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The Oxidative Amination of Tropone and Tropolone

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The reaction of tropone with aniline, *p*-toluidine, *p*-anisidine, and *p*-chloroaniline in the presence of copper(II) acetate gave 2-arylaminotropones and 2-arylamino-*N*-aryltroponeimines. However, when *o*-toluidine and *o*-anisidine were used, only the corresponding 2-arylaminotropones were obtained. The reaction of tropolone with methylamine, ethylamine, and isopropylamine afforded 3-aminotropolone derivatives, while the reaction with dimethylamine, pyrrolidine, and morpholine gave 3- and 5-aminotropolone derivatives, the latter being minor products.

Aminotropones and aminotropolones have usually been obtained 1) by the nucleophilic substitution of 2-alkoxy, 2-halo, and 2-tosyloxytropones; 2) by the reduction of the appropriate nitro, nitroso, or arylazotropolones; 3) by the hydrolysis of 3-(arylsulfonylamido)tropolones; and 4) by the reaction of 3-iodotropolone with liquid ammonia to give 4-aminotropolone.¹⁾ Recently, however, a novel nuclear amination of 3-dialkylaminotropones and 3-alkoxytropones under mild conditions to give 7-aminated tropone derivatives was reported.²⁾ Also, previously one of the present authors reported that the reaction of tropone and 2-phenyltropone with ammonia, methylamine, and dimethylamine in the presence of copper(II) salt gave 2-aminotropone derivatives and/or salicylaldehyde derivatives.³⁾ As one of a series of systematic investigations of the oxidative amination of seven-membered aromatics, the reaction of tropone with aromatic primary amines, and the reaction of tropolone with several kinds of primary and secondary amines in the presence of copper(II) salt were investigated; these results will be reported in this paper.

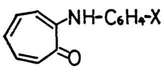
Results and Discussion

When tropone was treated in a closed vessel with a solution of copper(II) acetate and *p*-toluidine in methanol at room temperature for several days, 2-*p*-toluidinotropone (**1a**) and 1-(*p*-toluidino)-7-(*p*-tolylimino)-1,3,5-cycloheptatriene (**2a**)⁴⁾ were obtained in about 39 and 17% yields respectively. That the reaction must involve an oxidation step was suggested by the observations that the color of the solution gradually turned greenish brown from deep greenish blue, and that, in some instances, copper(I) oxide was separated on the wall of the reaction vessel. The yields of **1a** and **2a** *versus* the reaction times are listed in Table 1. The ratio of **1a** to **2a** remained almost constant after 5 days' reaction time. Moreover, the reaction of **1a** with *p*-toluidine in the presence or absence of copper(II) acetate was investigated, but in both cases **2a** was not obtained at all. Therefore, the possibility that **1a** was an intermediate for **2a** was eliminated. 7-*p*-Tolylimino-1,3,5-cycloheptatriene,⁵⁾ which formed at a slow and reversible step, is considered to be aminated to give **2a**, though the reaction of tropone and *p*-toluidine in the absence of copper(II) salt did not afford a detectable amount of the 7-*p*-tolylimino compound. A similar treatment of tropone with aniline, *p*-anisidine, and *p*-chloroaniline gave the corresponding 2-arylaminotropones (**1b**, **1c**, and **1d**) and, in addition, 1-arylamino-7-arylimino-1,3,5-cycloheptatrienes (**2b**, **2c**, and **2d**). However, the reaction of tropone with *o*-toluidine and *o*-anisidine afforded only the corresponding 2-arylaminotropone derivatives (**1e** and **1f**).

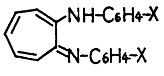
Table 1. The yields of **1a** and **2a** *versus* the reaction times[a)]

Reaction time (day)	Temp (°C)	Yields (%)[b)] **1a**		Yields (%)[b)] **2a**	
1.0	22—24	25.1	(21.4)	4.8	(3.8)
5.0	22—24	42.1	(36.8)	21.0	(16.1)
10.0	22—24	45.2	(39.1)	22.6	(16.6)
20.0	22—24	49.1	(41.1)	26.1	(18.2)

a) Tropolone (5 mmol), *p*-toluidine (20 mmol), copper(II) acetate (10 mmol), and methanol (10 ml) were used. b) The yields of **1a** and **2a** were estimated by the TLC separation of a known amount of the reaction product, followed by the measurement of the absorbance at 407 nm for **1a** and at 417 nm for **2a**. The isolated yields are indicated in parentheses.



