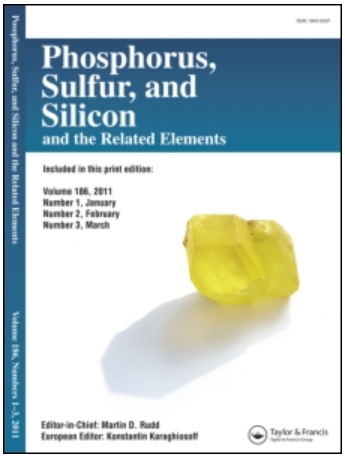

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MECHANISM OF THE REACTION OF SOME STABLE HEMIMERCAPTALS WITH *Secondary*-AMINES: EVIDENCE AGAINST THE INTERMEDIACY OF A METHYLENESULFONIUM ION

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MECHANISM OF THE REACTION OF SOME STABLE HEMIMERCAPTALS WITH *Secondary*-AMINES: EVIDENCE AGAINST THE INTERMEDIACY OF A METHYLENESULFONIUM ION

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(Received 10 December 1987)

The reaction of the arenethiols **4a–b** with formaldehyde and the *sec*-amines **5a–c** gave the aminomethyl aryl sulfides **6a–d**. The reaction of the hemimercaptals **3a–b** with **5a** in methanol gave **6a–b** in high yield. In acetonitrile reaction media, **6b** was obtained by the reaction of **3b** with **5a** which suggested that **7b** was not an intermediate in the formation of **6b** in methanolic media. The absence of **7b** in methanolic media suggests that the methylenesulfonium ion **8b** is not an reaction intermediate. The formation of **7b** was observed in the reaction of **3b** with methanol when catalyzed by the Lewis acid tetrafluoroboric acid diethyl ether complex. The experimental observations are best explained by a mechanism whereby **3a–b** are in rapid equilibrium with **4a–b** under the basic reaction conditions. Rapid reaction of the liberated formaldehyde with **5a** leads to the normal Mannich reaction pathway. Consistent with this mechanism, the reaction of a mixture of **3a–b** and **12** with **5a** gave both **6a–b** and **13**.

Key words: Hemimercaptal; Methylenesulfonium ion; Mannich reaction; Aminomethyl aryl sulfides; *sec*-Amines.

The reversibility of the addition of thiols to aldehydes to form hemimercaptals is well known in the literature.[1] In certain cases the resultant hemimercaptals have been isolated. As early as 1870, for example, Martius and Mendelssohn-Barthology reported the isolation of several stable hemimercaptals from the reaction of choral with thiols.[2] Levi reported the preparation of the stable hemimercaptals **1a–b** by the reaction of formaldehyde with octanethiol and benzenethiol, respectively, which were characterized by elemental analysis.[3]

Later, Poppelsdorf and Holt described the reaction of these hemimercaptals with activated methylene compounds under basic reaction conditions in the formal sulfur analog of a Mannich reaction.[4] The authors suggested the intermediacy of a methylenesulfonium ion **2**.

More recently, Field *et al.* reported an IR spectral study of the equilibration in solution of various hemimercaptals with their corresponding starting thiol and formaldehyde.[5] Grillot and Lau reported the isolation and IR spectrum of **1c**.[6] Recently, Ando and co-workers reported the isolation of a stable hemimercaptol.[7]

† Author to whom all correspondence should be addressed.

