

## A SERIES OF MODEL COMPOUNDS FOR THE STUDY OF AROMATIC REACTIONS<sup>1</sup>

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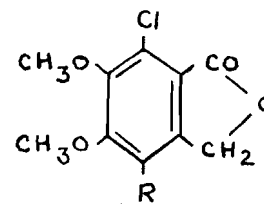
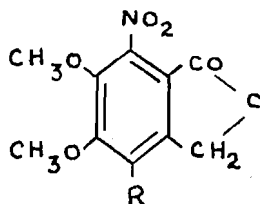
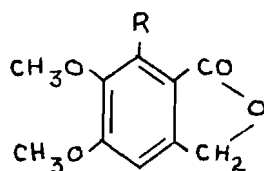
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### ABSTRACT

A series of halogenated phthalides was prepared in which there was a systematic variation in the identity, position, and degree of activation of the halogen, and in the activation of the methylene group. A study was made of the selective reductive removal of halogen in the presence of another halogen, or of a nitro group.

Metameconine (Ia) is admirably adapted to the study of competitive reactions. A rapid survey of its possibilities has shown that in several well-known aromatic reactions it could be used to drive currently favored theories into difficulties that were not easily resolved (1). The new compounds described in this paper formed a weapon that has since been used in a much more intensive attack upon two of these reactions.

One of these was the copper-catalyzed removal of halogen by aqueous hydroxide ion. Our previous work (1-6) had provided a set of compounds superbly suited to the study, as shown by the large number of new observations recorded in the next paper. More compounds needed in the investigation were provided in the present work. In particular, the synthesis of IIb, IIc, and II*d* was saved from triviality by two difficulties that had to be overcome. It was pointed out previously (1) that the nitro group in 4-amino-7-nitro-metameconine (IIe) was very easily extruded on diazotization. For example, when IIe was diazotized in dilute aqueous hydrochloric acid, reduction of the diazonium solution gave 7-chlorometameconine (IIIa), and treatment of the diazonium solution with potassium iodide gave 4-iodo-7-chlorometameconine (III*d*) (1). The same diazonium solution has now been shown to give 4,7-dichlorometameconine (IIIb) with cuprous chloride. However, cuprous bromide gave a mixture of compounds instead of pure IIIc. Thus the diazonium cation IIIe was conventional in its relative reactivities towards chloride, bromide, and iodide under the conditions used.



Ia. R = H	IIa. R = H	II <i>f</i> . R = OH	IIIa. R = H	IIIe. R = N <sub>2</sub> <sup>+</sup>
Ib. R = NHCOCH <sub>3</sub>	IIb. R = Cl	II <i>g</i> . R = OCH <sub>3</sub>	IIIb. R = Cl	III <i>f</i> . R = OH
Ic. R = N(COCH <sub>3</sub> ) <sub>2</sub>	IIc. R = Br	II <i>h</i> . R = NHCHO	IIIc. R = Br	III <i>g</i> . R = OCH <sub>3</sub>
Id. R = NHCHO	II <i>d</i> . R = I	II <i>i</i> . R = NO <sub>2</sub>	III <i>d</i> . R = I	
	IIe. R = NH <sub>2</sub>	II <i>j</i> . R = NHCOCH <sub>3</sub>		

<sup>1</sup>Most of the work was presented at the Annual Meeting of the Chemical Institute of Canada, in Toronto, June 7, 1963.

When sulfuric acid was used in the diazotization of *Ile* (in an attempt to avoid nucleophilic displacement of the nitro group) a diazonium salt was obtained whose resistance to thermal decomposition and to reduction has been recorded (1). The idea of using the poorly nucleophilic monovalent anions, nitrate and perchlorate, in place of sulfate, seemed most unattractive.<sup>2</sup> Fortunately, the diazonium sulfate prepared by the method of Hodgson and Walker (7, 8) was found to react under suitable conditions (8) with cuprous chloride, cuprous bromide, or potassium iodide to give good yields of the activated aromatic halides 4-chloro-7-nitrometameconine (*IIf*), 4-bromo-7-nitrometameconine (*IIf*), and 4-iodo-7-nitrometameconine (*IIf*), respectively.

