

was diluted with ethanol as before and submitted to ultraviolet analysis. Trituration of the oil with pentane and recrystallization from aqueous methanol and hexane-benzene yielded 0.32 g. of the ketone III, m.p. and mixed m.p. 58–59°.

A second rearrangement was carried out as above with amino alcohol, m.p. 84.5–85°, which had been recrystallized four more times from hexane-benzene. Again the neutral fraction was analyzed as described below.

Ultraviolet Analyses.—The quantitative results were obtained with a Beckman DU spectrophotometer. Determination of the extinction coefficients of solutions of known concentrations of ketones II and III (between 15 and 30 mg./l.) showed that Beer's law holds in this region. The

extinction coefficients of the unknown mixtures measured at four wave lengths together with the corresponding extinction coefficients of the authentic ketones (II and III) were used to set up four pairs of simultaneous equations which were solved for the concentrations of II and III. Weights were assigned to the values so obtained²² and the weighted averages together with the calculated probable errors are shown in Table I.

(22) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1943, p. 487 ff.

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Pyrolysis of Esters. II. Direction of Elimination in Pyrolysis of Tertiary Esters^{1,2}

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Pyrolysis of three tertiary esters, *t*-amyl acetate, dimethylisopropylcarbinyl acetate, and 1-methylcyclohexyl acetate, produced only the least highly alkylated olefin. A method is outlined for the isomerization of an internal double bond to the terminal position.

We have shown¹ that in the pyrolysis of esters of secondary alcohols the elimination follows the Hofmann rule, which predicts the formation of the least highly alkylated olefin. The pyrolysis of simple alkyl esters, however, in contrast to other elimination reactions, does not give a mixture of products but appears to produce only a single olefin. Thus, the only product isolated from the pyrolysis of methylisopropylcarbinyl acetate was 3-methyl-1-butene.

The esters previously studied, however, were all derived from secondary alcohols. In order to show that this selectivity is general, several tertiary esters were pyrolyzed. Pyrolysis conditions were again selected so that much less than 100% of the acetic acid was eliminated in order to make sure that no carbonization that could cause isomerization took place. It was previously shown⁶ that carbonization in the pyrolysis tube would cause isomerization of double bonds but that, if carbonization was avoided, the pyrolysis of esters could be used to synthesize 1,2-dimethylene-4-cyclohexene, an isomer of *o*-xylene. These mild conditions also appeared to produce the maximum selectivity in the direction of elimination. Pyrolysis of dimethylisopropylcarbinyl acetate (I), where the choice is between a primary and a tertiary hydrogen, produced only 2,3-dimethyl-1-butene (II). Since the properties of 2,3-dimethyl-2-butene differ markedly from those of II, it is certain that the product of this pyrolysis was at least 98% pure. The pyrolysis of *t*-amyl acetate (III), in which the competition

of abstraction is between primary and secondary hydrogens, yielded only 2-methyl-1-butene (IV). Because of the moderate difference in physical properties of IV and 2-methyl-2-butene (V) and the limit of accuracy of the method used to determine the purity, it can only be said that the IV obtained by pyrolysis was at least 95% pure. In accordance with the observation of Rehberg and Fisher,⁷ these tertiary esters decompose at a temperature at least 50° lower than the isomeric secondary esters.

In an effort to determine the strength of the driving force to produce only the least highly alkylated olefin, a case was found where the predicted olefin would be slightly strained. It has been shown that a double bond is more stable endocyclic to a cyclohexane than exocyclic to it.⁸ It appeared that derivatives of the tertiary alcohol, 1-methylcyclohexanol (VI), would provide a suitable test. Mosher⁹ had shown that dehydration of VI with iodine produced only 1-methylcyclohexene, and the fact that no formaldehyde was obtained on ozonolysis indicated the absence of any methylenecyclohexene (IX). The tertiary alcohol VI, which was prepared from cyclohexanone and methylmagnesium iodide, was acetylated with acetic anhydride and magnesium to produce 1-methylcyclohexyl acetate (VIII). Pyrolysis of VIII at 450° produced only the methylenecyclohexane (IX). Since the properties of the isomeric VII are moderately close to those of IX, the purity of IX was proved by independent synthesis. Cyclohexanecarboxylic acid (X) was reduced with lithium aluminum hydride to produce hexahydrobenzyl alcohol (XI), which was acetylated to give hexahydrobenzyl acetate (XII). Pyrolysis of XII at 530° produced pure IX. The infrared absorption spectrum of this methylenecyclohexane

(1) Previous paper in this series, *THIS JOURNAL*, **77**, 75 (1955).

