Reactions of isomeric 3,6- and 3,5-di-*tert*-butyl-*ortho*-benzoquinones with NH_3

V. B. Vol'eva,[a] T. I. Prokof'eva,[a] A. I. Prokof'ev,[b] I. S. Belostotskaya,[a] N. L. Komissarova,[a] and V. V. Ershov[a]*

[a]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 117977 Moscow, Russian Federation. Fax: +7 (095) 938 2156*

[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085*

The interaction of 3,6-di-*tert*-butyl-*ortho*-benzoquinone (**1**) and 3,5-di-*tert*-butyl-*ortho*-benzoquinone (**2**) with NH_3 in water—alcohol medium and with $(NH_4)_2CO_3$ in a solid phase has been studied. Redox processes with participation of a nucleophile of the medium take place for **1**, while **2** reacts with NH_3 at the carbonyl group with transformation of the quinone imide. The mechanism of redox transformation of **1** has been proposed.

Key words: 3,6-di-*tert*-butyl-*ortho*-benzoquinone, 3,5-di-*tert*-butyl-*ortho*-benzoquinone; quinone imine; aminoquinone; redox transformations, radical anion; indophenols; solid phase.

3,6-Di-*tert*-butyl-*ortho*-benzoquinone (**1**) and its 3,5-isomer (**2**) differ considerably in their reactivities. Reduction—oxidation transformations are more characteristic of quinone **1**, whereas reactions at the open carbonyl group are characteristic of isomer **2**.[1,2] This is confirmed by the results of investigation of the interaction of quinones **1** and **2** with ammonia in water—alcohol medium. In a NH_3—H_2O—MeOH (or EtOH) system quinone **1** forms 4-amino-3,6-di-*tert*-butyl-*ortho*-benzoquinone (**3**) as a final product of a multistage process including redox interaction between quinone **1** and a nucleophilic agent of the medium at the initial stage (Scheme 1).

This scheme is confirmed by ESR investigations. Initially, a signal of a product of single-electron reduction of quinone **1**, radical anion **4** (triplet with a_H = 3.3 Oe, which is caused by HFI with two ring protons) is registered in the reaction mixture spectrum. Then, the signal intensity decreases, and a spectrum appears that corresponds to 4-methoxysubstituted radical anion **5**. These spectra are identical with those obtained by single-electron reduction of previously known samples of quinones **1** and **6** in an alkali—alcohol solution (Fig. 1, see also Ref. 3).

Thus, a radical pair [**4** + MeO$^\cdot$] is formed as a result of a redox reaction between quinone **1** and an alcoholate ion. Registering ESR spectrum of compound **4** suggests that the radicals escape from solvent cells, and that the reason why the formation of alkoxysubstituted both radical anion **5** and quinone **6** is possible as a result of two parallel processes: (1) recombination of radicals **4** and MeO$^\cdot$, which is accompanied by rearrangement of compound **4** in the cell, followed by its oxidation with nonreacted quinone **1** or atmospheric oxygen; (2) addition of MeO$^\cdot$ to the initial quinone **1** in solvent bulk.

Appearance of methoxyquinone **6**, its unstable adduct with MeOH (**7**), and aminoquinone **3** in the reaction mixture is successively registered by TLC on Silufol plates. The presence of compound **7** as well as the fact that radical anions redox-conjugated with compound **3** are not registered in the ESR study of the reaction mixture, allow one to suppose that the formation of aminoquinone **3** proceeds according to an addition—elimination mechanism *via* an intermediate unstable adduct of methoxyquinone **6** with ammonia (see Scheme 1). Similar processes are characteristic of alkoxyquinones. Thus, during the reduction of methoxyquinone **6** in ethanol, an instant alkoxyl exchange is observed, and only spectrum of ethoxysubstituted radical anion is registered[3] (Scheme 2).

Although the stepwise mechanism of the formation of compound **3** seems more probable for the conditions involved, it is not, however, the only possible mechanism. Direct amination of compound **1** is an alternative.

Fig. 1. ESR spectra of semiquinone radical anions **4** (lines are marked with asterisks, triplet a_H = 3.3 Oe) and **5** (MeOH—conc. NH_3/H_2O (3 : 1), 25 °C).