The study also required a knowledge of the products of hydroxydehalogenation, and these were characterized in the present work. The uncatalyzed reaction of 7-chloro-4-iodometameconine (*IIIe*) with aqueous potassium hydroxide gave 7-chloro-4-hydroxymetameconine (*IIIg*), with selective replacement of iodine. One might have expected *IIf*, *IIf*, and *IIf* all to give 4-hydroxy-7-nitrometameconine (*IIf*) in the same reaction, but in fact with one exception the reactions took a more complex course. However, the copper-catalyzed reaction of the iodo compound (*IIf*) gave the expected hydroxy compound (*IIf*), accompanied by some 7-nitrometameconine (*IIf*); this competition between substitution and reduction is the main theme of the next paper. Phenols *IIf* and *IIIg* and their methyl ethers *IIf* and *IIIg* were synthesized for further comparative studies of anisoles and diphenyl ethers (9, 10).

It is odd that metameconine gives no 4-nitrometameconine on nitration (since 7-nitrometameconine readily gives 4,7-dinitrometameconine) (1), and we have now accumulated a considerable list of failures to nitrate at the 4-position. Over the course of 26 years, previous workers in this laboratory have repeatedly failed to nitrate 7-acetaminometameconine (*Ib*) (3)<sup>3</sup> and 7-diacetylamino metameconine (*Ic*) (3).<sup>3</sup> To this list of failures we have now added the known compound 7-chlorometameconine (*IIIa*) (5) and the new compound 7-formaminometameconine (*Id*). As a check, 4-formamino-7-nitrometameconine (*IIf*) and 4-acetamino-7-nitrometameconine (*IIf*) were made and found to be fairly stable. The difference between the 4- and 7-positions was also illustrated in another interesting way. The previous observations that 4- and 7-bromophthalides were subject to reductive dehalogenation (6) but that some related chloro compounds were not (5) led to the successful selective reduction of 7-chloro-4-iodometameconine (*IIIe*) to 7-chlorometameconine (*IIIa*) (1). We now find that 4,7-dichlorometameconine can also be selectively reduced in excellent yield, to the same 7-chlorometameconine (*IIIa*). Thus a difference in the identity of the two halogens is not required for selective removal of one of them.

The reductive removal of halogen in the presence of the easily reducible nitro group is of considerable interest, especially since the established method of Leslie and Turner (12) failed completely in the present series. Removal of the halogen of 4-iodo-7-nitrometameconine (*IIf*) with copper and aqueous potassium hydroxide has already been mentioned; it was (in this case) overshadowed by the substitution reaction. Better, but still moderate, yields of the reduced product (*IIf*) were obtained when 4-bromo-7-nitrometameconine (*IIf*) was heated with copper and molten benzoic acid at about 160°, according to the

<sup>2</sup>Diazotization of *IIf* in hydrobromic acid gave a crystalline diazonium salt showing diazonium and nitro bands at 2180 and 1547  $\text{cm}^{-1}$  in the infrared spectrum. It failed to give the Sandmeyer reaction, and it survived attempted reduction with hypophosphorous acid. While one sample remained unmelted at 250°, another exploded with quite a lot of noise, smoke, and flame, when touched by a spatula on the Buchner funnel. An analogous salt was obtained by diazotization of *IIf* in concentrated hydrochloric acid. Attempts to obtain fluoborates failed.

<sup>3</sup>Our early papers used the numbering scheme of Ráy and Robinson (11), the later ones the scheme of Chemical Abstracts.

method of Smith and Campanaro (13). In their examples bromine para to nitro was *not* removed. With the more delicate 4-iodo-7-nitrometameconine (II*d*), acetic acid was found to be preferable to benzoic acid as the source of hydrogen. Curiously, the addition of the very nucleophilic acetate ion did not appreciably lower the yield of the reduced product (II*a*); apparently the substitution reaction was much depressed in the acetic acid solvent.

Anbar, Guttman, and Friedman (14) recently found that cupric ion and ascorbic acid in neutral aqueous solutions were together very effective in the de-iodination of ortho-iodobenzoic acid. As is shown in the next paper, our experience differed sharply in nearly every respect from theirs. Nevertheless, 4-iodo-7-nitrometameconine (II*d*) was reduced smoothly and in good yield to 7-nitrometameconine (II*a*) by copper *metal* and ascorbic acid in alkaline solution. It is likely that this reduction system will prove very useful in preparative aromatic chemistry.