(2) Presented in part before the Division of Organic Chemistry at the 120th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

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(5) Office of Naval Research Fellow, Wayne University, 1948–1950; Research Corporation Fellow, Wayne University, 1950–1952.

(6) W. J. Bailey, J. Rosenberg and L. H. Young, *THIS JOURNAL*, **76**, 2251 (1954); W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).

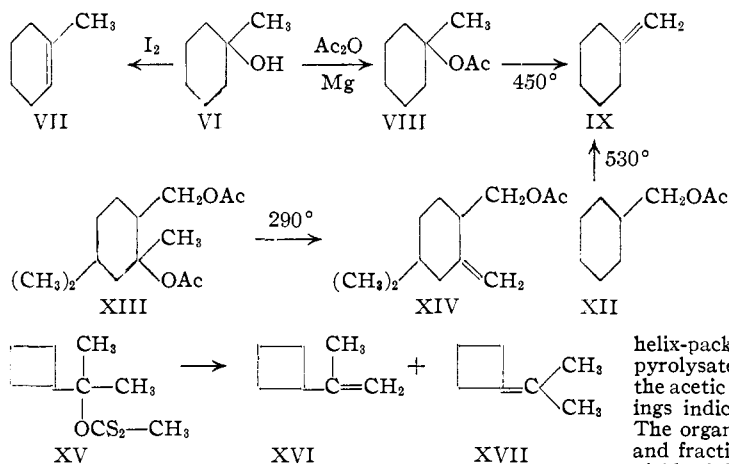
(7) C. E. Rehberg and C. H. Fisher, *ibid.*, **67**, 56 (1945).

(8) S. F. Birch, G. A. R. Kon and W. S. G. P. Norris, *J. Chem. Soc.*, 1361 (1923).

(9) W. A. Mosher, *THIS JOURNAL*, **62**, 552 (1940).

(IX) appeared to be practically identical with that of the IX produced from VIII. Arnold¹⁰ had previously shown that pyrolysis of XII produced IX. It can be concluded, therefore, that the driving force to produce the terminal olefin is so great that it is able to overcome the strain of the exocyclic double bond.

The direction of elimination in the pyrolysis of esters is surprising in view of the prediction of Barton. He suggested, on the basis of other *cis* eliminations, that the hydrogen should be extracted in the order $-\text{CH} > -\text{CH}_2 > -\text{CH}_3$.¹¹ Work is in progress to apply the present method of pyrolysis



to some of the cases, such as *l*-menthyl acetate, quoted in his paper.

The fact that the pyrolysis presumably gives the least stable olefin makes possible an excellent method for isomerizing a double bond from an internal position in a molecule to a terminal position. Since *t*-amyl alcohol or *t*-amyl acetate (III) can be synthesized from 2-methyl-2-butene (V), a very short procedure is available for isomerizing V to the isomeric 2-methyl-1-butene (IV). Presumably, this method will work for any olefin containing a methyl substituent.

Brenner and Schinz¹² have recently reported an application of the pyrolysis of a tertiary ester to the synthesis of cyclolavandulol acetate (XIV). Even though their pyrolysis was carried out in the liquid phase, heating the tertiary acetate XIII produced a 52% yield of the unsaturated XIV.

The vapor phase pyrolysis of esters appears to be superior to the liquid-phase Chugaev reaction for selectivity. Kazansky¹³ reported that thermal decomposition of the tertiary xanthate XV produced a mixture of the two isomeric olefins XVI and XVII.

Experimental¹⁴

Pyrolysis of Dimethylisopropylcarbinyl Acetate (I).—At a rate of 1 gram/minute 150 g. (1.04 moles) of dimethylisopropylcarbinyl acetate (I), b.p. 73° (80 mm.), n_{D}^{25} 1.4052 [reported¹⁵ b.p. 143–144°, n_{D}^{20} 1.4182], was pyrolyzed at

(10) R. T. Arnold, *THIS JOURNAL*, **70**, 2591 (1948).

