(48%) of methylenecyclohexane (IX), b.p. 100–101° (730 mm.), d^{25}_{25} 0.8000, $n^{25}D$ 1.4484. Infrared absorption spectrum of this methylenecyclohexane (IX) appeared to be identical with that of a sample of IX prepared from 1-methylcyclohexyl acetate (VIII).

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[Contribution from the Metcalf Chemical Laboratories, Brown University]

Selective Reduction of the Unsaturated Schiff Base System C=C—C=N; A Method for Reducing the Carbon–Carbon Double Bond of α,β-Unsaturated Aldehydes

By Eugene P. Goldberg[1] and Harold R. Nace

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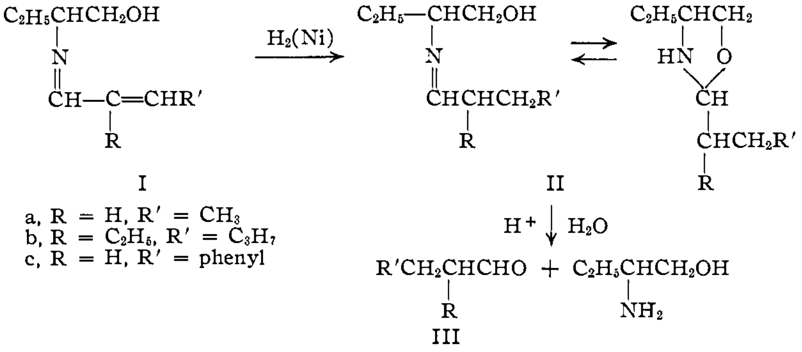
α,β-Unsaturated Schiff bases derived from 2-amino-1-butanol and crotonaldehyde, 2-ethyl-2-hexenal and cinnamaldehyde were hydrogenated at room temperature and 1–2 atmospheres using a Raney nickel catalyst. Only the C=C bond of the C=C—C=N system was saturated. This selective reduction is the basis for a new method of reducing α,β-unsaturated aldehydes to the corresponding saturated aldehydes.

In the course of a study of the reactions of 2-propyl-4-ethyloxazolidine and related compounds,[2a] it was found that the hydrogenation of 2-(2-ethyl-2-hexenylideneamino)-1-butanol with Raney nickel[2b] practically stopped after only the C=C bond had been saturated. This selective reduction of a C=C bond conjugated with a C=N bond suggested possible use as a method of reducing α,β-unsaturated aldehydes to the corresponding saturated aldehydes. In the past this has been accomplished by preparation of the aldehyde acetal, followed by reduction of the C=C bond and cleavage of the acetal, or, less satisfactorily, by direct hydrogenation of the aldehyde.

The reduction of α,β-unsaturated Schiff bases derived from 2-amino-1-butanol and three representative α,β-unsaturated aldehydes, crotonaldehyde (Ia), 2-ethyl-2-hexenal (Ib) and cinnamaldehyde (Ic) is reported here.



I

II

III

a, R = H, R' = CH_3
b, R = C_2H_5, R' = C_3H_7
c, R = H, R' = phenyl

2-(2-Butenylideneamino)-1-butanol (Ia) was prepared in ether in 66% yield from 2-amino-1-butanol and crotonaldehyde. When a methanol solution of Ia was subjected to room temperature, low pressure catalytic reduction with Raney nickel,[2b] a 57% yield of the previously reported[2a] 2-propyl-4-ethyloxazolidine (IIa-cyclic) was obtained. The reduction was rapid and hydrogen uptake practically ceased at one molar equivalent. When the resultant oxazolidine was itself subjected to comparable conditions of reduction, a 58% yield of 2-*n*-butylamino-1-butanol was obtained. The rate of this latter reduction was very slow and only 80% of the theoretical amount of hydrogen was used. These data indicate that saturation of only the C=C bond occurs because of a marked difference in the rates of reduction of the C=C and C=N bonds. The fact that a cyclic product was obtained from a Schiff base (IIa-cyclic from Ia) also is evidence for an oxazolidine–Schiff base equilibrium since IIa itself must equilibrate with IIa-cyclic.

Isolation of the unsaturated Schiff base Ia was found to be unnecessary since reduction of a methanolic solution of 2-amino-1-butanol and crotonaldehyde afforded a 77% yield of the oxazolidine (IIa-cyclic).