#### EXPERIMENTAL

Melting points marked (p) were determined on the precision capillary apparatus, the rest on the Kofler Micro Hot Stage; the values from the latter have been lowered 3–5° to bring them into agreement with the former (5), except for cases of polymorphism or decomposition at the melting point in which there is a real theoretical difference between the two methods. Infrared spectra for all of the new compounds and nuclear magnetic resonance (n.m.r.) spectra for some of them have been determined and are in agreement with the structures suggested.

##### *4,7-Dinitrometameconine (IIi)*

The yield (70.5%) and quality (151.3–152.0°) of the crude material were considerably better than reported before (1), due to the use of relatively larger amounts of nitrating acid and of purer metameconine. Fuming nitric acid (80 ml, 90%) and concentrated sulfuric acid (20 ml) were mixed and chilled to 0°. Metameconine (16.5 g, m.p. 157.5–158.5°) was added with stirring over 45 min. More fuming nitric acid (75 ml) was added, and the stirring continued 5 h longer, the mixture then being poured onto ice and water (300 ml). Crude product was recovered, washed, and dried; yield 17.0 g.

##### *4-Iodo-7-nitrometameconine (IId)*

The method resembled that used by Chalmers, Dickson, Elks, and Hems in the synthesis of a precursor of thyroxine (8). Sodium nitrite (0.42 g) was warmed with concentrated sulfuric acid (8 ml). The solution was chilled, diluted with glacial acetic acid (8 ml), and then stirred and cooled in an ice bath while a second cold solution, made from 4-amino-7-nitrometameconine (IIe) (1) (0.95 g, m.p. 230–231°), concentrated sulfuric acid (10 ml), and glacial acetic acid (10 ml), was added over a period of 1 h; stirring and cooling were continued for an additional 3 h. The cold solution of diazotized 4-amino-7-nitrometameconine was then added with stirring to a solution of potassium iodide (4 g), urea (2 g), and water (150 ml). The temperature rose to 58°. After being stirred for 0.5 h, the solution was treated with sodium bisulfite and chilled overnight; the light-yellow, crude product was recovered in a yield of 1.21 g (84%), m.p. 159.5–161.5°. When the cold solution of diazotized 4-amino-7-nitrometameconine from 3 g of the amine was poured into a mixture of water, chloroform, urea, potassium iodide, and iodine in the more elaborate procedure used in previous examples (8, 15), the total yield of once-crystallized product was only 76%. Three more recrystallizations of the first fraction of this material from ethanol gave the analytical sample, m.p. 161.3–161.9° (p).

Found: C, 32.96; 33.13; H, 2.27, 2.48; N, 3.66, 3.51; I, 35.00, 35.06. Calcd. for C<sub>10</sub>H<sub>8</sub>O<sub>6</sub>N<sub>1</sub>: C, 32.88; H, 2.23; N, 3.83; I, 34.79.

##### *4-Chloro-7-nitrometameconine (IIb)*

A cold solution of diazotized 4-amino-7-nitrometameconine (made approximately as above from 2.5 g of the amine) was added with swirling to a fresh solution of cuprous chloride (made from 5 g of copper sulfate pentahydrate) in concentrated hydrochloric acid (10 ml). Urea and water were added to the dark-purple mixture which was then warmed to 60–70°. Crude product was recovered from the cooled solution in a yield of 2.41 g (94%), m.p. 130–131°. Four recrystallizations from butanol gave the pale-yellow needles of the analytical sample, m.p. 132.8–133.3° (p).

Found: C, 44.12, 44.11; H, 2.74, 2.91; N, 5.24, 5.15; Cl, 12.81, 12.71. Calcd. for C<sub>10</sub>H<sub>8</sub>O<sub>6</sub>ClN: C, 43.88; H, 2.93; N, 5.12; Cl, 12.98.

##### *4-Bromo-7-nitrometameconine (IIc)*

A cold solution of diazotized 4-amino-7-nitrometameconine (made approximately as above from 1.0 g of the amine) was added with swirling to a solution of cuprous bromide (made from 2.5 g of copper sulfate pentahydrate) in hydrobromic acid (60%, 5 ml); urea was added and the mixture was warmed slightly,

diluted with water, and cooled. The recovered product after one recrystallization from butanol had a m.p. of 141.5–142.2°, yield 1.08 g (91%). Two more recrystallizations gave white plates, m.p. 140.5–141.5° (p).

