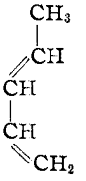
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Condensation of Piperylene with Acrylonitrile and Methyl Acrylate

BY JOHN S. MEEK AND JAMES W. RAGSDALE

When a diene such as piperylene (I) which possesses only one plane of symmetry undergoes the Diels–Alder reaction with an unsymmetrically substituted dienophile such as acrylonitrile (II) then possibly four different racemic nitriles might be formed. In this case these are *cis-* (III) and *trans*-1,2,5,6-tetrahydro-*ortho*-tolunitrile (IV) and *cis-* (V) and *trans*-1,2,3,6-tetrahydro-*meta*-tolunitrile (VI). The possibility of the formation of such isomers was recognized by Lehmann and Paasche.[1] However, in only a few cases have the adducts been identified as ortho or meta isomers and in no case has it been definitely proven whether these were *cis* or *trans* in nature. Lehmann and Paasche condensed acrolein with 4-*p*-xylyl-1,3-pentadiene and assigned to the resulting adduct the structure of an ortho isomer in which the aldehyde group and the *p*-xylyl group were *trans* to each other.[1] Their proof of structure was inconclusive and their adduct was not converted to any known compound.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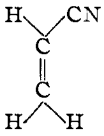
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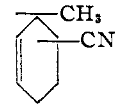
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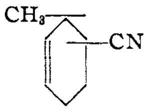
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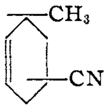
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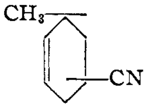
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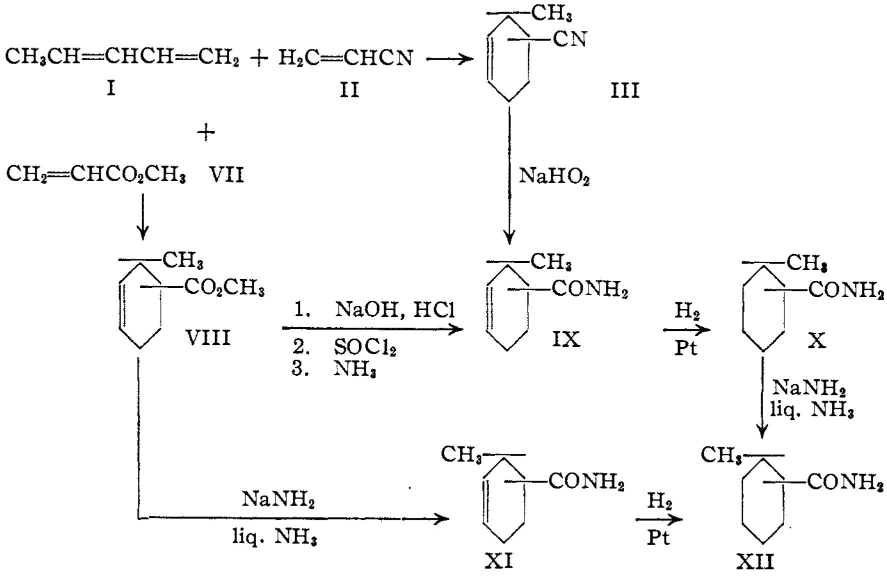

Recently it was found that the adduct of acrylonitrile and piperylene was a mixture of an ortho and a meta isomer and that the ortho isomer was roughly seven times as abundant as the meta isomer in the mixture.[2] Therefore, this reaction was chosen in an effort to learn if these isomers were *cis* or *trans* in nature, and at the same time it was planned to study the previously unreported condensation of piperylene and methyl acrylate (VII).

Methyl acrylate was found to condense readily with piperylene to give a 65% yield of an adduct (VIII). Dehydrogenation of VIII and subsequent hydrolysis produced *o*-toluic acid. No *m*-toluic acid was isolated. Saponification of VIII, conversion to the acid chloride, and treatment with ammonia gave a solid amide (IX). This upon hydrogenation gave the known *cis*-hexahydro-*o*-toluamide (X).[3] The over-all yield from the crude adduct to IX was 57%, showing that the majority of the adduct was the *cis*–ortho isomer VIII.