1a : X=*p*-CH_3
1b: X=H
1c : X=*p*-CH_3O
1d: X=*p*-Cl
1e : X=*o*-CH_3
1f : X=*o*-CH_3O



2a : X=*p*-CH_3
2b: X=H
2c : X=*p*-CH_3O
2d: X=*p*-Cl

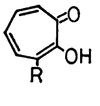
When tropolone and aqueous methylamine was allowed to react for a long period of time, 2-methylaminotropone (**3**) was obtained in a moderate yield. On the other hand, when tropolone was treated with methylamine in the presence of copper(II) sulfate in water, 3-methylaminotropolone (**4a**) and yellow prisms (**5**) were obtained besides **3**. The UV spectrum of **5** showed maxima at 229 (4.32), 277 (4.35), 360 (4.37), and 433 nm (log ε 3.88). In the IR spectrum, a carbonyl absorption appeared at 1595 cm^{-1}. A sharp *N*-methyl singlet (6H) appeared at 2.98 ppm besides the aromatic and NH protons in the NMR spectrum, indicating the symmetrical structure of **5**. The benzoylation of **5** gave monobenzoyl (**6**) and dibenzoyl compound (**7**). The alkaline hydrolysis of **6** gave 3-(*N*-benzoylmethylamino)tropolone (**8**), which was also obtained by the benzoyla-

Table 2. The yields of **3**, **4a**, and **5** *versus* the reaction temperature[a]

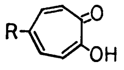
Reaction temp (°C)	Reaction time (day)	Yields (%) 3	4a	5	Recovery
8—10	30	0	6	23	34
18—20	10	0	3	21	18
30—32	10	11	15	21	8
50—52	2	13	25	5	8
70—72	1	27	25	0	0

a) Tropolone (20 mmol), copper(II) sulfate (40 mmol), and aqueous methylamine (30%, 25 ml) were allowed to react. The yields were based on the tropolone used.

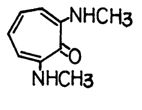
tion of **4a**, followed by the alkaline hydrolysis of the resulting product. These results indicate that **5** is 2,7-bis(methylamino)tropone. It is interesting here to note that raising the reaction temperature increases the yields of **3** and **4a**, and that at 70 °C **5** was not isolated at all (see Table 2). The further treatment of **3** or **4a** under similar conditions did not afford **5**; it is thought that **5** must be formed through a different reaction pathway. The reaction of tropolone with ethylamine and isopropylamine under similar conditions gave 3-ethylaminotropolone (**4b**) and 3-isopropylaminotropolone (**4c**) respectively.



4a : R=CH_3NH
4b: R=C_2H_5NH
4c : R=i-C_3H_7NH
4d: R=1-pyrrolidinyl
4e : R=morpholino
4f : R=$(CH_3)_2N$