Found: C, 38.12, 38.23; H, 2.50, 2.70; N, 4.44, 4.42; Br, 25.38, 25.09. Calcd. for  $C_{10}H_8O_6NBr$ : C, 37.74; H, 2.52; N, 4.40; Br, 25.16.

#### 7-Chloro-4-iodometameconine (III<sub>d</sub>) (1)

Pure 4-amino-7-nitrometameconine (3.0 g, m.p. 230–231°) was diazotized with sodium nitrite in aqueous hydrochloric acid (cf. ref. 1); the solution was poured into a rapidly stirred mixture of potassium iodide (10 g), urea (5 g), iodine (5 g), water (110 ml), and chloroform (140 ml). Crude product was recovered (in much the same way as in the second method used for 4-iodo-7-nitrometameconine above) in a yield of 3.08 g (74%), reduced after one recrystallization from methanol to 2.61 g (m.p. 140.5–145.5°). One more recrystallization raised the melting point to that of the pure material previously obtained (1), 148.5–153.5°, the range being due to the dimorphism observed on the Kofler hot stage (1), though usually not in the capillary method (1).

#### 4,7-Dichlorometameconine (III<sub>b</sub>)

Pure 4-amino-7-nitrometameconine (2.0 g) was diazotized in aqueous hydrochloric acid approximately as above. The solution was treated with urea and then added to a fresh solution of cuprous chloride (made from 5 g of copper sulfate pentahydrate) in concentrated hydrochloric acid (10 ml). After effervescence had ceased, the mixture was warmed to 60–70° and then chilled. The pale-yellow product was recovered and recrystallized from aqueous ethanol with charcoal. Colorless flat plates were obtained in a yield of 1.38 g (90%), m.p. 141.3–141.8° (with a trace at 138.8°). Four recrystallizations from butanol gave the analytical sample, m.p. 141.6–142.2° (p).

Found: C, 45.54; 45.39; H, 3.23, 3.07; (on another sample) Cl, 27.32, 27.19. Calcd. for  $C_{10}H_8O_4Cl_2$ : C, 45.65; H, 3.04; Cl, 27.00.

An attempt to convert the amine to the corresponding bromo compound (III<sub>c</sub>), using cuprous bromide in hydrobromic acid in place of cuprous chloride in hydrochloric acid, but retaining the diazotization in hydrochloric acid, gave a product which after two recrystallizations from acetic acid and two from butanol had m.p. 154.6–157.2°.

Found: C, 40.21, 40.21; H, 2.82, 2.99; Cl, 15.20, 15.39; Br, 19.25, 19.28. Calcd. for  $C_{10}H_8O_4ClBr$ : C, 39.09; H, 2.61; Cl, 11.40; Br, 26.06.

Reduction of this mixture yielded 7-chlorometameconine (III<sub>a</sub>).

#### Selective Dehalogenation of 4,7-Dichlorometameconine (III<sub>b</sub>)

4,7-Dichlorometameconine (0.10 g, m.p. 141–142°) was heated under reflux with water (15 ml), potassium hydroxide (1.5 g), and zinc dust (0.50 g) for 10 h. The mixture was filtered, the filtrate acidified with hydrochloric acid, and the long, white needles isolated in a yield of 0.075 g (79%), m.p. 193–194°. A mixture melting point with an authentic sample of 7-chlorometameconine (III<sub>a</sub>) (m.p. 194–195°) (5) showed no depression (194–195°). The reaction was not complete in a reaction time of 4 h.

#### 4-Hydroxy-7-nitrometameconine (II<sub>f</sub>)

4-Iodo-7-nitrometameconine (0.70 g, m.p. 160–161°) was dissolved in boiling 3% aqueous potassium hydroxide (35 ml, made in the proportion of 30 g potassium hydroxide (85% minimum) in 100 ml of water). Copper bronze (Kahlbaum's No. 02219, 0.34 g) was added and the mixture heated under reflux for 3 h with periodic stirring. The catalyst was removed by filtration. Then the filtrate was acidified with concentrated hydrochloric acid and cooled. Fluffy, yellow crystals, m.p. 167–197°, were recovered in a yield of 0.41 g. These were extracted with aqueous sodium bicarbonate, the insoluble material removed, and the filtrate acidified to give a white precipitate in a yield of 0.30 g (56%), m.p. 217–218° (with decomp.). Three recrystallizations from water gave the analytical sample of 4-hydroxy-7-nitrometameconine, m.p. 218.2–219° (p) (decomp.).

