and then all of the colored material went into the organic layer; the blue solid recovered could not be crystallized. Efforts to obtain material of analytical purity corresponding to IV were unsuccessful.

1-Benzyl-3-chloroazulene (V).—To a solution of 35.5 mg. (0.163 mmole) of 1-benzylazulene in 10 ml. of dimethylformamide was added 22 mg. (0.165 mmole) of N-chlorosuccinimide. The reaction mixture slowly turned green and after a few hours it was allowed to stand in a refrigerator (at *ca.* 10°) overnight. The mixture was poured into water, the whole extracted with ether, and the green ether layer was then washed several times with water. Removal of the solvent left a green oil which was chromatographed on basic alumina. Elution with petroleum ether developed a blue band and a green band. The blue band was eluted with a 25:1 petroleum ether–methylene chloride solvent and afforded 30 mg. (73%) of 1-benzyl-3-chloroazulene as a blue-green oil. A cyclohexane solution showed λ_{max} in mμ (D_{max}) in the ultraviolet at 238 (0.43), 287 (1.04), 328 (0.04), 336 (0.07), 343 (0.09), 351 (0.13), 368 (0.12) with a shoulder at 293 (0.85), and in the visible at 629 (1.31), 660 (1.12), 689 (1.10), and 772 (0.39) with shoulders at 584 (0.91), 609 (1.16), and 730 (0.49). The infrared spectrum was essentially identical to that of the product obtained from the sodium borohydride reduction of the presumed [1-(3-chloroazulyl)]tropenium fluoroborate (below). The n.m.r. spectrum showed resonance peaks centered at 5.65 p.p.m. (saturated hydrogens), 2.89 p.p.m. (phenyl hydrogens), and for the azulene ring hydrogens at 2.52 p.p.m. (2-position), 2.54 p.p.m. (6-position), 1.89 and 1.78 p.p.m. (4- and 8-positions). The peaks for the 5- and 7-hydrogens were partially covered by the large phenyl hydrogen peak and the centers for these could not be determined.

Reaction of Presumed [1-(3-Chloroazulyl)]tropenium Fluoroborate (IV) with Sodium Borohydride.—Freshly chromatographed 1-tropenyl-3-chloroazulene (117 mg., 0.463 mmole) and triphenylmethyl fluoroborate (149 mg., 0.452 mmole) were allowed to react in the same manner as described above. The acetonitrile was removed (rotary evaporator) and the residue was subjected to a pressure of *ca.* 0.3 mm. (vacuum pump) for several minutes. The almost black crystalline material was then triturated with two 50-ml. portions of dry petroleum ether, a 50-ml. portion of dry ether, and a further 50-ml. portion of petroleum ether. The last two extracts were almost colorless. Removal of the solvent from the combined triturates and chromatography of the residue gave 22.5 mg. (21%) of triphenylmethane, 61 mg. of 1-triphenylmethyl-3-chloroazulene (isolated and characterized as described above), and 7 mg. of a green oil.

The brown, semicrystalline residue was triturated with methylene chloride and the green solution decanted from undissolved tropenium fluoroborate (identified as previously described). The methylene chloride was removed *in vacuo* and about 20 ml. of dry acetonitrile distilled onto the residue. To the dark green solution which formed was added 15 mg. (0.396 mmole) of sodium borohydride. The color of the solution immediately turned to a dark blue, then to a lighter blue and finally to a blue-green, all within a few minutes. The reaction mixture was poured into water and the whole extracted with petroleum ether. Removal of the solvent from the extract left a blue-green oil which was chromatographed on basic alumina. Petroleum ether eluted 11.5 mg. of triphenylmethane and then two blue-green fractions. From the second fraction was obtained 11 mg. of a green oil. The first fraction was rechromatographed. Petroleum ether eluted an additional 3.5 mg. of triphenylmethane, and a blue band having a blue-green tail developed. The main portion of this band was removed with 20:1 petroleum ether–methylene chloride and afforded 36 mg. of a blue-green oil. Continued elution removed the trailing portion which gave an additional 11 mg. of the green oil obtained from the second blue-green fraction. This green oil and the one obtained from the petroleum ether trituration prior to reduction had essentially identical ultraviolet and visible spectra. A cyclohexane solution of each showed λ_{max} in mμ (D_{max}) in the ultraviolet at 240 (0.76), 283 (1.26), 288 (1.30), 295 (1.24), 300 (1.23), 354 (0.18), and 370 (0.18) with a shoulder at 347 (0.14), and in the visible at 630 (1.27), 660 (1.10), 690 (1.09), and 774 (0.39) with shoulders at 585 (0.93), 610 (1.14), and 735 (0.49). The infrared spectra of the two oils were slightly different. The ultraviolet, visible, and infrared spectra of both oils were very similar to those of 1-tropenyl-3-chloroazulene (III) and on this basis the oils are postulated to be tautomeric isomers of III. The elementary analysis was performed on the product isolated after reduction.

