2,3-Dihydrothiophene-3-carboxylic Acid (IIb). The electroreduction of 0.64 g of (Ib) [8] was run under the indicated conditions. The catholyte was separated, acidified with conc. HCl to pH 2, extracted with ether, and the extract was dried over $MgSO_4$ and evaporated in vacuo. We obtained 0.3 g (46%) of (IIb) as a colorless oil, R_f 0.46 (Silufol, 4:1 ether–hexane mixture). Infrared spectrum (ν, cm^{-1}): 945, 1280, 1428, 1710, 2940, 2965. Found: C 46.16; H 4.67; S 24.24%; M^+ 130. Calculated for $C_5H_6O_2S$: C 46.16; H 4.61; S 24.64%; mol. wt. 130.1.

2,3-Dihydroselenophene-3-carboxylic Acid (IIc). In a similar manner, from 0.8 g of (Ic) [9] we obtained 0.5 g (63%) of (IIc) as an amorphous powder, R_f 0.54 (Silufol, 2:3 hexane–ether mixture). Infrared spectrum (ν, cm^{-1}): 925, 1285, 1410, 1718, 2935, 2960. M^+ 177. Calculated for $C_5H_6O_2Se$: mol. wt. 176.9.

CONCLUSIONS

The electroreduction of the anions of five-membered heteroaromatic 2- and 3-carboxylic acids leads to the corresponding β,γ-unsaturated derivatives.

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NEW CATALYSTS FOR THE REDUCTION OF AROMATIC DIAZO COMPOUNDS BY ALCOHOLS TO HYDROCARBONS

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The reduction of aromatic diazo compounds to hydrocarbons is widely used in organic synthesis as a preparative method for replacing the amino group in an aromatic ring by hydrogen. The use of either primary or secondary alcohols as reducing agents for this purpose is well known [1]. However, the decomposition of diazo compounds in alcohols proceeds very slowly, often when heated, and is, especially in the case of methanol, nonspecific. Large amounts of phenol ethers are formed along with the hydrocarbons.

Recently we reported [2] that the nitrogen complex trans-$(dppe)_2W(N_2)_2$ (I) (dppe = $Ph_2PCH_2CH_2PPh_2$) is capable of catalyzing the reduction of aromatic diazo compounds by alcohols (including MeOH) to the corresponding hydrocarbons. The reaction proceeds at room temperature and is quite selective. Data on the catalytic activity of various nitrogen, carbonyl, and hydride complexes of Mo and W in this reaction are given in the present paper.

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EXPERIMENTAL

The aromatic diazo compounds ArN_2Cl were obtained by the diazotization of aromatic amines with isoamyl nitrite in acid alcoholic medium and, after isolation from solution, they were recrystallized. The starting cis-$(dppe)_2W(CO)_2$, trans-$(dppe)_2Mo(N_2)(CO)$, trans-$(dppe)_2Mo(N_2)_2$, trans-$(Ph_2MeP)_4Mo(N_2)_2$, cis-$(Me_3P)_4Mo(N_2)_2$, $(dppe)_2MoH_4$, $(dppe)_2WH_4$, $(Ph_2MeP)_4WH_4$, $[(Ph_2MeP)_4WH_5]ClO_4$, and $(dppe)_2WH_2Cl_2$ were synthesized as described in [3-6].

The experiments on the decomposition of the ArN_2Cl were run in an argon atmosphere at ~ 20°C. With stirring, a solution of 1.0 mmole of the ArN_2Cl in 5 ml of MeOH was added dropwise in 10 min to the appropriate amount of the complex in 5 ml of MeOH, after which the mixture was stirred for another 15-20 min. The N_2 evolution was practically ended by this time. Having measured the final volume of the evolved gas in a buret, the liquid reaction products and the solvent were separated by vacuum recondensation and the dry residue was extracted with ether. The condensate and ether extract were combined and analyzed by GLC on an LKhM-8M chromatograph (flame-ionization detector, and using N_2 as the carrier gas). To determine the benzene we used a 3 m × 3 mm column packed with Polysorb-4T (160°, internal standard = toluene). The anisole and chlorobenzene were analyzed at 110° on a 3 m × 3 mm column packed with 10% of poly(ethylene glycol adipate) deposited on Risorb BLK; internal standard = phenetole. The nitrobenzene and diphenyl were determined on the same column at 180°, and here diphenyl and nitrobenzene were respectively used as the internal standards.