9a : R=1-pyrrolidinyl
9b: R=morpholino
9c : R=$(CH_3)_2N$



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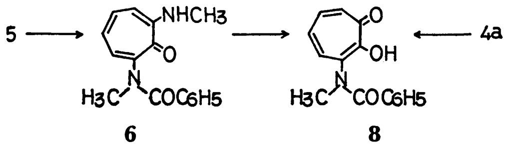
The reactions of tropolone and secondary amines have also been investigated. When tropolone was allowed to react with pyrrolidine in the presence of copper(II) sulfate, yellow prisms (**4d**) ($C_{11}H_{13}O_2N$, mp 98—99 °C) and yellow plates (**9a**) ($C_{11}H_{13}O_2N$, mp 236—238 °C (decomp.)) were obtained; the latter was a minor product. The elemental analysis and UV spectrum of **4d** showed it to be 3-(1-pyrrolidinyl)tropolone. The compound (**9a**) was also confirmed to have a tropolone nucleus from its UV spectrum and its characteristic iron(III) chloride test. The compound (**9a**) was also obtained when 5-bromotropolone was allowed to react with pyrrolidine in the presence of copper(II) acetate, though the yield was poor. Therefore, **9a** must be 5-(1-pyrrolidinyl)tropolone. Similar treatment of tropolone with morpholine and dimethylamine gave 3-(and 5-)-morpholinotropolones (**4e** and **9b**) and 3-(and 5-)-dimethylaminotropolones (**4f** and **9c**) respectively. The reaction of 5-chlorotropolone wtih pyrrolidine in the presence of copper(II) acetate gave 5-chloro-3-(1-pyrrolidinyl)tropolone (**10**), while the reaction of 3-bromotropolone with methylamine under similar conditions afforded 3-methylaminotropolone (**4a**).



6　**8**

Experimental

The Reaction of Tropone with Aniline, p-Toluidine, p-Anisidine, p-Chloroaniline, o-Toluidine, and o-Anisidine in the Presence of Copper(II) Acetate. Into a suspension of copper(II) acetate (2.00 g) in methanol (10 ml), *p*-toluidine (2.14 g) and tropone (0.530 g) were added successively with stirring. After several minutes, voluminous precipitates were separated. The mixture was allowed to stand for 10 days at 22—24 °C in an atmosphere of nitrogen. The reaction mixture was diluted with water, neutralized with dilute hydrochloric acid, and extracted thoroughly with chloroform. Hydrogen sulfide was passed through the chloroform solution, the copper(II) sulfide was filtered off, the filtrate was washed with water, and the solution was diluted with chloroform to 100 ml. A one-thousandth portion of this solution was separated on thin-layer chromatography using Merck Silica Gel PF_{254}. The fractions corresponding to 2-*p*-toluidinotropone (**1a**) and 1-(*p*-toluidino)-7-(*p*-tolylimino)-1,3,5-cycloheptatriene (**2a**) were eluted with methanol (10.0 ml), and the yields of **1a** and **2a** were estimated spectrophotometrically using the absorbances at 407 nm (for **1a**) and at 417 nm (for **2a**).

For the isolation of **1a** and **2a**, the solvent was removed under reduced pressure, and the residue was dissolved in a mixture of benzene and cyclohexane (1: 1) and chromatographed on a column containing 10 g of silica gel. The fraction eluted with the same solvent mixture gave orange crystals, which were subsequently recrystallized from the same solvent mixture to give 250 mg (17%) of **2a** as orange prisms; mp 139—140 °C (lit,[4] mp 143—144 °C). The fractions eluted with benzene and chloroform gave yellow crystals. Recrystallization from cyclohexane gave 415 mg (39%) of **1a**, mp 108—109 °C (lit,[6] mp 108.5—109.5 °C).

The reaction of tropone with aniline, *p*-anisidine, *p*-chloroaniline, *o*-toluidine, and *o*-anisidine was carried out in a similar manner to give the following 2-arylaminotropones and 2-arylamino-*N*-aryltroponeimines:

2-Anilinotropone (**1b**), oil, picrate; mp 141—142 °C (lit,[6] oil, picrate, mp 141—142 °C).

1-Anilino-7-phenylimino-1,3,5-cycloheptatriene (**2b**); mp 84—86 °C (lit,[4] mp 86—88 °C); yield, 22%.

2-*p*-Anisidinotropone (**1c**); mp 90—91 °C (lit,[7] mp 91—92 °C); yield, 22%.

1-(*p*-Anisidino)-7-(*p*-anisylimino)-1,3,5-cycloheptatriene (**2c**); mp 110.5—111.5 °C (lit,[4] mp 112.5—113.5 °C); yield, 31%.

2-*p*-Chloroanilinotropone (**1d**); mp 143—144 °C (lit,[4] 147 °C); yield, 37%.

1-(*p*-Chloroanilino)-7-(*p*-chlorophenylimino)-1,3,5-cycloheptatriene (**2d**); mp 165—166 °C (lit,[4] mp 168—170 °C); yield, 14%.