Anal. Calcd. for $C_{17}H_{13}Cl$: C, 80.79, H, 5.18. Found: C, 81.30; H, 5.55.

A cyclohexane solution of the blue-green oil (which was not analytically pure) exhibited λ_{max} in mμ in the ultraviolet at 239, 287, 328, 336, 343, 352, and 368 with a shoulder at 293 and in the visible at 630, 660, 690, and 773 with shoulders at 586, 610, and 732. A sample for analysis was obtained by taking a center cut of the band upon rechromatography and heating the recovered oil at 65° *in vacuo* (0.2 mm.) for 2 days. The infrared and n.m.r. spectra of this material were essentially identical to those of the product from the chlorination of 1-benzylazulene (above) and both are therefore indicated to be 1-benzyl-3-chloroazulene.

Anal. Calcd. for $C_{17}H_{13}Cl$: C, 80.79, H, 5.18. Found: C, 80.90; H, 5.48.

Acknowledgment.—The authors are indebted to M. T. J. Pratt and Dr. D. Bertelli for the triphenylmethyl fluoroborate used in this study.

Selective Catalytic Hydrogenation of Nitroölefins

WOLFGANG K. SEIFERT AND PAUL C. CONDIT

California Research Corporation, Richmond, California

Received July 16, 1962

The objective of this study was the catalytic hydrogenation of a straight-chain and a cyclic conjugated 1-nitroölefin to the corresponding oximes. The formation of nitroalkane was also investigated. 1-Nitro-1-octadecene and 1-nitrocycloöctene were chosen as model compounds. Their convenient synthesis was reported recently.[1]

The examples of catalytic hydrogenation of nitroolefins to oximes reviewed in the literature[2,3] are limited to compounds of the nitrostyrene type. Hydrogenation of substituted nitrostyrenes[4] with palladium on carbon in pyridine gives the corresponding oximes. Phenylacetaldoxime[5] was obtained from 1-phenyl-2-nitroethylene if the hydrogenation was carried out with platinum catalyst in alcohol containing a small amount of acid; the use of alcohol without the acid[5,6] leads to 1,4-dinitro-2,3-diarylbutane. The conversion of conjugated nitroölefins to nitroöalkanes by catalytic methods using neutral media has been studied[7] for various types of nitroölefins.

Table I summarizes our data on selective hydrogenation of 1-nitrocycloöctene I to cycloöctanoneoxime II and nitrocycloöctane III and of 1-nitro-1-octadecene IV to stearaldoxime V and 1-nitroöctadecane VI.

All reactions were carried out with palladium-on-carbon catalyst using 1.3–4 wt. % palladium metal based on nitroölefin. 1-Nitrocycloöctene I was quantitatively converted into a 5:1 mixture of cycloöctanone-oxime II and cycloöctanone VII. Whether 1.0 or 0.5 mole of hydrogen chloride was used per mole of I

(1) W. K. Seifert, *J. Org. Chem.*, **27**, 125 (1963), this issue.
(2) Houben-Weyl, "Methoden Der Organischen Chemie," Vol. XI/1, Georg Thieme Verlag, Stuttgart, 1957, pp. 382–394.
(3) N. Levy and J. D. Rose, *Quart. Rev.*, **1**, 385 (1947).
(4) B. Reichert and H. Marquardt, *Pharmazie*, **5**, 10 (1950), and previous papers.
(5) E. P. Kohler and N. L. Drake, *J. Am. Chem. Soc.*, **45**, 1281 (1923).
(6) A. Sonn and A. Schellenberg, *Chem. Ber.*, **50**, 1513 (1917).
(7) (a) H. Cerf de Mauny, *Bull. soc. chim. France*, [5], **7**, 133 (1940); (b) J. C. Sowden and H. O. L. Fischer, *J. Am. Chem. Soc.*, **69**, 1048 (1947); (c) C. D. Hurd, U. S. Patent 2,483,201 (September 27, 1949).

