anol solution was poured into 500 ml. of water. Extraction of the aqueous mixture with ether and removal of the ether gave olefinic material boiling between 108–110°: 0.5 g., n^{20}_D 1.4001. Olefin, having the same properties, is obtained from the dehydration of II.

New York 27, N. Y.

[Contribution from Chandler Laboratory, Columbia University]

2- and 3-Vinylpyridines as Dienophiles in the Diels–Alder Reaction[1]

By W. von E. Doering[2] and Sara Jane Rhoads[3]

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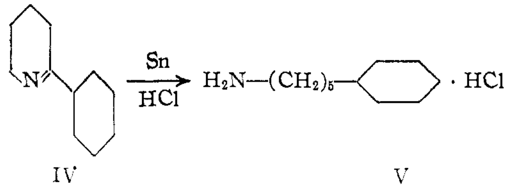
The Diels–Alder reactions of 2-vinylpyridine and of 3-vinylpyridine (the preparation of which has been improved) with butadiene and of 2-vinylpyridine with 2,3-dimethylbutadiene have been effected and compared with the styrene–butadiene reaction. The three dienophiles react at comparable temperatures. The structures of the adducts are 4-(α-pyridyl)-cyclohexene-1, 4-(β-pyridyl)-cyclohexene-1 and 4-(α-pyridyl)-1,2-dimethylcyclohexene-1.

The comparative reactivity of 2-vinylpyridine and 3-vinylpyridine as dienophiles in the Diels–Alder reaction is of theoretical interest in view of the marked electrophilicity of 2-vinylpyridine in contrast to the essentially neutral character of 3-vinylpyridine.[4] Until the recent report of the reaction of isoprene and 2-vinylpyridine to give 1-methyl-4-(α-pyridyl)-cyclohexene-1,[5] there have been no examples of the Diels–Alder reaction with vinylpyridines.

2-Vinylpyridine (I) and butadiene react to give an adduct, to which the structure, 4-(α-pyridyl)-cyclohexene-1 (II), is assigned on the basis of dehydrogenation with chloranil,[6] palladium black,[7] or, best with palladium-black and maleic acid[8] to 2-phenylpyridine and by analogy with the usual position assumed by the double bond in a Diels–Alder reaction. From the catalytic reduction of II in dilute hydrochloric acid a compound, m.p. 251–252.5°, is obtained, which is almost certainly 2-cyclohexylpiperidine hydrochloride (III), although Salathiel, *et al.*,[9] claim that this structure is to be assigned to a compound, m.p. 197–198°, which is the major product of the reduction of IV with tin and hydrochloric acid. Their compound is presumably V and not III.[10]



IV V

With 2,3-dimethylbutadiene, I reacts smoothly to give an adduct, 4-(α-pyridyl)-1,2-dimethylcyclohexene-1 (VI), which can be dehydrogenated to 4-(α-pyridyl)-1,2-dimethylbenzene (VII) and can be hydrogenated to a mixture of stereoisomers of 4-(α-piperidyl)-1,2-dimethylcyclohexane (VIII), the structural assignments being based on analogy and elementary analysis.

3-Vinylpyridine (IX) has been prepared in better yield by using a lower temperature (80°) in the reaction of trimethylamine and α-(3-pyridyl)-ethyl chloride hydrochloride, than that (125°) previously recommended,[4] the improvement being due to a large reduction in the amount of the undesirable by-product, α-(3-pyridyl)-ethyldimethylamine. IX reacts with butadiene, giving 4-(β-pyridyl)-cyclohexene-1 (X) which is converted by dehydrogenation to the known 3-phenylpyridine, and by hydrogenation to 3-cyclohexylpiperidine hydrochloride.

Styrene itself, reported by Alder and Rickert[11] to react with butadiene at 170–180°, in fact reacts appreciably at 125°.

