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REACTION OF *t*-BUTYLMAGNESIUM CHLORIDE WITH 1,4-DINITROBENZENE

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Abstract: *Whereas alkyl Grignard reagents generally react with 1,4-dinitrobenzene leading to redox or ring-alkylated products, t-butylmagnesium chloride gives substitution to the para position and/or 1,2 addition to the nitro group. Detailed ESR studies of the reaction are reported.*

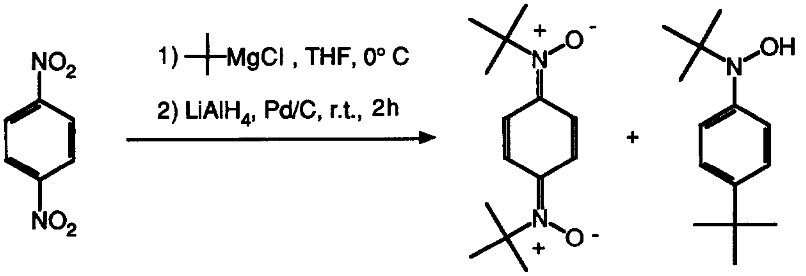
The course of the reaction of nitroarenes with Grignard reagents was demonstrated to depend strongly on the nature of the anionic framework. Alkylmagnesium halides, for example, predominantly give ring alkylated products from conjugate addition to the nitro group[1]. Although a wide spectrum of primary and secondary alkyl reagents was employed, only one example of *t*-butyl substituted nitroarenes was previously reported[2].

On the other hand, the reaction of nitrobenzene and *t*-butylmagnesium chloride was reported as one of the methods to prepare *N*-*t*-butyl-*N*-phenylnitroxyde[3] and other authors[4] detected the presence of ring-alkylated products as well.

Recently, we found[5] that the reaction of 1,4-dinitrobenzene (DNB) with alkyl Grignard reagents led essentially to two products: *trans*-5,6-dialkyl-1,4-dinitrocycloexa-1,3-dienes and starting DNB. This product-distribution was accounted for respectively as in-cage and out-of-cage products of a single electron transfer pathway. However, although evidence of it were found for all these kinds of reaction[6], when *t*-butylmagnesium chloride was used atypical results were discovered. In fact, carrying out the reaction under certain conditions, previously reported[5], only traces of *trans*-5,6-di-*t*-butyl-1,4-dinitrocycloexa-1,3-diene were detected in the aqueous layer (after treatment with sodium hypochlorite). On the contrary a very complex reaction-mixture was present in the organic layer (after bubbling with oxygen); the major product from it was the *N,N'*-di-*t*-butyl-1,4-benzoquinonediimmine *N,N'*-dioxide (**2**) instead of the expected DNB. The reaction of DNB with *t*-butylmagnesium chloride was previously studied, from an ESR point of view, by Rassat[7] and coworkers, and at least three main radical species were detected: only two structures $(Bu^t)_2N(O\cdot)$ (**A**) and p-$NO_2C_6H_4NBu^t(O\cdot)$ (**B**) were accounted for. These authors suggested a structure also for the third radical species p-$Bu^tC_6H_4NBu^t(O\cdot)$ (**C**) but they could not prove it. These results appeared to be in disagreement with our findings, therefore we decided to investigate in full this reaction.

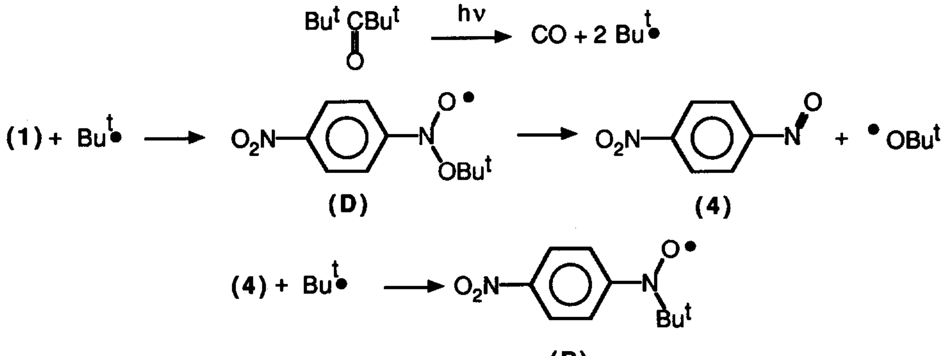
The reduction with lithium aluminium hydride and palladium on charcoal is reported to be a versatile method for the reduction of both nitronate adducts[8] and tetrahedral nitrogen adducts from 1,2 addition of Grignard reagents and nitroarenes[9]. Performing the reaction under these experimental conditions, a more simple product distribution was found (scheme 1): *N*-(4-*t*-butylphenyl)-*N*-*t*-butylhydroxylamine (**3**) and **2**. Both compounds in principle could be the reduced parent of the radical species (**C**) with a general structure p-X-$C_6H_4N(O\cdot)Bu^t$: a detailed ESR study was then achieved. If *N,N'*-di-*t*-butyl-1,4-benzoquinonediimmine *N,N'*-dioxide (**2**) was accountable of radical **C**, it should be possible to transform **2** in a biradical[10] (*N,N'*-di-*t*-butyl-*p*-phenylenebinitroxide), but all the attempts failed. To the contrary, the oxidation of hydroxylamine **3** leads to a radical species that confirms the right structure-assignment to **C**. Radical **B** was confirmed by comparison with the E.S.R. parameters of the radical species obtained in the photolytic reaction between DBN and $(Bu^t)_2CO$ (scheme 2).