Found: C, 47.06, 47.02; H, 3.49, 3.70; N, 5.36, 5.26. Calcd. for  $C_{10}H_9O_7N$ : C, 47.06; H, 3.53; N, 5.49.

The bicarbonate-insoluble material (0.07 g) had m.p. 172–179°, raised to 178–180° after one recrystallization from glacial acetic acid; mixture melting point with authentic 7-nitrometameconine (3, 11)<sup>3</sup> (m.p. 181–182°) (II<sub>a</sub>), 178–181°. In several repetitions of the experiment, the crude 7-nitrometameconine showed the same low melting point, indicating a third reaction product (see next paper).

#### 4-Methoxy-7-nitrometameconine (II<sub>g</sub>)

Pure 4-hydroxy-7-nitrometameconine (m.p. 219–220°, 1.0 g) was treated in ethereal solution with an excess of diazomethane. Some solid (0.21 g, m.p. 115–116.3°) deposited; more (0.72 g) was recovered by evaporation of the solvent (total yield 89%). Four recrystallizations from aqueous methanol gave the *light-sensitive* analytical sample, m.p. 113.6–114.5° (p).

Found: C, 48.64, 48.38; H, 4.12, 4.22; N, 5.26, 5.37. Calcd. for  $C_{11}H_{11}O_7N$ : C, 49.07; H, 4.09; N, 5.26.

#### 7-Chloro-4-hydroxymetameconine (III<sub>f</sub>)

Pure 7-chloro-4-iodometameconine (0.20 g, double m.p. 148.5–153.5°) was heated under reflux with potassium hydroxide (1.2 g) and water (15 ml) for 12 h. The cooled solution was acidified and the precipitate was recovered and treated with sodium bicarbonate solution. After filtration from a small amount

of insoluble material, the solution was acidified to give the product in a yield of 0.097 g (70%), m.p. 179.3–180.8°. Combined with a similar product from another reaction and thrice recrystallized from water, the sample gave short, white, stubby crystals, m.p. 179.3–180.0° (p).

Found: C, 48.91, 48.96; H, 3.84, 3.77; Cl, 13.93, 14.00. Calcd. for  $C_{10}H_9O_3Cl$ : C, 49.18; H, 3.64; Cl, 14.34.

#### 7-Chloro-4-methoxymetameconine (IIIg)

Treatment of 7-chloro-4-hydroxymetameconine (1.0 g, m.p. 180–181°) with excess ethereal diazomethane gave glistening white plates, 0.55 g, m.p. 108–109.5° (p), and 0.44 g, m.p. 110.4–111.2° (p), a total yield of 93%. Two recrystallizations from absolute ether gave the analytical sample, m.p. 109.0–109.8° (p).

Found: C, 51.47, 51.53; H, 4.45, 4.62. Calcd. for  $C_{11}H_{11}O_3Cl$ : C, 51.16; H, 4.22.

#### 4-Acetamino-7-nitrometameconine (IIj)

Pure 4-amino-7-nitrometameconine (IIe) (1) (1.0 g, m.p. 233–234.5°) was dissolved in warm glacial acetic acid (20 ml). The solution was kept at 80–100° for 40 min with acetic anhydride (3 ml) and then diluted with water (7 ml). Long, fine, white needles were recovered in a yield of 0.94 g (85%), m.p. 187–189°. Three recrystallizations from water gave the analytical sample, m.p. 187.8–188.3° (p). The sample quickly turned purple on exposure to daylight, and poor analytical results were obtained on a sample sent away. Satisfactory results were found on a sample analyzed immediately after preparation.

Found: C, 48.71, 48.47; H, 4.36, 4.34. Calcd. for  $C_{12}H_{12}O_7N_2$ : C, 48.65; H, 4.18.