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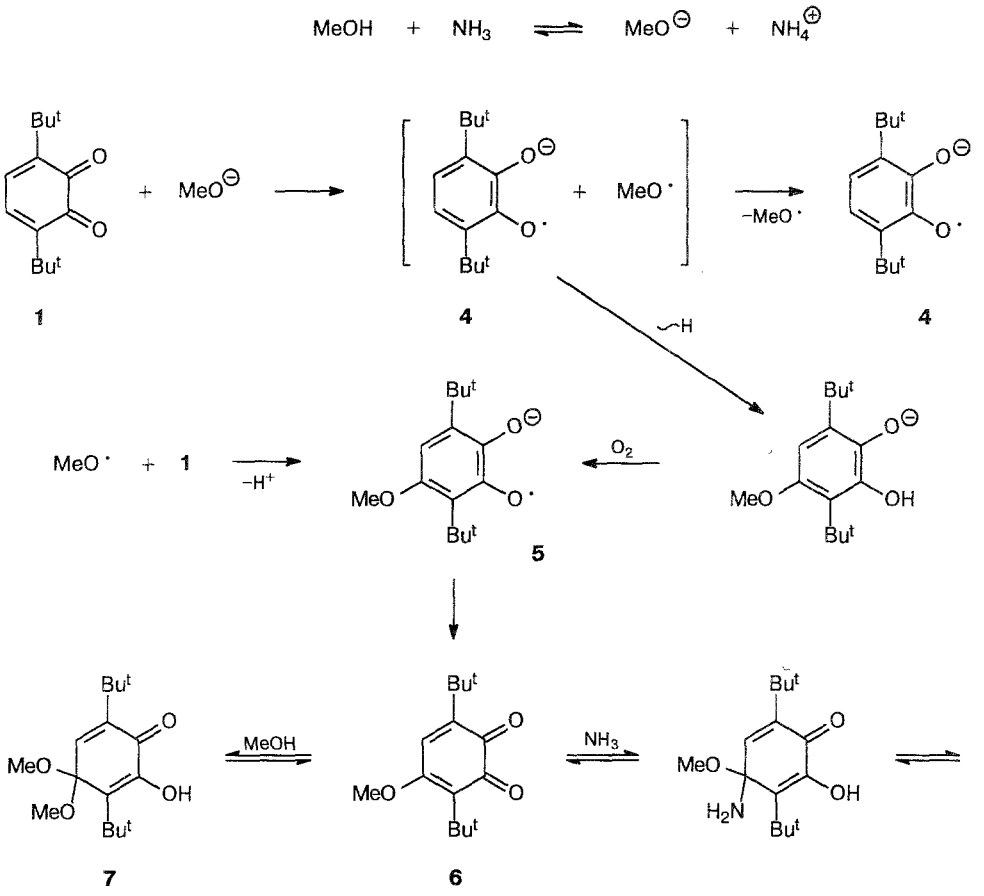
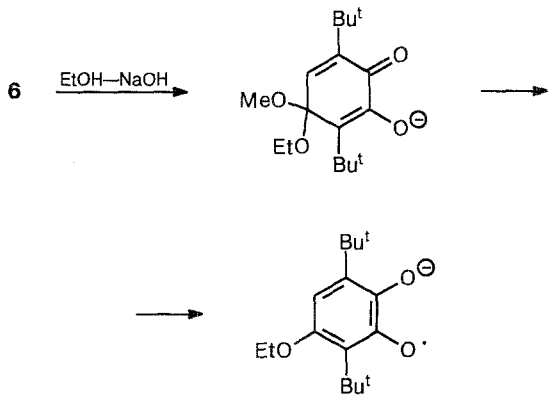
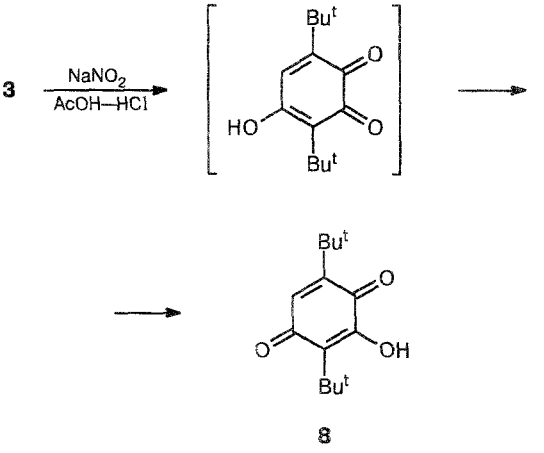
Scheme 1