2-(2-Ethyl-2-hexenylideneamino)-1-butanol (Ib) has been reported previously[2a] to give a 71% yield of IIb. Consequently, a methanolic solution of 2-ethyl-2-hexenal and 2-amino-1-butanol was catalytically reduced and an 84% yield of IIb was obtained. Isolation of 2-ethylhexanal from the above reduction mixture was accomplished in 60% yield by hydrolysis and continuous ether extraction.

The reduction of a methanolic solution of cinnamaldehyde and 2-amino-1-butanol, followed by hydrolysis and continuous ether extraction, afforded a 49% yield of hydrocinnamaldehyde. The reduction of this system did not stop completely at one molar equivalent of hydrogen. Instead a fourfold decrease in the reduction rate was evidenced.

The intermediate hydrocinnamaldehyde-2-amino-1-butanol anhydro product could not be isolated from the reduction mixture, obviously due to decomposition during distillation. Attempts to prepare this anhydro compound by azeotroping water from a refluxing benzene solution of hydrocinnamaldehyde and 2-amino-1-butanol resulted in a 60% yield of material which decomposed upon distillation and failed to give satisfactory analytical data.

2-(3-Phenyl-2-propenylideneamino)-1-butanol (IIc) was obtained as a white solid melting at 59–61°. However, it was not characterized by

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[2] (a) H. R. Nace and E. P. Goldberg, This Journal, **75**, 3646 (1953); (b) R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

analysis or spectrum. It was reduced with Raney nickel[2b] to give results comparable to those obtained with the aldehyde–aminoalcohol mixture. There appeared to be no advantage in isolating the unsaturated Schiff base.

It is evident from the work reported here that the rate of reduction of the $C{=}C$ bond in the system $C{=}C{-}C{=}N$ is very much greater than that of the $C{=}N$ bond under the conditions used. From hydrogen uptake *vs.* time curves it has been estimated that the ratio of the reduction rate of the $C{=}C$ bond to the $C{=}N$ bond is 20:1 in the case of Ia and Ib, but only about 4:1 with Ic.

A simple and satisfactory method for reducing the $C{=}C$ bond of an α,β-unsaturated aldehyde has thus been developed. The procedure involves the the solution of the aldehyde and amino alcohol in methanol,[3] reduction, hydrolysis and extraction. This method also appears to be superior in some respects to the acetal procedure since the isolation of intermediates is unnecessary and neutral conditions may be maintained until the final hydrolysis.

It is quite likely that unsaturated conjugated Schiff base systems which do not possess the β-hydroxyl group (derived from simple amines) will behave similarly in this type of reduction. The comparative stability of amino alcohol–aldehyde anhydro products, as opposed to Schiff bases formed from aliphatic amines and aldehydes, motivated the use of an amino alcohol in this investigation. Only 2-amino-1-butanol was studied and no information is available at present on the use of other amino alcohols for this purpose.

Experimental[4]

2-(2-Butenylideneamino)-1-butanol.—A solution of 7.0 g. (0.1 mole) of crotonaldehyde and 8.9 g. (0.1 mole) of 2-amino-1-butanol in 50 ml. of ether was refluxed for 1.5 hours with 15 g. of anhydrous potassium carbonate. After removing the solvent from the filtered solution, the residue was distilled through a 100-mm. Vigreux column to yield 9.3 g. (66%) of the colorless 2-(2-butenylideneamino)-1-butanol, b.p. 100–102°(8 mm.). Redistillation through a semi-micro column[5] afforded an analytical sample, b.p. 70° (0.15 mm.), n^{25}_D 1.4900, d^{25}_4 0.9145; M_D 44.64, calcd. 43.22; λ_{max} 3.06 (shoulder), 3.22 (medium OH and NH stretch), 6.02 (strong), 6.14 (medium), 9.41 (medium-strong; 1° OH deformation).

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.20; H, 10.67; N, 10.16.

No change in the refractive index of this Schiff base was noted after standing 24 hours. However, after 2 months the material had polymerized to a red-brown plastic mass.

