Fraction (7) was refractionated to give an analytical sample of acetylketene diethylacetal: b.p. 138.5–140.5° (21 mm.), $n^{25}_{\rm D}$ 1.4720, d^{25}_4 1.000, m.p. 7°.

Anal. Calcd. for $C_4H_4O(C_2H_5O)_2$: C, 60.74; H, 8.92; OC_2H_5, 56.9. Found: C, 60.78; H, 8.65; OC_2H_5, 53.3.

Treatment of acetylketene diethylacetal with ethanol containing a trace of acid, followed by heating and neutralization of the acidic catalyst by sodium ethoxide, gave after distillation ethyl orthoacetoacetate, b.p. 104–105° (21 mm.), d^{25}_4 0.962, $n^{25}_{\rm D}$ 1.4175.

Anal. Calcd. for $C_4H_5O(OC_2H_5)_3$: C, 58.80; H, 9.87; OC_2H_5, 66.1. Found: C, 58.33; H, 9.74; OC_2H_5, 66.3.

MADISON, WISCONSIN RECEIVED DECEMBER 8, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Diels–Alder Reaction of Isoprene with Styrene and 2-Vinylpyridine[1]

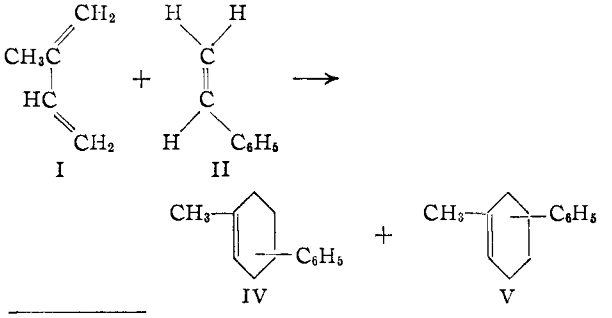
BY JOHN S. MEEK, RAYMOND T. MERROW AND STANLEY J. CRISTOL

When a monosubstituted ethylene is condensed with a monosubstituted diene in the Diels–Alder reaction, two or more isomers are possible as adducts. In reactions of this type, almost no work has been done with monoarylethylenes to determine which isomer will predominate in a given reaction. Therefore, the condensation of styrene and 2-vinylpyridine with isoprene was studied. Isoprene and styrene gave mainly 4-methyl-1,2,3,6-tetrahydrobiphenyl with a trace of 3-methyl-1,2,5,6-tetrahydrobiphenyl. The only adduct of isoprene and 2-vinylpyridine found was 1-methyl-4-(α-pyridyl)-cyclohexene.

The use of monoarylethylenes as dienophiles in the Diels–Alder reaction has been quite limited. Styrene has been found to condense with butadiene,[2] 2,3-dimethylbutadiene,[2] piperylcyclone,[3] tetraphenylcyclopentadienone[4] and hexachlorocyclopentadiene[5] to give Diels–Alder adducts. Since all of these dienes are symmetrical, no possibility exists for positional isomerism in the adducts, and the *exo–endo* isomerism was not determined. Since the presentation of our work, Alder and Haydn have reported the condensation of 2-phenyl-1,3-butadiene with styrene gives 1,4-diphenylcyclohexene and they did not isolate any isomeric 1,5-diphenylcyclohexene.[6]

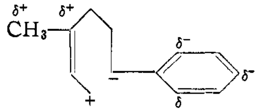
As a continuance of the work in our laboratory on the structure of Diels–Alder adducts, isoprene (I) was condensed with styrene (II), and with 2-vinylpyridine (III).

The condensation of I and II gave a 20% yield of oily adduct. On dehydrogenation with sulfur, followed by oxidation with permanganate, there was obtained a mixture of acids which consisted mainly of *p*-phenylbenzoic acid with a trace of the *m*-isomer. This showed that both 4-methyl-1,2,3,6-tetrahydrobiphenyl (IV) and 3-methyl-2,2,5,6-tetrahydrobiphenyl (V) were formed in the original Diels–Alder reaction.

