CHEMISTRY LETTERS, pp. 1823-1824, 1982. © The Chemical Society of Japan 1982

PALLADIUM ASSISTED N-METHYL ACTIVATION OF p-SUBSTITUTED N,N-DIMETHYLANILINES

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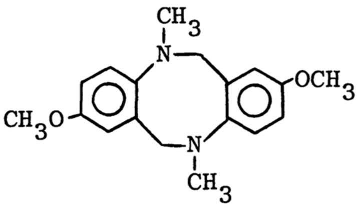
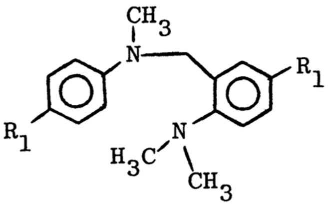
Intermediates in the reaction of N,N-dimethylanilines with palladium (II) acetate were trapped by acetate ion or oxygen to give N-methyl-oxygenated and demethylated products, while the trapping by other anilines gave homo- and cross-coupling cyclodimers. The reactions proceed via radical cation formation induced by the palladium salt.

The oxidative cyclodimerization of N,N-dimethylanilines containing a nobel carbon-carbon bond formation between N-methyl carbon and aromatic ring carbon was previously communicated.$^{1)}$ In a course of further investigation, trapping experiments of the reaction intermediates were carried out. Therein, some new reactions of the N-methyl group activated by a radical cation formation from N,N-dimethylaniline and palladium(II) acetate were found.

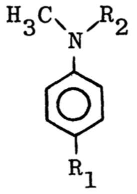
A mixture of palladium(II) acetate (5 mmole), sodium acetate (20 mmole), and N,N-dimethylanisidine (1a, 10 mmole) was heated at 80° for 5 h in a mixed solvent (80 ml) of acetic acid and benzene (1:1) under an atmosphere of nitrogen. After usual work-up, the aniline dimers, 2aa (10.2%) and 3a (28.3%) , were isolated together with 4a (3.4%), 5a (2.0%), and 6a (52.1%). A similar reaction of N,N-dimethyl-p-toluidine (1b) also gave rise to formation of 2bb (34.5%), 4b (2.5%), 5b (1.0%), and 6b (27.0%). The isolated dimer (3a) gave the cyclic dimer (2aa) quantitatively while 5a produced 6a in good yield (75%) by further oxidation with palladium(II) acetate.



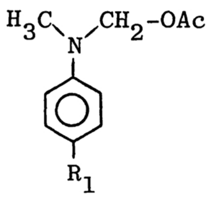
2aa



3 a (R_1 = OCH_3)
b (CH_3)



4 (R_2 = CHO)
5 (R_2 = H)
6 (R_2 = $NMeC_6H_4R_1$)



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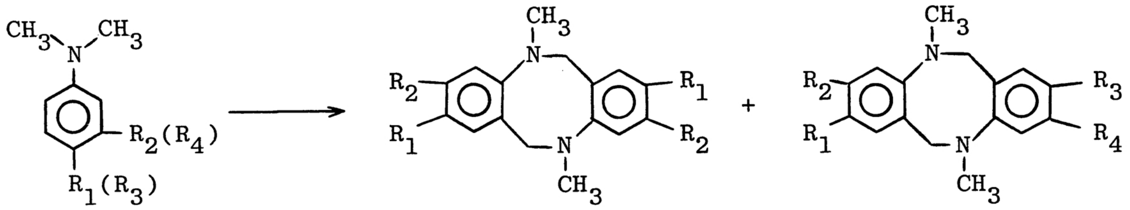
The formation of 4 and 5 suggests an intermediary of arylaminomethanol acetate (7) which may undergo ready hydrolysis and deformylation$^{2)}$ to give 5 or further acetoxylation and decomposition$^{3)}$ to form 4. The acetoxylation on N-methyl group may take place concurrently with the cyclodimerization.

