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REACTIONS OF 5,6-BENZO-1,2,3-TRIAZINE 3-OXIDES WITH PHENYLMAGNESIUM BROMIDE

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We have already reported that some of the 1,2-diazine N-oxides, different from other aromatic amine N-oxides, underwent a specific reaction with organometallic compounds. Namely, the reaction of pyridazine 1-oxide with phenylmagnesium bromide or phenyllithium2) afforded phenylated butadienes and vinylacetylenes, and cinnoline 2-oxides2) afforded phenanthrenes and stilbenes. These findings prompted us to investigate the reaction of triazine N-oxides with organometallic compounds, and some interesting results were obtained as follows.

To a solution of 4-methyl-5,6-benzo-1,2,3-triazine 3-oxide (Ia) dissolved in benzene was added at room temperature under stirring an ethereal solution of 2-3 moles of phenylmagnesium bromide. To a reaction mixture, water was added and worked up as usual. The products thus obtained were separated by column chromatography on alumina, affording five kinds of compounds: IIa; 1-(*o*-aminophenyl)-1-phenylethylene4), VIa; 2,2'-bis[(methylphenylhydroxy)-methyl]-*cis*-azobenzene, m.p. 196-197°, $C_{28}H_{26}O_2N_2$, M^+(m/e), 422, IR, 3500 cm^{-1}(KBr, OH), NMR ($CDCl_3$,δ), 1.88(6H, s.), 5.1(1H, broad, erased by D_2O), 6.4-7.7(19H, m.c.), VIIa; *trans*-isomer of VIa, m.p. 233-234°, $C_{28}H_{26}O_2N_2$, M^+(m/e) 422, IR, 3500 cm^{-1} (KBr, OH), NMR($CDCl_3$,δ), 1.88(6H, s.), 5.1(1H, broad, erased by D_2O), 6.4-7.7 (19H, m.c.), VIIIa; 4-methyl-3,4-diphenyl-3,4-dihydro-5,6-benzo-1,2,3-triazine, m.p. 162-163°, $C_{20}H_{17}N_3$, M^+(m/e), 299, UV(λ_{max}^{MeOH}), 252, 259, 268, and 317 mμ, NMR (CCl_4,δ), 1.90(3H, s.), 6.8-7.5(12H, m.c.), 8.05-8.3(2H, m.c.), IXa; 4-methyl-1,4-diphenyl-1,4-dihydro-5,6-benzo-1,2,3-triazine, m.p. 187-188°, $C_{20}H_{17}N_3$, M^+ (m/e), 299, UV(λ_{max}^{MeOH}), almost same as VIIIa, NMR(CCl_4,δ), 2.10(3H, s.), 6.8-7.5

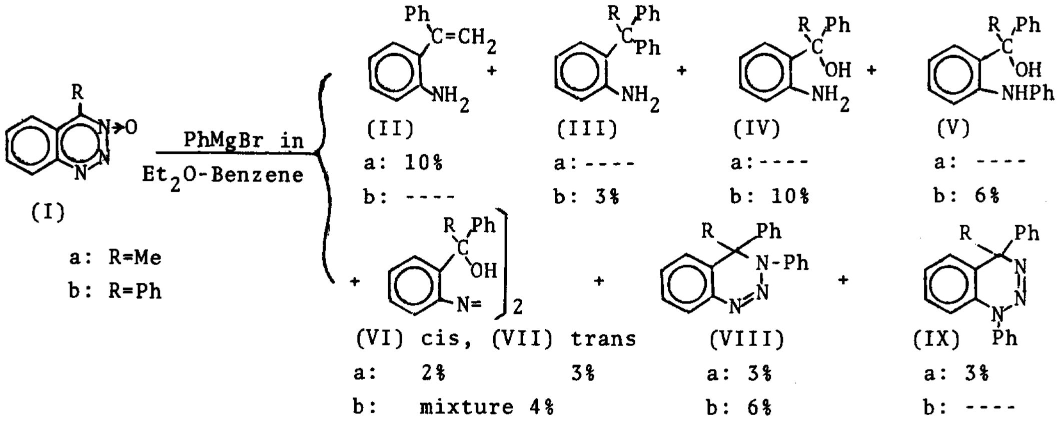


Chart 1.

(12H, m.c.), 7.9-8.2(2H, m.c.). Their yields are listed in Chart 1.

Then, similarly 4-phenyl-5,6-benzo-1,2,3-triazine 3-oxide[3,5] (Ib) was allowed to react with the reagent, affording six kinds of compounds: IIIb; o-aminophenyltriphenylmethane, m.p. 277-278°, $C_{25}H_{21}N$, M^+(m/e), 355, IR, 3360 and 3340 cm^{-1}(KBr, NH_2), NMR(CCl_4,δ), 3.1(2H, broad, erased by D_2O), 6.7-7.4(19H, m.c.), IVb; o-aminophenyldiphenylcarbinol[6], Vb; o-phenylaminophenyldiphenylcarbinol[6], a mixture of VIb and VIIb; *cis*- and *trans*-2,2'-bis[(diphenylhydroxy) methyl]-1,1'-azobenzene, $C_{38}H_{30}O_2N_2$, M^+(m/e), 546, IR, 3500 cm^{-1}(KBr, OH), NMR ($CDCl_3$,δ), 5.0(2H, broad, erased by D_2O), 6.5-7.5(28H, m.c.), VIIIb; 3,4,4-triphenyl-3,4-dihydro-5,6-benzo-1,2,3-triazine, m.p. 233°, $C_{25}H_{19}N_3$, M^+(m/e), 361, NMR(CCl_4,δ), 7.0-7.6(17H, m.c.), 8.1-8.3(2H, m.c.). Yields are listed in the Chart 1.

