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Reactions of Acrolein and Related Compounds. IX. Reactions with Ketimines

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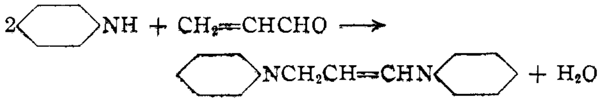
RECEIVED FEBRUARY 16, 1953

Novel conjugately unsaturated aldimines have been prepared by exchange reaction between N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine (II) and methacrolein or crotonaldehyde to give N-methallylidene- or N-crotylidene-1,3-dimethylbutylamine and methyl isobutyl ketone. From the reaction of acrolein or methacrolein with the same ketimine, cyclic condensation products, cyclohexenimines, also have been isolated.

Introduction

It has not been possible to prepare unsaturated aldimines directly from the reaction of unsaturated aldehydes such as methacrolein, acrolein or crotonaldehyde with amines. The reaction gives instead 1,3-diaminopropenes.[1] For example, piperidene was shown to react with acrolein as



Recently[2] Pollard and Parcell have reported the preparation of N-allylidenealkylamine by dehydrobromination of N-(2-bromoallyl)-dialkylamines.

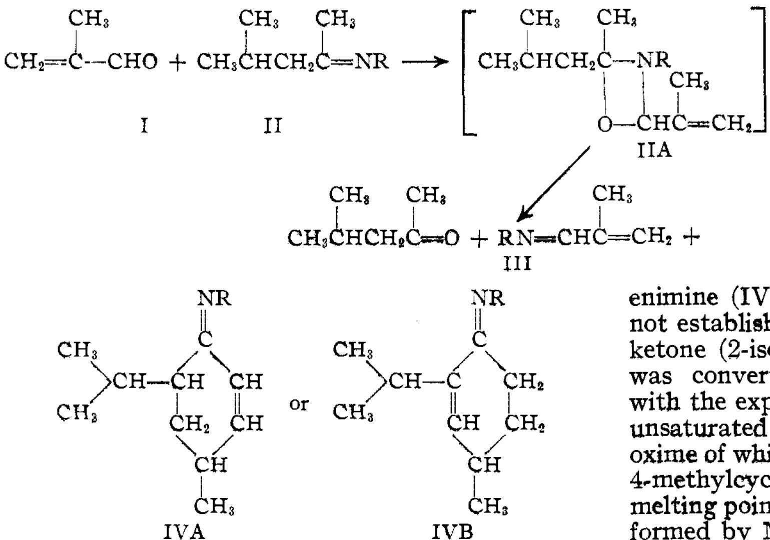
In unpublished studies in this Laboratory, Ballard, Haury and Norton have obtained aldimines and ketones by exchange reaction between saturated aldehydes and ketimines.

$$R'CHO + R_2C{=}NR \longrightarrow R'CH{=}NR + R_2CO$$

The behavior of methacrolein, acrolein and crotonaldehyde in this reaction constitutes the subject of this paper.

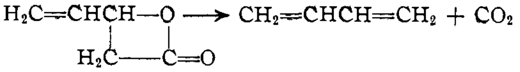
Discussion

In choosing an imine for study in these exchange reactions N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine (II) was selected rather than lower molecular weight products because the latter are considerably more sensitive to hydrolysis by absorption of moisture from the air.



$R = -CH(CH_3)CH_2CH(CH_3)_2$

Reaction with Methacrolein.—The reaction of methacrolein (I) with N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine (II) may be represented as shown. The first products above, N-methallylidene-1,3-dimethylbutylamine (III), and methyl isobutyl ketone are derived by simple metathesis. Heating equimolar amounts of the above reactants (I and II) at 50° for four hours has given an 89% yield of the unsaturated aldimine (III). The mechanism of this reaction has not been established. Obviously, it cannot be a simple hydrolysis to amine and ketone due to catalytic amounts of water since the amine would be expected to react with both linkages of the unsaturated aldehyde. It may be that the strong dipoles of imine and aldehyde align themselves as in IIA according to charge and then dissociate to form the more stable ketone and aldimine (III). A parallel for this addition would be the formation of β-lactams from ketene and imines or of β-lactones from ketene and ketones. A parallel for the cleavage is the conversion of β-lactones from acrolein, methacrolein, crotonaldehyde to carbon dioxide and diene.[3]



$$\begin{matrix} H_2C{=}CHCH{-}O \\ \quad\ | \qquad\ | \\ \quad H_2C{-}C{=}O \end{matrix} \longrightarrow CH_2{=}CHCH{=}CH_2 + CO_2$$

The N-methallylidene-1,3-dimethylbutylamine is surprisingly stable. There was no discoloration or obvious change on storage for several months. Only slight polymerization was noted upon heating the aldimine at 160° for several hours. Hydrogenation of the aldimine (III) gave N-isobutyl-1,3-dimethylbutylamine, the structure of which was established by mixed melting point of the monoöxalate with an authentic sample.