#### 4-Formamino-7-nitrometameconine (IIh)

The pure amino compound (IIe) (1.5 g, m.p. 230–231°) was heated under reflux with formic acid (90%, 25 ml) for 20 min, diluted with water (50 ml), and chilled. Fine, yellow needles were obtained in a yield of 1.42 g (86%), m.p. 188–188.5°. Three recrystallizations from water gave the analytical sample, m.p. 188.6–189.4° (p).

Found: C, 46.86, 47.01; H, 3.61, 3.67; N, 10.26, 10.03. Calcd. for  $C_{11}H_{10}O_7N_2$ : C, 46.83; H, 3.55; N, 9.93.

#### 7-Formaminometameconine (Id)

7-Aninometameconine (3, 11)<sup>3</sup> (0.84 g, m.p. 160.5–161.5°) was heated under reflux with formic acid (90%, 15 ml) for 20 min. The solution was diluted with water (40 ml) and chilled. White crystals were recovered in a yield of 0.78 g (82%), m.p. 211.9–213.4°. Three recrystallizations from water gave the analytical sample as long, white needles, m.p. 213.2–214.0° (p).

Found: C, 55.97, 56.05; H, 4.50, 4.66; N, 6.16, 6.27. Calcd. for  $C_{11}H_{11}O_5N$ : C, 55.46; H, 4.20; N, 5.88.

### Reductive Dehalogenations in the Presence of Nitro Groups

#### (a) With Copper and Benzoic Acid

The method is that of Smith and Companaro (13). Pure 4-bromo-7-nitrometameconine (0.20 g, m.p. 140–141°) (IIc) and benzoic acid (0.61 g) were heated together on an oil bath at 150–175°. Kahlbaum's copper bronze (No. 02219, 1.0 g) was added over a period of 5–10 min. The melt soon solidified. Heating was continued for a short time. The greenish mixture was then cooled, extracted with aqueous sodium carbonate (1.0 g in 5 ml), and filtered. The insoluble material was extracted with several small portions of boiling acetone. The product was recovered by evaporation of the acetone and recrystallized from glacial acetic acid with charcoal. Light-yellow crystals, m.p. 178–180°, were recovered (some from mother liquors) in a total yield of 0.06 g (40%), mixture melting point with authentic 7-nitrometameconine (3, 11)<sup>3</sup> (m.p. 181–182°), 178–181°.

#### (b) With Copper and Acetic Acid

Pure 4-iodo-7-nitrometameconine (0.114 g, m.p. 160–161°) (IIId) was heated under reflux for 12.5 h with glacial acetic acid (12 ml) and Kahlbaum's copper bronze (No. 02219, 0.15 g). The "catalyst" was then removed. The filtrate was concentrated to one-quarter of its original volume and diluted with water. The crude 7-nitrometameconine (IIa) so obtained had m.p. 175–178°, undepressed by admixture with authentic material. The yield was 0.05 g (68%). No reaction occurred in the absence of the copper bronze.

#### (c) With Copper and Acetate

The same iodo compound (0.25 g, m.p. 160–161°) (IIId) was heated under reflux for 6.5 h with glacial acetic acid (25 ml), potassium acetate (2.5 g), and Kahlbaum's copper bronze (0.25 g). The "catalyst" was removed. The markedly green filtrate was concentrated and then diluted with water to give a precipitate of crude 7-nitrometameconine in a yield of 0.086 g (53.5%). Its melting point of 177–179° was undepressed by admixture with authentic material.

#### (d) With Copper and Tetralin (12, 16)

The nitro-iodo compound (IIId) (0.25 g) was heated about 40 min with tetralin (2.5 ml) and copper bronze (0.25 g); attempts to isolate the product gave only an intractible, green gum.

#### (e) With Copper and Ascorbic Acid

Pure 4-iodo-7-nitrometameconine (0.200 g) (IIId), 4% aqueous potassium hydroxide (15 ml), ascorbic acid (0.100 g), and copper bronze (0.020 g) were heated together under reflux for 2 h. The reddish-orange solution was filtered from the catalyst (which was unchanged in appearance), and the product was isolated

in the usual way to give 7-nitrometameconine in a yield of 0.1025 g (78.6%), m.p. 179.5–182°, mixture melting point with authentic material (3, 11)<sup>3</sup> (m.p. 182–183°, 179–183.5°).

The method failed with the corresponding bromine compound (11c).

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