From the data of Table I, which summarizes all of our experiments, it is apparent that 2- and 3-vinylpyridine and styrene react with butadiene at comparable orders of magnitude and 2-vinylpyridine with its easily polarizable double bond[4] is not much more reactive than the other two.

Experimental[12]

Procedure for the Diels–Alder Reactions.—In Table I, reaction times and temperatures for the various reactions are listed. In a typical procedure, a charge of 10.5 g. (0.10 mole) of freshly distilled vinylpyridine, 10 cc. (0.12 mole) of butadiene and 0.1 g. of hydroquinone was heated in a sealed tube. The reaction mixture, a dark, viscous oil, was leached with ether to yield a turbid solution which deposited appreciable quantities of ether-insoluble polymers on standing. It was found advisable to dilute the ethereal solution to a volume of *ca.* 300 cc. in order to remove as much of the polymeric material as possible; otherwise, emulsion formation in subsequent steps rendered the working of the product extremely tedious. The clear ethereal solution, decanted from insoluble polymers, was extracted with 2 *N* hydrochloric acid. Treatment of the acid extracts with excess 10% sodium hydroxide, liberated an oil which was dissolved in

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[1] From a dissertation submitted July 30, 1948, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

[3] Vassie James Hill Fellow of the American Association of University Women, 1947–1948.

[4] W. von E. Doering and R. A. N. Weil, This Journal, **69**, 2461 (1947).

[5] J. S. Meek, R. T. Merrow and S. J. Cristol, *ibid.*, **74**, 2667 (1952).

[6] R. T. Arnold and C. J. Collins, *ibid.*, **61**, 1407 (1939); R. T. Arnold, C. J. Collins and W. Zenk, *ibid.*, **62**, 983 (1940).

[7] R. P. Linstead, A. F. Millidge, S. L. S. Thomas and A. L. Walpole, *J. Chem. Soc.*, 1146 (1937); R. P. Linstead and S. L. S. Thomas, *ibid.*, 1127 (1940).

[8] S. Akabori and T. Suzuki, *Bull. Chem. Soc. Japan*, **4**, 200 (1929); S. Akabori and K. Saito, *Ber.*, **63**, 2245 (1930).

[9] R. Salathiel, J. M. Burch and R. M. Hixon, This Journal, **59**, 984 (1937).

[10] They report the isolation of a small amount of material, characterized only by m.p. 250°, which may well have been III.

[11] K. Alder and H. F. Rickert, *Ber.*, **71**, 379 (1938).

[12] Microanalyses were performed by Miss Lois May, Columbia University. Melting points are corrected. The purity of the 2-vinylpyridine, obtained from the Reilly Tar and Chemical Corporation, was confirmed by boiling point and conversion to the picrate.

TABLE I

Expt.	Diene	Dienophile	Time, hr.	Temp., °C.	Yield,[a] %	Dienophile recovered
1	Butadiene	2-Vinylpyridine	16	125	31 (44)	29
2	Butadiene	2-Vinylpyridine	24	125	34 (45)	24
3	Butadiene	2-Vinylpyridine	40	125	41 (46)	12
4	Butadiene	2-Vinylpyridine	40	60–70	2.5 (12.5)	80
5	2,3-Dimethylbutadiene	2-Vinylpyridine	19	130–150	41	0
6	2,3-Dimethylbutadiene	2-Vinylpyridine	32	100–130	32	0
7	Butadiene	3-Vinylpyridine	24	125	15 (19)	23
8	Butadiene	3-Vinylpyridine	40	125	33	0
9[b]	Butadiene	Styrene	14	170–180	33	0
10	Butadiene	Styrene	40	125	11 (38)	70

[a] The first figure is the percentage of theoretical yield, based on the amount of dienophile originally used in the reaction; the percentage in parentheses is calculated on the basis of the dienophile not recovered from the reaction mixture. [b] Reference 11.

ether. Distillation was used to separate unreacted starting material from the product.

