cals, KA-101)[10] is a quasiamorphous alumina, as determined by X-ray diffraction,[11] which can be referred to as χ-ρ alumina. The X-ray pattern is diffuse and intermediate between amorphous ρ and the more crystalline χ, but distinct from each.[11] A minor phase (*ca.* 20–30%) which coexists with the above dominant phase resembles γ-alumina but is more diffuse. The catalyst is supplied as pellets, 8–14 mesh, with a surface area of 360 m^2/g. Sodium content is 0.40%, expressed as Na_2O.

Catalyst C (Houdry HA-100S)[12] is a γ-alumina catalyst which has been described as essentially nonacidic,[13] while catalyst B (Harshaw AL-0104)[14] is also a γ-alumina, classed as weakly acidic. Both B and C have been utilized as dehydration catalysts in a large number of published examples by several different workers.[13] C has a sodium content of 0.1–0.2%, while B has a content of 0.4% expressed as Na_2O.

Catalysts were prepared by heating at the dehydration temperature for a period of 1 hr under reduced pressure (20–25 mm). After this period they were used directly as described below.

Dehydration of Cyclohexanone (1).—Cyclohexanone[15] (20 g, 0.21 mol) was added dropwise at a rate of 0.25 ml/min through a 22-mm Pyrex tube packed to a depth of either 18 or 26 cm with alumina and externally heated with a Lindberg Hevi-Duty split-tube furnace. A pressure of 20–25 mm was maintained in the system to facilitate rapid removal of the product from the column. The product was trapped in a flask immersed in a Dry Ice–acetone bath, and subsequently warmed to room temperature, washed with water, filtered through anhydrous magnesium sulfate, and analyzed immediately by glpc (12.8 g, 72%).[16] No attempt was made to maximize this yield, although we recognize that this method discriminates against isolating phenolic-type products. High-boiling materials were also condensed on the inside of the exit tube from the dehydration chamber. This was shown to consist mainly of phenolic material and higher-boiling residues. Since our main interest was in the hydrocarbon fraction, we made no further effort at a complete material balance for all products.

The dehydration products were identified by collecting each peak emanating from the chromatograph in glass V tubes immersed in cooling baths: (1) in isooctane for uv analysis, and (2) in $CDCl_3$ for nmr analysis. In each case, the product was identified by comparison of the uv, nmr, and glpc retention times to those of authentic samples in our laboratories.

Dehydration of 4-Methylcyclohexanone (3).—Methylcyclohexanone[17] (20 g, 0.18 mol) was dehydrated at 400° as described above for cyclohexanone, yielding 14.9 g (87%)[18] of the product, which was analyzed immediately by glpc.

Dehydration of 2-Methylcyclohexanone (2).—2-Methylcyclohexanone[19] (15 g, 0.13 mol) was dehydrated at 400° as described above, yielding 9.3 g (73%)[20] of product, which was immediately analyzed by glpc.

Thermolysis of 4-Methyl-1-cyclohexene (22).—4-Methyl-1-cyclohexene (10 g) was thermolyzed by passage through an 18-cm column packed with either A, B, or C, at 400°. Immediate glpc of the recovered product (>95% in all three cases) revealed that the only new product was 1-methyl-1-cyclohexene (2–5%).

Registry No.—**1**, 108-94-1; **2**, 583-60-8; **3**, 589-92-4; alumina, 1344-28-1.

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[10] Kaiser Chemicals, Division of Kaiser Aluminum and Chemical Corp.

[11] Private communication, Dr. Robert B. Emerson, Staff Research Associate, Chemical Aluminas, Kaiser Chemicals, Baton Rouge, La.

[12] Houdry Process and Chemical Co.

[13] See, for example, L. Klemm, J. Shabtai, and D. Taylor, *J. Org. Chem.*, **33**, 1480 (1968), and references therein.

[14] The Harshaw Chemical Co., Division of Kewanee Oil Co.

[15] J. T. Baker Chemical Co.

[16] For catalyst A (26-cm column) the following total product analysis was obtained: recovered **1**, 21.8%; total dehydration products, 78.2%. The hydrocarbon analysis is shown in Table I, recalculated on the basis of 100% total hydrocarbon content.