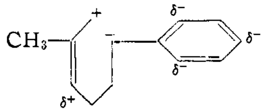


The reaction of I with III gave an adduct in 33% yield. Dehydrogenation converted the adduct to 2-(*p*-tolyl)-pyridine, which was identified through the picrate. None of the *m*-isomer was found in the dehydrogenation product. Since the tolylpyridines were unknown, they were synthesized by the reaction of the corresponding lithium compound with pyridine.

The predominance of 1,4-disubstituted adducts with 2-substituted dienes and monosubstituted dienophiles is reasonable when one assumes transition states such as VI and VII. The transition state VI would be stabilized to a greater degree by resonance than VII. Transition states similar to VI and VII in the Diels–Alder reaction have been discussed by Branch and Calvin,[7] Dewar[8] and Remick.[9]



VI



VII

Experimental

The isoprene used was purchased from the Phillips Petroleum Company, the styrene was a gift from the Dow Chemical Company, and the 2-vinylpyridine was bought from the Reilly Tar and Chemical Corporation. The styrene was distilled just before using, and the 2-vinylpyridine was purified by steam distillation and was then dried over magnesium sulfate.

Condensation of I and II.—Thirty-four grams (0.5 mole) of I, 52.0 g. (0.5 mole) of II and 1 g. of *p*-*t*-butylcatechol were heated to 150–160° in a Parr hydrogenation bomb for 24 hours under autogenous pressure. Distillation of the reaction mixture yielded 17.0 g. (19.7%) of crude adduct, b.p. 118–119° (6 mm.), $n^{20}_{\rm D}$ 1.5351.

Anal. Calcd. for $C_{18}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.19; H, 9.05.

Dehydrogenation of the Condensation Product of I and II.—Three grams of the adduct mixture and 1.15 g. of sul-

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[1] This work was supported by the Office of Naval Research and was presented in part at the 115th Meeting of the American Chemical Society, March, 1949.

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

[3] B. A. Arbuzov and D. A. Akhmed-Zade, *J. Gen. Chem.* (*U. S. S. R.*), **12**, 212 (1942) [*C. A.*, **37**, 2733 (1943)].

[4] V. S. Abramov and T. L. Mitropolitanskaya, *J. Gen. Chem.* (*U. S. S. R.*), **10**, 207 (1940); **34**, 7284^6 (1940).

[5] Velsicol Corporation, British Patent 614,931; *C. A.*, **43**, 4693*d* (1949).

[6] K. Alder and J. Haydn, *Ann.*, **570**, 201 (1950).

[7] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," 5th printing, Prentice-Hall, Inc., New York, N. Y., 1946, p. 489.

[8] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, England, 1949, p. 151.

[9] A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 447.

fur were heated in a Heymann dehydrogenation tube[10] at 260–265° for 25 hours, followed by 20 minutes of heating with zinc dust. Filtration with suction gave 2.0 g. of a dark viscous liquid.

This crude dehydrogenated product was refluxed with 4.75 g. of potassium permanganate in 250 ml. of water for 8 hours until all of the permanganate color had disappeared. The mixture was steam distilled until the distillate was no longer oily, and then the manganese dioxide was filtered off. The filtrate was concentrated to about $^{2}/_{3}$ its volume and acidified with concentrated hydrochloric acid. A white solid immediately precipitated out. The crude acid weighed 1.40 g. and melted from 181–220°. Recrystallization from methanol-water gave 0.80 g. of *p*-phenylbenzoic acid, m.p. and mixed m.p.[11] 220.5–221.5°, and only a trace of the *m*-isomer, m.p. and mixed m.p.[11] 163–164°.

Adduct of Isoprene and 2-Vinylpyridine (VIII).—In the Parr bomb were placed 40.8 g. (0.6 mole) of I, 52.5 g. (0.5 mole) of III, 1 g. of *p*-*t*-butylcatechol and 30 ml. of acetone. The mixture was heated to 170° for 24 hours. Distillation of the mixture gave 29.0 g. (33.5%) of crude adduct, b.p. 103–107° (6 mm.). The yield of purified adduct was 26.9%, b.p. 103–104° (6 mm.), $n^{20}\text{D}$ 1.5390, d^{20} 0.9961; *MR* calcd. 54.49, found 56.13.

