REACTION OF SECONDARY AMINES WITH CYCLIC 1,3-DIENES, CATALYZED BY NICKEL COMPLEXES

U. M. Dzhemilev, A. Z. Yakupova, and G. A. Tolstikov

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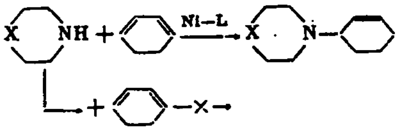
We were the first to study the reaction of secondary amines with cyclic 1,3-dienes in the presence of nickel complexes and activating additives. 1-Morpholyl-2-cyclopentene (I) is formed in 60% yield when cyclopentadiene (CPD) is reacted with morpholine in the presence of $Ni(acac)_2 - Al(C_2H_5)_3 - P(C_4H_9)_3 - CF_3CO_2H$, 1 : 2 : 3 : 10 (80°C, 5 h). The reaction is complicated by the formation of dicyclopentadiene (DCP), which lowers the yield of (I) substantially. Compound (I) is not formed in the absence of CF_3COOH.

Under the optimum conditions (80°, 5 h), piperidine when reacted with CPD in the same catalytic system is converted to 1-piperidyl-2-cyclopentene (II) in 50% yield. After reaction the catalyzate contains, together with (II), unreacted piperidine, DCP, and 5% of CPD. The yield of (I) and (II) could not be increased by increasing the temperature and reaction time due to the competing dimerization of CPD to DCP. At the decomposition temperature of DCP (180-190°) the yield of (I) and (II) is low, probably because of the decomposition of the catalytically active complex.

X = O(I), CH_2(II)

When CPD is replaced by 1,3-cyclohexadiene the yields of amines (III) and (IV) are, respectively, 90 and 80%. In contrast to CPD, 1,3-cyclohexadiene also reacts with piperidine and morpholine in the absence of CF_3CO_2H, but here the yield of the amines does not exceed 10%.



X = CH_2(III), O(IV)

In our experiments we were unable to make 1,3-cyclooctadiene react with amines.

EXPERIMENTAL

The employed dienes were at least 99.5% pure. The amines were analyzed on a Chrom-31 chromatograph, using a 2-m long column, packed with Silicone Elastomer E-301 deposited on Celite, and nitrogen as the carrier gas. The UR spectra were taken on a UR-20 spectrophotometer (as a film). The NMR spectra were recorded on a Tesla BS-480B instrument using CCl_4 solutions and HMDS as the internal standard. The mass spectra were taken on an MKh-1306 instrument using ionizing electrons with an energy of 50 eV and an ionization chamber temperature of 200°.

To a solution of 0.5 mmole of $Ni(acac)_2$, 1.5 mmoles of $P(C_4H_9)_3$, and 1.0 ml of butadiene in 3 ml of dry benzene at 0°, in an argon stream, was added 1.0 mmole of $Al(C_2H_5)_3$ and the mixture was stirred for 0.5 h. The catalyst solution was transferred to a 17-ml steel autoclave, which had previously been loaded with 50 mmoles of the amine, 50 mmoles of the 1,3-cyclodiene, and 5 mmoles of CF_3CO_2H, and the mixture was heated at 80° for 5 h. After cooling, the catalyzate was washed with water, filtered through 10 g of Al_2O_3 (III activity), and washed with benzene. The benzene eluates were combined with the main filtrate, the solvent was evaporated, and the residue was vacuum-distilled.

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1-Morpholyl-2-cyclopentene (I). Bp 86° (7 mm); n_D^{20} 1.4934. Infrared spectrum (ν, cm^{-1}): 720, 3060 (cis-CH=CH). NMR spectrum (δ, ppm): 1.7 m (2H, CH_2); 2.1 m (2H, $CH_2C=$); 2.29 m (4H, CH_2N); 3.2 m (1H, $-\overset{|}{C}HN-$); 3.45 m (4H, CH_2O); 5.67 m (2H, CH=CH); m/e 153. Found: C 70.6; H 9.7; N 9.2%. $C_9H_{15}NO$. Calculated: C 70.59; H 9.8; N 9.15%. Hydrochloride, mp 199-201°. Found: C 56.71; H 8.58; N 7.32; Cl 18.65%. $C_9H_{16}NOCl$. Calculated: C 56.99; H 86.44; N 7.39; Cl 18.73%.