In an attempt to get a better conversion of VIII to IX, ammonolysis was tried. None appeared to take place with alcoholic ammonia solutions. The use of liquid ammonia with ammonium chloride was next tried,[4] but no identifiable product could be obtained. The use of sodium amide in liquid ammonia gave a small yield of a compound (XI) which was identified as *trans*-1,2,5,6-tetrahydro-*o*-toluamide by hydrogenation to the known *trans*-hexahydro-*o*-toluamide (XII).[3] A subsequent experiment showed that under similar conditions the *cis* amide was converted to the *trans* isomer.

The crude adduct of piperylene and acrylonitrile was treated with sodium hydroxide and hydrogen peroxide in alcohol. An 85% yield of IX was obtained and thus the majority of the adduct was shown to be III. Attempts to isolate an amide

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[1] Lehmann and Paasche, *Ber.*, **68**, 1146 (1935).

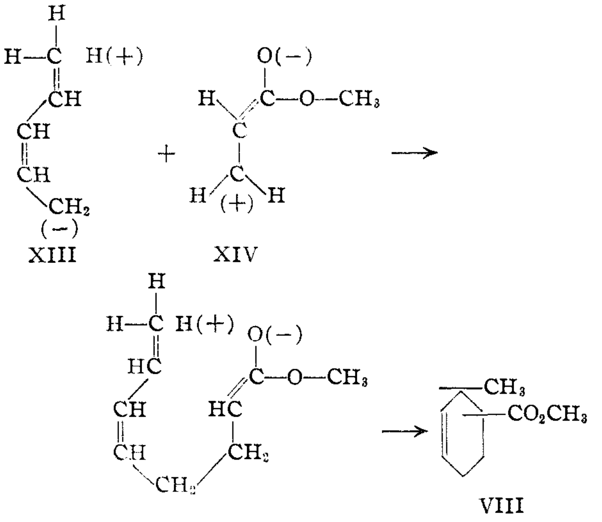
[2] Frank, Emmick and Johnson, THIS JOURNAL, **69**, 2313 (1947).

[3] Skita, *Ann.*, **431**, 1 (1923); v. Auwers, *J. prakt. Chem.*, [2] **124**, 209 (1930).

[4] Fellinger and Audrieth, THIS JOURNAL, **60**, 579 (1938).

derived from either IV, V or VI have failed so far although it has been shown that V or VI if not both must be present in the reaction mixture.[2]

From these two examples it appears that piperylene condenses with a negatively substituted unsymmetrical ethylene to give chiefly the *cis*-ortho isomer. This is what one would expect on the basis of resonance and inductive effects in the compounds studied. For in piperylene it has been shown that the inductive and hyperconjugative effect of the methyl group causes a negative charge to reside on the terminal carbon atom[5] (XIII). In methyl acrylate, as well as many other negatively substituted ethylenes, the β-carbon atom is positive when compared to the α-carbon atom due to mesomeric effects (XIV). Thus the molecules may line up as pictured below to form the ortho isomer, the negative end of one being attracted by the positive end of the other. In the piperylene molecule (XIII) hyperconjugation of the methyl group results in its having a positive charge. This charge attracts it to the negative charge on the carbonyl group resulting from resonance, and thus a *cis* configuration results.



XIII XIV

VIII

The formation of the meta isomer in the case above would require the positive end of the dienophile to join with the positive end of the diene which would need a higher energy of activation than that required for the formation of the ortho isomer.

Experimental

The piperylene, methyl acrylate and acrylonitrile used in these experiments were Eastman Kodak Company practical grade, and they were used without further purification. About 70% of the piperylene was the *trans* isomer.

Adduct of Piperylene with Methyl Acrylate (VIII).—A mixture of 57 g. (0.67 mole) of methyl acrylate, 45.5 g. (0.67 mole) of piperylene and 0.1 g. of hydroquinone were placed in a Parr hydrogenation bomb under 1200 pounds of hydrogen pressure and heated for six hours at 200°. The hydrogen was used to test for leaks in the apparatus, and also in the hope that it would cut down peroxide formation and the diffusion of the piperylene which might result in polymerization taking place around the valves of the bomb head. No such polymerization was encountered and the use of the bomb avoided the dangers of sealed glass tubes and permitted the use of larger amounts of materials. The product was distilled through a short Vigreux column and 67.4 g. (65%) of adduct was obtained, b. p. 180–205° (627 mm.). A small portion was redistilled and the fraction boiling at 181–183° (622 mm.), $n^{20}\text{D}$ 1.432 was taken for analysis.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.13; H, 9.15. Found: C, 70.28; H, 8.98.