Scheme 2



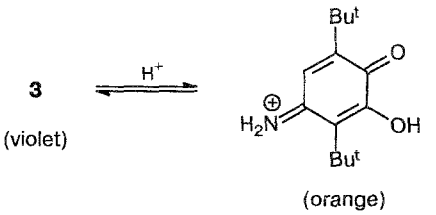
Scheme 3



The formation of aminoquinone **3** under the conditions which exclude the participation of any intermediate substances, *e.g.*, while rubbing together quinone **1** and ammonium carbonate in the absence of a solvent, confirms this possibility.

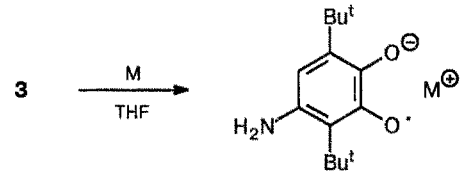
Aminoquinone **3** which have not been described earlier was identified on the basis of elemental analysis and spectral data as well as by a chemical method, by its transformation into oxyquinone **8** (Scheme 3).

It is found that aminoquinone **3** changes reversibly its color, depending on changes in the pH values of the medium:



Single-electron reduction of aminoquinone **3** on metal mirror surfaces (Na, K) gives radical anions (Scheme 4) characterized by ESR spectrum, in which a doublet of triplets (a_H = 4.05 Oe, a_N = 2.05 Oe, Fig. 2) is registered. HFI with protons of NH_2 group is absent, that suggests its planar position relatively to aromatic ring. In the case of sodium semiquinolate, HFI with ^{23}Na nucleus (a_{Na} = 0.4 Oe, see Fig. 2) is observed, that attests to a contact nature of ionic pairs.

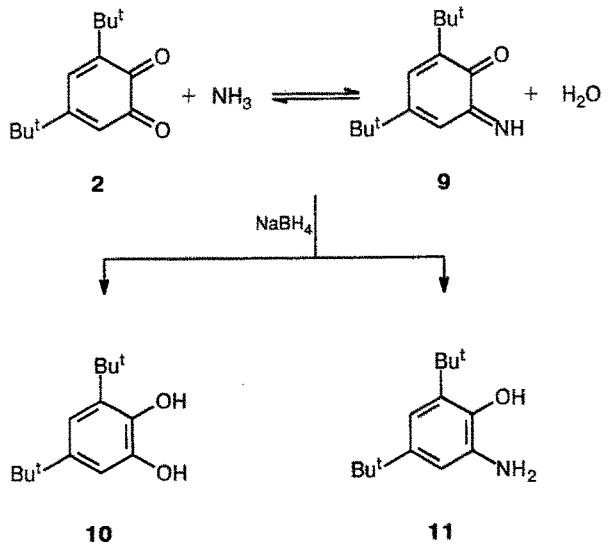
Scheme 4



M = Na, K

In contrast to quinone **1**, isomer **2** reacts with ammonia in water—alcohol medium reversibly. When the solvent is removed, the initial quinone **2** is regenerated. The equilibrium is shifted completely to quinonimine **9** at the treatment with an excess of NH_3. An "instantaneous photo" of the equilibrium position can be obtained by treating the solution with sodium borohydride (Scheme 5).

Scheme 5



When there is a sufficient excess of NH_3, aminophenol **11** is formed almost quantitatively (>90 %), that can be used as a convenient method for its preparation. The alternative variant, which was used in another synthesis of aminophenol **11** (Scheme 6), gave poorer results.