Reduction of 2-(2-Butenylideneamino)-1-butanol.—A solution of 7.05 g. (0.05 mole) of the Schiff base in 40 ml. of dry methanol was hydrogenated (room temperature, 1–2 atmospheres) with 1 g. of Raney nickel.[2b] After 30 minutes, the hydrogen uptake had almost ceased and 0.051 mole of hydrogen had been used. The catalyst and solvent were removed and the residue was distilled through a 100-mm. Vigreux column to yield 4.10 g. (57%) of 2-propyl-4-ethyloxazolidine, b.p. 65–69° (8 mm.), n^{25}_D 1.4393. The oxazolidine was characterized further by its infrared spectrum.

When 2.60 g. (0.018 mole) of the above oxazolidine, in 25 ml. of dry methanol, was hydrogenated with 0.5 g. of Raney nickel[2b] as reported previously,[2a] the reduction proceeded very slowly and only 0.014 mole of hydrogen was used after 3.5 hours. 2-*n*-Butylamino-1-butanol was isolated in 58% yield.

Reduction of a Mixture of 2-Amino-1-butanol and Crotonaldehyde.—A solution of 8.4 g. (0.12 mole) of crotonaldehyde and 10.7 g. (0.12 mole) of 2-amino-1-butanol in 100 ml. of dry methanol was shaken with 1 g. of Raney nickel[2b] as above. Reduction was complete after 60 minutes and 0.11 mole of hydrogen was consumed. Removal of the solvent and catalyst, followed by distillation of the residue through a 200-mm. Vigreux column, yielded 13.2 g. (77%) of 2-propyl-4-ethyloxazolidine, b.p. 65–70° (8 mm.), n^{25}_D 1.4391. The oxazolidine was characterized by its infrared spectrum and by hydrolysis in 2,4-dinitrophenylhydrazine reagent to the 2,4-dinitrophenylhydrazone of *n*-butyraldehyde (identified by mixture m.p. with an authentic sample).

Reduction of a Mixture of 2-Amino-1-butanol and 2-Ethyl-2-hexenal.—A solution of 8.90 g. (0.1 mole) of 2-amino-1-butanol and 12.60 g. (0.1 mole) of 2-ethyl-2-hexenal in 50 ml. of dry methanol was hydrogenated with 2 g. of Raney nickel[2b] as above. The reduction stopped after 1.5 hours and 0.098 mole of hydrogen had been used. After removal of the catalyst and solvent, the residue was divided into two equal parts. The first half was distilled through the semi-micro column[5] to afford 8.39 g. (84%) of 2-(2-ethyl-hexylideneamino)-1-butanol, b.p. 82–88° (0.25 mm.), n^{25}_D 1.4515. The α-naphthylurea derivative[6] melted at 123.5–126°, mixture m.p. with the α-naphthylurea of an authentic sample (m.p. 124.5–126°) 123.5–126°.

The second half of the above reduction residue was added to 30 ml. of 10% hydrochloric acid and allowed to stand 2.5 hours. Additional water was added and the resulting mixture was extracted with three 25-ml. portions of ether. The ether solution was washed with water and dried over anhydrous magnesium sulfate. Distillation through the semi-micro column yielded 1.32 g. (21%) of 2-ethylhexanal, b.p. 52–54° (15 mm.), n^{25}_D 1.4132. The 2,4-dinitrophenylhydrazone melted at 117–118.5°, mixture m.p. with the 2,4-dinitrophenylhydrazone of 2-ethylhexanal (m.p. 116.5–118°) 116.5–118.5°.

Repetition of the above reduction followed by continuous ether extraction of the acidic aqueous solution for 12 hours increased the yield of 2-ethylhexanal to 60%.

Reduction of 2-(3-Phenyl-2-propenylideneamino)-1-butanol.—2-Amino-1-butanol was treated with an equivalent amount of cinnamaldehyde in refluxing benzene as above to yield an oil which crystallized from heptane as white crystals, m.p. 59–61° (59%). This was assumed to be the Schiff base, 2-(3-phenyl-2-propenylideneamino)-1-butanol, although it was not characterized. A solution of 10.60 g. (0.052 mole) of this material in 60 ml. of dry methanol was hydrogenated with 1 g. of Raney nickel as above. The reduction was stopped after 20 minutes (0.057 mole of hydrogen had been used) when a decrease in the rate of hydrogen uptake was noted. The residue remaining after removal of the solvent and catalyst was hydrolyzed by warming for 15 minutes on a steam-bath with 20 ml. of hydrochloric acid in 150 ml. of water. The hydrolysis mixture was extracted with three 50-ml. ether portions. Distillation of the dried ether solution gave 2.96 g. (43%) of hydrocinnamaldehyde, b.p. 61–63° (0.5 mm.), n^{25}_D 1.5141. The semicarbazone melted at 125.5–127.5°, mixture m.p. with the semicarbazone of hydrocinnamaldehyde (m.p. 127–129°) 126–128°.