TABLE 1. Decomposition of PhN_2Cl in Methanol Using Various Mo and W Complexes (PhN_2Cl:Complex = 100:1)

Complex	Yield in % when based on PhN_2Cl		Complex	Yield, in % when based on PhN_2Cl	
	N_2	PhH		N_2	PhH
$(dppe)_2Mo(N_2)_2$	100	96	$(dppe)_2MoH_4$	100	89
$(dppe)_2Mo(CO)(N_2)$	100	94	$(Ph_2MeP)_4WH_4$	97	76
$(dppe)_2W(N_2)_2$	100 *	93 *	$[(Ph_2MeP)_4WH_5]ClO_4$	56	51
$(dppe)_2W(CO)_2$	94	88	$(dppe)_2WH_4$	52	46
$(Ph_2MeP)_4Mo(N_2)_2$	94	83	$(dppe)_2WH_2Cl_2$	47	34
$(Me_3P)_4Mo(N_2)_2$	96	85			

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* Data from [2].

TABLE 2. Decomposition Products of PhN_2Cl in Methanol and Its Deutero Derivatives Using $(PH_2MeP)_4WH_4$ (PhN_2Cl:W ratio = 50:1)

Alcohol	Yield of N_2, in % when based on PhN_2Cl	Yield of organic products, in % when based on PhN_2Cl			
		benzene	anisole	chlorobenzene	diphenyl
CH_3OH	100	84	2,9	0.6	3,4
CH_3OD	100	77	1,7	0,1	3,6
CD_3OD	55	19	14,1	4,7	5,1

TABLE 3. Decomposition of Aryldiazonium Chlorides in Methanol Using $(dppe)_2W(CO)_2$ and $(Ph_2MeP)_4WH_4$

ArN_2Cl	Mole ratio ArN_2Cl : W	Yield of products in % when based on ArN_2Cl			
		$(dppe)_2W(CO)_2$		$(Ph_2MeP)_4WH_4$	
		N_2	ArH	N_2	ArH
p-$NO_2C_6H_4N_2Cl$	50 : 1	100	85	100	97
	100 : 1	100	83	100	88
	200 : 1	100	79	—	—
	300 : 1	—	—	100	85
$C_6H_5N_2Cl$	50 : 1	100	97	100	84
	100 : 1	94	88	97	76
	200 : 1	90	82	—	—
	300 : 1	81	71	—	—
	500 : 1	45	—	—	—
p-$CH_3OC_6H_4N_2Cl$	50 : 1	100	91	52	34
	100 : 1	60	48	23	—

The isotope analyses were run by mass spectrometry on a Varian MAT CH-8 instrument at 20 eV.

DISCUSSION OF RESULTS

The data on the catalytic activity of the studied complexes when PhN_2Cl is reduced by methanol are given in Table 1. The reaction proceeds with a fast rate at room temperature. The nitrogen and carbonyl complexes of Mo and W are the most active and selective in this reaction, and also the molybdenum hydride complex $(dppe)_2MoH_4$. The yield of benzene is nearly quantitative when they are used. The hydride complexes of W are less efficient.

When PhN_2Cl is decomposed in MeOH using $(Ph_2MeP)_4WH_4$ we also determined the other catalytic decomposition products of the diazo compound (Table 2). We found that together with benzene, the main product, small amounts of anisole, diphenyl, and chlorobenzene are formed.

As in the case of the nitrogen complex (I) [2], the decomposition of diazo compounds catalyzed by hydride and carbonyl complexes is strongly inhibited by atmospheric oxygen, although all of the studied complexes are quite stable in the air. Thus, if the reaction is run in the presence of air, then only 26% of the N_2 is evolved when PhN_2Cl is decomposed in MeOH using $(Ph_2MeP)_4WH_4$ for the standard length of time (25 min), and only 16% in the case of $(dppe)_2W(CO)_2$ (PhN_2Cl:W ratio = 50:1).