[17] Chemical Samples Co.

[18] For catalyst A (26-cm column) the following total product analysis was obtained: recovered **3**, 39.7%; total dehydration products, 60.3%. The hydrocarbon analysis is shown in Table I, recalculated on the basis of 100% total hydrocarbon present.

[19] Aldrich Chemical Co.

[20] For catalyst A (26-cm column) the following total product analysis was obtained: recovered **2**, 54.5%; total dehydration products; 45.5%. The hydrocarbon analysis is shown in Table I, recalculated on the basis of 100% total hydrocarbon present.

Mechanism of Redox Decomposition of Oxymercurated *cis*-2-Butene in Aqueous Solution

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Olefins are oxidized by mercuric ion in aqueous acid to yield unsaturated aldehydes,[1-4] saturated aldehydes,[2,3] allylic alcohols,[4] or saturated ketones.[5] Saturated ketones are obtained under milder conditions than unsaturated aldehydes or allylic alcohols. For example, acetone is obtained from propene at about 50° and methyl ethyl ketone from *trans*- or *cis*-2-butene below room temperature,[6] whereas acrolein and crotonaldehyde are formed at about 80°[1] and allyl alcohol at 90°.[4] These reactions proceed as the redox decomposition of hydroxymercurated olefins,[7] and their reaction rates are first order with respect to the mercurials,[1,8] without depending on free mercuric ion in the case of ketone formation.[8]

Since hydroxymercurated *cis*-2-butene is sufficiently stable at low temperatures, the reaction process can be pursued by nmr spectroscopy *in situ* after the temperature of the solution is raised abruptly. Time-sequential spectra following the redox decomposition of hydroxy- and deuteroxymercurated *cis*-2-butene are shown in Figure 1.[9]

It is obvious in Figure 1 that methyl ethyl ketone is the sole product and, interestingly, no deuterium is incorporated into the product from the solvent D_2O. Therefore, reaction equations are presented as follows, where the mechanism of two electron transfer, *i.e.*, no association of free mercuric ion, is postulated on the basis of the reaction kinetics.[8]

$$CH_3CH(OH)CHCH_3Hg^+ \xrightarrow[H_2O]{} CH_3COCH_2CH_3 + H^+ + Hg(0) \quad (1)$$

$$CH_3CH(OD)CHCH_3Hg^+ \xrightarrow[D_2O]{} CH_3COCH_2CH_3 + D^+ + Hg(0) \quad (2)$$

The reaction product from the D_2O solution was analyzed by mass spectroscopy and the following deuterium distribution was obtained: $d_0 = 97.3\%$, $d_1 = 2.4\%$, $d_2 = 0.3\%$, $d_3 = d_4 = \cdots = d_8 = 0.0\%$. Thus the result shown in eq 2 was confirmed unequivocally. A concerted mechanism is, therefore, suggested, whereby an intramolecular hydrogen shift occurs and

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[1] B. C. Fielding and J. Roberts, *J. Chem. Soc. A*, 1627 (1966).

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[5] Y. Saito and M. Matsuo, *ibid.*, **10**, 527 (1967).

[6] Y. Saito, 1st Japan–U. S. S. R. Seminar on Catalysis, Novosibirsk, July 1971.

[7] W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

[8] M. Matsuo and Y. Saito, *Bull. Chem. Soc. Jap.*, **44**, 2889 (1971).

[9] Chemical shifts of α, β, γ, and β' protons of both hydroxy- and deuteroxymercurated *cis*-2-butenes were δ 3.01, 3.86, 1.19, and 1.38, respectively, and their coupling constants for the sets of $\alpha\beta$, $\beta\gamma$, and $\alpha\beta'$ protons were 4.0, 6.0, and 7.6 Hz, respectively, where designation of α, β, β', etc., was made from the mercurated carbons.