2-*o*-Toluidinotropone (**1e**). Recrystallization from cyclohexane gave yellow prisms; mp 52—53 °C; yield, 14%. UV (methanol) max: 238 (log ε 4.36), 341 (4.09), and 404 nm (4.19). Found: C, 79.61; H, 6.16; N, 6.45%. Calcd for $C_{14}H_{13}ON$: C, 79.59; H, 6.20; N, 6.63%.

2-*o*-Anisidinotropone (**1f**). Recrystallization from a mixture of benzene and cyclohexane gave yellow prisms; mp 111—113 °C; yield, 44%. UV (methanol) max: 234 (log ε 4.33), 345 (4.04), and 406 nm (4.21). Found: C, 74.19; H, 5.80; N 6.02%. Calcd for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77; N, 6.16%.

The Reaction of Tropolone with Methylamine Tropolone (1.22 g) was dissolved in aqueous methylamine (40%, 10 ml), and the mixture was allowed to react at room temperature for 15 days. The reaction mixture was diluted with water, neutralized with dilute hydrochloric acid, and extracted with chloroform. The chloroform solution was extracted with a sodium hydroxide solution and dilute hydrochloric acid successively. The alkaline solution gave 475 mg of tropolone (mp 48—50 °C), while the acidic solution afforded 683 mg (51%) of 2-methylaminotropone (**3**) (mp 80—82 °C). A similar reaction of tropolone with aqueous pyrrolodine, however, did not afford 2-(1-pyrrolidinyl)tropone.

The Reaction of Tropolone with Primary Amines in the Presence of Copper(II) Salt. The example to be cited is the reaction of tropolone with methylamine. A deep blue solution obtained by dissolving tropolone (2.44 g) and copper(II) sulfate (10.0 g) in aqueous methylamine (30%, 25 ml) was heated at 50—52 °C for 48 h, during which time the color of the solution turned greenish brown and brown crystals began to separate. Water (75 ml) was then added to the reaction mixture, and the precipitate was collected by filtration.

The precipitate was dried and dissolved in chloroform, and hydrogen sulfide was passed through the solution. The copper(II) sulfide was filtered off, and the filtrate was washed successively with an excess of a dilute sodium hydroxide solution and dilute hydrochloric acid. The alkaline solution was acidified with acetic acid, and the yellow crystals (**A**, 850 mg, mp 100—110 °C) that separated were collected by filtration. The filtrate was extracted with chloroform, the chloroform solution was washed with water and dried, and the solvent was evaporated to give a red oil (**B**, 164 mg).

The acid solution was neutralized with sodium hydrogencarbonate, and the yellow crystals that separated were collected, washed, and dried. These crystals were dissolved in a mixture of benzene and chloroform (1:1) and chromatographed on an alumina column to obtain yellow crystals (**C**, 154 mg, mp 117—127 °C). The aqueous solution was extracted with chloroform, the chloroform solution was washed with water and dried, and the solvent was removed to give brown crystals (505 mg). These crystals were dissolved in a mixture of benzene and cyclohexane and treated with a copper(II) acetate solution. The copper(II) complex that was thus obtained was again treated with hydrogen sulfide to regenerate copper-free yellow crystals (**D**, 400 mg, mp 74—80 °C). The portion which did not afford copper(II) salt gave further crops of yellow crystals (**C**, 40 mg; mp 115—124 °C).

The aqueous solution, obtained at first by the dilution of the reaction mixture and the filtration of the precipitate, was acidified with dilute hydrochloric acid and extracted with chloroform, while the chloroform solution was similarly treated to give yellow crystals (**A**, 10 mg), a red oil (**B**, 380 mg), and a small amount of yellow crystals (a mixture of **C** and **D**).

The recrystallization of **A** from ethanol gave 3-methylaminotropolone (**4a**) as yellow plates; mp 113.5—115 °C (lit,[8] mp 113—114 °C; yield, 765 mg (25.3%). (Found: C, 63.67; H, 6.04; N, 8.94%).