The catalytic activity of the carbonyl and hydride complexes in the reduction of substituted aromatic diazo compounds was studied for the example of $(dppe)_2W(CO)_2$ and $(Ph_2MeP)_4WH_4$. As can be seen from Table 3, when $p\text{-}NO_2C_6H_4N_2Cl$ is decomposed in MeOH, the greatest catalytic activity is displayed by $(Ph_2MeP)_4WH_4$, whereas $(dppe)_2W(CO)_2$ is more efficient in the decomposition of $p\text{-}CH_3OC_6H_4N_2Cl$. In both cases these complexes are superior to $(dppe)_2W(N_2)_2$ in their activity (cf. [2]) and the yield of the hydrocarbon approaches 100%.

The alkyl group of the alcohol is the source of the hydrogen for forming the ArH, which is confirmed by the experiments with the deuterated alcohols. Thus, when PhN_2Cl is decomposed using $(Ph_2MeP)_4WH_4$ in CH_3OD (98.0 at.% of D) the amount of C_6H_5D in the formed benzene exceeds the natural amount by only 1-2%. If the reaction is run in CD_3OD (98.2 at.% D), then the formed benzene analyzes 84% of the monodeuterated derivative C_6H_5D and 16% of C_6H_6. A smaller amount of D in the benzene when compared with the starting CD_3OD is explained by the kinetic isotope effect. A decrease in the yield of benzene and the total efficiency of the decomposition of PhN_2Cl in CD_3OD (see Table 2) is apparently also caused by the isotope effect and indicates that the cleavage of hydrogen from the alkyl group of the alcohol is the limiting step of the catalytic process. A slowing up of the main reduction reaction when the decomposition is run in CD_3OD is accompanied by an increase in the role of side processes, as a consequence of which the yields of anisole and chlorobenzene increase. It should be mentioned that the use of CH_3OD does not lead to either a substantial decrease in the efficiency of the decomposition or a change in the ratio of the main and secondary products (see Table 2). A similar picture was also observed during catalysis by complex (I) [2].

As a result, various nitrogen, carbonyl, and hydride complexes of Mo and W are capable of catalyzing the reduction of aromatic diazo compounds by alcohols to hydrocarbons. The efficiency of this reaction depends on the character of the starting metal complex, the nature of the diazo compound, and other factors. With the proper choice of catalyst the selectivity of the reaction is very high and the yield of the hydrocarbon ArH approaches 100%.

CONCLUSIONS

Some new efficient catalysts were found for the reduction of aromatic diazo compounds by alcohols to the corresponding hydrocarbons.

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REACTION OF COPPER DERIVATIVES OF MONOSUBSTITUTED ACETYLENES WITH BENZOYL CHLORIDE

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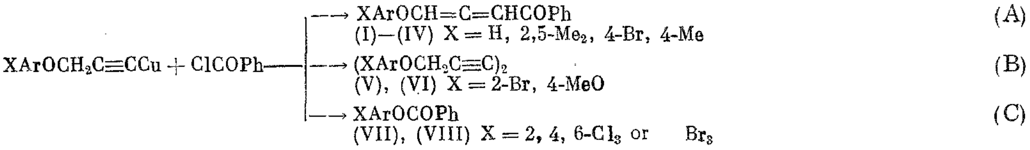
Copper acetylides RC≡CCu are widely used in the synthesis of various classes of compounds [1-4]. The reaction of the copper derivatives of the propargyl and ethynyl phenyl ethers with benzoyl chloride was studied in the present paper. The reaction was run under the conditions described in [5] for copper phenylacetylide, which is converted here to phenylbenzoylacetylene. In contrast to this acetylide, the reaction of the studied copper aroxypropynylides, depending on the substituents X, proceeded in the following directions:



