

and  $\log K_2$  values for the complexation of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{NH}_4^+$  with (II) in methanol are most representative [6]. The qualitative behavior described for (I) relative to the complexation constants with these monovalent cations is valid for (II), i.e., the addition of a benzo ring to (II) with the formation of (I) does not significantly affect the mechanism for ligand complexation.

From a practical viewpoint, we may note that among the cations studied,  $\log K_1$  for  $\text{Ca}^{2+}$  and  $\log K_2$  for  $\text{Na}^+$  have high values. This may be used for the separation of cations in non-aqueous media.

### CONCLUSIONS

1. In a calorimetric study of the thermodynamics of the complexation of benzo-12-crown-4 with lithium, sodium, potassium, ammonium, and calcium thiocyanates, this ligand was found to have a tendency for partial filling of the coordination sphere of these cations.

2. The thermodynamic parameters are not in accord with the concept relating complex stability with the correspondence of the diameters of the metal cation and cavity of the crown ether.

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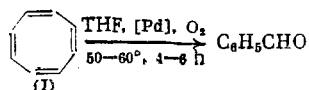
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### EFFICIENT METHOD FOR THE PREPARATION OF SUBSTITUTED BENZALDEHYDES BY THE OXIDATION OF CYCLOOCTATETRAENE, CYCLOHEPTATRIENE AND THEIR DERIVATIVES BY MOLECULAR OXYGEN IN THE PRESENCE OF PALLADIUM COMPLEXES

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The oxidation of linear and cyclic olefins by molecular  $\text{O}_2$  catalyzed by palladium, rhodium, and iridium complexes is an efficient method for the synthesis of carbonyl compounds under mild conditions with high yields [1-5]. In this regard, we studied the possibility of the oxidation of cyclooctatetraene (I), 1,3,5-cycloheptatriene (II), and their derivatives by molecular oxygen in the presence of a  $\text{PdCl}_2\text{-CuCl}$  catalyst. High selectivity and high oxidation product yields are observed for (I) when the reaction is carried out in THF at 50-60°C for 4-6 h and Pd:Cu:(I) ratio = 1:10:10. Under these conditions (I) is converted to benzaldehyde in 80% yield with the formation of a small amount of benzoic acid.



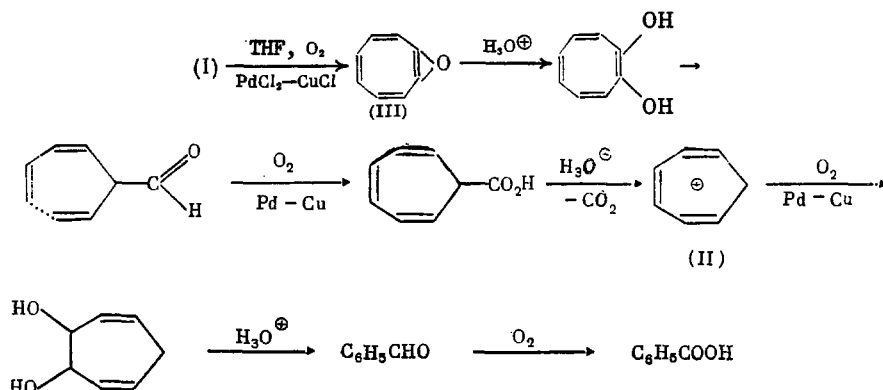
Institute of Chemistry, Bashkir Science Center, Urals Branch, Academy of Sciences of the USSR, Ufa. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 10, pp. 2403-2405, October, 1988. Original article submitted July 31, 1987.

TABLE 1. Oxidation of Cyclopolyenes by Molecular Oxygen in the Presence of the PdCl<sub>2</sub>-CuCl Catalytic System

Starting compound	T, °C*	Reaction product	Yield, %
(I)	50	C <sub>6</sub> H <sub>5</sub> CHO	80
(II)	50	C <sub>6</sub> H <sub>5</sub> CHO	95
(III)	60	C <sub>6</sub> H <sub>5</sub> CHO	95
(IV)	60	(V)	15
		(VI)	80
		(VII)	5
(VIII)	60	(IX)	15
		(X)	80
		(XI)	5
(XII)	60	(XIII)	90

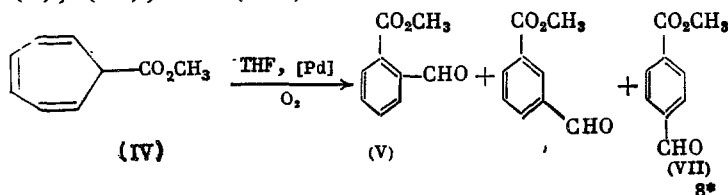
\*The reaction time was 4 h at 50°C and 6 h at 60°C.