The recrystallization of **C** from ethanol gave 2,7-bis(methylamino)tropone (**5**) as yellow needles; mp 128—130 °C; yield, 4.8%. Found: C, 65.67; H, 7.50; N, 16.92%. Calcd for $C_9H_{12}ON_2$: C, 65.83; H, 7.37; N, 17.06%.

The recrystallization of **D** from a mixture of benzene and cyclohexane gave 2-methylaminotropone (**3**); mp 81—82 °C; yield, 13%.

The red oil (**B**) was dissolved in chloroform and washed with dilute hydrochloric acid to remove the basic compounds. The chloroform solution was washed with water and dried, and the solvent was removed. The recrystallization of the crystalline residue from cyclohexane gave 205 mg of tropolone as pale yellow crystals.

The reaction of tropolone with ethylamine and isopropylamine was carried out in a similar manner.

3-Ethylaminotropolone (**4b**); yellow plates (from ethanol); mp 57—58 °C (lit,[8] mp 51—53 °C); yield, 20%. (Found: C, 65.75; H, 6.82; N, 8.42%).

3-Isopropylaminotropolone (**4c**); yellow prisms (from dilute methanol); mp 72—73.5 °C (lit,[8] 72—73 °C); yield, 23%. (Found: C, 66.48; H, 7.28; N, 7.75%).

Benzoylation of 2,7-Bis(methylamino)tropone (5). Into a solution of **5** (600 mg) in pyridine (5 ml), benzoyl chloride (2.5 ml) was added under ice cooling and with stirring. After 1 h, the reaction mixture was poured into water, acidified with hydrochloric acid, and extracted with chloroform. The solution was washed with water, the solvent was removed, and the crystalline residue was washed with benzene. The crystals were recrystallized from 1-butanol to give 2,7-bis(*N*-benzoylmethylamino)tropone (**7**) as yellow prisms; mp 230—232 °C. UV (methanol) max: 282 (log ε 4.00), and 355 nm (3.81). Found: C, 73.70; H, 5.51; N, 7.31%. Calcd for $C_{23}H_{20}O_3N_2$: C, 74.17; H, 5.41; N, 7.52%.

The benzene solution was chromatographed on a silica gel column, and the fraction eluted with chloroform was recrystallized from benzene to give 2-(*N*-benzoylmethylamino)-7-methylaminotropone (**6**) as yellow prisms; mp 183—184 °C; yield, 202 mg. UV (methanol) max: 253 (log ε 4.25) 345 (4.04), and 420 nm (4.20). Found: C, 71.40; H, 6.10; N, 10.34%. Calcd for $C_{16}H_{16}O_2N_2$: C, 71.62; H, 6.01; N, 10.44%.

Alkaline Hydrolysis of 6. A solution of **6** (150 mg) in ethanol (3 ml) was refluxed with 10% aqueous sodium hydroxide (0.6 ml) for 4 h. The reaction mixture was then diluted with water, acidified with acetic acid, and extracted with chloroform. The evaporation of the solvent gave a crystalline residue, which was recrystallized from a mixture of benzene and cyclohexane to give 65 mg of 3-(*N*-benzoylmethylamino)-tropolone (**8**) as pale yellow prisms; mp 115—116 °C. UV (methanol) max: 331 (log ε 3.79) and 368 nm (3.78). Found: C, 70.52; H, 5.12; N, 5.32%. Calcd for $C_{15}H_{13}O_3N$: C, 70.58; H, 5.13; N, 5.49%.

3-(N-Benzoylmethylamino)tropolone (8) from 4a. Into a solution of **4a** (100 mg) in pyridine (1 ml), benzoyl chloride (0.6 ml) was added under ice cooling and with stirring. After 1 h, the mixture was poured into water, and a viscous oily product was separated from the water. This oil was, without further purification, dissolved in ethanol (5 ml) and refluxed with an excess of an aqueous sodium hydroxide solution for 2 h. The mixture was then diluted with water, acidified with acetic acid, and extracted with chloroform. The solvent was removed, and the residue was chromatographed on a silica gel column. The fraction eluted with chloroform gave **8** (58 mg); mp 114—116 °C, which was identical with that obtained from **5**.