SCHEME 1



(1) (2) (3)

SCHEME 2



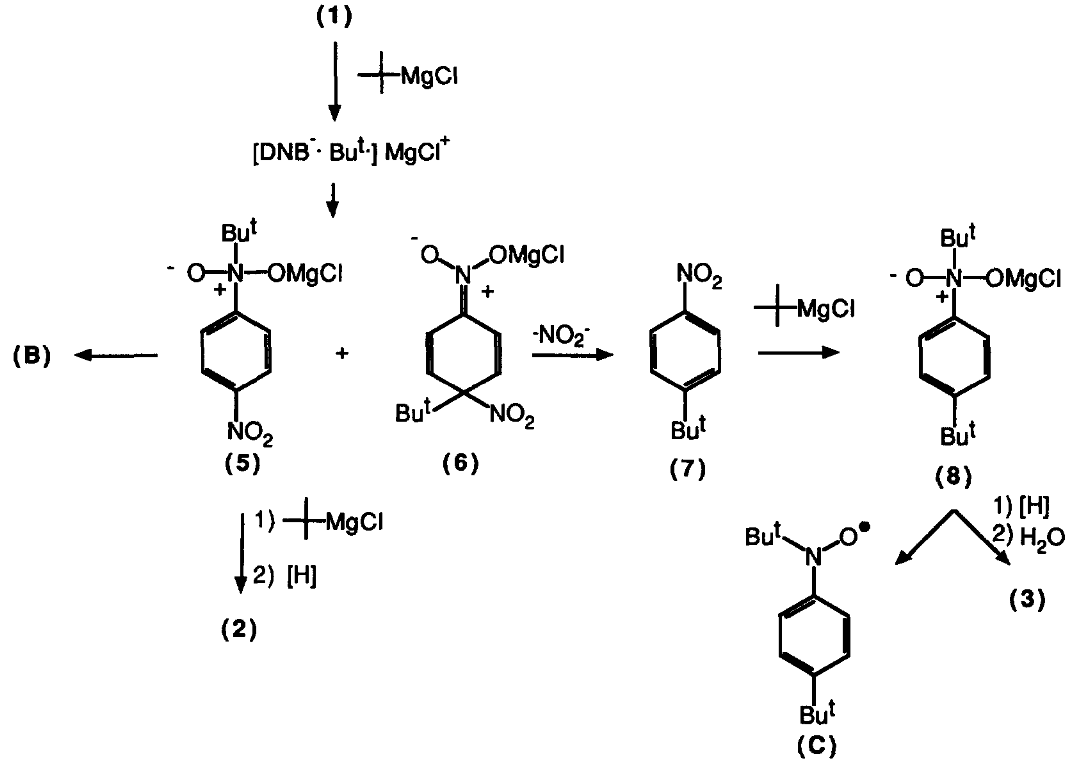
(D) (4) (B)

The concentration of these radical species depends on DNB to Bu^tMgCl ratio in agreement with that previously reported[7b]. If DBN concentration is preponderant, radical **B** is the most intense and only a very poor extra signal, attributable to $Bu^t_2NO\cdot$ (**A**), is present; when equimolecular amount or excess of Bu^tMgCl is used, radical **C** becomes dominant. From a mechanistic point of view for this reaction, a full polar pathway might be invoked, as suggested in previous works[9,12] to justify the *N*-alkylated products obtained from the reaction of Grignard reagents and nitroarenes. However, a single electron transfer mechanism could describe this reaction as well. In fact, being the *ortho* positions of the benzene-ring hindered by the oxygen atoms of the nitro substituents, the bulky *t*-butyl radical prefers an attack at the less hindered nitrogen. The formation of product **3** can also be explained in terms of single electron transfer interaction: such pathway was already observed in the substitution-reaction of the nitro group in 1,4-dinitrobenzene-system[11] and suggested in this reaction[7]. The steps to obtain products **2** and **3** are depicted in scheme 3.The reduction of intermediates **5** and **8** can be performed by lithium aluminum hydride or by the nitrous ion which is formed during the reaction. For this reason, compound **2** can be separated from the reaction mixture without adding reductants.