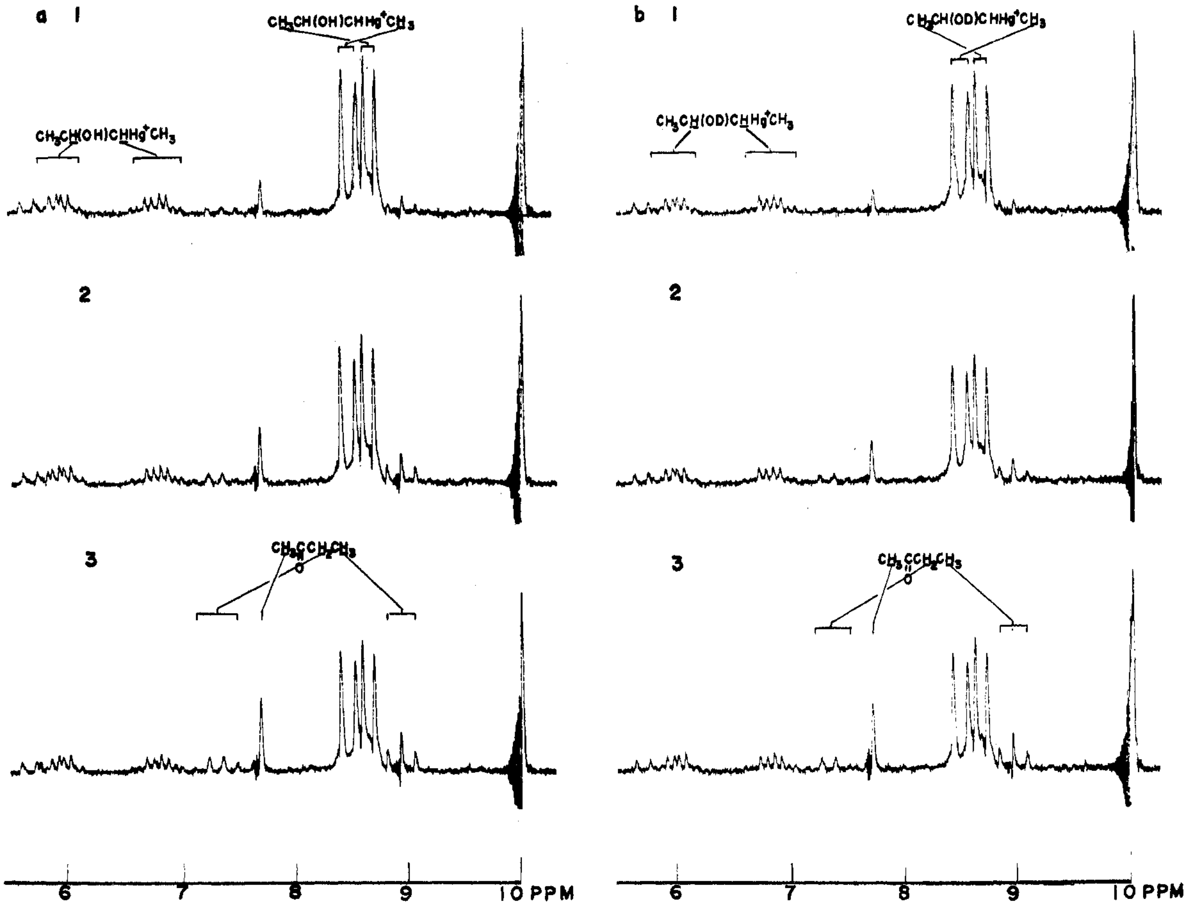

Figure 1. The time-sequential nmr spectra obtained *in situ* for the redox decomposition of oxymercurated *cis*-2-butene in H_2O solution (a) and D_2O solution (b). These spectra were taken after (a) (1) 20.0 min, (2) 38.0 min, (3) 57.5 min, and (b) (1) 5.5 min, (2) 28.0 min, (3) 55.0 min from the moment of raising the solution temperature.

two electrons are transferred along the carbon–mercury bond simultaneously.

