

sulfoxide, 7605-18-7; 2,4-dinitrophenylhydrazone of 5, 7605-19-8; 2,4-dinitrophenylhydrazone of corresponding sulfone, 7649-30-1; IV (X = CO, Z = SO₂), 3166-15-2; IV (X = CO, Z = S), 492-22-8; IV (Z = SO, X = S), 2362-50-7; IV (Z = SO, X = O), 948-44-7; IV

(Z = SO, X = CHOH), 7605-20-1; IV (Z = SO, X = SO-*cis*), 2748-51-8; IV (Z = SO, X = SO-*trans*), 2748-50-7.

Acknowledgment.—We wish to acknowledge the technical assistance of Miss Marilyn Pérez-Arzola.

The Reaction of Active Methylene Compounds with Carbon Disulfide in the Presence of Ammonia. I. The Reaction of Cyclohexanone

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Received August 3, 1966

Cyclohexanone, in the presence of ammonia, easily reacted with carbon disulfide to give a characteristic sulfur compound containing nitrogen. Cyclohexylideneammonium 2-cyclohexylideneamino-1-cyclohexene-1-dithiocarboxylate (I) was proposed for this compound. Compound I was easily converted into its isomer, for which 1'-amino-1'-cyclohexyl 2-cyclohexylideneamino-1-cyclohexene-1-dithiocarboxylate (II) was proposed. Both I and II easily gave a derivative of thiazine which was assigned 4-thiono-1,2,5,6,7,8-pentahydro-3,1,2-benzothiazine-2-spirocyclohexane (III). Compound I was remarkably sensitive to cupric and a few other metal ions. In relation to the present reaction, several new compounds are described. It is suggested that two of these compounds, 2,4-dithiono-1,2,5,6,7,8-pentahydro-3,1,2-benzothiazine (IV) and 9-thiono-10-azanonahydroanthracene (V), may have *meso*-ion structure.

The present investigation was directed to exploring the reaction of active methylene compounds with carbon disulfide in the presence of ammonia. Here, cyclohexanone was chosen as one of the model active methylene compounds.

Cyclohexanone readily reacted with the above reagents to give a characteristic and rather unstable compound, C₁₉H₃₀N₂S₂ (I), which formed yellow needles and melted at 115–116° (slow heating) and 135–136° (rapid heating) and was very sensitive to cupric ion. Compound I, when treated with acidic reagents, was readily converted into long orange plates, C₁₃H₁₉N₂S₂ (III), mp 197–198°, and cyclohexanone (Scheme I). The same compound, on treatment with methanol or such as dimethylformamide for a short time was converted into an isomeric compound, short orange prisms, C₁₉H₃₀N₂S₂ (II), mp 143–144° dec (slow heating) and 162° dec (rapid heating). In these transformations I was sensitive to trivial conditions and other complex compounds have been obtained from the former; these problems will be reported in a separate paper. When I was heated with morpholine, elimination of dithiocarboxyl group occurred to give a dithiocarbamate.³

Compound II, on treatment with acid, also changed into III and cyclohexanone.

Generally, III was most easily obtained in these transformations. When the crude product mentioned above was treated with acetic acid, III was obtained in almost quantitative yield. The compound was rather stable and easily soluble in hydrochloric acid or alcoholic alkali; the greater part could be regenerated from the solution by neutralization.

In order to determine the structure of these compounds, III was subjected to oxidation and desulfuration. Oxidation with permanganate gave cyclohexanone and cyclohexanedione. Desulfuration afforded

2-methylcyclohexanone and N-cyclohexyl-2-methylcyclohexylamine (VII). Picryl and benzoyl derivatives of III, and methyl, ethyl, and benzylidene derivatives of II were also prepared.

The presence of a thiocarbonyl group in I, II, and III was inferred from their ultraviolet absorption spectra. The presence of an amino group in II and an imino group in III was considered from their infrared absorption spectra. It seemed that I had neither amino nor imino group and broad bands which may be assigned to ⁺NH₂= or —⁺NH= group were observed.