TABLE I

THE SELECTIVE HYDROGENATION OF 1-NITROCYCLOÖCTENE AND 1-NITRO-1-OCTADECENE[a]

Run	Nitro-olefin	Solvent	HCl/nitro-olefin (moles)	Wt. % pyridine in methanol	Mole % composition of crude products: Oxime II	Oxime V	Nitroalkane III	Nitroalkane VI	Carbonyl compound VII[d]	Carbonyl compound (VIII)[e]	H_2/nitro-olefin (moles)
1	I	Methanol	1	..	83[b]	..	0	..	17[b]	..	2.1
2	IV	Methanol	0.5	..	..	73	..	2	..	13[c]	1.8
3	I	Pyridine	..	..	60[b]	..	3	..	Trace	..	2.5[f]
4	IV	Pyridine	..	..	..	60	..	..	..	..	1.9[f]
5	I	Methanol	..	1.3	Trace	..	83	..	10	..	1.0
6	IV	Methanol	..	2.0	..	Trace	..	50[c]	..	10[e]	1.1

[a] See Experimental for conditions and analytical procedures. [b] The analytical values were confirmed by isolation of the pure compounds by distillation. [c] Isolated by chromatography. [d] VII = cycloöctanone. [e] The values are estimated and based on the assumption that the carbonyl compound is stearaldehyde VIII. [f] The amounts of consumed hydrogen given are corrected for hydrogenation of pyridine which was determined separately.

had no effect on the product composition. If, however, only 0.05 mole of hydrogen chloride was employed, the initial rate of hydrogenation was faster than in the experiments with the higher acidity at constant catalyst concentration and the yield of oxime II decreased, while the amount of ketone VII stayed constant. The infrared spectrum of the crude product of run 2 showed a carbonyl absorption: if the latter is assigned to stearaldehyde VIII (its formation would be analogous to the formation of ketone VII from nitro-olefin I), the amount of VIII is estimated at about 13%.

With pyridine as solvent, the rate of hydrogenation of both nitroölefins (runs 3 and 4) was significantly slower than with acidic methanol. Pyridine itself was hydrogenated slowly under the conditions of the reaction. Piperidine can add[8] to nitroölefins. Reactant stability tests in pyridine without hydrogen and with amounts of added piperidine corresponding to that assumed to be formed by hydrogenation of pyridine showed that the straight-chain nitroölefin IV was much less stable than the cyclic nitroölefin I. The latter had been found to be perfectly stable in acidic methanol. Thus, the lower yields of oximes in pyridine are explained.

The selective hydrogenation of the double bond succeeded to a different extent with both nitroölefins (runs 5 and 6). The rate of hydrogenation of the cyclic nitroölefin I decreased sharply after one mole of hydrogen had been consumed per mole of nitroölefin. In the reduction of 1-phenyl-2-nitroethylene in neutral alcohol[5] or acetic acid[6] solvent with platinum catalyst, 1,4-dinitro-2,3-diarylbutane had been obtained. A molecular weight determination of the isolated product of run 6 showed that it was monomeric VI. Other workers[7a] had reported a good yield of 1-nitroöctane by hydrogenation of 1-nitro-1-octene with a small amount of platinum in acetone. With 1-nitro-1-octadecene IV and amounts of platinum from 1–10%, our analyses indicated the presence of 34–43% of 1-nitro-1-octadecane VI in the crude product.

The origin of cycloöctanone VII in run 1 is of interest. Theoretically, it might arise (1) from hydrolysis of oxime II since water is formed in the reaction, (2) from hydrogenation of some oxime II to the imine and subsequent hydrolysis, or (3) from 1,4-addition of hydrogen to I and subsequent Nef[9] decomposition of the resulting *aci*-form of III to nitrous oxide and VII. The first possibility was excluded since it was shown that pure oxime II was not hydrolyzed under the conditions of run 1 with added water and without hydrogen; oxime V was stable to hydrolysis under the work-up conditions of run 2. While the Nef reaction of III was not investigated, further hydrogenation of oxime II was found to occur to some extent since one mole of cycloöctanone-oxime hydrochloride consumed two moles of hydrogen during thirty hours under conditions of run 1.