1-Piperidyl-2-cyclopentene (II). Bp 76° (7 mm); n_D^{20} 1.4903. Infrared spectrum (ν, cm^{-1}): 720, 3060 (cis-CH=CH). NMR spectrum (δ, ppm): 1.54 m (8H, CH_2); 2.2 m (6H, CH_2N, $CH_2C=$); 3.32 m (1H, $-\overset{|}{C}HN-$); 5.53 (2H, CH=CH); m/e 151. Found: C 79.50; H 11.20; N 9.30%. $C_{10}H_{17}N$. Calculated: C 79.47; H 11.26; N 9.27%. Hydrochloride, mp 218-220°. Found: C 63.52; H 9.63; N 7.34; Cl 19.5%. $C_{10}H_{18}NCl$. Calculated: C 64.00; H 9.60; N 7.47; Cl 18.93%.

1-Piperidyl-2-cyclohexene (III). Bp 55° (1 mm); n_D^{20} 1.5008. Infrared spectrum (ν, cm^{-1}): 730, 3030 (cis-CH=CH). NMR spectrum (δ, ppm): 1.41 br. s (10H, CH_2); 1.85 br. s (2H, $CH_2C=$); 2.4 m (4H, CH_2N-); 3.03 m (1H, $-\overset{|}{C}HN-$); 5.54 s (2H, CH=CH); m/e 165. Found: C 80.1; H 11.5; N 8.3%. $C_{11}H_{19}N$. Calculated: C 80.00; H 11.51; N 8.48%. Hydrochloride, mp 229-231°. Found: C 65.44; H 10.01; N 6.82; Cl 17.7%. $C_{11}H_{20}NCl$. Calculated: C 65.50; H 9.93; N 6.95; Cl 17.62%.

1-Morpholyl-2-cyclohexene (IV). Bp 61° (1 mm); n_D^{20} 1.5015. Infrared spectrum (ν, cm^{-1}): 730, 3025 (cis-CH=CH). NMR spectrum (δ, ppm): 1.56 m (2H, CH_2); 1.87 br. s (2H, $CH_2C=$); 2,42 m (4H, CH_2N); 3.01 m (1H, $-\overset{|}{C}HN-$); 3.48 m (4H, CH_2O); 5.57 s (2H, CH=CH); m/e 167. Found: C 72.3; H 10.2; N 8.4%. $C_{10}H_{17}NO$. Calculated: C 71.86; H 10.18; N 8.38%. Hydrochloride, mp 194-195°. Found: C 59.04; H 8.84; N 6.83; Cl 17.4%. $C_{10}H_{18}NOCl$. Calculated: C 58.97; H 8.85; N 6.88; Cl 17.44%.

CONCLUSIONS

The reaction of piperidine and morpholine with cyclopentadiene and 1,3-cyclohexadiene in a system that contains nickel acetylacetonate, tri-n-butylphosphine, triethylaluminum, and trifluoroacetic acid (1 :3 :2 :10) leads to cycloalkenylpiperidines and morpholines.

REACTION OF ALLYLMERCURY HALIDES WITH PLATINUM COMPOUNDS

A. Z. Rubezhov, A. S. Ivanov,
and S. P. Gubin

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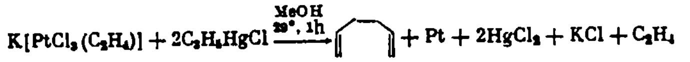
Allyl compounds of mercury are universal allylating agents for metal halides of the Pt group (Ru, Os, Ir, Rh, Pd) [1-5]. We studied the reaction of allylmercury halides with Pt(IV), Pt(II), and Pt(0) compounds.