When II was alkylated (the methyl derivative, IIa, and the ethyl derivative, IIb), one of the two NH₂ stretching bands disappeared; the benzylidene deriva-

TABLE I
APPEARANCE AND MELTING POINTS
OF THE COMPOUNDS INVESTIGATED

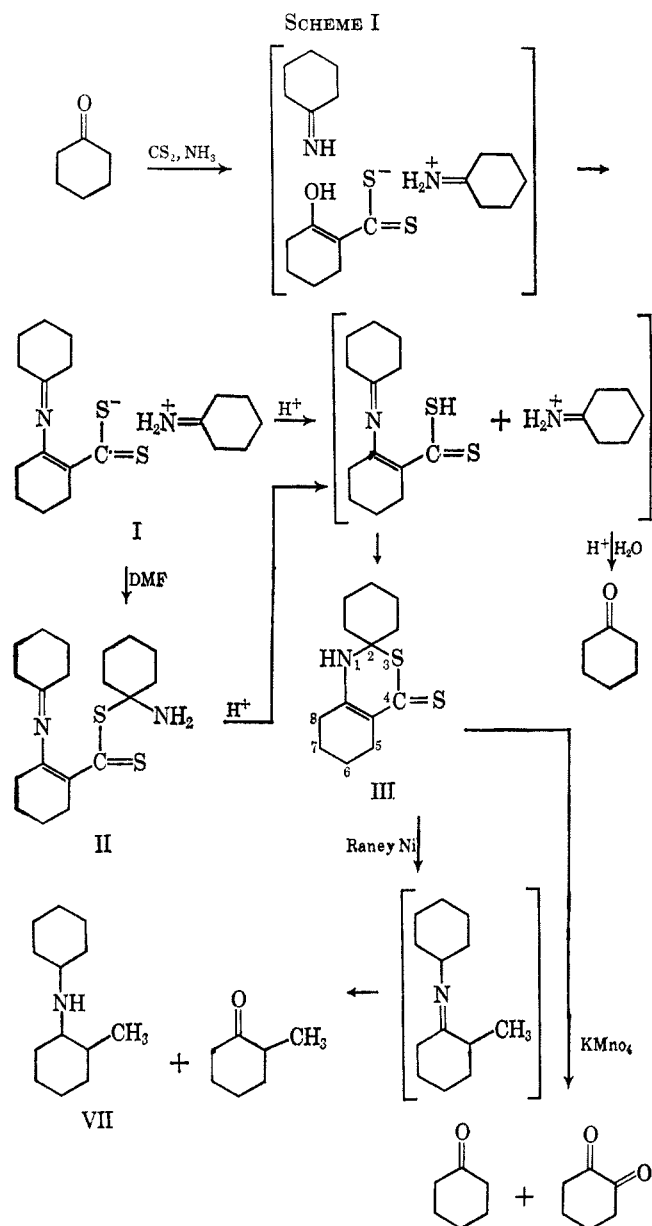
Compd ^a	Appearance	Mp, °C (cor)
I	Yellow needles	115–116 (slow heating) 135–136 (rapid heating)
II	Short orange prisms	143–144 dec (slow heating) 162 dec (rapid heating)
IIa	Yellow needles	204–205
IIb	Yellow needles	201–202
IIc	Orange-red plates	183–184
III	Long orange plates	197–198
IIIa	Yellow crystals	136–138
IIIb	Yellow needles or plates	165–166 dec
IIIc	Orange thick plates	194–195
IV	Lustrous red plates	202–203 dec
V	Light flesh colored crystals	ca. 250 dec
VI	Light pink needles	275–276
Hydrochloride of VII	Colorless thick plates	265–266 (in sealed tube)

^a IIa, methyl derivative of II; IIb, ethyl derivative of II; IIc, benzylidene derivative of II; IIIa, benzoyl derivative of III (hydrochloride); IIIb, picryl derivative of III (hydrochloride); IIIc, the compound prepared from 4-methylcyclohexanone (corresponds to III).

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(3) Colorless needles, mp 233–234° (in sealed tube), possibly O(CH₂CH₂)₂-NCSS · H₂N⁺(CH₂CH₂)₂O. Details may be reported in a separate paper.



tive lacked both bands, and instead showed a C=N band (Table I).

On the basis of the above arguments, the scheme of reaction and the structure I (cyclohexylideneammonium 2-cyclohexylideneamino-1-cyclohexene-1-dithiocarboxylate), II (1'-amino-1'-cyclohexyl 2-cyclohexylideneamino-1-cyclohexene-1-dithiocarboxylate), and III (4-thiono-1,2,5,6,7,8-pentahydro-3,1,2-benzothiazine-2-spirocyclohexane) were proposed. Compounds I, II, or III could not be obtained in the reaction of 2-cyclohexylidene-cyclohexanone with carbon disulfide and ammonia. This fact may also support the structure III in which the two carbon rings are not directly combined. The present reaction also was conducted with respect to 2-, 3-, and 4-methylcyclohexanone. 2- and 3-methylcyclohexanone were sluggish to react; this may be due to the steric effect of the methyl group. The behavior of 4-methylcyclohexanone was similar to that of cyclohexanone; the product, on recrystallization from methanolic acetic acid, yielded thick orange plates, $C_{15}H_{23}NS_2$ (IIIc), mp 194–195°; the infrared absorption spectrum was almost identical with that of compound III.