The higher-boiling by-product (IV) obtained in 5% conversion to product was identified as N-(1,3-dimethylbutyl)-2-isopropyl-4-methylcyclohexenimine (IV A or B, location of ethylenic bond is not established). Hydrolysis gave an unsaturated ketone (2-isopropyl-4-methylcyclohexenone) which was converted to a 2,4-dinitrophenylhydrazone with the expected analysis. Hydrogenation of the unsaturated ketone gave a saturated ketone the oxime of which was identified as that of 2-isopropyl-4-methylcyclohexanone by melting point and mixed melting point. The by-product (IV) is presumably formed by Michael-type addition of the activated methyl or methylene group in the ketone part of the imine (I) to the ethylenic linkage of meth-

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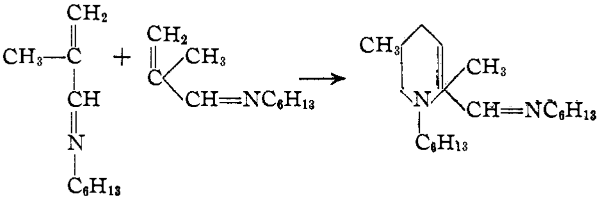
[1] C. Mannich, K. Handke and K. Roth, *Ber.*, **69B**, 2112 (1936).

[2] C. B. Pollard and R. F. Parcell, THIS JOURNAL, **73**, 2925 (1951).

[3] H. J. Hagemeyer, *Ind. Eng. Chem.*, **41**, 765 (1949).

acrolein. The terminal aldehyde then condenses on the remaining activated methyl or methylene group by aldol condensation to give IV A or B. There seems little evidence for favoring either structure A or B. Since the derived 2,4-dinitrophenylhydrazone melted sharply, the by-product does not appear to be a mixture.

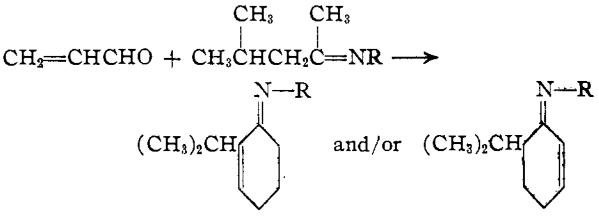
At 200° N-methallylidene-1,3-dimethylbutylamine (III) has given a 17% conversion to dimer whose structure has not been determined. The structure may be analogous to those of acrolein and methacrolein thermal dimers.[4]



If the above structure is correct, we have an example of the unusual involvement of a conjugated imine linkage in a Diels–Alder type reaction.

No reaction was observed upon heating a mixture of the imine (III) with acrylonitrile at 100° for 17 hours or on passing ketene into the imine (III) at 30° for two hours. Reaction with maleic anhydride resulted in tar formation. The imine (III) did not polymerize alone or in admixture with methyl methacrylate or styrene using benzoyl peroxide or boron trifluoride–ether complex as catalyst. The boron trifluoride precipitated as a complex with the imine.

Reaction with Acrolein.—No aldimine was observed in the reaction of acrolein with N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine (II) and the only product isolated was N-(1,3-dimethylbutyl)-2-isopropylcyclohexenimine (V A and/or V B) in 5% conversion to product. Except for a 32% recovery of imine charged the remaining materials were converted to "resins."

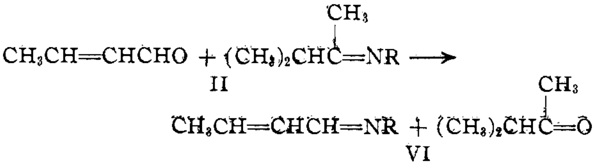


V A V B

R = —CH(CH$_3$)CH$_2$CH(CH$_3$)$_2$

With the addition of anhydrous potassium carbonate the conversion to product was increased to 14% and the yield was 28%. The product from simultaneous hydrolysis and hydrogenation of the cyclohexenimine gave a semicarbazone whose melting point was in agreement with that in the literature[5] for the semicarbazone of 2-isopropylcyclohexanone.