Depending on the character of their reaction with $CH_2=CHCH_2HgCl$, and Pt(IV) and Pt(II) compounds can be subdivided into two groups. The first group includes saltlike compounds of the M_2PtCl_6 and M_2PtCl_4 type (M = K, Na), Zeise salt, and its dimer $(C_2H_4PtCl_2)_2$. These Pt(II) and Pt(IV) derivatives react with allylmercury chlorides (AMC) to give Pt, Hg(II) salts, and the liberation of biallyl (BA).



(1)

The second group of compounds includes complexes of type L_2PtX_4 and L_2PtX_2, where L = PhCN or PPh_3.

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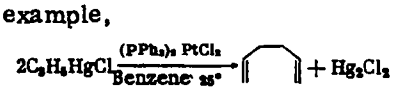
These Pt(II) and Pt(IV) derivatives react with AMC to give BA and Hg(I) salts. The starting Pt compounds remain unchanged during reaction, for example,

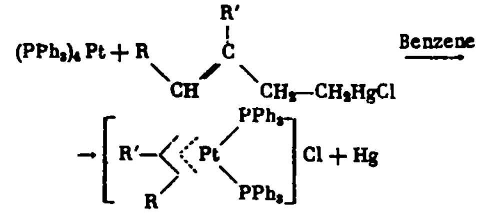


(2)

It is possible that reaction (2) proceeds under the influence of the free ligand L that is present in the benzene solution [6], which is capable of functioning as a symmetrizing agent. The diallylmercury that is formed during symmetrization decomposes under the reaction conditions to give BA and Hg, and the latter reacts with $HgCl_2$ to give calomel. Actually, we were able to isolate Hg in a number of cases.

$$\begin{gathered} 2C_3H_5HgCl \rightarrow C_3H_5{-}Hg{-}C_3H_5 + HgCl_2 \\ C_3H_5HgC_3H_5 \rightarrow C_3H_5{-}C_3H_5 + Hg \\ HgCl_2 + Hg \rightarrow Hg_2Cl_2 \end{gathered} \tag{3}$$

L_4Pt ($L = PPh_3$) reacts instantly with allylmercury halides in benzene at ~20°. Evaporation of the reaction mixture gave π-allyl cation complexes. When reacted with $(PPh_3)_4Pt$ under analogous conditions the alkyl and aryl derivatives of Hg(II) form the σ-complexes $(PPh_3)_2PtR(X)$ (R = alkyl, aryl) [7].



(4)

R = R' = H; R = H, R' = Me; R = H, R' = Ph; R = Me, R' = H; R = Ph, R' = H; R = Ac, R' = Me

The obtained π-allyl complexes are stable colorless compounds that are difficultly soluble in organic solvents and are soluble only in chloroform to give the (1 : 1) adducts with the solvent. Despite the fact that the method proposed by us for the synthesis of the π-allylbis(triphenylphosphine) complexes of platinum [at least for π-allylbis(triphenylphosphine)platinum chloride] is less convenient than the reaction of L_4Pt with allyl halides [8], the latter cannot be used to obtain a wide selection of substituted π-allyl complexes (for example, for the synthesis of the 2-phenyl- or 1-acetyl-2-methyl derivatives), since the corresponding substituted allyl halides are not available.

EXPERIMENTAL

The starting allylmercury halides were obtained as described in [9]; the synthesis of the Pt compounds was described in [10]. The IR spectra were measured on a UR-10 instrument as KBr pellets, while the NMR spectra were taken on an NR-2305 instrument (60 MHz).

Preparation of π-Allylbis(triphenylphosphine)platinum Chlorides (General Method). To the orange-yellow solution of 0.0004 mole of $(PPh_3)_4Pt$ in 50 ml of benzene was added in drops, at ~20°C, in an argon atmosphere, a colorless solution of 0.0004 mole of the allylmercury halide in 20 ml of benzene. The mixture decolorized within 5 min and a gray precipitate of Hg deposited. The mixture was stirred for another hour, filtered, and the filtrate was diluted with ether until all of the reaction product had precipitated, which was filtered, washed well on the filter with ether to remove the PPh_3, and dried in vacuo. The obtained white compound was recrystallized.*