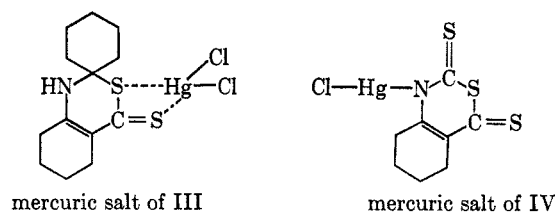
Further, the reaction of cyclohexanone with carbon disulfide was carried out using sodium amide in place of ammonia. In this case three different compounds were produced, though in poor yield, in addition to I, II, or III. The compounds were lustrous red plates, $C_8H_9NS_3$ (IV), mp 202–203° dec; orange needles, $C_{40}H_{56}N_4S_5$, mp 185–186°; and light pink needles, $C_{13}H_{20}N_2S$ (VI), mp 275–276°. The last compound seemed to be 1-[2-(1-cyclohexen-1-yl)-1-cyclohexen-1-yl]-2-thiourea.⁴

Compound IV was tentatively assigned the structure of 2,4-dithiono-1,2,5,6,7,8-pentahydro-3,1,2-benzothiazine on the basis of infrared and ultraviolet absorption spectra (Tables II and III).

Compounds I–IV all afforded the respective mercuric or other metallic salts (consult Experimental Section).

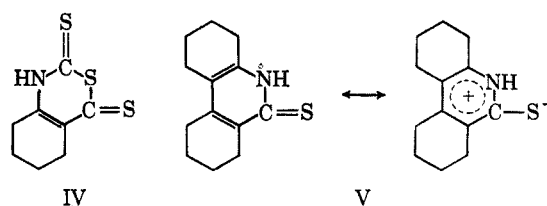
These metal salt reactions may be reasonably explained by the structures proposed. Of the complex salts, those which were produced by the reaction with mercuric chloride were obtained in apparently pure state; the mercuric salts of III and IV gave the most distinct analytical figure ($C_{13}H_{19}NS_2HgCl_2$ and $C_8H_8NS_3HgCl$). These mercuric salts were indifferent toward silver nitrate; it seemed that they have no ionized chlorine.

The salt formation, except that of IV, may be due to the coordination of the two sulfur atoms with the metal atom. As to IV, the infrared spectrum of its mercuric salt lacked NH bands which were present in the case of the parent compound. Viewed from the acidic nature of IV, together with the spectral result, the salt probably results from the replacement of the imino hydrogen with the metal atom. The following structures were tentatively assigned to the two salts which were produced by the reaction of mercuric chloride with III and IV respectively.



The sensitiveness of I toward cupric ion may be explained by its structure which is analogous to sodium diethyldithiocarbamate, a valuable analytical reagent; I is a vinylol of a dithiocarbamate.

When 2-cyclohexylidene-cyclohexanone was treated with carbon disulfide in the presence of sodium amide, a small amount of light flesh colored crystals, $C_{13}H_{17}NS$ (V), mp ca. 250° dec, was produced; from spectral data



(4) The melting point was identical with the literature value of 1-[2-(1-cyclohexen-1-yl)-1-cyclohexen-1-yl]-2-thiourea, mp 274–276°, and the infrared and ultraviolet spectra measured also were almost identical with those reported: C. Podesva, E. J. Tarlton, and A. F. McKay, *Can. J. Chem.*, 1403 (1962).