(11) D. H. R. Barton, *J. Chem. Soc.*, 2174 (1949).

(12) A. Brenner and H. Schinz, *Helv. Chim. Acta*, **35**, 1333 (1952).

(13) B. A. Kazansky, *Ber.*, **69B**, 950 (1936).

(14) The authors are indebted to Vivian Kapuscinski for the analyses.

(15) L. Henry, *Bull. Acad. roy. Belg.*, 285 (1907).

400° over a period of 90 minutes, as previously described.¹ Titration of the aqueous extracts of the pyrolysate indicated that 81% of the acetic acid had been liberated. Fractionation of the dried organic layer through a 6-inch, helix-packed column yielded 64 g. (76%) of 2,3-dimethyl-1-butene (II) in thirty-eight fractions, b.p. 55.5–57.8°, n_{D}^{20} 1.3888–1.3915 [reported b.p. 55.0–57.5° (760 mm.)],¹⁶ n_{D}^{20} 1.3912,¹⁷ 1.3897¹⁸. Physical constants reported for the isomeric hydrocarbon, 2,3-dimethyl-2-butene, are b.p. 72.3–72.6° (747 mm.) and n_{D}^{20} 1.4115.¹⁹

Pyrolysis of *t*-Amyl Acetate (III).—Two hundred grams (1.54 moles) of *t*-amyl acetate (III), b.p. 62–64° (97 mm.), n_{D}^{20} 1.3980 [reported²⁰ b.p. 124–125°, n_{D}^{25} 1.3995], was pyrolyzed at 400° over a period of 2 hours, as previously described. Titration of the aqueous extracts with standard base indicated that 65% of the acetic acid was liberated.

Fractionation through a 6-inch, helix-packed column yielded forty fractions, amounting to 64 g. (59%) of 2-methyl-1-butene (IV), b.p. 30–33° (748 mm.), n_{D}^{20} 1.3775–1.3798 [reported b.p. 31–33° (760 mm.)],²¹ n_{D}^{20} 1.3783²². Data for the isomeric hydrocarbon, 2-methyl-2-butene (V), are b.p. 38–40° (760 mm.)²³ and n_{D}^{20} 1.3878.²²

Pyrolysis of 1-Methylcyclohexyl Acetate (VIII).—With the pyrolysis apparatus that has been previously described, 114 g. (0.73 mole) of 1-methylcyclohexyl acetate (VIII), b.p. 177–178° (740 mm.), n_{D}^{25} 1.4355, $d_{\text{4}^{25}}$ 0.9545 [reported²⁴ b.p. 182–187°, $d_{\text{4}^{18}}$ 0.954, n_{D}^{18} 1.4386], was pyrolyzed over a 135-minute period by dropping the liquid through a 12-inch,

helix-packed Vycor tube externally heated at 450°. The pyrolysate was extracted several times with water to remove the acetic acid. Titration of an aliquot of the aqueous washings indicated that 66% of the acetic acid was liberated. The organic layer was dried over anhydrous sodium sulfate and fractionated through a 6-inch, helix-packed column to yield 40.0 g. (56%) of methylenecyclohexane (IX), b.p. 101–102° (738 mm.), n_{D}^{25} 1.4484, $d_{\text{4}^{25}}$ 0.8004 [reported²⁵ b.p. 101–102° (738 mm.), $d_{\text{4}^{25}}$ 0.803, n_{D}^{20} 1.448].

Data for the isomeric 1-methylcyclohexene (VII) are b.p. 110° (769 mm.), n_{D}^{20} 1.450 and $d_{\text{4}^{20}}$ 0.811.⁹

Hexahydrobenzyl Alcohol (XI).—To 80.0 g. (2.1 moles) of lithium aluminum hydride and 1 liter of anhydrous ether in a 3-liter, three-necked flask, equipped with a stirrer, a dropping funnel and a reflux condenser, 256 g. (2.0 moles) of cyclohexanecarboxylic acid (X) was added dropwise. After the reaction mixture had been stirred overnight, the complex was decomposed with 5% hydrochloric acid. The ether layer was washed with a saturated sodium bicarbonate solution, then with water, and was dried over anhydrous sodium sulfate. The ether was removed by distillation and the residue was fractionated through a 6-inch, helix-packed column to yield 171 g. (75%) of hexahydrobenzyl alcohol (XI), b.p. 92–93° (24 mm.), $d_{\text{4}^{25}}$ 0.9203, n_{D}^{25} 1.4628 [reported²⁶ b.p. 88–89° (22 mm.), $d_{\text{4}^{25}}$ 0.9215, n_{D}^{25} 1.4640].