As is well known, undeuterated acetaldehyde is obtained by palladium(II) oxidation of ethylene in D_2O solution.[10] Redox decomposition of the 2-hydroxyethylpalladium(II) σ complex to acetaldehyde is sufficiently fast that no deuterium isotope effect is observed for deuterated ethylene.[11] The rate-determining step in this reaction is ascribed to the σ-complex formation from an olefin–palladium(II) π complex.[12] This is in sharp contrast to the mercury(II) case, since hydroxymercuration of olefin is much more rapid[13] than the redox decomposition.[6] A resemblance can be seen, therefore, between mercury(II) and palladium(II) oxidation of olefins to ketones not only because of the common reaction mechanism of intramolecular hydrogen shift during the redox decomposition process but also because of the reaction scheme olefin → π complex → σ complex → saturated ketone.

The reaction rates of the redox decomposition were obtained as first order with respect to the mercurials, as reported previously,[5,6,8] with the rate constants determined as 2.8×10^{-5} and 2.7×10^{-5} sec^{-1} for the H_2O and D_2O solutions, respectively.

Large solvent isotope effects were reported for the reaction of deoxymercuration affording the original olefins. For example, the value of $k(D_2O)/k(H_2O)$ for the dehydroxymercuration of 2-hydroxypropylmercuric iodide was 2.16.[14] Similar results were obtained for deoxymercuration affording ethylene,[15] propylene,[14] and cyclohexene;[16] they are $k(D_2O)/k(H_2O)$ = 3.32, 2.80, and 3.2, respectively. These large inverse solvent isotope effects can be explained by assuming fast prototropic preequilibrium during deoxymercuration.[7] Since the magnitude of the solvent isotope effect for the present reaction is negligibly small, no acidic assistance during the redox decomposition of hydroxymercurated *cis*-2-butene could be concluded.

Experimental Section

Materials.—All the reagents were of GR grade, prepared by Tokyo Kasei Kogyo Co. Ltd. (Tokyo), and were used without further purification. Absence of impurities was confirmed by gas chromatography using a β,β'-dioxypropionitrile column for *cis*-2-butene prepared by Takachiho Kagaku Kogyo Co. Ltd. (Tokyo).

Procedure.—Mercuric solutions were prepared by dissolving mercuric nitrate in concentrated nitric acid and diluting with ion-exchange water to a given concentration. The concentration of mercuric ion was determined by titration with potassium thiocyanate. *cis*-2-Butene was introduced from the cylinder into the solution maintained at 0°. In order to prepare $CH_3CH(OH)CHCH_3Hg^+$, a solution consisting of 0.25 g (4.00 mmol) of HNO_3, 1.32 g (4.00 mmol) of $Hg(NO_3)_2$, and 1.80 g (100 mmol) of H_2O was used, while a solution consisting of 0.25 g (4.00 mmol)

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[13] J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

[14] M. M. Kreevoy, *ibid.*, **81**, 1099 (1959).

[15] M. M. Kreevoy and L. T. Ditsch, *J. Org. Chem.*, **25**, 134 (1960).

[16] M. M. Kreevoy and F. R. Kowitt, *J. Amer. Chem. Soc.*, **82**, 739 (1960).

of DNO_3, 1.32 g (4.00 mmol) of $Hg(NO_3)_2$, and 2.00 g (100 mmol) of D_2O was used to prepare $CH_3CH(OD)CHCH_3Hg^+$.

A part of the solution maintained at 0° was quickly transferred to an nmr sample tube and put in the probe of the spectrometer kept at 4.3°, with the temperature regulated by blowing cooled nitrogen gas and nmr calibrated by the relative chemical shifts of 1,3-propanediol. The redox decomposition reaction was pursued by taking spectra in sequence with a JEOL C-60 nmr spectrometer. The concentrations of oxymercurated *cis*-2-butene and methyl ethyl ketone were determined from the peak intensities by comparing them with that of the external tetramethylsilane reference. A Hitachi RMU-S mass spectrometer was used for analysis of methyl ethyl ketone produced in D_2O solution, which was separated from the solution by vacuum distillation at 0°.

Registry No.—$CH_3CH(OH)CHCH_3Hg^+$, 35184-47-5; $CH_3CH(OD)CHCH_3Hg^+$, 35184-48-6.