TABLE II

INFRARED DATA OF THE COMPOUNDS INVESTIGATED

Compd ^a	Frequency, cm ⁻¹		Tentative assignment
	KBr	CHCl ₃	
I	~2660 (w, br)	~2720 (w, br)	=NH ₂ ⁺ stretching
	1593 (s)	1590 (sh)	Conj C=N stretching
	1575 (vs)	1576 (vs)	Conj C=C stretching
II	1488 (s)	1485 (m)	Ring stretching
	1450 (m)	1450 (m)	
	3332 (s)	3381 (m)	
IIa	3255 (m)	3305 (w)	NH ₂ stretching
	1590 (s)	1575 (sh)	{ Conj C=N stretching, NH ₂ deformation, Conj C=C stretching
	1553 (vs)	1545 (s)	
1492 (vs)	1495 (vs)		
IIb	1452 (s)	1454 (s)	Ring stretching
	3270 (m)		NH stretching
	1590 (vs)		{ Conj C=N stretching, Conj C=C stretching
IIc	1481 (s)		Ring stretching
	3275 (m)		NH stretching
	1586 (vs)		{ Conj C=N stretching, Conj C=C stretching
III	1480 (s)		Ring stretching
	1636 (s)		C=N stretching
	1600 (w)		{ Benzene C=C stretching, Conj C=N stretching, Conj C=C stretching
IIIa	1580 (w)		{ Benzene C=C stretching, Ring stretching
	1536 (s)		NH stretching
	1500 (vs)		
1449 (s)			
IIIb	3190 (s)	3387 (s)	Conj C=C stretching
	1536 (s)	1539 (vs)	(probable)
	1517 (vs)	1517 (s)	Ring stretching
IIIc	1449 (m)	1453 (m)	NH ⁺ stretching
	2280 (m)		
	1893 (m)		
IV	1839 (m)		C=O stretching (benzoyl)
	1692 (vs)		Conj C=C stretching
	1626 (s)		Benzene C=C stretching
V	1590 (w)		{ Benzene C=C stretching, Ring stretching
	1581 (m)		NH ⁺ stretching
	1494 (s)		
1448 (s)			
VI	~2310 (m, br)		{ Conj C=C stretching, Benzene C=C stretching
	~1800 (w, br)		
	1600 (s)		
VII	3200 (s)		NH stretching
	1537 (sh)		{ Conj C=C stretching, Ring stretching
	1519 (vs)		{ Ring stretching, Ring stretching, Asym CH ₂ deformation
VIII	1455 (m)		NH stretching
	3112 (s)	3310 (m)	{ Conj C=C stretching, Ring stretching
	1591 (vs)	1598 (s)	NH stretching
IX	1505 (vs)	1485 (vs)	Conj C=C stretching
	3163 (w)		Ring stretching
	1610 (m)		Conj C=C stretching
X	1585 (vs)		Ring stretching
	1435 (m)		{ NH ₂ stretching, NH stretching
	3322 (m)		C=C stretching ^b
XI	3182 (s)		{ NH ₂ deformation, S=C-N- group vibration
	1687 (m)		Ring stretching
	1672 (m)		NH ₂ ⁺ stretching
1547 (vs)			
1457 (m)			
XII	~2710 (w, br)		NH ₂ ⁺ stretching
	2650 (w)		
	2515 (m)		
XIII	2435 (m)		NH ₂ ⁺ stretching
	2160 (w)		
	2045 (w)		
XIV	1933 (w)		NH ₂ ⁺ stretching

^a See footnote *a* in Table I. ^b It is well known that the conjugated C=C stretching mode appears near 1600 cm⁻¹, but this compound gave absorptions more closely corresponding to the nonconjugated double-bond frequency; in the literature cited in ref 2, the two double bonds are claimed to be conjugated.

structure V (9-thiono-10-azonanhydroanthracene) was tentatively proposed. It may be suggested that IV and V have a possibility of being *meso* ions.

TABLE III

ULTRAVIOLET DATA OF THE COMPOUNDS INVESTIGATED

Compd ^a	λ _{max} ^{ethanol} , mμ	λ _{max} ^{cyclohexano} , mμ
	(log ε)	(log ε)
I	307 (3.82)	313
	403 (4.32)	406
II	340 (3.74)	343
	419 (4.36)	409
IIa	315 (3.88)	
IIb	399 (4.30)	324 (4.00)
	319 (3.93)	402 (4.43)
IIc	401 (4.40)	402 (4.43)
	253 (4.23)	252 (4.26)
III	343 (3.60)	343 (3.59)
	421 (4.36)	415 (4.38)
IIIc	340 (3.74)	348
	411 (4.32)	394
IV	340 (3.70)	
	411 (4.30)	
V	302 (4.28)	303
	416 (3.95)	400
VI	279 (3.93)	239
	362 (3.88)	296
VI	272 (3.94)	

^a See footnote *a* in Table I.

Experimental Section

Preparation of I, II, and III in the Presence of Ammonia. Isolation of III.—A mixture of cyclohexanone (80 g, 0.82 mole), carbon disulfide (76 g, 1 mole) and 260 ml of aqueous ammonia (28%) was shaken at room temperature for a few hours. The yellow solid product was collected, washed with water, methanol, and ether, and dried: yield *ca.* 90 g. When the crude product was recrystallized from acetic acid, *ca.* 60 g of long orange plates (III) was obtained: yield *ca.* 90% (the crude product was assumed to mainly consist of I). Compound III was further recrystallized from methanol, mp 197–198°. *Anal.* Calcd for C₁₃H₁₃NS₂: C, 61.61; H, 7.56; N, 5.53; S, 25.31; mol wt (vapor pressure osmometry, vpo), 253.41. Found: C, 61.62; H, 7.50; N, 5.28; S, 25.45; mol wt, 256 (in acetone).