4-(α-Pyridyl)-cyclohexene-1 (II).—By the general procedure, experiments 1, 2, 3 and 4 (Table I) afforded the adduct II, b.p. 77–80° at 0.5 mm. and b.p. 66–67° at 0.4 mm. on redistillation.

A sample of II was converted to the **picrate** by treating with the calculated amount of picric acid in dry benzene. The crude picrate, m.p. 112–115°, was obtained as dark yellow needles, m.p. 114.5–115°, after two recrystallizations from benzene.

Anal. Calcd. for $C_{17}H_{16}N_4O_7$: C, 52.6; H, 4.2; N, 14.4. Found: C, 52.7; H, 4.3; N, 14.6.

Heated in a sealed tube with 0.05 g. of hydroquinone for 40 hr. at 125°, 5.0 g. of II darkened somewhat, but could be recovered substantially unchanged (4.44 g., 89%, b.p. 89° at 2 mm.), no I being detected.

Dehydrogenation of 4-(α-Pyridyl)-cyclohexene-1 (II). (a) **With Chloranil.**—According to the method of Arnold, *et al.*,[6] a solution of 1.0 g. (0.0063 mole) of II and 5.6 g. (0.023 mole) of chloranil in 20 cc. of xylene was refluxed gently for 10 hr. The reaction mixture was filtered, diluted with ether, and extracted with 10 cc. of 3 *N* hydrochloric acid. Treatment of the acid extracts with excess 10% sodium hydroxide separated a dark red oil, which was extracted with ether. The ethereal solution, dried over anhydrous potassium carbonate, was evaporated, the residual oil being distilled *in vacuo* to yield 0.2 g. of 2-phenylpyridine, b.p. 91–94° at 0.1 mm., 21% yield. A sample was converted to the crude picrate (90% yield, m.p. 170–173°), which was crystallized from ethanol to give a product, m.p. 175–176°, showing no depression in m.p. on admixture with an authentic sample of the picrate of 2-phenylpyridine (reported m.p. 169–170°[13] and 175–176°[14]).

(b) **With Palladium-black.**—According to the procedure of Linstead, *et al.*,[7] a solution of 0.70 g. (0.004 mole) of II in 30 cc. of β-methylnaphthalene was refluxed with 0.5 g. of palladium-black in a vigorous stream of carbon dioxide for 6 hr. Isolated as before, the product was evaporatively distilled at 3 mm. to give fraction 1, 0.25 g. at a jacket temperature of 77–85°, and fraction 2, 0.26 g. at 85–105°. The crude picrate of fraction I, m.p. 120–150°, evidently contained unchanged II and/or disproportionation products, whereas the crude picrate of fraction 2, m.p. 172–175°, showed no depression in m.p. when mixed with an authentic sample of the picrate of 2-phenylpyridine.

(c) **With Palladium-black and Maleic Acid.**—Following the method of Akabori, *et al.*,[8] a mixture of 0.16 g. (0.001 mole) of II, 0.45 g. (0.004 mole) of maleic acid in 6 cc. of water and 0.25 g. of palladium-black was refluxed for 5 hr., filtered, made strongly alkaline with 20% sodium hydroxide and extracted with ether. After removal of the ether, the basic residue was converted to the **picrate**; heavy, yellow needles from ethanol: 0.2 g., 52% yield, m.p. 169–174°, m.p. 175–176° after one recrystallization from ethanol.

2-Cyclohexylpiperidine Hydrochloride (III).—A solution of 3.0 g. (0.019 mole) of II in 40 cc. of 1.5 *N* hydrochloric acid was reduced in the presence of 0.1 g. of platinum oxide catalyst in an Adams–Parr hydrogenation apparatus in 5 hr. Treatment of the filtered solution with excess alkali liberated a basic oil which was dissolved in ether and dried over anhydrous potassium carbonate. After removal of the ether, the oil was evaporatively distilled at 0.8–1.0 mm. and a jacket temperature of 80–85° to give 2.3 g. (74%) of a colorless product with a strong piperidine-like odor, which gave a positive Hinsberg test for secondary amines. Dissolved in anhydrous ether and treated with dry hydrogen chloride, the base was converted to the hydrochloride III, m.p. after one crystallization from ether–ethanol 251–252.5° with dec.