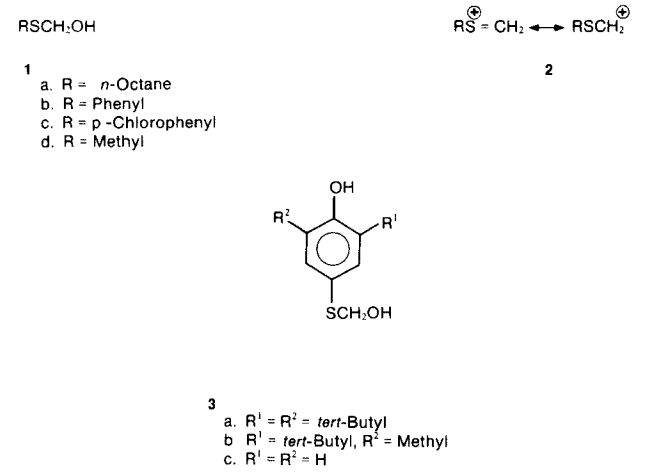


FIGURE 1

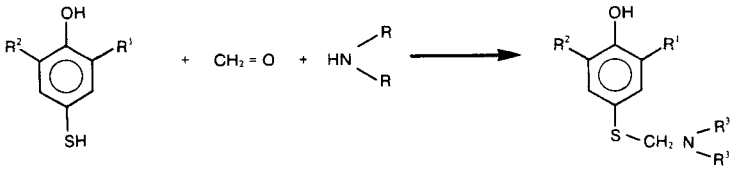
Quite recently, we reported the isolation and spectral characterization of the stable hemimercaptals **3a–c**.[8] ^{1}H NMR spectral studies of **3a–b** demonstrated that equilibration with starting thiol and formaldehyde in neutral solution was slow on the NMR time scale as evidenced by $^3J_{HCOH}$ coupling in the ^{1}H NMR spectra of **3a–b**. In a very recent report by Jones and co-workers, a similar coupling was observed in the hemimercaptal **1d**.[9] Investigation of the chemistry of **3a–c**, however, led to the suggestion that these hemimercaptals were in rapid equilibrium with starting thiol and formaldehyde *under basic reaction conditions*.[8]

The results of these studies led us to question the original suggestion of Poppelsdorf and Holt that methylenesulfonium ions were intermediates under *basic* reaction conditions. Pollak and Grillot provided evidence against methylenesulfonium ions in the reaction of both thioaminals and thiomercaptals under *acidic* conditions.[10] We report in this paper evidence against the involvement of methylenesulfonium ions in the reaction of the hemimercaptals **3** with *sec*-aromatic amines.

RESULTS AND DISCUSSION

The reaction of the arenethiol **4a** with **5a** and 37% aqueous formaldehyde in a methyl alcohol reaction medium afforded the aminomethyl aryl sulfide **6a** (91% recrystallized) (see Scheme I). The TLC and ^{1}H NMR spectrum of the reaction product prior to recrystallization indicated that the formation of **6a** was essentially quantitative (uncrystallized **6a** gave correct elemental analysis).

The structure of **6a** rests on the following observations. In the IR spectrum of **6a**, an absorption was observed at 3620 cm^{-1} that was assigned to the hydroxyl stretching frequency of the hindered phenol. In the ^{1}H NMR spectrum a singlet resonance was observed at δ 5.15 that was assigned to the methylene protons of **6a**. In the ^{13}C {^{1}H} NMR spectrum of **6a**, a singlet resonance was observed at



4
a. $R^1 = R^2 =$ *tert*-Butyl
b. $R^1 =$ *tert*-Butyl; R^2 = Methyl
c. $R^1 = R^2 = H$

5
a. R = Phenyl
b. R = Methyl
c. R = n-Butyl

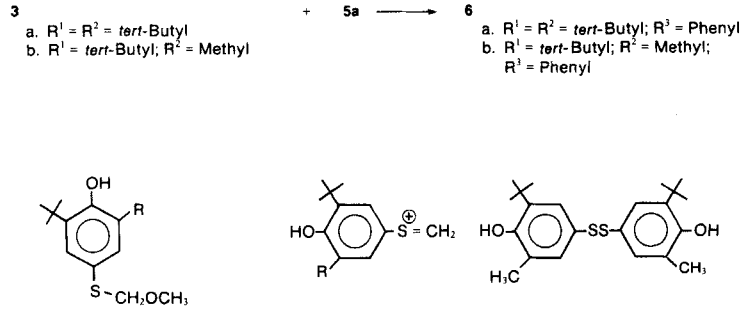
6
a. $R^1 = R^2 =$ *tert*-Butyl; R^3 = Phenyl
b. $R^1 =$ *tert*-Butyl; R^2 = Methyl; R^3 = Phenyl
c. $R^1 = R^2 =$ *tert*-Butyl; R^3 = Methyl
d. $R^1 = R^2 =$ *tert*-Butyl; $R^3 =$ *n*-Butyl

SCHEME I

δ 61.3 that was assigned to the methylene carbon atom bonded to both nitrogen and sulfur. The MS displayed a molecular ion at 419 mass units. The spectral and elemental analysis data were fully in accord with the proposed structure.