The Reaction of Tropolone with Secondary Amines in the Presence of Copper(II) Salt. The example cited will be for the reaction of tropolone with pyrrolidine. A deep blue solution obtained by dissolving copper(II) sulfate (5.00 g), ammonium chloride (3.00 g), and tropolone (1.22 g) in a mixture of pyrrolidine (12 ml), and water (12 ml) was heated at 50—55 °C for 5 days. Water (150 ml) was added to the reaction mixture, neutralized with hydrochloric acid, and the precipitate was collected by filtration. The filtrate was extracted with chloroform, the precipitate and chloroform extract were combined, and hydrogen sulfide was passed through the solution. The copper(II) sulfide was removed, and the filtrate was washed with a dilute sodium hydroxide solution. The aqueous layer was acidified with acetic acid, and the precipitate (**A**) was filtered and washed with water. The filtrate was extracted with chloroform, and the chloroform solution was washed with water and dried. The subsequent evaporation of the solvent and distillation of the residue under reduced pressure afforded 496 mg of tropolone; mp 48—51 °C.

The crystals (**A**, 763 mg) were distilled under reduced pressure (2 Torr). The **B** fraction (distilled at a bath temperature of 120—130 °C) was recrystallized from methanol to give 552 mg (29%) of 3-(1-pyrrolidinyl)tropolone (**4d**), while the **C** fraction (sublimed under a free flame) was recrystallized from methanol, followed by dimethylformamide, to give 95 mg (5%) of 5-(1-pyrrolidinyl)tropolone (**9a**).

3-(1-Pyrrolidinyl)tropolone (**4d**); yellow prisms (from methanol); mp 98—99 °C. UV (methanol) max: 269 (log ε 4.34), 361 (4.19), and 422 nm (3.79). Found: C, 69.26; H, 7.18; N, 7.48%. Calcd for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.33%.

5-(1-Pyrrolidinyl)tropolone (**9a**); yellow plates (from dimethylformamide); mp 236—238 °C (dec). UV (methanol) max: 240 (log ε 4.32), 286 (3.51), 374 (4.29), and 394 nm (sh, 4.23). Found: C, 69.30; H, 7.09; N, 7.40%. Calcd for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.33%.

The reaction of tropolone with morpholine and dimethylamine was carried out in a manner similar to that described above, and the following 3- and 5-aminotropolone derivatives were obtained.

3-Morpholinotropolone (**4e**); yellow plates (from cyclohexane); mp 84—86 °C; yield, 21%. UV (methanol) max: 226 (log ε 4.24), 273 (4.19), and 355 nm (4.03). Found: C, 64.17; H, 6.42; N, 6.99%. Calcd for $C_{11}H_{13}O_3N$: C, 63.75; H, 6.32; N, 6.76%.

5-Morpholinotropolone (**9b**); yellow prisms (from dioxane); mp 201—202 °C; yield, 2%. UV (methanol) max: 236 (log ε 4.32), 283 (3.54), and 363 nm (4.12). Found: C, 63.39; H, 6.39; N, 6.95%. Calcd for $C_{11}H_{13}O_3N$: C, 63.75; H, 6.32; N, 6.76%.

3-Dimethylaminotropolone (**4f**); yellow prisms (from cyclohexane); mp 54.5—56 °C; yield, 24%. UV (methanol) max: 226 (log ε 4.14), 271 (4.26), and 360 nm (4.04). Found: C, 65.62; H, 6.95; N, 8.44%. Calcd for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48%.

5-Dimethylaminotropolone (**9c**); yellow needles (from ethanol); mp 163—164.5 °C (lit,[9] 160—162 °C); yield, 2%. (Found: C, 65.36; H, 6.73; N, 8.66%).