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A Mild and Effective Two-Step Conversion of Disubstituted Cyanamides to Secondary Amines

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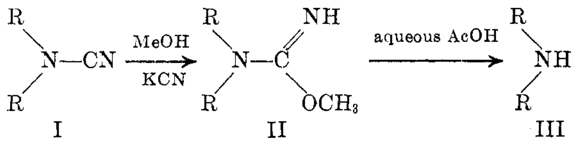
One limitation in the synthesis of secondary amines by the cyanamide method arises from the frequent difficulty of cleaving the N-CN bond.

In a previous paper,[1] we have reported on a KCN-promoted addition of methanol to disubstituted cyanamides to give isourea-type compounds (II), which could be hydrolyzed easily to secondary amines by refluxing in aqueous acetic acid.



In this manner, we were able to prepare some secondary terpenylamines not available by the usual decyanation procedures.[1,2]

This note reports further results (Table I) and experimental details from the application of this method to the synthesis of various secondary amines (including cyclic amines III-10, III-11), as well as an elucidation of the mechanism involved in the formation of the intermediate *O*-methylisoureas (II).

Satisfactory yields of disubstituted cyanamides are obtained from halides and cyanamide using sodium methylsulfinylmethide in dimethyl sulfoxide as deprotonating agent. Besides the mildness of the reaction conditions, one important advantage of this procedure over the conventional method[3] is the avoidance of isomeric products arising from allylic rearrangements or from cyclopropylcarbinyl interconversion reactions. The intermediate *O*-methylisoureas (II) are obtained by heating the corresponding cyanamides with potassium cyanide in methanol. In practice, these intermediates can be isolated, purified, and then hydrolyzed in the subsequent step, or hydrolyzed directly as crude products. The second step is carried out by refluxing the intermediates II in aqueous acetic acid. Under these conditions, the *O*-methylisoureas undergo a facile hydrolysis to secondary amines.

The formation of isoureas (II) may be regarded as a base-catalyzed addition of methanol to the cyano group, the role played by potassium cyanide being to provide a low, but sufficient, concentration of MeO^- ions.

$$CN^- + MeOH \rightleftarrows MeO^- + HCN$$

$$R_2NCN + MeO^- \longrightarrow R_2N\underset{OMe}{C}{=}N^- \xrightarrow{MeOH} R_2N\underset{OMe}{C}{=}NH + MeO^-$$

This mechanism is supported both by the successful replacement of equimolar potassium cyanide with catalytic amounts of sodium methoxide and by the analogy with the mechanism observed for the base-catalyzed conversion of nitriles to methyl imidates.[4]

The absence of strong acids or bases in the two steps makes this modification of the cyanamide method suitable to be used with sensitive substrates. Furthermore, the fact that disubstituted cyanamides are also key intermediates in the von Braun degradation suggests potential applications.[5]

Experimental Section

Boiling points are uncorrected. Melting points are uncorrected and were taken on a Büchi capillary melting point apparatus. Ir spectra were run on a Perkin-Elmer 337 spectrophotometer, nmr spectra on a Varian A-60A spectrometer (Me_4Si) (0.00 ppm).

Materials.—All the halides used for the synthesis of disubstituted cyanamides were bromides, except for 3,4,5-trimethoxybenzyl chloride and 3,4-methylenedioxybenzyl chloride. They were synthesized by known procedures. Dimethyl sulfoxide was dried by distillation from calcium hydride.

General Methods. Disubstituted Cyanamides (I).—Cyanamide (0.1 mol) was added portionwise to a stirred suspension of sodium methylsulfinylmethide[6] prepared *in situ* from 0.22 mol of a 80% dispersion of sodium hydride in mineral oil and 150 ml of dry dimethyl sulfoxide. The mixture was stirred at room temperature for 30 min and then 0.22 mol of the appropriate halide (0.11 mol for I-10 and I-11) was added slowly. Generally, the reaction temperature rose to 50–60° while a white precipitate formed. After an additional 1-hr stirring at room temperature, the mixture was poured into ice–water and extracted with ether. The ether extract was washed with water, dried over $MgSO_4$, and concentrated, and the residue was distilled or crystallized from a suitable solvent.

N,N-Disubstituted *O*-Methylisoureas (II).—A mixture of 0.1 mol of the appropriate I, 0.1 mol of potassium cyanide, and 200

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