Although cycloöctanone VII can be separated by distillation from its oxime II, the ketone VII was converted quantitatively to oxime II by treatment of the crude reduction product of run 1 with hydroxylamine and a sodium acetate–acetic acid buffer in methanol solvent, thus giving II in >90% yield of theory. The hydrogenation of crude 1-nitrocycloöctene I, as prepared by addition of dinitrogen tetroxide to cyclooctene and elimination with triethylamine,[1] has provided cycloöctanoneoxime in an over-all yield of at least 83% (based on olefin).

Experimental

Melting points are uncorrected.

Analytical Technique.—The data of Table I were determined by quantitative infrared analysis. They represent mole per cent composition of the crude yields which were 94–97% for runs 1–5 and 90% for run 6. In several cases (footnotes *b* and *c*, Table I), the pure compounds were isolated from the crude products; the isolated yields were 1–5% lower than the analytical values. The methods applied are described in a previous paper.[1]

All spectra were measured in carbon tetrachloride. The amounts of compounds III, VI, and VII were determined by the ratio method.[1] Oxime V was analyzed by measuring the intensity of the free OH absorption. Oxime II was analyzed by both methods, and the two types of analyses agreed within 5% in all cases. The free OH absorptions of the oximes were determined at concentrations of $<0.4 \times 10^{-3}$ mole/l., using *dry* carbon tetrachloride solvent and 9-cm. quartz cells. In concentrations $> 0.4 \times 10^{-3}$ mole/l., hydrogen bonding disturbed the measurements. The oximes were analyzed with a Beckman IR 4 infrared spectrophotometer. A Perkin–Elmer Infracord spectrophotometer served for the determination of the other compounds.

Hydrogenation.—The reactions were carried out on a 2–50 mmole scale at room temperature and 10–60 p.s.i. hydrogen pressure using a Parr hydrogenator with 80–500 ml. reaction vessels. In runs 1, 2, 5, and 6, catalyst and solvent were prehydrogenated. The catalyst was 5% palladium on carbon; its percentage, as given below, is wt. % palladium metal based on nitroölefin.

Cycloöctanoneoxime (II) (Run 1).—A solution of 5.43 g. (35 mmoles) of 1-nitrocycloöctene[1] in 175 ml. methanol containing 35 mmoles of dry hydrochloric acid was hydrogenated with 3.25 g. of catalyst (3% palladium). During 6 min., the reaction temperature increased from 26 to 32° and 2 moles of hydrogen was consumed per mole of nitroölefin. The reaction was continued

(8) D. E. Worral, *J. Am. Chem. Soc.*, **49**, 1598 (1927).

(9) (a) W. E. Noland, *Chem. Rev.*, **55**, 137 (1955); (b) H. Feuer and A. T. Nielsen, *J. Am. Chem. Soc.*, **84**, 688 (1962).

for 10 min. longer with very small consumption of hydrogen. After addition of 35 mmoles of sodium acetate, the catalyst was filtered and extracted with methanol. The combined methanolic solutions were vacuum-concentrated to about 20 ml. After addition of 200 ml. of water, the mixture was extracted with ether and the combined ethereal solutions were washed with sodium bicarbonate solution and water. After vacuum evaporation of the ether and water, 4.61 g. (96% yield) of crude product was obtained which analyzed (infrared) for 83% cycloöctanoneoxime and 17% cycloöctanone. The vapor phase chromatogram of this crude product showed that the two major compounds were nearly uncontaminated with other by-products. An aliquot of the mixture was separated by microdistillation to give 78% oxime II and 16% ketone VII. The infrared spectrum of cycloöctanone VII, which was isolated by preparative vapor phase chromatography also, was identical with that of authentic material ($\epsilon_{5.88\mu}/\epsilon_{3.40\ \mu} = 1.44$). The infrared spectrum of the oxime II was identical with that of authentic cycloöctanoneoxime obtained by a 16-hr. reaction of equimolar amounts of cycloöctanone, hydroxylamine hydrochloride, and sodium acetate in water–methanol solvent at room temperature and subsequent work-up as described above; b.p. 63° (0.08 mm.), m.p. 41.7–42.7° (reported[10] m.p. 26–28°), $\epsilon_{2.74\ \mu} = 1.19 \times 10^2$ l. cm.$^{-1}$ mole^{-1}, $\epsilon_{2.74\ \mu}/\epsilon_{3.40\ \mu} = 0.52$.