Bis(triphenylphosphine)-π-allylplatinum Chloride $[(PPh_3)_2Pt(C_3H_5)]Cl$. Yield 70%, mp 194-198° (decompn.), mp 195° (decompn.) [8]. Found: C 58.51; H 4.36; Cl 4.90%. $C_{39}H_{35}PtP_2Cl$. Calculated: C 58.83; H 4.43; Cl 4.45%. Infrared spectrum (ν, cm^{-1}): 3080, 3050, 3020, 2995, 1590, 1480, 1435, 1400, 1315, 1280, 1190, 1170, 1125, 1100, 1080, 1030, 1005, 945, 930, 870, 850, 760, 730, 700, 545, 510. NMR spectrum ($CHCl_3$, δ, ppm): 3.56 (unresolved signal, 4H); 6.10 m (1 H).

Bis(triphenylphosphine)-π-2-phenylallylplatinum Chloride $[(PPh_3)_2Pt(C_9H_9)]Cl \cdot CHCl_3$. Yield 70%, mp 287-293° (decompn.). Found: C 55.39; H 3.92; Cl 14.00; P 6.80%. $C_{43}H_{40}PtP_2Cl_4$. Calculated: C 55.71; H 4.06; Cl 14.30; P 6.25%.

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*In the case of AMC the obtained complex was recrystallized from benzene. In all of the other cases the complexes are insoluble in hot benzene and were recrystallized from chloroform.

Bis(triphenylphosphine)-π-1-acetyl-2-methylallylplatinum Chloride $[(PPh_3)_2Pt(C_6H_9O)]Cl \cdot CHCl_3$. Yield 54%, mp 295-300° (decompn.). Found: C 53.14; H 3.92; Cl 14.02; P 6.20%. $C_{43}H_{40}PtP_2Cl_4O$. Calculated: C 53.15; H 4.15; Cl 14.58; P 6.38%. Infrared spectrum (ν, cm^{-1}): 3080, 3060, 3030, 3010, 2990, 1680-1650, 1590, 1580, 1485, 1435, 1315, 1195, 1165, 1100, 1035, 1005, 760, 700, 620, 555, 535, 520, 505.

Bis(triphenylphosphine)-π-1-methylallylplatinum Chloride $[(PPh_3)_2Pt(C_4H_7)]Cl \cdot CHCl_3$. Yield 70%, mp 268-274° (decompn.). Found: C 52.85; H 3.79; Cl 14.98; P 6.33%. $C_{41}H_{38}PtP_2Cl_4$. Calculated: C 52.97; H 4.12; Cl 15.25; P 6.66%.

Bis(triphenylphosphine)-π-2-methylallylplatinum Chloride $[(PPh_3)_2Pt(C_4H_7)]Cl \cdot CHCl_3$. Yield 65%, mp 290-295° (decompn.) Found: C 52.81; H 3.94; Cl 15.10; P 6.28%. $C_{41}H_{38}PtCl_4P_2$. Calculated: C 52.97; H 4.12; Cl 15.25; P 6.66%.

Reaction of Pt(II) and Pt(IV) Compounds with AMC (General Method). To a solution of 0.003 mole of the Pt compound in 100 ml of CH_3OH at ~20°, in an argon atmosphere, was added a solution of 0.003 mole of AMC in 50 ml of MeOH, after which the mixture was stirred for 3-4 h and then filtered. The filtrate was diluted with water and extracted with chloroform. The aqueous layer was evaporated and the residue was analyzed for the presence of Hg^{2+} or Hg^{+} by the addition of NaOH. The organic layer was evaporated, collecting the condensate in a cooled (—78°) receiver. After distilling off the solvent the residue was recrystallized and analyzed in the usual manner. The condensate was analyzed by GLC for the presence of biallyl.

CONCLUSIONS

1. A study was made of the reaction of allylmercury halides with Pt(0), Pt(II), and Pt(IV) compounds.

2. The π-allylbis(triphenylphosphine) complexes of Pt were synthesized by the allylation of tetrakis(triphenylphosphine)platinum with substituted allylmercury halides.

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