EXPERIMENTAL

^1H-NMR spectra were recorded with a Varian EM360L instrument. Chemical shifts are given in p.p.m. from Me_4Si in $CDCl_3$ solutions. IR spectra were recorded with a Perkin-Elmer FTIR1600 spectrometer. Mass spectra were recorded with a VG 7070 spectrometer or with an HP 59970 workstation. Melting points are uncorrected and were determined with a Büchi apparatus. THF was dried by refluxing over sodium wires until the blue color of benzophenone ketyl persisted and then distilling into a dry receiver under nitrogen atmosphere. Commercial DNB was recrystallized and commercial solutions of *t*-butylmagnesium chloride were titrated before use.

SCHEME 3



Reaction A: To a stirred solution of DNB (6 mmol) in THF (15 mL) cooled at 0 °C, 12 mmol of *t*-butylmagnesium chloride were added dropwise under inert atmosphere. The reaction was stirred for 5 minutes before adding 18 mmol of lithium aluminuim hydride and 2 mmol of palladium on charcoal. The reaction was allowed to stand at room temperature for 2 h and then quenched with saturated ammonium chloride, extracted with dichloromethane, dried over anhydrous sodium sulphate and evaporated under reduced pressure. The residue was submitted to a chromatographic separation over a silica gel column eluted with a 3/2 mixture of hexane and ethyl acetate.

N-(4-*t*-butylphenyl)-*N*-*t*-butylhydroxylamine (**3**): 30%, syrup, ^{1}H-NMR ($CDCl_3$) δ 1.10 (s, 9H); 1.30 (s, 9H); 6.20 (bs, 1H, OH); 7.27 (bs, 4H, arom), IR (film) ν_{OH} 3251cm^{-1}, *m/z* 221.17802 (M$^+$, calcd for $C_{14}H_{23}NO$ 221.17796), 190, 165, 150 (base), 57. Decomposed on standing.

N,N'-di-*t*-butyl-1,4-benzoquinonediimmine *N,N'*-dioxide (**2**): 31%, mp 175 °C (dec), ^{1}H-NMR ($CDCl_3$) δ 1.67 (s, 18H); 7.57 (s, 4H), *m/z* 250.16804 (M$^+$, calcd for $C_{14}H_{22}N_2O_2$ 250.16813), 203, 163, 130 (base), 57, 41.

Reaction B: The residue of the organic layer of a reaction carried out under the reported conditions^5 was submitted to a chromatographic separation over a silica gel column eluted with a 3/2 mixture of hexane and ethyl acetate leading to a 16% of **2** and large amounts of tars. The aqueous layer, extracted with dichloromethane and evaporated under reduced pressure, led to traces (<4%) of *trans*-5,6-di-*t*-butyl-1,4-dinitrocicloexa-1,3-diene [*m/z:* 267 (M$^+$-15); FTIR ν_{NO_2}1550 and 1340 cm^{-1}].

E.S.R experiments: The experiments were run matching the conditions used in the current preparative reaction. A "U" sample tube, to keep separate the two reactants was used and the THF solution of Bu^{t}MgCl was deoxygenated with the freeze-thaw technique in a vacuum line. The reagents were mixed directly in the E.S.R. sample tube, at the desired temperature, and then introduced in the spectrometer cavity previously settled at the same temperature. The h.f.c. parameters of the two main radical species are: *p*-NO$_2$-C$_6$H$_4$N(O·)Bu^t (**B**) [a$_N$ (*p*) = 0.6 G., a$_H$ (2H *m*) = 0.9 G., a$_H$ (2H *p*) = 2.25 G., a$_N$ =10.45 G. g-factor =2.0060] and *p*-Bu^t-C$_6$H$_4$N(O·)Bu^t (**C**) [a$_H$ (2H *m*) =0.9 G., a$_H$ (2H *o*) =1.9 G., a$_N$ =12.3 G. g-factor= 2.0058]. A very poor extra signal, attributable to Bu$^t_2$NO· (**A**)[13], is present in defect of Grignard reagent. The experiment with DBN and Bu$^t_2$CO, to confirm the structure of radical (**B**), was run photolysing directly in the E.S.R. cavity a deoxygenated benzene solution of the two reactants, at room temperature; it is noteworthy that radical p-NO$_2$C$_6$H4NO-Bu^t(O·) (**D**) [a$_N$ (*p*)= 0.8 G., a$_H$ (2H *m*) =1.05 G., a$_H$(2H *o*)=2.9 G., a$_N$=12.05 G., g-factor= 2.0050] intermediate in this reaction, is also present in our system. The structure of radical **C** was confirmed by oxidation, with molecular oxygen, of a THF solution of pure hydroxylamine (**3**).

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