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TRANSANNULAR OXIDATION OF BIS-ARYLHYDRAZONES OF CYCLODECAN-1,6-DIONE

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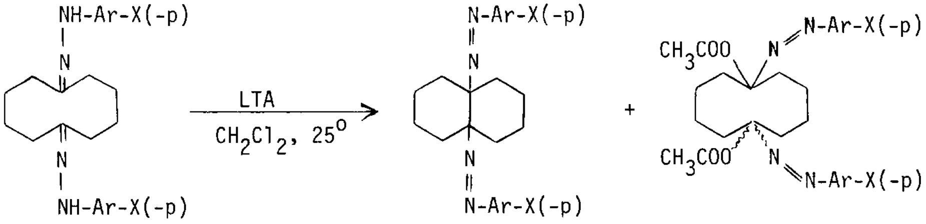
Summary Oxidation of the title compounds (1) with lead tetraacetate at room temperature leads to the formation of 9,10-bis-arylazo-decalines (2) via a transannular reaction, as well as to 1,6-bis-acetoxy-1,6-bis-arylazo-cyclodecanes (3)

It is well known[2] that ten-membered ring is a suitable system for transannular reactions For this reason and in the course of our further work[3] we have undertaken the preparation and oxidation with lead tetraacetate (LTA) of some bis-arylhydrazones of cyclodecan-1,6-dione

The hydrazones (1) were prepared upon treatment of cyclodecan-1,6-dione with two equivalents of arylhydrazine in ethanol solution at room temperature The oxidation of hydrazones (1) was carried out with LTA at room temperature in dichloromethane and the reaction was complete in about 2 hrs The reaction products after column chromatography were 9,10-bis-arylazo-decalines (2) and 1,6-bis-acetoxy-1,6-bis-arylazo-cyclodecanes (3), in various yields depended on the electronic effect of the substituent X (Table) When the oxidation took place with Ag_2O in ether under reflux for 30 hrs the transannular products (2) were only isolated in 80-90% yield



(1) (2) (3)

A X=H, B X=CH_3, C X=OCH_3, D X=NO_2, E X=Cl

Both products (2) and (3) are coloured and exhibit in visible absorption peaks at 418-445 and at 404-413 nm respectively On the other hand the products (3) show in IR a peak at 1735-1740 cm^{-1} (νCO) and in NMR ($CDCl_3$) a singlet at 2 13-2 15 δ for methyl protons The compounds (2) show in mass spectra a low intensity peak for molecular ion followed by another one $[M-ArN_2]^+$, whereas the ion ArN_2^+ is usually the base peak The compounds (3) show in the mass spectra the presence of the ion $[M-58]^+$ instead of that of molecular ion M^+

Table Products (2) and (3) Obtained from the Oxidation of Hydrazones (1) with LTA

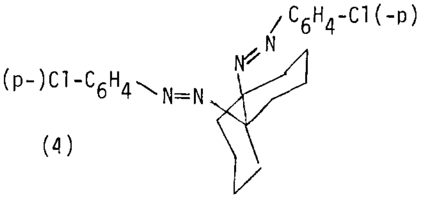
Hydrazone (1)	Reaction Products[a]			
	(2)		(3)	
	m p (^oC)	Yield %	m p (^oC)	Yield %
A	91- 93	63		
B	124-126	60		
C	119-121	35[b]		
D	163-165	25	201-205	53
E	121-123	44[c]	132-135[c]	23
	227-229	2	175-177	15

[a] All products (2) and (3) had satisfactory elemental analyses (C, H, N ± 0 3) and spectroscopic data (UV, IR, NMR, MS) in agreement with proposed structures

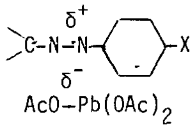
[b] Yield based on the diketone used for the preparation of the hydrazone (1C), which was not isolated, since oxidized in the air

[c] Two isomers (cis-trans) were isolated

From the oxidation of the hydrazone (1E) two isomers (2) were isolated and it has been shown by an X-ray analysis[4] that the compound (2E) (m p 121-123°) has the cis-decaline structure (4) An analogous cis-structure it is assumed for the other compounds (2) Furthermore, for the pair of compounds (3E) a cis-trans isomerism should be assigned, but this problem is under further consideration From the Table it is seen that electron-releasing substituents X favour the formation of transannular products (2), whereas electron-withdrawing groups X favour the formation of (3) This could be explained assuming an intermediate[5] like (5) during the oxidation



(4)



(5)

Thus, if X is $-NO_2$ the positive charge rather belongs to C-atom, which is attacked by CH_3COO^- giving the product (3) If X is $-CH_3$ or $-OCH_3$ the positive charge mostly is spread in the aromatic ring with a preferencial formation of the transannular product (2)

REFERENCES

1 E M - X , Ph D Thesis, to be submitted to the University of Thessaloniki

2 A C Cope, M M Martin, and M A Kervey, Quart Rev , 20, 119 (1966)

3 J Stephanidou-Stephanatou, E Varella, E D Micromastoras, and N E Alexandrou, J Heterocyclic Chem , 16, 1373 (1979)

4 C Cavounis and P J Rentzeperis, to appear in Z Kristallogr

5 R N Butler, F L Scott, and T A F O'Mahony, Chem Rev , 73, 93 (1973)

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