Anal. Calcd. for $C_{11}H_{22}ClN$: C, 64.8; H, 10.9; Cl, 17.4; N, 6.9. Found: C, 64.8, 64.8; H, 11.1, 11.1; Cl, 17.3; N, 6.7.

4-(α-Pyridyl)-1,2-dimethylcyclohexene-1 (VI).—Experiments 5 and 6 (Table I) worked in the usual manner, afforded VI, b.p. 108–112° at 2.5 mm. and b.p. 128–130° at 6 mm. on redistillation.

The picrate of VI, prepared in ethanolic solution, melted at 106.5–107.5°.

Anal. Calcd. for $C_{19}H_{20}N_4O_7$: C, 54.9; H, 4.9; N, 13.5. Found: C, 54.8; H, 4.9; N, 13.5.

VI was best dehydrogenated by method (c) above, methods (a) and (b) giving quite impure products, purified only by repeated crystallization. The product, 4-(α-pyridyl)-1,2-dimethylbenzene (VII), was isolated as the picrate; deep yellow needles from benzene; m.p. (crude) 178–180°, m.p. 179–180° after two recrystallizations from benzene.

Anal. Calcd. for $C_{19}H_{16}N_4O_7$: C, 55.3; H, 3.9; N, 13.6. Found: C, 55.3; H, 3.8; N, 13.8.

4-(α-Piperidyl)-1,2-dimethylcyclohexane (VIII).—Dissolved in 60 cc. of 2 *N* hydrochloric acid, 4.1 g. (0.021 mole) of VI was catalytically reduced with platinum oxide catalyst, 94% of four mole equivalents having been absorbed in 9 hr. The addition of fresh catalyst and continued shaking over a period of 12 hr., produced no further hydrogen uptake. The filtered solution was treated with excess alkali, extracted with ether, dried and concentrated. The product was distilled *in vacuo*, to give 3.0 g. (72%) of a colorless oil with a piperidine-like odor, b.p. 97–98° at 1.5 mm., showing a positive Hinsberg test for secondary amines.

Anal. Calcd. for $C_{13}H_{25}N$: C, 79.9; H, 12.9. Found: C, 79.6; H, 12.7.

A mixture of 0.5 g. of the distilled, hydrogenated product and 0.6 g. of picric acid was dissolved in hot benzene, and treated with *n*-hexane to induce cloudiness. Cooling with scratching produced a light yellow, crystalline mixture of picrates, m.p. 115–120°, from which 15 recrystallizations from a benzene–hexane mixture afforded a picrate, m.p. 157–159°.

Anal. Calcd. for $C_{19}H_{28}N_4O_7$: C, 53.8; H, 6.7; N, 13.2. Found: C, 54.1; H, 6.9; N, 12.8.

Concentration of the filtrates enriched in the more soluble component(s) gave crude picrates which were combined and recrystallized once from a benzene–hexane mixture. The mixture, m.p. 113–120°, was analyzed without attempting further separation.

Anal. Found: C, 53.8; H, 6.6.

Both samples of picrates required extended drying *in*

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[13] F. W. Bergstrom and S. H. McAllister, THIS JOURNAL, **52**, 2845 (1930).

[14] J. W. Haworth, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 349 (1940).

vacuo to remove traces of solvent before acceptable analytical data could be obtained.

3-Vinylpyridine (IX).—IX was prepared by the method of Doering and Weil[4] with constructive modifications. α-(3-Pyridyl)-ethyl chloride hydrochloride (XI) which is strongly deliquescent, was purified by sublimation at 0.5–0.7 mm. and 70–80° rapidly, and without decomposition, to give long, colorless, prismatic needles, m.p. 111–112° (reported[4] m.p. 109–110°) in a yield of 53.0% from β-pyridylmethylcarbinol.