Compound III was easily soluble in pyridine, hydrochloric acid (yellow), and alcoholic alkali (greenish yellow), and hardly soluble in ether and water; the color of solution in a common organic solvent was yellowish orange or red. Dissolved in an appropriate solvent, III readily decolorized bromine water. It was easily regenerated from the solution in hydrochloric acid or in alcoholic alkali by neutralization.

Isolation of I.—The above crude product was dissolved in chloroform in the cold and filtered and an equal volume of methanol was added; the mixture was kept overnight in an icebox. About 3 g of yellow needles (I) was obtained from 10 g of the crude crop: mp 115–116° (slow heating) and 135–136° (rapid heating), much less soluble in pyridine than III. *Anal.* Calcd for C₁₉H₂₀N₂S₂: C, 65.09; H, 8.63; N, 7.99; S, 18.29; mol wt (vpo), 350.58. Found: C, 65.22; H, 8.35; N, 8.30; S, 18.16; mol wt, 355 (in acetone).

Compound I could be recrystallized from a solvent such as cold, freshly distilled tetrahydrofuran, but generally was not stable enough for recrystallization and easily changed into III, II, or other compounds. Dissolved in ethanol, I instantly decolorized bromine water. Compound III could be obtained by concentration of the mother liquor in the case of crystallization of the crude crop.

Compound I was remarkably sensitive to cupric ion producing brown precipitates or coloration (sensitivity, *ca.* 1 ppm) which was easily extracted with a common organic solvent such as ether; it seemed that an addition of pyridine to the extracting solvent is preferable. The same applied to a few other specific metal ions (Table IV).

TABLE IV

COLOR REACTION OF I AND II TOWARD METALLIC IONS

	Cu ²⁺	Hg ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺
I	Dark brown	Gray	Deep red	Deep reddish brown	Russet
II	...	Gray	Deep red

Isolation of II.—When the above crude crop of I was recrystallized from hot dimethylformamide, short orange prisms or thick plates (II) were quantitatively produced; recrystallization from pyridine or methanol gave a product of mp 143–144° dec (slow heating) and 162° dec (rapid heating). *Anal.* Calcd for $C_{19}H_{30}N_2S_2$: C, 65.09; H, 8.63; N, 7.99; S, 18.29; mol wt (vpo), 350.58. Found: C, 65.25; H, 8.45; N, 7.71; S, 18.34; mol wt, 365 (in chloroform).

Compound II, dissolved in ethanol, readily decolorized bromine water and was much less soluble in piperidine or morpholine than I.

Modified Method of the Preparation.—The present reaction also was conducted by passing ammonia gas through the mixture of cyclohexanone and carbon disulfide; almost the same result as that of the preceding preparation was obtained.

The Derivatives of I, II, and III. Methyl Derivative (IIa) of II.—Compound II was methylated using methyl *p*-toluenesulfonate in an usual way. The N-methyl derivative produced was recrystallized from ethanol–acetone: yellow needles or long plates, mp 204–205°. *Anal.* Calcd for $C_{20}H_{32}N_2S_2$: C, 65.90; H, 8.85; N, 7.69; S, 17.56. Found: C, 65.97; H, 9.19; N, 7.71; S, 17.44.

Compound IIa was much more easily made from I by the above method.

Ethyl Derivative (IIb) of II.—Likewise, the derivative was prepared from I or II in an usual way using diethyl sulfate. Recrystallization from benzene gave yellow needles, mp 201–202°. *Anal.* Calcd for $C_{21}H_{34}N_2S_2$: C, 66.63; H, 9.05; N, 7.40; S, 16.91. Found: C, 66.84; H, 8.96; N, 7.40; S, 16.90.

Benzylidene Derivative (IIc) of II.—Compound II and an equivalent amount of benzaldehyde was dissolved in a requisite amount of chloroform and warmed. After the solution was allowed to stand for 1 hr, methanol was added. The orange-red plates (IIc) which separated from the solution were recrystallized from methanol–chloroform: mp 183–184°, easily soluble in chloroform and difficultly soluble in methanol. *Anal.* Calcd for $C_{26}H_{34}N_2S_2$: N, 6.39. Found: N, 6.42.

Benzoyl Derivative (IIIa) of III.—The crude hydrochloride IIIa, prepared in an usual way, was dissolved in a small amount of hot acetic acid and then acetone was added. The yellow crystals that separated had mp 136–138°. *Anal.* Calcd for $C_{20}H_{24}ONS_2Cl$: C, 60.97; H, 6.14; N, 3.56; S, 16.28; Cl, 9.00. Found: C, 61.30; H, 6.22; N, 3.44; S, 16.08; Cl, 9.04.