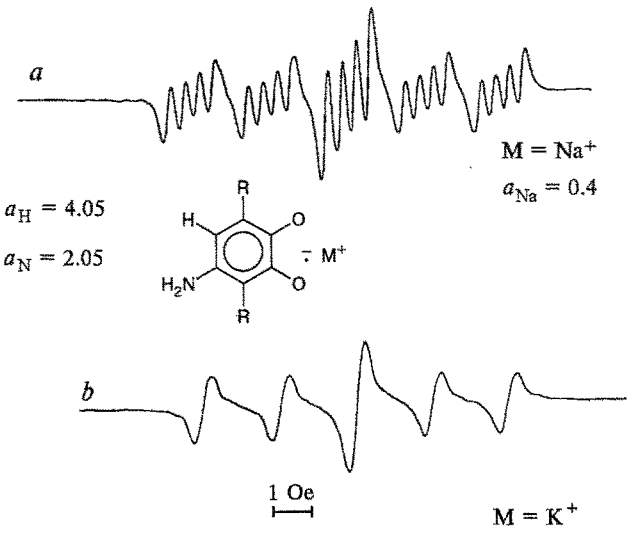
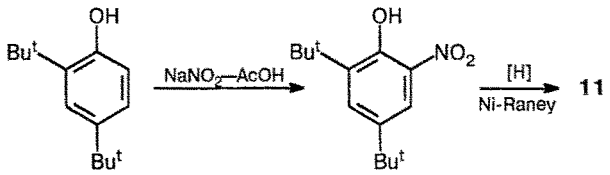


Fig. 2. ESR spectra of semiquinone radical anion obtained by reduction of aminoquinone **3** on mirror surfaces of Na (*a*) and K (*b*) (THF, 25 °C).

Scheme 6



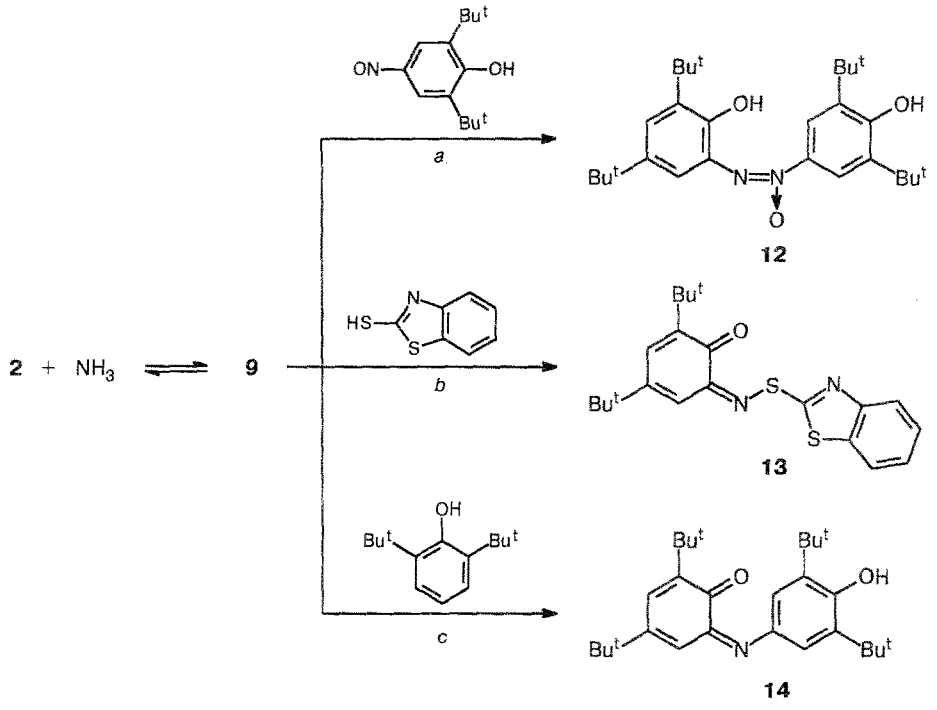
Quinonimine **9** is chemically high-reactive compound. The possibility of its synthetic application *in situ* is illustrated by reactions with *p*-nitrozophenol (Scheme 7, *a*) and by dehydrocoupling with readily oxidizable organic compounds (Scheme 7, *b* and *c*).

A new simple and suitable method of synthesis of asymmetrical indophenols and relative compounds was elaborated on the basis of the reaction (*c*). An interesting feature of indophenol **14**, the product of the reaction with 2,6-di-*tert*-butylphenol, was discovered. It was found that individual compound **14** in ammonia—alcohol medium underwent a radical exchange, some kind of metathesis, and two new compounds, **15** and **16** (Scheme 8), appeared in the solution along with compound **14**, which are identified by TLC with previously known compounds. The sample **15** was obtained by reaction of quinonimine **9** with 3,5-di-*tert*-butylpyrocatechol (**10**), indophenol **16** was obtained by combination of 2,6-di-*tert*-butylphenol with 2,6-di-*tert*-butyl-*para*-benzoquinone in ammonia—alcohol medium (see Scheme 8).