The reaction of a mixture of 1a (10 mmole) and 1b (10 mmole) with palladium(II)



1m and 1n 2mm (or 2nn) 2mn

m (or n): a. $R_1(R_3)$= OCH_3, $R_2(R_4)$= H; b. $R_1(R_3)$= CH_3, $R_2(R_4)$= H;
c. CH_3, CH_3; d. Cl, H.

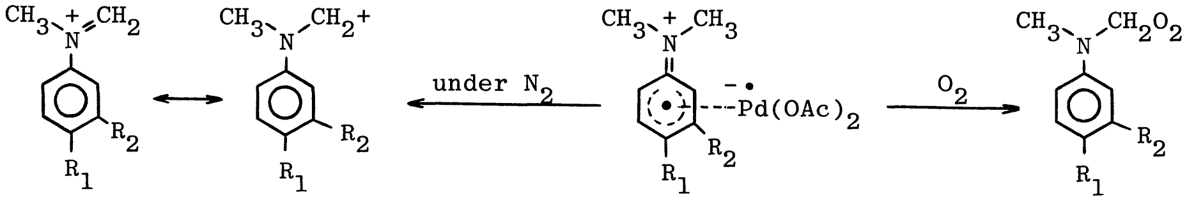
Table 1. Formation of Homo- and Cross-coupling Cyclodimers.

Reactants[a]	Products			
(1m and 1n)	Cyclodimers (%)[b]	Composition (%)		
1a - 1b	52.2	2aa (26.2)	2bb (50.6)	2ab (23.2)
1a - 1c	17.8	2aa (8.2)	2cc (59.0)	2ac (32.8)
1a - 1d	8.7	2aa (84.2)	2dd (5.8)	2ad (10.1)
1c - 1d	19.7	2cc (91.8)	2dd (0.0)	2cd (8.1)

a. Equimolar amounts of 1m and 1n were used to react with a half equivalent of Pd(II) acetate. b. Total yields of isolated cyclodimers based on moles of used $Pd(OAc)_2$

acetate (5.0 mmole) was carried out at 80° for 5 h in a solvent (80 ml) of acetic acid -benzene (1:1) under nitrogen. The work-up of the reaction mixture gave the homo-coupling dimers, 2aa (13.7%) and 2bb (26.4%), and the cross-coupling dimer 2ab (12.1%), along with recovered 1a (79.5%) and 1b (55.9%). The compound 2ab was characterized as follows; mp 136-137°C, nmr ($CDCl_3$, TMS): δ(ppm) 2.85 (s, 3H, N-CH_3), 2.89 (s, 3H, N-CH_3), 2.33 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 4.33 (s, 4H, -CH_2-), and 6.95-7.37 (m, 6H, Ar-H), 10M mass; $C_{18}H_{22}N_2O$ (m/e 282.1729). Analogous reactions are summarized in Table 1. The relative reactivity ratio of used N,N-dimethylanilines for cyclodimerization was calculated as 1a (1.0), 1b (1.64), 1c (3.07), and 1d (0.12), respectively. It is notable that 1b or 1c is more reactive than 1a. The fact clearly indicates that the more electron-rich are o-positions, the more efficiently does the reactant 1 result in cyclodimerization,4) and thus that the cyclodimerization may proceed via an attack of cationic species derived from N-methyl groups onto aromatic o-positions.

On the other hand, the reaction of 1a under a stream of air gave 4a (10%), 5a (23 %), and 6a (32%), but no cyclodimers were detected. The formation of cationic N-methyl species (9) may be disturbed by oxygen. Consequently, the present reactions may contain an initial cation radical intermediate (8) generated by SET from 1 to Pd(II).



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References 1) T. Sakakibara and H. Matsuyama, Chem. Lett., 1980, 1331. 2) O. Ogawa, Y. Kawazoe, and Y. Sawanishi, Chem. Pharm. Bull. (Japan), 28, 3029 (1980). 3) T. Itahara and T. Sakakibara, Bull. Chem. Soc., Jpn., 52, 631 (1979). 4) Methyl group (σ_m value, -0.07) activates m-positions more than methoxy group (+0.12); H. H. Jaffe, Chem. Rev., 53, 191 (1953).

(Received August 25, 1982)