Anal. Calcd. for $C_8H_{15}NO$: C, 67.99; H, 10.71; N, 9.92. Found: C, 67.66; H, 10.42; N, 9.69.

In another run, 4.05 g. of a crude hydrogenation product containing 70% of oxime II, 23% of cycloöctanone VII, and 7% of impurity was converted to cycloöctanoneoxime by treatment with a mixture of 2.8 g. (40 mmoles) of hydroxylamine hydrochloride, 10.8 g. (80 mmoles) of sodium acetate trihydrate, 40 ml. of methanol, and 15 ml. of water for 40 min. at 50°. After work-up as described above and drying of the product for 24 hr. at 5 mm., 3.76 g. (91%) of material was obtained, which analyzed for 93% oxime II and 0% ketone VII.

Cycloöctanoneoxime was also prepared by hydrogenating 5.5 wt. % 1-nitrocycloöctene in pyridine (run 3) with 1.3% palladium for 16 hr. The product was worked up as described above with the difference that the pyridine was removed by azeotropic distillation with heptane after the catalyst had been filtered and extracted with ether.

Stearaldoxime (V) (Run 2).—A solution of 594 mg. (2 mmoles) of 1-nitro-1-octadecene[1] in 10 ml. of methanol containing 1 mmole of dry hydrochloric acid was hydrogenated with 183 mg. of catalyst (1.3% palladium). During 20 min., 1.8 moles of hydrogen was consumed per mole of nitroölefin and the rate of hydrogenation decreased sharply. After addition of 2 mmoles of sodium acetate, the mixture was worked up as described for cycloöctanoneoxime. The isolated crude product (528 mg., 94% yield) analyzed for 73% stearaldoxime content. If the carbonyl absorption, present at 5.75 μ in the crude product, is assigned to stearaldehyde, the amount of the latter is estimated at 13%. Pure stearaldoxime, m.p. 88.0–89.8° (reported[11] m.p. 89°), $\epsilon_{2.74\mu} = 1.30 \times 10^2$ l. cm.$^{-1}$ mole^{-1}, was obtained by recrystallization from methanol and hexane.

Hydrogenation of 3.7 wt. % 1-nitro-1-octadecene in pyridine (run 4) for 9 hr. using 4% palladium and subsequent work-up as described for II gave a crude product (96% crude yield) which contained 60% stearaldoxime.

Nitrocycloöctane (III) (Run 5).—A solution of 2.15 g. (13.8 mmoles) of 1-nitrocycloöctene in 100 ml. of methanol and 1 g. of pyridine was hydrogenated with 0.94 g. of catalyst (2.2% palladium). The rate of hydrogenation dropped when slightly less than 1 mole of hydrogen had been consumed (10 min.) per mole of nitroölefin. After filtration, methanolic extraction of the catalyst, and vacuum evaporation of the solvents with added heptane, 2.05 g. (96% crude yield) of crude product was obtained which analyzed for 83% nitrocycloöctane and10% cycloöctanone. Pure nitrocycloöctane, n^{20}D 1.4819 (reported[12] n^{20}D 1.4812), $\epsilon_{6.45\mu}/\epsilon_{3.40\mu} = 3.29$, was obtained by preparative vapor phase chromatography (6 ft. × 3/4 in. o.d. column packed with 25% GE-30 silicone gum rubber on Chromosorb W; helium flow rate, 200 ml./min.; temperature, 165°; retention time, 12 min. for VII, 37 min. for III). The isolated cycloöctanone was spectrally identified (100% pure).

(10) N. A. Rosanow and M. Belikow, *J. Russ. Phys. Chem. Soc.*, **61**, 2303 (1929); *Chem. Abstr.*, **24**, 3765 (1930).

