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THE REDUCTIVE COUPLING OF DIBENZYLIDENACETONE BY OSMIUM (IV) SALTS

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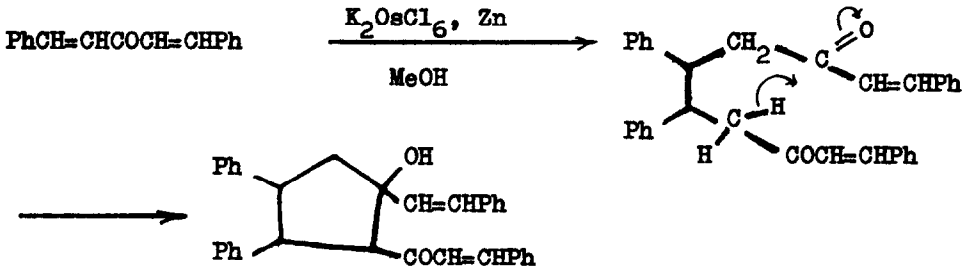
It has been known that dibenzylidenacetone (DBA) complexes with palladium(0) and platinum(0) [1,2].

In this work some attemps to prepare DBA complexes of osmium are presented. The interaction of the DBA with osmium (IV) salt in the presence of the Zn-dust as reductant has been studied.

In a typical experiment the solution of DBA (0.1 mol) in metanol (200 ml) was stirred with a mixture of the K_2OsCl_6 (0.1 mol) and Zn-dust (0.3 mol) at reflux temperature. After 3h initial DBA was completely consumed (from data of TLC). Some white fine powder was isolated on cooling; this and K_2OsCl_6-Zn unreacted were transferred to the shott-filter, washed with methanol and extracted with boiling $CHCl_3$ in the Soxhlet apparatus.

The white fine crystalline compound (~100% yield) was obtained from the $CHCl_3$-extraction and was recrystallized from $CHCl_3$ [3]. It should be noted that only Zn depleted totally during the reaction; osmium salt remained unchanged, and may be reused time and again for analogous reactions on adding of freshly prepared Zn-dust.

The product was poorly soluble in most organic solvents, m.p. 205-206°C. Mol.weight: M^+, m/e 470. Its infrared spectrum showed characteristic bands at 3550 (ν_{OH}), 1680 ($\nu_{C=O}$) and 1640 ($\nu_{C=C}$) cm^{-1}. NMR-spectrum (60 Mcs, HMDS as external standard) exhibited, in the vinylic region, two magnetic unequivalent -CH=CH-groups at δ 7.33 and 7.57 ppm. The compound did not contain osmium according to microanalytical data. It absorbed two moles of hydrogen over Raney Ni (ethyl acetate, 25°, 1 at) giving the known 3,4-diphenyl-1-phenetyl-5-phenetylcarbonylcyclopentan-1-ol [4]. It dissolved in CF_3COOH yielding a brightly violet solution; the latter on dilution with water and subsequent extraction with ether yields the known triene - 3,4-diphenyl-1-styryl-5-cinnamoylcyclopent-5-ene [5]. Based on these results it is safe to say that the product obtained is - 3,4-diphenyl-1-styryl-5-cinnamoylcyclopentan-1-ol. Its formation occurs as DBA reductive coupling is followed by cyclisation of the intermediate linear dimer via an intramolecular aldol condensation:



The reduction product of the intermediate linear dimer - 1,5,6,10-tetraphenyldecan-3,8-dione [5] was isolated with poor yield (~5%) along with the cyclisation product.

The occurrence of small quantities of such products from DBA in reductive conditions has been reported [4], but only as a side reaction. The main course of the reaction was reduction of the α,β -double bond.

Other α,β -unsaturated ketones react with K_2OsCl_6 and Zn-dust in exactly the same manner as DBA. For example chalcone yields 1,3,4-triphenyl-5-benzoylcyclopentan-1-ol [6] along with small quantities of 1,4,5,6-tetraphenylhexan-1,6-dione. By this means the reaction performed may be used as a preparative method for the synthesis of the cyclic ketols from α,β -unsaturated ketones.

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References and notes.

1. Y.Takahashi, Ts.Ito, S.Sakai, Y.Ishii, J.Chem.Soc., Chem.Communs. 1065 (1970).
2. K.Moseley, P.M.Maitlis, J.Chem.Soc., Chem.Communs., 982 (1971).
3. According to microanalytic data this compound contains one molecule of water. Calculated for $C_{34}H_{30}O_2H_2O$: C, 83.47; H 6.66. Found: C, 83.05: H, 6.17
4. M.Boyer, C.R.Acad.Sci.(C), 1960, 263, 1072
5. White crystalline compound, m.p. 180°. Calculated for $C_{34}H_{34}O_2$: C,86.29; H, 7.17. Found: C, 86.56; H, 7.23. IR (KBr): 1705, 1600, 1590 cm^{-1}.
6. White crystalline, m.p. 280°. Calculated for $C_{30}H_{26}O_2.H_2O$: C, 83.04; H, 1.45. Found: C, 83.33; H, 6.16. IR (KBr): 3500, 1680, 1600, 1590cm^{-1}.