According to Reppe et al., [6], C<sub>6</sub>H<sub>5</sub>CHO and C<sub>6</sub>H<sub>5</sub>COOH may be obtained by the oxidation of (I) by KMnO<sub>4</sub> or H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. In accord with the scheme proposed by Azatyan and Esayan [7], the oxidation of (I) by molecular O<sub>2</sub> in the presence of the PdCl<sub>2</sub>-CuCl system may be represented as follows:

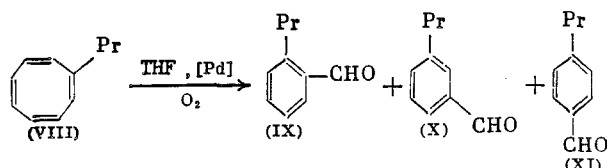


In order to support this hypothesis, we carried out the oxidation of (II) and 1,2-epoxycyclooctatriene (III), which are intermediates in the conversion of (I) under the conditions selected according to the above scheme. Thus, (II) and (III) give benzaldehyde in 95% yield upon oxidation.

In order to expand the range of application of this method, we studied the oxidation of substituted cyclooctatetraene and cycloheptatriene. In our experiments, 1-methoxycarbonyl-2,4,6-cycloheptatriene (IV) was converted in quantitative yield to o-, m-, and p-methoxycarbonylbenzaldehydes (V), (VI), and (VII) in 15:80:5 ratio.



Thus, 1-propyl-1,3,5,7-cyclooctatetraene (VIII) was converted to a mixture of o-, m-, and p-propylbenzaldehydes (IX), (X), and (XI) in 98% yield. The content of the meta isomer (X) in the product mixture was 80%. The oxidation of substituted cyclooctatetraenes gives mainly meta-substituted benzaldehydes.



We were unable to carry out the oxidation of bicyclo[6.1.0]nona-2,4,6-triene (XII) to benzaldehyde since, under our conditions, (XII) undergoes skeletal rearrangement to bicyclo[4.3.0]nona-2,4,7-triene (XIII).

The structure of the benzaldehydes obtained was demonstrated by comparison with authentic samples using gas-liquid chromatography and spectral methods [8-11].

#### EXPERIMENTAL

Samples of polyenes (II), (III), (IV), (VIII), and (XII) were obtained according to reported procedures [6, 12-15]. The purity of these samples was 99% as demonstrated by gas-liquid chromatography. The gas-liquid chromatographic analysis was carried out on a Chrom-5 chromatograph using a flame ionization detector and a 1.2-m column packed with 5% SE-30 on Interton-Super (0.16-0.20 m) with helium as the gas carrier. The preparative separation of the mixtures was carried out on a Perkin-Elmer F-21 preparative chromatograph using a flame ionization detector and 5-m column packed with 20% PEG-6000 on Chromosorb A. The column temperature was 170°C and helium served as the carrier gas.

General Procedure for the Oxidation of Cyclopolyenes. A sample of 5 ml water and 0.085 mole cyclopolyene was added to a mixture of 1.5 g (0.0085 mole) PdCl<sub>2</sub> and 8.36 g (0.085 mole) CuCl in 50 ml THF. The mixture was heated to 50-60°C and oxygen was bubbled through with stirring at a rate of 5 liters/h. The catalyzate was diluted with chloroform and washed with 5% hydrochloric acid and then water until the wash water was neutral. The organic layer was dried over MgSO<sub>4</sub>. The solvent was evaporated and the residue was distilled in vacuum. The substituted benzaldehyde isomers were preparatively separated (Table 1).

#### CONCLUSIONS

1. An efficient preparative method has been developed for the synthesis of benzaldehydes by the oxidation of cyclooctatetraenes and cycloheptatrienes by molecular oxygen in the presence of the PdCl<sub>2</sub>-CuCl system.

2. Monosubstituted cyclooctatetraenes are converted predominantly to meta-substituted benzaldehydes. A mechanism was proposed for this reaction.

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