Pyrolysis of Hexahydrobenzyl Acetate (XII).—By the procedure described above, 86 g. (0.554 mole) of hexahydrobenzyl acetate (XII), b.p. 111° (44 mm.), $d_{\text{4}^{25}}$ 0.9566, n_{D}^{25} 1.4427 [reported¹⁰ b.p. 195–196° (745 mm.)], that was prepared by heating the hexahydrobenzyl alcohol (XI) with acetic anhydride, was pyrolyzed at 530°. The pyrolysate was extracted several times with water, and titration of an aliquot of the combined aqueous extracts indicated that 51% of the acetic acid was liberated. The organic layer was dried over anhydrous sodium sulfate and fractionated through a 6-inch, helix-packed column to yield 25.5 g.

(16) C. G. Schmitt and C. E. Boord, *THIS JOURNAL*, **54**, 751 (1932).

(17) I. N. Nassurov, *Ber.*, **69B**, 18 (1936).

(18) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughn, *THIS JOURNAL*, **58**, 137 (1936).

(19) I. Schurman and C. E. Boord, *ibid.*, **55**, 4930 (1933).

(20) J. C. Munch, *ibid.*, **43**, 997 (1926).

(21) J. F. Norris and J. M. Houbert, *ibid.*, **49**, 873 (1927).

(22) M. Siemons, Thesis, Mount Holyoke College, 1929.

(23) J. F. Norris and R. Reuter, *THIS JOURNAL*, **49**, 2624 (1927).

(24) W. Ipatiew, *Ber.*, **45**, 3217 (1912).

(25) G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publ. Corp., New York, N. Y., 1940, pp. 160, 326.

(26) G. S. Hiers and R. Adams, *THIS JOURNAL*, **48**, 2388 (1926).

(48%) of methylenecyclohexane (IX), b.p. 100–101° (730 mm.), d_{20}^{25} 0.8000, n_D^{25} 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

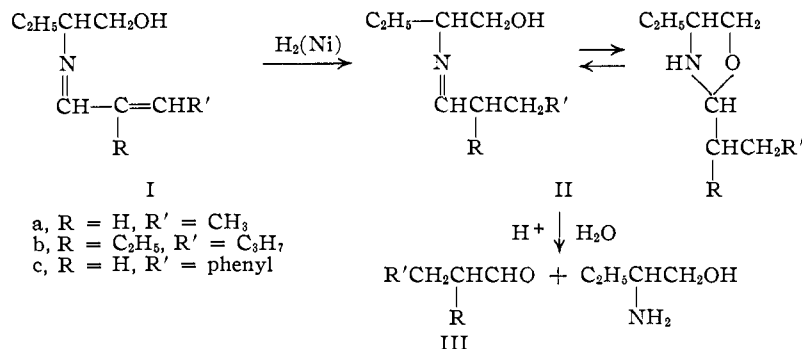
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α,β -Unsaturated Schiff bases derived from 2-amino-1-butanol and crotonaldehyde, 2-ethyl-2-hexenal and cinnamaldehyde were hydrogenated at room temperature and 1–2 atmospheres using a Raney nickel catalyst. Only the C=C bond of the C=C—C=N system was 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.



2-(2-Butenylideneamino)-1-butanol (Ia) was prepared in ether in 66% yield from 2-amino-1-butanol and crotonaldehyde. When a methanolic 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

(1) Brown University Fellow 1952–1953; New Product Development Laboratory, General Electric Co., Pittsfield, Mass.

(2) (a) H. R. Nace and E. P. Goldberg, *THIS JOURNAL*, **75**, 3646 (1953); (b) R. Mazingo, *Org. Syntheses*, **21**, 15 (1941).