Similarly, **6b–d** were obtained by the reaction of **4a–b** with the corresponding amines **5a–c** and formaldehyde. The formation of **6a–d**, of course, is not surprising as Grillot and Schaffrath reported that the reaction of thiophenols with formaldehyde and aryl amines gave aminomethyl aryl sulfides.[11] The literature suggests that these reactions proceed through a Mannich-type reaction mechanism, although iminium ions do not appear to be intermediates in neutral or basic reaction media.[12–15]

Previously, we reported the preparation of **3a–c** in high yield by the reaction of **4a–c** with 37% aqueous formaldehyde in a methyl alcohol reaction medium under basic conditions. These results suggested that **3a–b** may be intermediates in the formation of **6a–b**. Indeed, the reaction of either **3a** or **3b** with **5a** in a methanol reaction medium gave **6a–b**, respectively (see Scheme II). Similarly, the reaction of **3b** with **5a** in acetonitrile reaction media *in the absence of methanol* gave **6b** in high yield.



3
a. $R^1 = R^2 =$ *tert*-Butyl
b. $R^1 =$ *tert*-Butyl; R^2 = Methyl

6
a. $R^1 = R^2 =$ *tert*-Butyl; R^3 = Phenyl
b. $R^1 =$ *tert*-Butyl; R^2 = Methyl; R^3 = Phenyl

7
a. R = *tert*-Butyl
b. R = Methyl

8
a. R = *tert*-Butyl
b. R = Methyl

9

SCHEME II

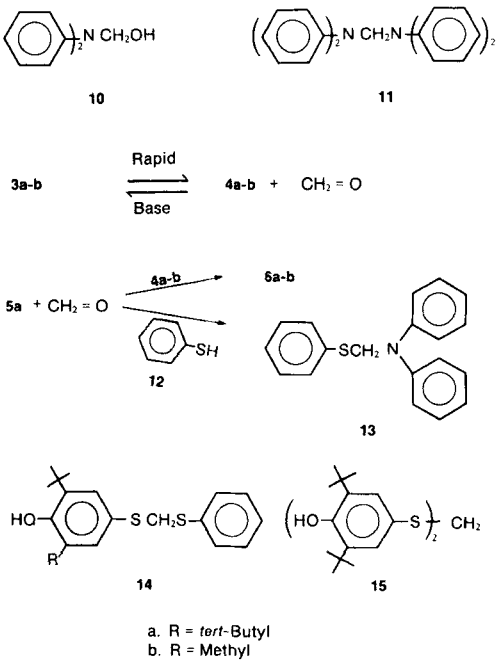
The reaction of **3b** with **5a** in acetonitrile ruled out **7b** as a plausible intermediate in methanolic media. The formation of **7b** would be expected to arise by electrophilic capture of methanol if the methylenesulfonium ion **8b** was an intermediate in the formation of **6b**. The absence of **7b** in the reaction of **3b** with **5a** in methanol strongly suggests that methylene sulfonium ions are *not* reaction intermediates, although the rapid equilibration **7** $\rightleftharpoons$ **8** is not excluded.

The stability of **3b** under basic reaction conditions was ascertained in a control experiment. A solution of **3b** and triethylamine in methanol was stirred for 24 hours at room temperature. In the ^{1}H NMR spectrum of the reaction mixture, resonances were observed for **3b** along with a minor quantity of disulfide **9**. The dilsulfide **9** was probably obtained by oxidation of **4b** with adventitious oxygen. The observation of **9** supports the previous contention that these hemimercaptals are in rapid equilibrium with formaldehyde and thiol under basic reaction conditions.[8]