Picryl Derivative (IIIb) of III.—A saturated solution of III in chloroform was combined with that of picryl chloride (equivalent amount) in benzene and warmed for a while. The whole turned dark red and then yellow crystals separated from the solution; they collected and recrystallized from ethanol containing methanol. The derivative was obtained as the hydrochloride IIIb as yellow plates or needles: mp 165–166° dec, easily soluble in methanol and rather hardly soluble in ethanol and benzene. *Anal.* Calcd for $C_{19}H_{21}O_6N_4S_2Cl$: C, 45.55; H, 4.23; N, 11.18; S, 12.80; Cl, 7.08. Found: C, 45.69; H, 4.27; N, 10.63; S, 12.55; Cl, 6.92.

The free base was obtained by crystallizing hydrochloride IIIb with pyridine: brown plates, mp *ca.* 232° dec. Rigid purification was not achieved.

Mercuric Derivatives of I, II, and III.—Compounds I, II, and III reacted with mercuric chloride to give the respective yellow salts. These salts, dissolved in ethanol or dimethylformamide, were indifferent toward silver nitrate. Of these salts, that of III afforded the most distinct analytical figure.

Compound III reacted with mercuric chloride in concentrated hydrochloric acid or in methanol. The yellow crystals produced were collected and washed with hot methanol and then ether: mp *ca.* 234° dec, easily soluble in dimethylformamide and pyridine. *Anal.* Calcd for $C_{13}H_{19}NS_2HgCl_2$: C, 29.74; H, 3.65; N, 2.67; S, 12.22; Cl, 13.51. Found: C, 30.11; H, 3.49; N, 2.69; S, 11.60; Cl, 13.28.

Conversion of I and II into III.—Compound I or II (0.5 g) was dissolved in a mixture of 5 ml of *ca.* 0.14 *N* sulfuric acid and 10 ml of methanol and refluxed for a while. Compound III separated quantitatively from the solution (III was much more easily produced from II); the orange plates produced were identified by mixture melting point, infrared spectrum, and elemental analysis. The mother liquor, from which III was removed, contained a considerable amount of cyclohexanone which was obtained as the 2,4-dinitrophenylhydrazone; the mother liquor, after an addition of a saturated solution of sodium chloride, was extracted with ether; and the organic portion was

concentrated and treated with 2,4-dinitrophenylhydrazine to give yellow flattened needles, mp 161–162°, which did not depress the melting point of an authentic specimen of cyclohexanone 2,4-dinitrophenylhydrazone.

Oxidation of III.—Compound III (2 g) was suspended in water (20 ml) and to this was gradually added a solution of potassium permanganate (6 g in 150 ml of water) over a period of several hours with stirring at room temperature. The stirring was continued for an additional 15 hr. The reaction mixture was acidified, sodium bisulfite was added, the mixture and filtered. The yellow filtrate was extracted with ether. A considerable amount of cyclohexanone, in the form of the 2,4-dinitrophenylhydrazone, was obtained from the extract: mp 161–162°, undepressed by the addition of an authentic specimen. In addition, a small amount of 1,2-cyclohexanedione was detected as the 2,4-dinitrophenylhydrazone which was much less soluble than the cyclohexanone 2,4-dinitrophenylhydrazone and thus easily fractionated from the latter; recrystallization from pyridine gave red crystals, mp 227–229° dec, undepressed by the addition of an authentic specimen.

Desulfuration of III.—Compound III (10 g) was refluxed with Raney nickel (100 g) in ethanol (250 ml) for a few hours. The decolorized reaction mixture was separated from nickel by decantation and centrifuge. The nickel was washed with ethanol and the washings were also centrifuged. Both the ethanolic portions were combined and concentrated under diminished pressure and fractionated into three portions: (1) bp 40–60° (8 mm), *ca.* 1.2 g; (2) bp 60–65° (8 mm), *ca.* 1 g; (3) bp 70–84° (8 mm), *ca.* 0.3 g.

From the low-boiling fraction was obtained 2-methylcyclohexanone as the 2,4-dinitrophenylhydrazone and the semicarbazone; the 2,4-dinitrophenylhydrazone was recrystallized from methanol to give orange yellow plates, mp 137–138°, undepressed by the addition of an authentic specimen; the semicarbazone was recrystallized from ethanol to give colorless plates, mp 193–197° dec (rapid heating) and 186–190° dec (slow heating), undepressed by the addition of an authentic specimen. *Anal.* Calcd for $C_8H_{15}N_3O$: C, 56.78; H, 8.94; N, 24.83. Found: C, 57.04; H, 9.06; N, 24.61. The above semicarbazone was converted into the 2,4-dinitrophenylhydrazone which was identical with the preceding derivative (mixture melting point test).