The Reaction of 5-Chlorotropolone and 5-Bromotropolone with Pyrrolidine in the Presence of Copper(II) Salt. 5-Chlorotropolone (0.64 g) was added to a solution obtained by dissolving copper(II) acetate (1.60 g) in pyrrolidine (4 ml) and ethanol (10 ml), and the mixture was heated at 55—60 °C for 24h. The mixture was then diluted with water, and the precipitate was collected by filtration. The filtrate was neutralized with dilute hydrochloric acid and extracted with chloroform. The precipitate and the chloroform extract were then combined, and hydrogen sulfide was passed through the solution. Copper(II) sulfide was filtered off, and the filtrate was treated with a dilute sodium hydroxide solution. The separated sodium salt and the aqueous solution were combined, acidified with acetic acid, and extracted with chloroform, and the chloroform solution was again treated with 6M-hydrochloric acid. The acid-insoluble portion gave 232 mg of 5-chlorotropolone. The acid-soluble portion was neutralized with sodium hydrogencarbonate to give 215 mg of yellow crystals. These crystals were recrystallized from ethanol to give 5-chloro-3-(1-pyrrolidinyl)tropolone (**10**) as yellow crystals; mp 90—92 °C; yield, 190 mg (21%). UV (methanol) max: 277 (log ε 4.38), 368 (4.19), and 430 nm (3.82). Found: C, 58.68; H, 5.53; N, 6.19%. Calcd for $C_{11}H_{12}O_2NCl$: C, 58.54; H, 5.37; N, 6.21%.

A solution of copper(II) acetate (1.60 g), pyrrolidine (6 ml), methanol (6 ml), and 5-bromotropolone (0.80 g) was heated at 55—60 °C for 24 h, after which the reaction mixture was treated much as above. The portion soluble in both the sodium hydroxide solution and 6M-hydrochloric acid gave 30 mg of 5-(1-pyrrolidinyl)tropolone (**9a**) as yellow crystals (mp 235—237 °C (dec)) identical with the sample obtained by the reaction of tropolone and pyrrolidine described above.

The Reaction of 3-Bromotropolone with Methylamine in the Presence of Copper(II) Salt. To a deep blue solution obtained by dissolving copper(II) acetate (2.00 g) in methanol (10 ml) and methylamine (30%, 5 ml), 3-bromotropolone (1.00 g) was added, after which the mixture was heated at 60—65 °C for 20 h. The precipitate was then removed, and the filtrate was concentrated under reduced pressure. The residue was diluted with water, and hydrochloric acid was added to the solution to adjust the pH at about 3. The precipitate that formed was filtered and washed with water, while the filtrate was extracted with chloroform. The precipitate and chloroform extract were then combined, hydrogen sulfide was passed through, and the copper(II) sulfide was filtered off. The filtrate was washed with 4M-hydrochloric acid, and the acid-soluble portion was neutralized with sodium hydrogencarbonate. The crystals that separated out were recrystallized from ethanol to give yellow scales (mp 111—113 °C; 85 mg) which were identical with 3-methylaminotropolone (**4a**).

References

1) a) T. Nozoe, K. Takase, and H. Matsumura, "Dai-Yuki Kagaku," Vol. 13, Asakura Publishing Co., Tokyo (1960), Chaps., 7, 8, and 11; b) F. Pietra, *Chem. Rev.*, **73**, 293 (1973).

2) B. Ricciarelli, R. Cabrino, F. D. Cima, C. A. Veracini, and F. Pietra, *J. Chem. Soc., Chem. Commun.*, **1974**, 723.

3) K. Kikuchi, *Bull. Chem. Soc. Jpn.*, **40**, 385 (1967).

4) W. R. Brasen, H. E. Holmquist, and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961).

5) a) Y. Kitahara, T. Asao, and M. Funamizu, Japanese Patent 17824 and 17825 (1964); b) K. Sanechika, S. Kajigaeshi, and S. Kanemasa, *Synthesis*, **1977**, 202.

6) T. Nozoe, Y. Kitahara, T. Ando, S. Masamune, and H. Abe, *Sci. Repts. Tohoku Univ. Ser. I.* **36**, 166 (1952).

7) a) T. Mukai and M. Kimura, *Tetrahedron Lett.*, **1970**, 717; b) M. Kimura, Ph. D. Thesis, Tohoku University, Sendai, Japan, 1969.

8) K. Takase, M. Yasunami, and H. Okino, unpublished results.

9) K. Takase, M. Yasunami, and T. Yamatani, unpublished results.