and F. G. Stoune, J. Chem. Soc., A, 3019 (1969).
8. A. N. Nesmeyanov, L. S. Isaeva, and L. N. Morozova, Inorg. Chim. Acta, 29, 1210 (1978).
9. I. S. Isaeva, T. A. Peganova, P. V. Petrovskii, et al., J. Organomet. Chem., 258, 367 (1983).
10. R. A. Schuun, Inorg. Synth., 13, 124 (1972).

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# SYNTHESIS OF ISOTHIOAMIDES OF Alk—C(SAr)=NAr BY RADICAL ARYLATION OF THIOAMIDES

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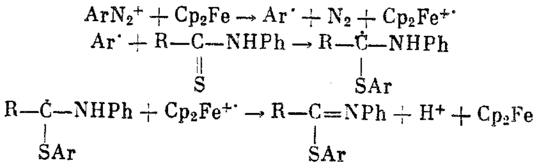
Esters of imidothioacids (isothioamides, ITA's) are highly reactive compounds used as intermediates in organic synthesis, particularly in the synthesis of alkaloids [1]. Methods for obtaining ITA's ($R^1$—$C(SR^2)$=$NR^3$) depend significantly on the nature of the substituents. For compounds with $R^1$ = Alk and $R^2$ = Ar there are no general synthetic methods. The usual method, the Chapman reaction [2], i.e., substitution of the chlorine in the corresponding imidoyl chlorides by an SAr group, is difficult due to their extreme instability when $R^1$ = Alk [3]. Other recently proposed methods [4-6] are less general. They start from compounds already containing the SAr group, i.e., derivatives of aromatic thiols, which are relatively inaccessible.

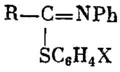
In this work we obtained $\mathrm{Alk{-}\underset{\diagdown SAr}{C}{=}NAr}$ bearing ITA's by applying a method previously developed by us involving radical arylation of thioamides [7] using diazonium fluoroborates as the aryl radical source, which are easily obtained from accessible and cheap anilines, in combination with catalytic amounts of ferrocene. Previously by this method ITA's derived from atomatic thioacids were obtained [8]. The reaction scheme is as follows:



$$ArN_2^+ + Cp_2Fe \rightarrow Ar^{\cdot} + N_2 + Cp_2Fe^{+\cdot}$$
$$Ar^{\cdot} + R{-}\underset{\underset{S}{\|}}{C}{-}NHPh \rightarrow R{-}\underset{\underset{SAr}{|}}{\dot{C}}{-}NHPh$$
$$R{-}\underset{\underset{SAr}{|}}{\dot{C}}{-}NHPh + Cp_2Fe^{+\cdot} \rightarrow R{-}\underset{\underset{SAr}{|}}{C}{=}NPh + H^+ + Cp_2Fe$$

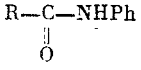
As seen from Table 1 the above reactions proceed with high conversion of the starting substance and in 3 h they give the target compounds (I) with 40-85% yields.

At the same time noticeable amounts of the corresponding amides (II) and diaryldisulfides (III) are formed and in some cases (expts. 2-6, Table 1) also thiol esters (IV) and aniline (V)



$$R{-}\underset{\underset{SC_6H_4X}{|}}{C}{=}NPh$$

(I)

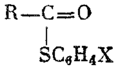


$$R{-}\underset{\underset{O}{\|}}{C}{-}NHPh$$

(II)

$(XC_6H_4S)_2$

(III)



$$R{-}\underset{\underset{SC_6H_4X}{|}}{C}{=}O$$

(IV)

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