Reaction with Crotonaldehyde.—The reaction of crotonaldehyde with N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine (II) gave a product in 68% yield the analysis of which is in agreement with N-crotylidene-1,3-dimethylbutylamine (VI). In this case there was no indication of the cyclohexenimines formed with acrolein and methacrolein.



$$CH_3CH{=}CHCHO + \underset{II}{(CH_3)_2CH\overset{CH_3}{\overset{|}{C}}{=}NR} \longrightarrow CH_3CH{=}CHCH{=}NR + (CH_3)_2CH\overset{CH_3}{\overset{|}{C}}{=}O$$

VI

R = —CH(CH$_3$)CH$_2$CH(CH$_3$)$_2$

With acrolein the only product isolated was the cyclohexenimine (V); with methacrolein both the aldimine (III) and the cyclohexenimine (IV) were obtained; with crotonaldehyde only the aldimine (VI) was obtained. These reactions are in line with other observations which show that acrolein and methacrolein undergo Michael-type reaction readily, but that the β-methyl group of crotonaldehyde interferes with the Michael reaction.

Experimental

Reaction of Methacrolein with N-(1,3-Dimethylbutylidene)-1,3-dimethylbutylamine (II).—In unpublished investigation in these laboratories N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine, b.p. 128.8° (100 mm.), n^{20}D 1.4237, d^{20} 0.7842, has been prepared from methyl isobutyl ketone and 1,3-dimethylbutylamine.

Anal. Calcd. for $C_{12}H_{25}N$: C, 78.61; H, 13.75; N, 7.64. Found: C, 78.12; H, 13.65; N, 7.52.

A mixture of 70 g. (1 mole) of methacrolein and 183 g. (1 mole) of N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine was allowed to stand at room temperature overnight and then heated at 50° for four hours. Distillation of the product gave 84 g. of methyl isobutyl ketone, 12 g. of unreacted N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine, 127 g. of N-methallylidene-1,3-dimethylbutylamine boiling at 46–50° (10 mm.), n^{20}D 1.4550, d^{20} 0.7845, and 11 g. of a material boiling at 74–77° (0.5 mm.). The conversion to N-methallylidene-1,3-dimethylbutylamine (III) is 83% and the yield is 89%.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N, 9.14; neut. equiv., 153. Found: C, 78.18, 78.13; H, 12.56, 12.54; N, 8.52, 8.54; neut. equiv., 156.

The infrared spectrum had bands at 6.13 and 6.20 μ which may be expected from conjugated double bonds and is at distinct variance with the absorption of N-allylideneëthylamine as reported by Pollard and Parcell[2] with the strong "Unusual" band at 5.65 μ and the weak band at 6.06 μ. The ultraviolet absorption spectrum had a band at 2200 Å. with a molecular extinction coefficient of 18645 l./mole cm. which might be expected from the conjugated system.

The material boiling at 74–77° (0.5 mm.) was formed in 5% conversion to product and gave an analysis which except for carbon was in close agreement with that to be expected for N-(1,3-dimethylbutyl)-2-isopropyl-4-methylcyclohexenimine (IV A or B).

Anal. Calcd. for $C_{16}H_{29}N$: C, 81.63; H, 12.42; N, 5.95; neut. equiv., 235. Found: C, 80.66, 80.63; H, 12.19, 12.31; N, 5.82, 5.86; neut. equiv., 238.

The infrared and ultraviolet spectra of this material and of N-(1,3-dimethylbutyl)-3,3,5-trimethyl-5-cyclohexenimine[6] were run for comparison and provide further evidence for the designated structure.

	N-(1,3-Dimethylbutyl)-2-isopropyl-4-methyl-cyclohexenimine	N-(1,3-Dimethylbutyl)-3,3,5-trimethyl-5-cyclohexenimine
Infrared, μ	6.13 (s)[a]	6.10 (s)
Ultraviolet, at 2280 Å.	E_M 20885 l./mole cm.	E_M 13541 l./mole cm.

[a] A weak band at 5.88 μ is attributed to carbonylic impurity.

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(4) R. R. Whetstone, U. S. Patent 2,479,283 (1949).