That the ketone was already present, at least to a certain degree, in the low-boiling fraction, was inferred by the infrared spectrum. Perhaps it was formed from the corresponding ketimine structure (2-methylcyclohexylideneaminocyclohexane) by the action of water which was contained in the solvent or absorbed by the nickel.

The high-boiling fraction was dissolved in ether and into this was passed dry hydrogen chloride. The resulting precipitates were collected and recrystallized from pentanol or ethanol containing a small amount of hydrochloric acid; colorless thick plates [N-cyclohexyl-2-methylcyclohexylamine (VII) hydrochloride], mp 265–266° (in sealed tube), were soluble in methanol, ethanol, and acetic acid, less soluble in cold water, and hardly soluble in ether, benzene, and dioxane; the melting point was undepressed on admixture with an authentic specimen (see next item). The infrared spectra of both specimens also were quite identical. The compound showed no positive test toward bromine water. *Anal.* Calcd for $C_{13}H_{26}NCl$: C, 67.35. H, 11.31; N, 6.04; Cl, 15.30. Found: C, 67.27; H, 11.22; N, 6.46; Cl, 15.64.

In addition, *o*-toluidine was detected in the above high-boiling fraction or the middle fraction. To the fraction was added excess picryl chloride and the mixture was allowed to stand for 7 days in an icebox. A small amount of the orange-red crystals produced was recrystallized from methanol as red needles: mp 168–169°, undepressed by the addition of an authentic specimen. Rigid purification was not achieved owing to lack of material, but analyses were carried out by way of precaution. *Anal.* Calcd for $C_{13}H_{10}N_4O_6$: C, 49.06; H, 3.17; N, 17.66. Found: C, 48.95; H, 2.85; N, 17.04.

Synthesis of VII.—2-Methylcyclohexanone (23 g, 0.2 mole) and cyclohexylamine (20 g, 0.2 mole) were refluxed with potassium fluoride (60 g, 1 mole) for 20 hr. The reaction mixture was filtered and fractionally distilled under reduced pressure. A fraction distilling at 114–115° (7 mm) was collected (22 g), colorless liquid (turned yellow to dark on standing). The freshly distilled material (10 g) was refluxed with tetralin (15 g) and palladium black (0.5 g) for 10 hr. The reaction mixture, freed

from the catalyst, was fractionally distilled under reduced pressure to give a fraction boiling at *ca.* 70–90° (26 mm): yield *ca.* 4 g. To this product was passed dry hydrogen chloride and the white precipitates obtained were recrystallized twice from pentanol: colorless plates, mp 264–265° (in sealed tube).

The hydrogenation mentioned above also was conducted by means of lithium aluminum hydride (in ether) to give the same product. *Anal.* Calcd for $C_{13}H_{23}NCl$: C, 67.35; H, 11.31; N, 6.04; Cl, 15.30. Found: C, 67.26; H, 11.29; N, 6.33; Cl, 15.19.

The Reaction Product (IIIc) from 4-Methylcyclohexanone.—The same method as that used in the preparation of III was applied. The yield was somewhat less than that in the case of cyclohexanone. The crude product was recrystallized from methanolic acetic acid and then from methanol: orange thick plates (IIIc), mp 194–195°. The nature and the infrared and the ultraviolet absorption spectra were almost identical with those of III. *Anal.* Calcd for $C_{15}H_{23}NS_2$: C, 64.00; H, 8.24; N, 4.98; S, 22.78. Found: C, 64.22; H, 8.26; N, 4.83; S, 22.78.

Reaction of Cyclohexanone with Carbon Disulfide in the Presence of Sodium Amide.—To a mixture of carbon disulfide (830 g, *ca.* 6.3 moles) and sodium amide (100 g, *ca.* 2.6 moles) was added dropwise cyclohexanone (256 g, *ca.* 2.6 moles) under cooling (ice water) and vigorous stirring (the reaction vessel was fitted with reflux condenser). The stirring was continued for an additional several hours after the addition was complete. In the course of reaction, some ammonia and hydrogen sulfide evolved. The solid product was filtered, washed with water (the washings were red and set aside), and dried (*ca.* 70 g); an additional amount (70 g) of this crude solid product was obtained by concentrating the above organic filtrate. The water-insoluble crude crop consisted mainly of a mixture of I, II, and III; the amount of I contained was small and the greater part seemed to consist of III. The crude crop, on recrystallization from methanol, afforded the long orange plates which were identified with III by mixture melting point test, infrared spectrum, and elemental analysis.