Three reactions of sublimed XI (15.0 g., 0.084 mole), 23 cc. of trimethylamine[15] and 40 cc. of absolute methanol were placed in a sealed tube for 48 hr. at room temperature, for 10 hr. at 80° and for 10 hr. at 125°, respectively. The reaction mixtures were worked as previously described.[4] From the first run, 65% of the starting material was recovered. From the second and third, 4 and 54% of the theoretical amount of α-(3-pyridyl)-ethyldimethylamine was obtained by ether extraction of the solvent-free residue in 8% aqueous sodium hydroxide. In the usual way, solid potassium hydroxide was added to raise the concentration to 40–50%, and the solution of residual quaternary hydroxide was boiled vigorously to give 3-vinylpyridine in 28, 65 and 38% yields, respectively.

4-(β-Pyridyl)-cyclohexene-1 (X).—From experiments 7 and 8 (Table I), X was isolated by distillation, b.p. 98–100° at 3 mm., and was converted to the **picrate**, m.p. 117–118.5° after one recrystallization from absolute ethanol.

Anal. Calcd. for $C_{17}H_{16}N_4O_7$: C, 52.6; H, 4.2; N, 14.4. Found: C, 52.8; H, 4.1; N, 14.9.

3-Phenylpyridine.—X was dehydrogenated by boiling a solution of 0.50 g. (0.003 mole) and 0.70 g. (0.007 mole) of maleic acid in 10 cc. of water for 8 hr., in the presence of 0.5 g. of palladium-black. The reaction product was converted directly to the crude picrate: 0.70 g., 61%, m.p. 157–159° with softening from 145°. One recrystallization from ethanol afforded long, fine, yellow needles, m.p. 161–163° with softening beginning *ca.* 150°. Repeated recrystallization from acetone was required to eliminate this softening behavior; reported values of m.p.: 161–163.5°,[16] 162–164°,[17] 159–160°,[14] 162–163°.[18]

3-Cyclohexylpiperidine Hydrochloride.—The catalytic reduction of 0.32 g. (0.002 mole) of X, dissolved in 40 cc. of 1.5 *N* hydrochloric acid in the presence of 0.1 g. of platinum oxide, was complete in 3.5 hr., a total of four equivalents of hydrogen being absorbed. The filtered solution was evaporated to dryness under reduced pressure, the crude hydrochloride being crystallized several times from dry acetone, m.p. 161.5–162.5°. The free amine gave a positive Hinsberg test for secondary amines.

Anal. Calcd. for $C_{11}H_{22}ClN$: C, 64.8; H, 10.9. Found: C, 64.9; H. 11.0.

4-Phenylcyclohexene-1.—This compound was prepared by the method of Alder and Rickert[11] (expt. 9, Table I). A mixture of 20.8 g. (0.20 mole) of styrene (freshly distilled, b.p. 64° at 45 mm.), 28 cc. (0.34 mole) of butadiene and 0.2 g. of hydroquinone was heated in a sealed tube at 125° for 40 hr. Distillation of the product gave 14.65 g. (70.4%) of unchanged styrene, b.p. 45–50° at 27 mm., and 3.50 g. (11.1%) of 4-phenylcyclohexene-1; b.p. 103–110° at 11 mm., reported b.p. 98–115° at 11 mm.[11]

Dehydrogenation of 1.0 g. with selenium according to Alder and Rickert[11] afforded 0.6 g. (61%) of pure biphenyl, m.p. 70–71°, undepressed on admixture with an authentic sample.

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[15] Purified using the phosphorus pentoxide method of Ingram, M.S. Dissertation, University of Chicago, 1940.

[16] Z. H. Skraup and A. Cobenzyl, *Monatsh.*, 456 (1883).

[17] R. Forsyth and F. L. Pyman, *J. Chem. Soc.*, 2912 (1926).