The compounds (Ia and Ib) afforded also sevsral kinds of compounds other than those mentioned above, but their separations and identifications have not yet been carried out on account of small quantities. The structural proof of the compounds (IIa, IVb, and Vb) were confirmed in comparison of the authentic samples, respectively.

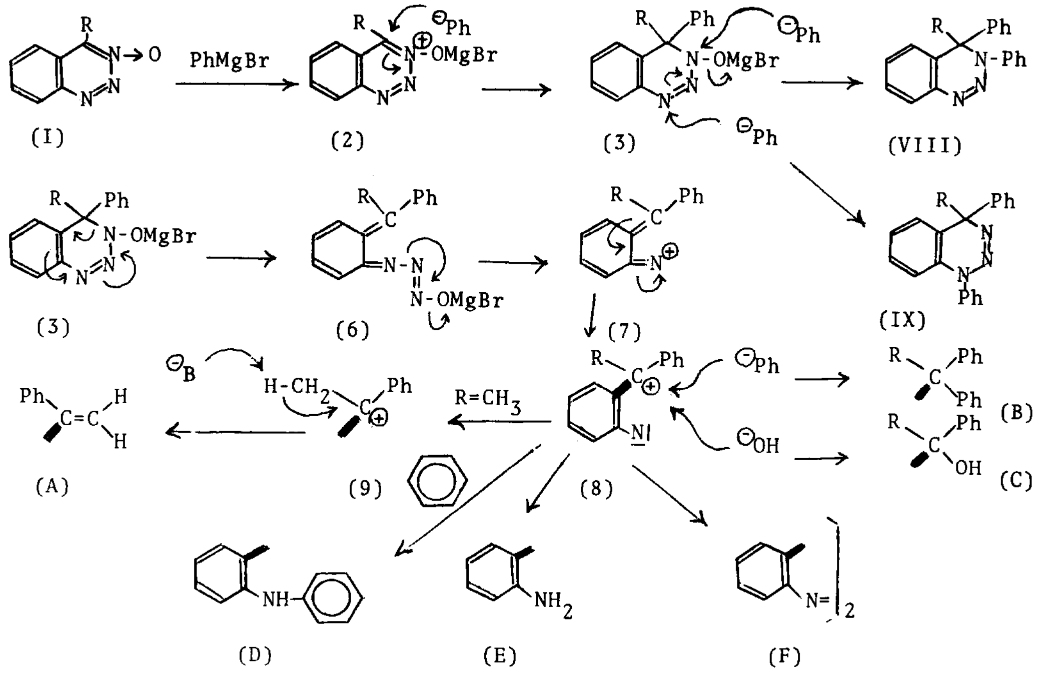
The UV spectra of the hydroxy compounds in conc. H_2SO_4, exhibited specific absorptions at 350-500 $m\mu$, due to the methyldiphenyl-methyl cations in the cases of VIa and VIIa, and due to the triphenyl-methyl cations in the cases of IVb, Vb, and a mixture of VIb and VIIb.

As for the azo-dimers, the compound having lower melting point was assumed to be the cis-dimer (VIa) in (a) group. In (b) group, two kinds of compounds (VIb and VIIb) were obtained in the state of a mixture, but their isolations were difficult.

Concerning the dihydrotriazines, the structures were inferred from the fact that in (VIIIa), the NMR chemical shift of the methyl group was observed rather in higher field, and that of H_8-proton was observed in lower field than those of the corresponding isomer (IXa), respectively. Since the chemical shift of H_8-proton of (VIIIb) is approximately the same as that of (VIIIa), the structure of VIIIb is inferred to be 3-phenylated compound, but a possibility of being 1-phenylated structure (IXb) can not be denied.

Concerning the formation of these compounds, the following mechanism can be proposed as the most reasonable[7].

The compound (3) is formed by the 1,3-dipolar addition of the reagent to I, followed by the attack of a phenyl anion at the 3-position to form VIII, by the attack at the 1-position to form IX. The fission and the elimination of the nitrogen molecule of the compound (3), similar to the case of the 1,2-diazines,



results in the formation of the compound (8) having both di- or tri-phenylmethyl cation and nitrene *via* the compound (7). Addition of a phenyl or an hydroxy anion to the cation affords (B) and (C). When R is the methyl group, abstraction of a proton of the methyl group by the base results in the formation of (A).

On the other hand, the nitrene moiety is likely converted8) into amino compound (E), azo compound (F), and the compound (D), formed by the insertion of the nitrene to carbon-hydrogen bond of the solvent benzene. The compound (D) is also considered to be formed by the reaction of (7) with a phenyl anion.

As for the number of the products, there are combinations of A,B,C, and D,E,F. Without consideration of stereoisomerism, there must be six kinds of products in (b) group and nine kinds in (a) group. But in the present work, four kinds of products in (b) group and two kinds in (a) group were isolated. Further investigations, including the structural elucidation of the uncertain compounds, are now underway.

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7) By heating (I) with water or dil. H_2SO_4, fission of the ring occurred to form o-azidoacetophenone, followed by elimination of the nitrogen molucule to form anthranils via nitrene, on which a report3) was published. There is probability that the intermediate of this reaction was allowed to react with PhMgBr to form the same hydroxy compounds as we obtained. But in our present condition, in Et_2O-benzene, any decomposition occurred even if the reaction mixture was heated, suggesting the reaction pathway of the above report should be denied.
8) " Nitrene " edited by W.Lwowski, Interscience Publishers (1970), and references cited therein.