Isolation of VI.—Besides I, II, and III, a few other compounds, though in poor yield, were isolated from the above reaction product. From the red aqueous washings of the crude solid product, a small amount of yellow precipitates separated on standing; collection and recrystallization from ethanol gave light pink needles (VI), mp 275–276°. *Anal.* Calcd for $C_{13}H_{20}N_2S$: C, 66.07; H, 8.53; N, 11.86; S, 13.54. Found: C, 65.96; H, 8.45; N, 11.60; S, 13.57.

Isolation of IV.—From the preceding washings from which VI was removed, *ca.* 4.5 g of red crystals was obtained on long standing, by neutralization with dilute hydrochloric acid, or by extraction with ether. Recrystallization from benzene gave lustrous red plates (IV): mp 202–203° dec, easily soluble in pyridine, acetone, and aqueous alkali (yellow) and hardly soluble in hydrochloric acid. Compound IV, when dissolved in concentrated sulfuric acid, produced red coloration. *Anal.* Calcd for $C_8H_9NS_3$: C, 44.62; H, 4.21; N, 6.51; S, 44.67; mol wt (Rast), 215.35. Found: C, 44.41; H, 4.33; N, 6.20; S, 44.67; mol wt, 208.

The mercuric derivative was made from IV and mercuric chloride in ethanol. The brown plates produced was washed with methanol, mp *ca.* 140° dec; the solution of the compound in ethanol or dimethylformamide was indifferent toward silver nitrate. *Anal.* Calcd for $C_8H_9NS_3HgCl$: C, 21.33; H, 1.79; N, 3.11; S, 21.35; Cl, 7.85. Found: C, 21.31; H, 1.88; N, 3.05; S, 21.07; Cl, 7.59.

Likewise, red precipitates of the lead derivative were formed from an ethanolic solution of IV by addition of lead acetate.

Isolation of an Additional Compound.—The red organic filtrate, from which the crude crop of a mixture of I, II, and III was removed, on concentration, yielded a small amount of another crystalline compound. Recrystallization from methanol gave orange needles, mp 185–186°, $\lambda_{max}^{ethanol}$ 370 and 409 m μ . *Anal.* Calcd for $C_{40}H_{56}N_4S_3$: C, 63.81; H, 7.50; N, 7.44; S, 21.25. Found: C, 63.88; H, 7.46; N, 7.38; S, 21.24.

Reaction of 2-Cyclohexylidenecyclohexanone with Carbon Disulfide in the Presence of Sodium Amide.—To a mixture of carbon disulfide (252 g, 3.3 moles) and sodium amide (6 g, 0.16 mole) was added 2-cyclohexylidenecyclohexanone [bp 152–155° (20 mm); 20 g, 0.12 mole] over a period of 1 hr with stirring at room temperature; the stirring was continued for an additional 20 hr. The brown-yellow solid product which was easily soluble in water, was not investigated further. The red organic filtrate was concentrated. About 1 g of yellow crystals was obtained; recrystallization from dimethylformamide gave light flesh colored crystals (V) which decomposed gradually above *ca.* 250° and was very easily soluble in pyridine, hydrochloric acid, concentrated sulfuric acid (yellow), easily soluble in chloroform, slightly soluble in cold dimethylformamide (easily soluble in hot one), and hardly soluble in water, dilute hydrochloric acid, aqueous alkali, and other common organic solvent. The compound, dissolved in appropriate solvent, readily decolorized bromine water and was positive toward tetranitromethane. *Anal.* Calcd for $C_{13}H_{17}NS$: C, 71.20; H, 7.82; N, 6.39; S, 14.59. Found: C, 71.27; H, 7.82; N, 6.10; S, 14.60.

Registry No.—Carbon disulfide, 75-15-0; cyclohexanone, 108-94-1; III, 7616-97-9; I, 7630-81-1; II, 7641-48-7; IIa, 7650-64-8; IIb, 7660-83-5; IIc, 7650-65-9; IIIa, 7650-74-0; IIIb, 7650-72-8; IIIb hydrochloride, 7650-66-0; 2-methylcyclohexanone 2,4-dinitrophenylhydrazone, 5138-30-7; 2-methylcyclohexanone semicarbazone, 4549-20-6; 2-methylcyclohexanone, 583-60-8; VII, 7616-98-0; VII hydrochloride, 7650-68-2; *o*-toluidine picryl derivative, 7616-99-1; IV, 7650-70-6; IV mercury derivative, 7617-00-7; V, 7650-71-7.

Acknowledgment.—The authors are indebted to Dr. Hiroshi Midorikawa (The Institute of Physical and Chemical Research) for his generous aid in many respects. Thanks are also due to Dr. Y. Okumura, Miss H. Asaba, and Messrs. T. Imamoto and K. Uotsu for their kind advice and assistance.