[18] G. Ciamician and P. Silber, *Ber.*, **20**, 191 (1887).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Reactions of Acetylenic Compounds Catalyzed by Sulfonated Polystyrene Resins

BY MELVIN S. NEWMAN

RECEIVED MAY 8, 1953

The rearrangement of 1-ethynylcyclohexanol to 1-acetylcyclohexene is brought about in excellent yield by heating in aqueous acetic acid with Dowex-50, a sulfonated polystyrene resin. It is shown that neither 1-ethynylcyclohexene nor 1-acetylcyclohexanol is an intermediate in this rearrangement. If Dowex-50 is treated with small amounts of mercuric ion a resin (Hg–resin) is obtained which is remarkably effective in promoting hydration of the acetylenic linkage. Several examples are given, including the hydration of acetylene to acetaldehyde.

It is well known that ethynylcarbinols are converted into α,β-unsaturated ketones on heating with formic acid.[1] Several different reagents have been used to effect this change. In the case of 1-ethynylcyclohexanol (I) the yield of 1-acetylcyclohexene (II) is about 60–70%.[2] In this work, it is shown that 84–87% yields of II may be obtained from I by heating with a stirred suspension of Dowex-50[3] in about 90% acetic acid for a short time. Similarly, diethylethynylcarbinol and 1-ethynyl-2,2,6-trimethylcyclohexanol[4] were converted into 3-ethyl-3-penten-2-one[5] (84%) and 2,6,6-trimethyl-1-acetylcyclohexene[6] (75%), respectively. On similar treatment of 3-hydroxy-3-phenyl-1-butyne a reaction leading, presumably, to 3-phenyl-3-buten-2-one occurred, but only polymer was obtained.[7] Further work is required to establish the generality of this method.

In homogeneous solution it is believed that the eneyne, formed by dehydration of the ethynylcarbinol, is the first intermediate and that this is then hydrated to the α,β-unsaturated ketone.[8] In the study of the rearrangement of I into II by means of

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[1] See (a) J. D. Chanley, THIS JOURNAL, **70**, 244 (1948), and (b) A. W. Johnson, "The Chemistry of the Acetylenic Compounds, Vol. I, The Acetylenic Carbinols," Edward Arnold and Co., London, 1946, p. 124 ff. This reaction is usually called the Rupe reaction, although Rupe believed the rearranged products were unsaturated aldehydes.

[2] See J. H. Saunders, *Org. Syntheses*, **29**, 1 (1949).

[3] A sulfonated polystyrene polymer with about 12% cross linking obtained from the Dow Chemical Co. The sample used was 200–400 mesh.

[4] The author is indebted to Professor E. R. H. Jones for a generous gift of 2,2,6-trimethylcyclohexanone.

[5] R. Locquin and R. Heilman, *Bull. soc. chim.*, **45**, 1112 (1929); R. Heilmann, *Compt. rend.*, **215**, 112 (1942).

[6] H. B. Henbest and G. Woods, *J. Chem. Soc.*, 1150 (1952), showed that the crude ketone obtained by treating the ethynylcarbinol with formic acid consisted of 2,6,6-trimethyl-1-acetylcyclohexene, (b.p. 88–90° at 20 mm., n^{20}D 1.4775, when pure) which did not form a 2,4-dinitrophenylhydrazone, and a small amount of a compound, presumably 2,2,6-trimethylcyclohexylideneacetaldehyde, which formed a red 2,4-dinitrophenylhydrazone, m.p. 214–215°.

[7] C. D. Hurd and R. E. Christ, THIS JOURNAL, **59**, 118 (1937), reported a similar experience.

[8] (a) G. F. Hennion, R. B. Davis and D. E. Maloney, *ibid.*, **71**, 2813 (1949). See also (b) J. C. Hamlet, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 2652 (1951). It should be pointed out that the qualitative evidence presented should be supported by kinetic measurements. We are presently engaged in such a study.