(5) A. Kotz and A. Michels, *Ann.*, **350**, 214 (1906).

(6) Prepared in this Laboratory from isophorone and 1,3-dimethylbutylamine by Ballard, Haury and Norton: b.p. 118° (18 mm.), n^{20}D 1.4801, d^{20} 0.8535. *Anal.* Calcd. for $C_{15}H_{27}N$: C, 80.64; H, 13.08; N, 6.27. Found: C, 80.54; H, 13.05; N, 6.27.

Acidification and steam distillation of a sample of N-(1,3-dimethylbutyl)-2-isopropyl-4-methylcyclohexenimine gave an oil from which was derived a bright-red 2,4-dinitrophenylhydrazone, m.p. 151.2–152.2°.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.8; H, 6.1; N, 16.9. Found: C, 57.4, 57.4; H, 6.2, 6.1; N, 16.4, 16.5.

A portion of the ketone produced by hydrolysis of the imine was hydrogenated over Raney nickel at 25° and 30 p.s.i. The 2-isopropyl-4-methylcyclohexanone obtained by distillation boiled at 208° and gave an oxime which melted at 105° in exact agreement with the known oxime of 2-isopropyl-4-methylcyclohexanone.[5]

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.95; H, 11.31; N, 8.28. Found: C, 71.5; H, 11.6; N, 8.15.

For an authentic sample of oxime for mixed melting point, 2-isopropyl-4-methylphenol was prepared by alkylation of *p*-cresol with isopropyl alcohol in liquid hydrogen fluoride.[7] The fraction, 78 g., boiling at 220–245°, was hydrogenated in ethanol over Raney nickel at 150° and 1500 p.s.i.g. A heart cut of the product, 40 g., b.p. 205–220°, containing 2-isopropyl-4-methylcyclohexanol was oxidized with dichromate. An oxime of the product melted sharply at 105° in agreement with the oxime of 2-isopropyl-4-methylcyclohexanone. A mixture with the derivative from N-(1,3-dimethylbutyl)-2-isopropyl-4-methylcyclohexenimine gave no depression of melting point.

Dimerization of N-Methallylidene-1,3-dimethylbutylamine.—One-half mole, 77 g., of N-methallylidene-1,3-dimethylbutylamine was heated at 200° for one hour. Distillation gave 33 g. of starting imine and 13 g. (17% conversion to product, 38% yield) of dimer which may be N,N′-bis-(1,3-dimethylbutyl)-2,5-dimethyl-1,2,3,4-tetrahydropyridine-2-carboxaldimine, b.p. 101–102° (0.5 mm.), $n^{20}D$ 1.4770, d^{20} 0.8693.

Anal. Calcd. for $C_{20}H_{38}N_2$: C, 78.36; H, 12.50; N, 9.14; neut. equiv., 153. Found: C, 78.24, 78.45; H, 12.41, 12.48; N, 8.94, 8.91; neut. equiv., 159.

The infrared absorption spectrum showed a band at 6.01 μ as might be expected from non-conjugated olefinic and imine linkages.

Hydrogenation of N-Methallylidene-1,3-dimethylbutylamine.—A 20-g. sample of N-methallylidene-1,3-dimethylbutylamine in 25 ml. of dioxane was hydrogenated over Raney nickel at 50–150° and 1500 p.s.i.g. Distillation gave 13 g. of N-isobutyl-1,3-dimethylbutylamine, b.p. 167–170°, $n^{20}D$ 1.4180.

The monoöxalate of the N-isobutyl-1,3-dimethylbutylamine was prepared by mixing equimolar amounts of the amine and an alcoholic solution of oxalic acid. After recrystallization from alcohol the derivative melted at 186–186.5°.

Anal. Calcd. for $C_{12}H_{25}NO_4$: C, 58.27; H, 10.19; N, 5.66. Found: C, 58.37, 58.30; H, 10.25, 10.24; N, 5.31, 5.38.

The boiling point of N-isobutyl-1,3-dimethylbutylamine[8] is 172.8°, $n^{20}D$ 1.4180.

There was no depression of melting point upon mixing with the monoöxalate of an authentic sample of N-isobutyl-1,3-dimethylbutylamine.