The reaction of **3b** under acidic conditions was investigated to probe the possible involvement of a methylenesulfonium ion. To a solution of **3b** in methanol at −40°C was added tetrafluoroboric acid diethyl ether complex. After the reaction mixture was warmed to 14°C, the examination of an aliquot taken from the reaction mixture showed only unreacted **3b**. Upon stirring overnight at room temperature, however, the methoxy derivative **7b** (14%) was obtained by fractional recrystallization of the crude product. The TLC of the crude reaction mixture indicated the presence of three components of which **7b** appeared to be the major component. Unreacted **3b** was not present in the final reaction mixture. Although other mechanistic pathways are possible, the formation of **7b** may proceed through the intermediacy of the methylenesulfonium ion **8b** formed directly from **3b** under the acidic reaction conditions. In this regard, however, Pollak and Grillot have shown evidence against the intermediacy of a methylenesulfonium ion derived from **1b** under acidic reaction conditions.[10]

The above observations rule out the intermediacy of either **7a–b** or the methylenesulfonium ion **8a–b** as plausible intermediates for the formation of **6a–b** from **3a–b** under basic reaction conditions. A reasonable mechanism for the formation of **6a–b** from **3a–b** is shown in Scheme III. Under the basic reaction conditions, **3a–b** are in rapid equilibrium with **4a–b** and formaldehyde. Rapid reaction of the liberated formaldehyde with **5a** leads to the normal Mannich reaction pathway. Mannich reactions of formaldehyde with diphenylamine and an appropriate substrate have been reported in the literature.[16] The precise mechanistic pathway of Mannich reactions with aromatic amines under basic conditions, however, is still not fully elucidated, although previous work would suggest that in the present study either the hemiaminal **10** or animal **11** may be an intermediate under basic reaction conditions.[12–15,17–19]

In a crossover experiment designed to ascertain whether the mechanism illustrated in Scheme III is operative, the reaction of a mixture of **3a** and **12** with **5a** would be expected to give a mixture of both **6a** and **13**[20] because the Mannich intermediate generated would react with both **4a** and **12**. Major differences in the nucleophilicity of **4a** and **12** toward the Mannich intermediate would not be anticipated. Indeed, the reaction of a mixture of **3a** and **12** with **5a** gave both **6a** and **13**. Similarly, the reaction of a mixture of **3b** and **12** with **5a** gave a mixture of



a. R = *tert*-Butyl
b. R = Methyl

SCHEME III

both **6b** and **13**. These results are consistent with the mechanism illustrated in Scheme III. The absence of observable quantities of the dithioketals **14a–b** in these crossover experiments provide further evidence against the involvement of the methylenesulfonium ions **8a–b**, which would be expected to react with **12** to an appreciable extent. Dithioketals are stable to acidic conditions. The absence of the dithioketal **15** in the reaction of **4a** with formaldehyde and **5a** provides further evidence against the involvement of methylenesulfonium ions in these reactions.

The results of this study show that hemimercaptals are not intermediates in the reaction of the thiols **4a–b** with formaldehyde and **5a–c**, although **3a–b** may form in a rapidly reversible reaction. This study further demonstrates that methylenesulfonium ions are not intermediates in the reaction of the hemimercaptals **3** with amines *under basic reaction conditions.* Evidence is presented that suggests the hemimercaptals **3a–b** are in rapid equilibrium with thiol and formaldehyde. The reaction of the liberated formaldehyde with the amine and thiol then proceeds through the usual Mannich mechanism.

EXPERIMENTAL

All melting points were determined in open capillary tubes with a Thomas-Hoover melting-point apparatus and are uncorrected. IR spectra (1% solution in sodium chloride cells) were recorded on a Perkin–Elmer Model 710 or 1300 spectrophotometer. ^{1}H NMR spectra were taken on a Jeol FX-90Q, Varian Model XL-200, or Varian model CFT-20 spectrometer. ^{13}C NMR Spectra were obtained on a Varian Model XL-200 spectrometer using a 55° flip angle, a 0.8-s repetition rate with no pulse delay, and with full proton decoupling. All ^{1}H and ^{13}C NMR spectra are reported relative to tetramethylsi-

lane, where a positive sign is downfield from the standard. MS were obtained on a Finnegan Model 8200 mass spectrometer.

Whatman DSC-1F silica gel was used for dry-column chromatography. MERCK 9385 silica gel 60 (230–400 mesh) was used for flash chromatography.[21] MERCK pre-coated (0.25) silica gel 60 F-254 plates were used for TLC. Preparative HPLC was carried out with a Waters Prep 500A HPLC.