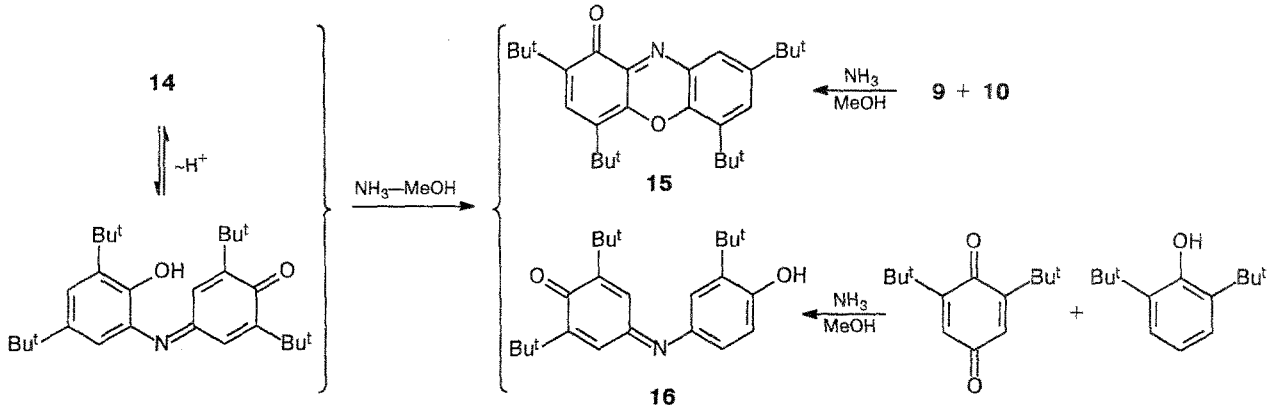
Experimental

^1H NMR and ESR spectra were registered on a Bruker P-80 WY and a Varian E-12A spectrometers. The reduction of

Scheme 7



Scheme 8



quinones on metal mirror surfaces was carried out *in vacuo* in THF solutions in special ESR tubes. The analysis of the reaction mixtures was carried out by TLC in hexane—ether (4:1) or in hexane—ether—$CHCl_3$ (4:4:1) systems on Silufol UV-254 plates.

Reactions of quinones 1 and 2 with ammonia were carried out in saturated solutions of compounds **1** and **2** in mixtures of alcohol (MeOH or EtOH) with conc. NH_3/H_2O (3:1).

Synthesis of aminoquinone 3. NH_3/H_2O (15 mL) was added to a solution of 1.1 g ($5 \cdot 10^{-3}$ mol) of quinone **1** in 45 mL of MeOH; ~0.5 mL of ammonia—alcohol solution was taken for ESR investigations, the rest was kept at ~20 °C until initial compound **1** and its alkoxysubstituted derivatives **6** and **7** disappeared completely (TLC control). Precipitated violet crystals were filtered off, dried, and sublimed at >200 °C. Yield 1 g (84 %). Found (%): C, 71.54; H, 9.12; N, 5.79. $C_{14}H_{21}O_2N$. Calculated (%): C, 71.48; H, 9.00; N, 6.00. ^1H NMR ($CDCl_3$), δ: 1.24 and 1.42 (18 H, Me_3C); 5.24 (2 H, NH_2); 6.28 (1 H, ring H).

Solid phase amination of quinone 1. A mixture of 2.2 g ($1 \cdot 10^{-2}$ mol) of compound **1** and 10 g (~$1 \cdot 10^{-1}$ mol) of $(NH_4)_2CO_3$ was submitted to abrasion in an electrical mixer for friable solid bodies, equipped with Z-shaped knife (rotation rate is 3600 rpm for 2 h with periodic interruptions (1—1.5 min). Organic products were extracted with methylene chloride and divised into individual components by preparative TLC. Initial compound **1** (~98 %) and aminoquinone **3** (~1.5 %) were isolated, which were identical to the pattern samples.

