CONCLUSIONS

1. The possibility of using iodobenzoyl diacetate in methanolic alkali for the epoxidation of α,β-unsaturated ketones was demonstrated for the first time in the case of dehydropregnenolone.

2. The relatively low reactivity of Δ^4-3-ketosteroids in reactions of $PhI(OAc)_2/MeOH/KOH$ was determined.

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FORMATION OF CARBENE AND CARBYNE SPECIES IN THE REACTION OF BENZALDEHYDE WITH METALS IN THEIR LOW-VALENCE STATE

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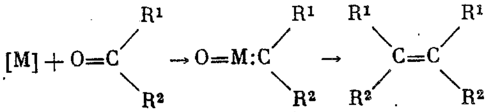
The reactions of carbonyl compounds with molybdenum, tungsten, and chromium carbonyls as well as with tungsten halides with tungsten in its low-valence state are accompanied by the formation of unsaturated hydrocarbons [1, 2].

The initial step in these reactions is presumably the oxidative addition of the carbonyl compound to the metal with the formation of a carbene complex. We studied the reaction of



benzaldehyde with Mo, W, Cr, and Re carbonyls and with tungsten compounds with tungsten in its low oxidation state formed upon the reaction of WCl_6 with sec-butyllithium. In all cases, unreacted benzaldehyde remains in the systems, while the only hydrocarbon product is stilbene. Table 1 shows that the greatest stilbene yield is observed upon the use of $Mo(CO)_6$. An increase in the reaction temperature with other conditions equal did not lead to an increase in the stilbene yield, which reaches 60% with the $Mo(CO)_6/PhCHO$ mole ratio equal to 20.

$Re(CO)_{10}$ does not display activity in this reaction. The formation of an unstable intermediate complex of phenylcarbene is indicated by the isolation of 5-6% toluene (relative to PhCHO introduced) upon carrying out the reaction in the presence of ethanol.

The reaction of benzaldehyde with tungsten compounds featuring tungsten in its low oxidation state obtained by the reduction of WCl_6 by sec-butyllithium leads to the formation

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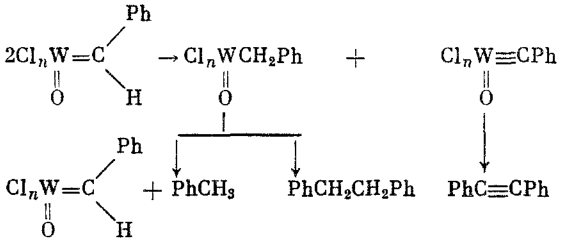
TABLE 1. Reaction of Metal Carbonyls with Benzaldehyde at 25°C, M/PhCHO Mole Ratio = 5

Metal carbonyl	Solvent	Time, h	Stilbene yield, % rel. to PhCHO	
			cis-	trans-
$Mo(CO)_6$	Benzene	24	5	19
	Pentane	2	4	17
	»	24	10	38
	»	72	10	38
$W(CO)_6$	Benzene	24	3	6
	Pentane	24	4	8
$Cr(CO)_6$	Benzene	24	1	3
	THF	24	0,5	8

of stilbene and tolan in 4:1 mole ratio. The total yield of these products is 20-28% relative to benzaldehyde introduced after 2 h reaction.

The formation of tolan, which was observed for the first time in this reaction, may be related to the disproportionation of the initially generated carbene complexes. Gas-liquid chromatographic analysis of the reaction products indicate the formation of 1% toluene and 2.5% dibenzyl. Tungsten chloride reduced by sec-butyllithium in combination with benzaldehyde [W/PhCHO = 120] initiates the polymerization of cyclopentene with ring opening.



EXPERIMENTAL

The reactions of benzaldehyde with metal carbonyls was carried out by the addition of 1 M solutions of benzaldehyde in benzene, pentane, or THF at 25°C to solid carbonyls (the metal/PhCHO mole ratio = 5). The reactions were run for from 2 to 72 h at 25°C. At the end of the reaction, the solvent was removed in a vacuum. The residue was extracted by ether and the ethereal fraction was analyzed chromatographically on an LMKh-8-MD5 chromatograph using 3-m column packed with E-301 on Chromosorb W and a 3-m column packed with Apieson L on Chromosorb W.

The reaction of benzaldehyde with tungsten compounds with tungsten in a low oxidation state was carried out as follows. A 0.5 M solution of sec-butyllithium in hexane (W/Li = 0.25) was added to 0.07 M WCl_6 in benzene at 25°C. After 0.5 h, the gaseous products were removed in a vacuum. A 1 M solution of benzaldehyde in benzene (PhCHO/W = 1) was added to the resulting suspension of the reduced tungsten compound in benzene at 25°C. The reaction was carried out for 2 h. The chromatographic analysis of the products was analogous to that described above.

CONCLUSIONS

The reactions of benzaldehyde with Mo, W, and Cr carbonyls and tungsten chlorides with tungsten in its low oxidation state are accompanied by the separation of stilbene or stilbene and tolan, respectively, which is attributed to the formation of intermediate complexes of phenylcarbene and phenylcarbyne.

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