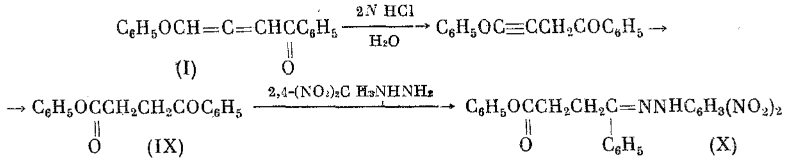
$$\mathrm{XArOCH_2C{\equiv}CCu + ClCOPh} \longrightarrow \begin{cases} \longrightarrow \mathrm{XArOCH{=}C{=}CHCOPh} \quad \text{(I)—(IV) } X = \mathrm{H,\ 2,5\text{-}Me_2,\ 4\text{-}Br,\ 4\text{-}Me} & \text{(A)} \\ \longrightarrow \mathrm{(XArOCH_2C{\equiv}C)_2} \quad \text{(V), (VI) } X = \mathrm{2\text{-}Br,\ 4\text{-}MeO} & \text{(B)} \\ \longrightarrow \mathrm{XArOCOPh} \quad \text{(VII), (VIII) } X = \mathrm{2,\ 4,\ 6\text{-}Cl_3} \text{ or } \mathrm{Br_3} & \text{(C)} \end{cases}$$

The results of studying the obtained compounds (I)-(VIII) are given in Table 1.

Direction (A) was observed when X = H, Me, 2,5-Me_2, and 4-Br. The structure of the allenic γ-ketoethers (I)-(IV) was established employing mass spectrometry, PMR, and IR spectroscopy, and by the formation of hydrazones. Either the absence or the weak manifestation of the vibration bands of the allenic grouping in the IR spectra of compounds (I)-(IV) proved unexpected. The presence of this grouping in these compounds was confirmed by the PMR spectra (see Table 1), while the presence of a C=O group, conjugated with the allenic system and the benzene ring, was confirmed by the presence of an absorption band at 1630 cm^{-1} in their IR spectra.

The mass spectrum of 1-phenoxy-3-benzoylpropadienone (I) contains peaks that correspond to the following ions: M^+ 236 (92%), $(M - C_6H_5)^+$ – 59 (100%), $(M - COC_6H_5)^+$ – 131 (47%), $(C_6H_5C_3H_2)^+$ – 115 (38%), $(C_6H_5C_3H)^+$ – 114 (13%), $(C_6H_5CO)^+$ – 105 (63%), $(C_6H_5C_2H)^+$ – 103 (28%), $(C_6H_5OH)^+$ – 94 (10%), and $(C_6H_5)^+$ – 77 (25%), which confirms its structure.

When treated with 2,4-dinitrophenylhydrazine, compound (I) is converted to the 2,4-dinitrophenylhydrazone of the phenyl ester of 3-benzoylpropionic acid (X). When compared with the starting (I), an absorption band in the 1720 cm^{-1} region appeared in the IR spectrum of (X), which is characteristic for an unconjugated carbonyl group. Its appearance is related to the hydration of (I) to the phenyl ester of 3-benzoylpropionic acid (IX):



$$\underset{\text{(I)}}{\mathrm{C_6H_5OCH{=}C{=}CH\overset{}{\underset{\underset{\displaystyle O}{\|}}{C}}C_6H_5}} \xrightarrow[\mathrm{H_2O}]{2N\ \mathrm{HCl}} \mathrm{C_6H_5OC{\equiv}CCH_2COC_6H_5} \rightarrow$$

$$\rightarrow \underset{\text{(IX)}}{\mathrm{C_6H_5O\underset{\underset{\displaystyle O}{\|}}{C}CH_2CH_2COC_6H_5}} \xrightarrow{2,4\text{-}(\mathrm{NO_2})_2\mathrm{C_6H_3NHNH_2}} \underset{\text{(X)}}{\mathrm{C_6H_5O\underset{\underset{\displaystyle O}{\|}}{C}CH_2CH_2\underset{\underset{\displaystyle C_6H_5}{|}}{C}{=}NNHC_6H_3(NO_2)_2}}$$

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