Reaction of Acrolein with N-(1,3-Dimethylbutylidene)-1,3-dimethylbutylamine.—One mole (56 g.) of acrolein was mixed with one mole (183 g.) of N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine. The mixture warmed slowly but was held at 35–40° by cooling for one hour. At this time 59 g. (32% recovery) of N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine was distilled to a kettle temperature of 100° (2 mm.). Very little lower boiling material was found. The residue was acidified and extracted with ether. The ether extract was discarded. The amines were liberated with sodium hydroxide and extracted with ether. The ether extract was dried and distilled to give 11 g. of N-(1,3-dimethylbutyl)-2-isopropylcyclohexenimine (V A or B) boiling at 84–85° (1 mm.), (5% conversion to product in 7% yield).

Anal. Calcd. for $C_{15}H_{27}N$: C, 81.4; H, 12.3; N, 6.3; neut. equiv., 221. Found: C, 80.9, 80.8; H, 12.1, 12.4; N, 6.3, 6.5; neut. equiv., 224.

Another run was made to determine the effect of anhydrous potassium carbonate on the reaction. One mole of N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine, one mole of acrolein and 100 g. of anhydrous potassium carbonate were mixed and stirred at 35–40° for four hours. The potassium carbonate was removed by filtration. Distillation of the filtrate gave 91 g. of N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine and 31 g. (14% conversion to product in 28% yield) of N-(1,3-dimethylbutyl)-2-isopropylcyclohexenimine boiling at 80–85° (0.5 mm.), $n^{20}D$ 1.4805.

In order to determine if any N-allylidene-1,3-dimethylbutylamine was formed but destroyed on distillation a third run was made identical with the first reaction of this series, except that the crude reaction product was immediately hydrogenated over Raney nickel at 150° and 1500 p.s.i. The hydrogenated product was acidified and steam distilled. Redistillation of the acid-insoluble material gave, besides 38 g. of 4-methyl-2-pentanol, a 16-g. fraction boiling at 111–113° (50 mm.), $n^{20}D$ 1.4599, d^{20} 0.9125. Analysis of this fraction indicates it to be an approximately equal mixture of 2-isopropylcyclohexanone and 2-isopropylcyclohexanol.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50; carbonyl 0.715 eq./100 g. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.75; hydroxyl, 0.705 eq./100 g. Calcd. for 46.8% $C_9H_{16}O$ and 53.2% $C_9H_{18}O$: C, 76.50; H, 12.07; carbonyl, 0.350 eq./100 g.; hydroxyl, 0.316 eq./100 g. Found: C, 76.34, 76.40; H, 12.12, 12.12; carbonyl, 0.350 eq./100 g.; hydroxyl, 0.316 eq./100 g.

The ketone and alcohol were probably formed during the hydrogenation by hydrolysis (due to water remaining in the Raney nickel catalyst) followed by partial hydrogenation of the cyclohexanone. A semicarbazone melted at 186° in agreement with the melting point of the semicarbazone of 2-isopropylcyclohexanone.[5] A light-orange 2,4-dinitrophenylhydrazone, m.p. 134–136°, gave an analysis in agreement with the 2,4-dinitrophenylhydrazone of 2-isopropylcyclohexanone.

Anal. Calcd. for $C_{15}H_{20}N_4O_4$: C, 56.2; H, 6.3; N, 17.5. Found: C, 56.0, 56.2; H, 6.3, 6.5; N, 17.0, 17.1.

Reaction of Crotonaldehyde with N-(1,3-Dimethylbutylidene)-1,3-dimethylbutylamine.—A mixture of 137 g. (0.75 mole) of N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine and 53 g. (0.75 mole) of crotonaldehyde was set aside to react at room temperature overnight. Distillation gave 69 g. of a mixture of crotonaldehyde and methyl isobutyl ketone and 79 g. of a product, b.p. 62° (10 mm.), 68% yield, whose analysis is in agreement with N-crotylidene-1,3-dimethylbutylamine.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N, 9.14. Found: C, 77.87, 77.77; H, 12.77, 12.74; N, 8.97, 8.94.

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[7] Adaptation of method of Calcott, Tinker and Weinmayr, THIS JOURNAL, **61**, 1010 (1939).

[8] Unpublished results of Ballard, Haury and Norton of this Laboratory. *Anal.* Calcd. for $C_{10}H_{23}N$: C, 76.36; H, 14.74; N, 8.91; neut. equiv., 157.3. Found: C, 76.43; H, 14.74; N, 8.89; neut. equiv., 157.8.