(11) H. Stephen, *J. Chem. Soc.*, 1876 (1925).

(12) Badische Anilin-u.-Soda-Fabrik, British Patent 720,646 (December 22, 1954).

1-Nitroöctadecane (VI) (Run 6).—A solution of 672 mg. (2.26 mmoles) of 1-nitro-1-octadecene in 10 ml. of methanol and 0.17 g. of pyridine was hydrogenated with 1.3% palladium. Since there was no break in the hydrogen uptake/time curve, the reaction was terminated after 1.1 moles of hydrogen had been consumed per mole of nitroölefin (11 min.). After work-up, as described for III, 612 mg. of crude product (90% crude yield) was isolated. When 489 mg. of this material was chromatographed on silicic acid, using *n*-hexane containing 10% benzene as eluent, 255 mg. (yield about 50%) of pure 1-nitroöctadecane VI, m.p. 39.5–41°, $\epsilon_{6.44\ \mu}/\epsilon_{3.40\mu} = 0.91$, was isolated.

Anal. Calcd. for $C_{18}H_{37}NO_2$: C, 72.18; H, 12.45; N, 4.67; mol. wt. (in benzene), 299.5. Found: C, 72.16; H, 12.41; N, 4.56; mol. wt. (in benzene), 308.

N-Methyl-1,2,3,4,4a,9a-hexahydrocarbazoles by Catalytic Hydrogenation

KARL H. BLOSS AND CHARLES E. TIMBERLAKE[1]

The George Washington Carver Foundation, Tuskegee Institute, Alabama[2]

Received July 27, 1962

For forty years N-methyl-1,2,3,4,4a,9a-hexahydrocarbazole,[3] prepared by tin–hydrochloric acid reduction of N-methyl-1,2,3,4-tetrahydrocarbazole,[4] has been the only known N-methylated 1,2,3,4,4a,9a-hexahydrocarbazole, although a respectable number of 1,2,3,4-tetrahydrocarbazoles, with or without methyl groups in 9-position, have been obtained by Fischer indole synthesis and its improved versions.[5] When metal–acid, including sodium and ethanol, was applied to N-methyl-1,2,3,4-tetrahydrocarbazoles, the benzene ring of which had been substituted by one or more methyl groups, the corresponding hexahydrocarbazoles were actually found, but the yields failed to exceed 13%. An estimation of the equilibria involved in the catalytic hydrogenation of tetrahydrocarbazoles suggested the application of low hydrogen pressure together with an acidic solvent, which would both favor the formation of hexahydrocarbazoles and inhibit their overreduction to 1,2,3,4,5,6,7-8-octahydrocarbazoles.

With Adams' platinum oxide,[6] 9-methyl- and the (5–8),9-dimethyl-1,2,3,4-tetrahydrocarbazoles gave the corresponding 1,2,3,4,4a,9a-hexahydrocarbazoles in yields of 85% and better. Glacial acetic acid served as the solvent; occasionally a small amount of hydrochloric acid had to be added. Prolonged hydrogenation under these conditions led to other acid-soluble oils, presumably dodecahydrocarbazoles, which were not investigated. The formation of acid-insoluble by-products was negligible. The hydrogenation rates were nearly identical for all reactions.

The N-methyl-1,2,3,4,4a,9a-hexahydrocarbazoles are basic liquids,[7] virtually insoluble in water or aqueous

(1) A portion of this work was submitted to Tuskegee Institute as a M.S. thesis.

(2) Presented at the Southeastern Regional Meeting of the American Chemical Society in Birmingham, Ala., November 4, 1960.

(3) J. v. Braun and H. Ritter, *Ber.*, **55**, 3795 (1922).

(4) W. H. Perkin, Jr., and S. G. P. Plant, *J.Chem. Soc.*, **125**, 1509 (1924).

(5) W. Freudenberg, "Heterocyclic Compounds," Vol. 3, R. C. Elderfield, ed., J. Wiley and Sons, Inc., New York, N. Y., 1952, p. 304.

(6) R. Adams, V. Vorhees, and R. L. Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 463.

(7) Exception: 6,8,9-trimethyl-1,2,3,4,4a,9a-hexahydrocarbazole, m.p. 59–60°, glassy prisms; J. C. Kelley, in progress.