Anal. Calcd. for $C_{12}H_{15}N$: C, 83.19; H, 8.73. Found: C, 83.25; H. 8.48.

Dehydrogenation of VIII.—Two and three-tenths grams of purified adduct and 0.83 g. of sulfur were heated together at 180–185° for 26 hours, and for 24 hours at 210–220°, until the evolution of hydrogen sulfide had ceased. After 30 minutes of heating with zinc dust, the mixture was filtered and the filtrate distilled at reduced pressure. One and one-tenth grams of material which did not decolorize permanganate in the cold was obtained, b.p. 156–157° (12 mm.). This compound was converted quantitatively by an ethanolic solution of picric acid to the picrate (IX). After recrystallization from acetone, the picrate melted at 176–177°.

Anal. Calcd. for $C_{18}H_{14}N_4O_7$: C, 54.27; H, 3.54. Found: C, 54.36; H, 3.54.

Preparation of 2-(*p*-Tolyl)-pyridine.—An attempt to prepare 2-(*p*-tolyl)-pyridine by coupling the diazonium salt of 8.5 g. of *p*-toluidine with pyridine using the procedure for 2-phenylpyridine[12] gave, after distillation *in vacuo*, 2.1 g. of an oil, m.p. 3–12°. This was treated with methanol saturated with picric acid and the resulting solid was fractionally recrystallized from acetone. The first and major fraction of 0.40 g. melted at 198.5–199.5° and depressed the melting point of IX. The second picrate weighed 0.11 g. and melted at 197–198° and depressed the m.p. of IX and that of the first picrate. A third picrate amounted to 0.011 g. and melted at 178–180° and gave no depression with IX. The first two picrates were presumably derived from 3- and 4-(*p*-tolyl)-pyridine. These picrates were not investigated further.

The method of Evans and Allen[13] for preparing 2-phenylpyridine was next followed to prepare 2-(*p*-tolyl)-pyridine. To 3.5 g. (0.5 gram-atom) of lithium ribbon cut in small pieces in 100 ml. of dry ether, was added 43 g. (0.25 mole) of *p*-bromotoluene in 50 ml. of dry ether. Then 40 g. of dry[13] pyridine in 100 ml. of dry toluene was added and the ether distilled. The remaining mixture was heated to 105–110° with stirring for 8 hours, cooled, and extracted with water. The non-aqueous layer was dried over potassium hydroxide and distilled, yield 20.1 g. (47.5%) of crude product, b.p. 121–128° (6 mm.). Redistillation gave 17.9 g. (40.4%) of pure product, b.p. 108–109° (4 mm.).

Anal. Calcd. for $C_{12}H_{11}N$: C, 85.17; H, 6.55. Found: C, 84.89; H, 6.68.

The picrate of this compound was formed quantitatively in ethanol and melted at 178–179°.

Anal. Calcd. for $C_{18}H_{14}N_4O_7$: C, 54.27; H, 3.54. Found: C, 54.68; H, 3.27.

A mixed melting point of this picrate with IX was not depressed.

2-(*m*-Tolyl)-pyridine.—The same procedure, using *m*-bromotoluene, lithium and pyridine, gave a 20% yield of product, b.p. 106–107° (2 mm.).

Anal. Calcd. for $C_{12}H_{11}N$: C, 85.17; H, 6.55. Found: C, 85.25; H, 6.47.

The picrate of 2-(*m*-tolyl)-pyridine prepared from methanolic picric acid melted at 175.5–177° and depressed considerably the melting point of IX.

Anal. Calcd. for $C_{18}H_{14}N_4O_7$: C, 54.27; H, 3.54. Found: C, 54.53; H, 3.30.

Acknowledgment.—The microanalyses were performed by the Clark Microanalytical Laboratory, Urbana, Illinois.

BOULDER, COLORADO RECEIVED JULY 2, 1951

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

[13] J. C. W. Evans and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 517.