Deamination of aminoquinone 3. Compound **3** (0.235 g, $1 \cdot 10^{-3}$ mol) was dissolved in 10 mL of AcOH, several drops of HCl were added (the color of the mixture thereby changed from violet to orange), and a solution of $NaNO_2$ ($0.07 \cdot 10^{-3}$ mol) in AcOH was added dropwise (release of gas

bubbles was observed). The formation of a single product, oxyquinone **8**, identical to a previously known sample, was established by TLC.

Reaction of quinone 2 with ammonia. *A.* Compound **2** (11 g, $5 \cdot 10^{-2}$ mol) was dissolved in 300 mL of MeOH; 100 mL of conc. NH_3/H_2O was added. Change from red to yellowish-orange color of the solution was observed; however, only the initial quinone **2** was present according to TLC data. Powder of $NaBH_4$ was added to the solution in small portions until it turned completely colorless; white needle crystals precipitated, were filtered off, washed with a mixture of MeOH and conc. NH_3/H_2O, dried, and precipitated again from $CHCl_3$ with hexane. Compound **11** (10 g, 91 %) was obtained, m.p. 162 °C (see Ref. 5). An alternative synthesis was carried out by reduction of 2-nitro-4,6-di-*tert*-butylphenol (it was obtained by a procedure described earlier[6]) with hydrogen over Raney Ni. The m.p. is not depressed in a mixture with sample **11**. Yield ~75 %. (It should be noted that only one of three experiments on catalytic reduction was successful; the formation of deep colored mixtures of compounds, which were difficult to separate and in which phenoxazyne derivatives **15** were identified along with compound **11**, was observed in the other cases.)

***B. Isolation of compound* 12.** 4-Nitroso-2,6-di-*tert*-butylphenol (0.24 g, $1 \cdot 10^{-3}$ mol) was added to an ammonia—alcohol solution of compound **2** (0.22 g, $1 \cdot 10^{-3}$ mol), and the mixture was kept until the initial compound **2** disappeared. A product was precipitated with water, filtered off, dried, and crystallized from acetone. Compound **12** (0.34 g, 74 %) as canary-yellow crystals was obtained, m.p. 179 °C. Found (%): C, 73.60; H, 9.05; N, 5.82. $C_{28}H_{42}O_3N_2$. Calculated (%): C, 73.91; H, 9.30; N, 6.18.

***C. Isolation of compound* 13.** Mercaptobenzene (0.17 g, $1 \cdot 10^{-3}$ mol) was added to an ammonia—alcohol solution of compound **2** (0.22 g, $1 \cdot 10^{-3}$ mol); the mixture was kept until the initial compound **2** disappeared. A product was precipitated with water, dried, and purified by preparative TLC. Compound **13** (0.3 g, 80 %) as brick-red crystals was obtained, m.p. 164 °C (from acetone). Found (%): C, 65.41; H, 6.03; N, 6.91. $C_{21}H_{24}ON_2S_2$. Calculated (%): C, 65.50; H, 6.28; N, 7.30.

***D. Isolation of compound* 14.** 2,6-Di-*tert*-butylphenol (1.1 g, $5 \cdot 10^{-3}$ mol) was added to an ammonia—alcohol solution of compound **2** (1.1 g, $5 \cdot 10^{-3}$ mol), and the mixture was kept for 24 h. A product was precipitated with water, dried, and purified by preparative TLC. Compound **14** (1.5 g, ~70 %) was isolated, m.p. 133 °C (see Ref. 7). When compound **14** was kept in an ammonia—alcohol solution over 24 h, the formation of two new colored products was observed. The products were identified as indophenol **16** (red) and 1-*H*-oxo-2,4,6,8-tetrakis(*tert*-butyl)phenoxazine **15** (blue) by TLC with authentic samples. Reference sample **16** was obtained by condensation of 2,6-di-*tert*-butyl-*para*-benzoquinone with 4-amino-2,6-di-*tert*-butylphenol in ammonia—alcohol medium; compound **15** was obtained by the action of NH_3 on 3,5-di-*tert*-butylpyrocatechine in MeOH or by condensation of compound **2** with compound **11** in the presence of NH_3.

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