Reagents were purchased from commerical laboratory supply houses. Solvents were dried prior to use. Reactions were carried out in flame-dried apparatus under an atmosphere of nitrogen. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY Corporation, Ardsley, N.Y.

N-(3,5-Di-tert-butyl-4-hydroxyphenylthiomethyl)-N,N-diphenylamine, (**6a**)

Method A

To a stirred solution of 144 g (0.85 mol) of **5a** and 203 g (0.85 mol) of **4a** in 1 L of methanol was added dropwise 69 g (0.85 mol) of 37% aqueous formaldehyde at room temperature. The reaction mixture was stirred at room temperature for 18 h. To the reaction mixture was added an additional 7 g (85 mmol) of 37% aqueous formaldehyde and then the reaction mixture was heated at 60°C for 1 h. The solvent was removed *in vacuo* and the residue was recrystallized from petroleum ether (bp 35–60°C) to give 324 g (91%) of a white crystalline solid: mp 77–80°C; IR (CCl_4) 3620 (OH) cm^{-1}; ^1H NMR ($CDCL_3$) δ 1.38 (s, $C(CH_3)_3$, 18H), 5.20 (s, CH_2, 2H), 5.22 (s, OH, 1H), 6.84–7.38 (complex m, ArH, 12H); ^{13}C NMR ($CDCl_3$) δ 29.7, 33.7, 61.3, 122.3, 122.4, 125.0, 129.9, 132.1, 138.1, 147.7, 154.8; MS m/z $419^{+\cdot}$. Anal. Calcd for $C_{27}H_{33}NOS$: C, 77.3; H, 7.9; N, 3.3. Found: C, 77.3; H, 7.8; N, 3.3.

Method B

A solution of 5.00 g (18.6 mmol) of **3a** and 3.15 g (18.6 mmol) of **5a** in 25 mL of methanol was heated at reflux for 18 h. The solid that precipitated upon cooling was collected to give 5.00 g (64%) of a white solid identical in every respect to that prepared by method A.

N-(3-tert-Butyl-4-hydroxy-5-methylphenylthiomethyl)-N,N-diphenyl-amine, (**6b**). To a solution of 20 g (102 mmol) of **4b** and 17.2 g (102 mmol) of **5a** in 200 mL of methanol was added dropwise 8.3 g (102 mmol) of 37% aqueous formaldehyde. After the addition was complete, the reaction mixture was heated at reflux for 4 h. The solvent was removed *in vacuo* and the residue was recrystallized from petroleum ether to give 26 g (68%) of a white solid: 58–63°C; IR (CCl_4) 3615 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 9H), 2.15 (s, 3H), 4.77 (s, OH, 1H), 5.21 (s, 2H), 7.08 (complex m, 12H). Anal. Calcd for $C_{24}H_{27}NOS$: C, 76.3; H, 7.2; N, 3.7; S, 8.5. Found: C, 76.6; H, 7.3; N, 3.6; S, 8.7.

Method B: Methanol Solvent

A solution of 2.26 g (10 mmol) of **3b** and 1.69 g (10 mmol) of **5a** in 10 mL of methanol was stirred at room temperature for 72 h. The solvent was removed *in vacuo* and the residue was recrystallized from petroleum ether to give 2.41 g (64%) of a white solid identical in every respect to that prepared by method A.

Method C: Acetonitrile Solvent

A solution of 2.26 g (10 mmol) of **3b** and 1.69 g (10 mmol) of **5a** in 10 mL of acetonitrile was stirred at room temperature for 72 h. The solvent was removed *in vacuo* and the residue was recrystallized from petroleum ether to give 3.23 g (85%) of a white solid identical in every respect to that prepared by method A.