Reduction of a Mixture of 2-Amino-1-butanol and Cinnamaldehyde.—A solution of 13.2 g. (0.1 mole) of cinnamaldehyde and 8.9 g. (0.1 mole) of 2-amino-1-butanol in 50 ml. of dry methanol was hydrogenated with 0.5 g. of Raney nickel as above. After 60 minutes there was a decrease in the reduction rate and 0.1 mole of hydrogen had been used. The solvent and catalyst were removed and the residue was hydrolyzed by warming on a steam-bath for 10 minutes with 25 ml. of hydrochloric acid in 100 ml. of water. The resulting oil was extracted with three 75-ml. portions of ether. The ether extract was washed with sodium bicar-

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[3] Evidently the Schiff base is formed and reduced in solution.

[4] Melting points are corrected; boiling points are uncorrected. Infrared spectra were determined with a double beam spectrophotometer, described by D. F. Hornig, G. E. Hyde and W. A. Adcock, *J. Opt. Soc. Am.*, **40**, 497 (1950), using a sodium chloride prism. Liquid film samples, formed by pressing between polished calcium fluoride plates, were used. Microanalyses were performed by Mr. S. M. Nagy and Associates, Microchemical Laboratory, Mass. Institute of Technology, Cambridge, Mass.

[5] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

[6] The Schiff base reacts as the cyclic oxazolidine isomer yielding derivatives expected of a 2° amine. See E. P. Goldberg and H. R. Nace, THIS JOURNAL, **75**, 6260 (1953).

bonate solution, dried over magnesium sulfate and the ether residue distilled through the semi-micro column to yield 2.60 g. (20%) of hydrocinnamaldehyde; b.p. 62–63° (0.3 mm.), n^{25}_D 1.5182. The semicarbazone melted at 127.5–129°, mixture m.p. with the semicarbazone of hydrocinnamaldehyde (m.p. 127–129°) 127.5–129°.

Repetition of the above reduction, followed by continuous ether extraction of the acidified reduction residue for 21 hours, afforded 6.51 g. (49%) of hydrocinnamaldehyde; b.p. 83–86° (6 mm.), n^{25}_D 1.5200.

The intermediate 2-amino-1-butanol-hydrocinnamaldehyde anhydro compound could not be isolated from the hydrogenation mixture due to decomposition during distillation. Attempts to prepare this anhydro compound from 2-amino-1-butanol and hydrocinnamaldehyde gave a 50% yield of material, 2-(3-phenylpropyl)-4-ethyloxazolidine, that decomposed when distilled and could not be obtained analytically pure; b.p. 113–114° (0.2 mm.), n^{25}_D 1.5120, d^{25}_4 0.9990; M_D 61.75, calcd. 61.69.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.31; H, 9.36; N, 6.01.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

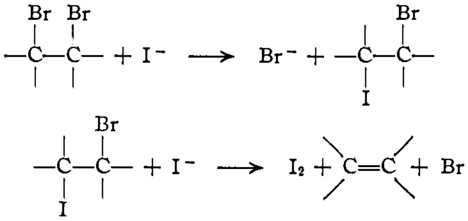
The Mechanism of the Transformation of Vicinal Dihalides to Olefins by Reaction with Iodide Ion[1]

BY JACK HINE AND W. H. BRADER, JR.

RECEIVED MAY 19, 1954

It is shown that the dehalogenation of ethylene bromide, propylene bromide and 1,2-dibromobutane by iodide ions is largely initiated by an S_N2 attack to form a bromoiodide which is directly dehalogenated. The dehalogenation of the 2,3-dibromobutanes is believed to be largely direct as previously suggested. In evidence is quoted the fact that ethylene bromide is the most reactive of the dibromides mentioned. Furthermore it is shown that the rate constant for the reaction of ethylene bromide is in excellent agreement with that which would be predicted for the S_N2 reaction of the compound with iodide ion under the conditions employed. It is improbable that a very large fraction of the reaction follows a path involving the formation of a vicinal diiodide. It is proposed that the dehalogenation reaction proper involves the formation of an intermediate in which one of the halogen atoms is bound equally to two carbon atoms.

The reaction of vicinal dihalides, particularly dibromides, with iodide ion to yield iodine and olefins has been known for some time. It has been suggested that the reaction involves the intermediate formation of a diiodide followed by its deiodination[2] and also that only the bromoiodide is an intermediate, and that this is transformed to the olefin directly[3] (mechanism I).

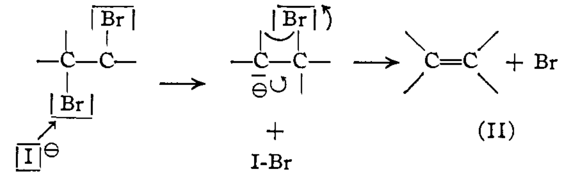


(I)

$$-\overset{Br}{\underset{|}{C}}-\overset{Br}{\underset{|}{C}}- + I^- \longrightarrow Br^- + -\overset{|}{\underset{I}{C}}-\overset{Br}{\underset{|}{C}}-$$

$$-\overset{|}{\underset{I}{C}}-\overset{Br}{\underset{|}{C}}- + I^- \longrightarrow I_2 + \rangle C{=}C\langle + Br^-$$

In addition Winstein, Pressman and Young[4] have proposed that the reaction is a direct dehalogenation of the dihalide and has a mechanism (II) somewhat analogous to the E2 mechanism[5] for β-elimination reactions.



(II)

I-Br + $2I^- \longrightarrow I_3^- + Br^-$

Evidence for Mechanism I.—Kinetic data are available to show that the reaction follows good second-order kinetics, first order in iodide ion and alkyl halide, for a considerable variety of dibromides when allowance is made for the combination of the iodine formed with unreacted iodide ion.[2–4,6,7] Mechanisms involving the intermediate formation of the diiodide and/or the bromoiodide would give uncomplicated second-order kinetics only if the first step, which would have to be a bimolecular nucleophilic attack (S_N2)[8] by iodide ion on carbon, were rate controlling and the subsequent steps comparatively rapid. Since simple second-order kinetics are observed, it seems unlikely that much of the reaction proceeds by the diiodide mechanism because this would require the second bromine atom to undergo S_N2 displacement much more rapidly than the first, implying that it is activated by the first iodine atom introduced. This seems unreasonable, since in the only case which appears to have been studied, β-fluorine, -chlorine and -bromine all have about the same effect on S_N2 reactivity,[9] and the effect of all four halogens has been found to be approximately the same in the γ-position.[10]

In order for mechanism I to fit the observed kinetics the initial S_N2 displacement must be slow compared to the subsequent dehalogenation of the bromoiodide. That this subsequent reaction of the bromoiodide is indeed relatively fast is shown by the fact that the dehalogenation of ethylene bromoiodide[11] proceeds about ten times as rapidly

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(1) Paper IV in the series "The Effect of Halogen Atoms on the Reactivity of Other Halogen Atoms in the Same Molecule." For paper III see ref. 9.

(2) C. F. van Duin, *Rec. trav. chim.*, **43**, 341 (1924); **45**, 345 (1926); **47**, 715 (1928).

(3) E. Biilmann, *ibid.*, **36**, 313 (1917).

(4) S. Winstein, D. Pressman and W. G. Young, THIS JOURNAL, **61**, 1645 (1939).

(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, chap. VIII.

(6) T. L. Davis and R. Heggie, *J. Org. Chem.*, **2**, 470 (1937).

(7) R. T. Dillon, THIS JOURNAL, **54**, 952 (1932).

(8) For the significance of this term see C. K. Ingold, ref. 5, chap. VII.

(9) J. Hine and W. H. Brader, Jr., THIS JOURNAL, **75**, 3964 (1953).

(10) W. H. Brader, Jr., Ph.D. Thesis, Georgia Institute of Technology, 1954.

(11) A. Slator, *J. Chem. Soc.*, **85**, 1697 (1904).