N-(3,5-Di-tert-butyl-4-hydroxyphenylthiomethyl)-N,N-dimethylamine, (**6c**). To a suspension of 5.96 g (25 mmol) of **4a** in 10 mL of toluene was added sequentially 4.51 g (25 mmol) of 25% aqueous dimethylamine and 2.03 g (25 mmol) of 37% aqueous formaldehyde. After the initial exothermic reaction was complete, the resultant two-phase reaction mixture was heated at 100°C for 2 h. The reaction mixture was cooled and the organic phase was separated. The aqueous phase was extracted with diethyl ether (1 × 100 mL) and the combined organic phases were dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was recrystallized from acetonitrile to give 4.0 g (54%) of a white solid: mp 69–73°C; IR (CH_2Cl_2) 3640 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (s, 18H), 2.36 (s, 6H), 4.37 (s, 2H), 5.20 (s, 1H), 7.32 (s, 2H). Anal. Calcd for $C_{17}H_{29}NOS$: C, 69.1; H, 9.9; N, 4.7. Found: C, 69.1; H, 9.8; N, 4.8.

N-(3,5-Di-tert-butyl-4-hydroxyphenylthiomethyl)-N,N-di-n-butylamine, (**6d**). By the method used to prepare **6c**, compound **6d** was prepared from 11.92 g (50 mmol) of **4a**, 4.10 g (50 mmol) of 37% aqueous formaldehyde, and 6.46 g (50 mmol) of **5c**. The residue was purified by flash chromatography (dichloromethane eluent) to give 12.35 g (67%) of a colorless liquid: IR (CH_2Cl_2) 3640 (OH)cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, $^3J_{HCCH} = 7$ Hz, 6H), 1.26 (complex m 4H), 1.43 (s, 18H), 1.45 (complex m, 4H), 2.52 (t, $^3J_{HCCH} = 7$ Hz, 4H), 4.46 (s, 2H), 5.14 (s, 1H), 7.30 (s, 2H). Anal. Calcd for $C_{23}H_{41}NOS$: C, 72.8; H, 10.9; N, 3.7; S, 8.4. Found: C, 72.9; H, 11.0; N, 3.4; S, 8.3.

1-(3,5-Di-tert-butyl-4-hydroxyphenylthio)-1-(methoxy)methane, (**7b**). To a solution of 4.52 g (20 mmol) of **3b** in 25 mL of methanol at −40°C was added 1 ml of tetrafluoroboric acid-diethyl ether complex. The reaction mixture was allowed to warm to room temperature and then it was stirred overnight at room temperature. The reaction mixture was added to a solution of dilute aqueous sodium bicarbonate and the resultant heterogeneous mixture was extracted with diethyl ether. The ether extract was dried over anhydrous sodium sulfate and the solvent was removed *in vacuo*. The residue was recrystallized from acetonitrile to give 0.65 grams (14%) of a white solid: 98–101°C; IR ($CHCl_3$) 3610, 3400 (OH) cm^{-1}; ^1H NMR δ 1.40 (s, 9H), 2.16 (s, 3H), 3.46 (s, OCH_3, 3H), 4.88 (s, 2H), 4.96 (s, OH, 1H), 7.16 (d, 1H), 7.30 (d,1H). Anal. Calcd for $C_{13}H_{20}O_2S$: C, 65.0; H, 8.4. Found: C, 64.6; H, 8.3.

N,N-Diphenyl-N-(phenylthiomethyl)amine, (**13**). To a solution of 11.02 g (100 mmol) of **12** and 8.1 g (100 mmol) of 37% aqueous formaldehyde in 100 mL of methanol was added 16.90 g (100 mmol) of **5a**. The reaction mixture was stirred overnight at room temperature. Upon dilution of the resultant two-phase reaction mixture with methanol, the white solid which precipitated was collected by filtration. The crude product was recrystallized from methanol to give 11.36 g (39%) of white crystals: mp 80–82°C; ^1H NMR ($CDCl_3$) δ 5.37 (s, 2H), 7.24 (complex m, 15H). Anal. Calcd for $C_{19}H_{17}NS$: C, 78.3; H, 5.9; N, 4.8; Found: C, 78.0; H, 5.7; N, 4.7.

Reaction of **3b** *with* **5a** *and* **12**. A solution of 9.0 g (40 mmol) of **3b**, 4.1 mL (40 mmol) of **12**, and 6.8 g (40 mmol) of **5a** in 50 ml of methanol was stirred at room temperature for 6 days. The solvent was removed *in vacuo* and the mixture was separated by preparative HPLC (silica gel; 98:2 hexane:ethyl acetate eluent) to give 3.4 g (29%) of **13** and 8.5 g (58%) of **6b**.

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