The adduct was dehydrogenated by heating under reflux with a 25% palladium on charcoal catalyst. Saponification of the resulting oil and acidification gave *o*-toluic acid. This was identified by means of a mixed melting point with an authentic sample and by preparing the *p*-bromophenacyl ester derivative.

Adduct of Piperylene with Acrylonitrile (III).—A mixture of 38.5 g. (0.72 mole) of acrylonitrile, 58 g. (0.85 mole) of piperylene and a trace of hydroquinone and iodine were placed in the bomb as in the above procedure and were heated at 130° for eight hours. Distillation of the resulting product gave 18.7 g. of crude piperylene, 18.4 g. of acrylonitrile, and 47.6 g. (54%) of crude adduct. Frank, Emmick and Johnson[2] have reported a 56% yield when equivalent amounts of *trans*-piperylene and acrylonitrile were heated for twenty-four hours on a steam-bath. Fractionation of our adduct through a column possessing 12 theoretical plates failed to separate the position isomers shown to be present but not isolated by those authors. The adduct boiled at 190–191° (620 mm.), $n^{20}\text{D}$ 1.4710.[6]

***cis*-1,2,5,6-Tetrahydro-*o*-toluamide (IX).**—To a solution of 2.1 g. of VIII in 15 ml. of methanol was added a solution of 1.6 g. of potassium hydroxide in 3 ml. of water. The mixture was allowed to stand in the cold for forty hours. This was then acidified with hydrochloric acid and extracted with ether. This extract was then warmed to remove the ether and any methanol present, and the residual oil was heated with 6 g. of thionyl chloride for thirty minutes. The acid chloride was poured into ice-cold concentrated ammonium hydroxide and the resulting solid was isolated by means of filtration and washed with water. Recrystallization from hot water gave 1.1 g. (58%) of amide, m. p. 143°.

This same amide was prepared from the adduct of acrylonitrile and piperylene by the action of alkaline hydrogen peroxide using the procedure given for converting *o*-tolunitrile to the amide[7] with 18.1 g. (0.15 mole) of the adduct being used. A yield of 16.1 g. (85%) of the amide was obtained, m. p. 140–142°. Recrystallization from 10% methanol gave crystals melting at 143° as before and a mixed melting point of the two was not depressed.

Anal. Calcd. for $C_8H_{13}NO$: C, 69.02; H, 9.41; N, 10.06. Found: C, 69.1; H, 9.20; N, 10.13.

Methyl *cis*-Hexahydro-*o*-toluate.—Hydrogenation of a small quantity of VIII showed that about 2% more than the theoretical amount of hydrogen was absorbed at room conditions with Adams catalyst being used. Hydrogenation of 20 g. (0.13 mole) of VIII in 40 ml. of methanol with 50 mg. of platinum oxide was carried out. The platinum was removed by means of filtration and the filtrate was distilled through a short Vigreux column. The main fraction boiled at 181–183° (623 mm.) and weighed 15.2 g. (75%); $n^{20}\text{D}$ 1.432; d^{24} 0.956.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.15; H, 10.46.

***cis*-Hexahydro-*o*-toluamide (X).**—The 15.2 g. of hydrogenated ester prepared above were allowed to stand

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(5) Hannay and Smyth, *ibid.*, **65**, 1931 (1943).

(6) We are indebted to Mr. Robert C. Ronald for this fractionation.

(7) Noller, "Organic Syntheses," Col. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 586.

almost two days with 6 g. of sodium hydroxide in aqueous ethanol. The mixture was acidified with hydrochloric acid and then ether extracted. Fractional distillation gave 10 g. (72%) of *cis*-hexahydro-*o*-toluic acid, b. p. 119–121° (9 mm.), $n^{20}D$ 1.4572; reported,[8] b. p. 122–123° (10 mm.), $n^{20}D$ 1.458. A small amount of the acid was heated with thionyl chloride, the excess reagent was removed by distillation and the acid chloride was poured into ice-cold ammonium hydroxide. The amide obtained was recrystallized twice from a methanol–water mixture and melted sharply at 149.5°; reported[8] m. p. 151–153°.

Twelve grams of IX prepared from the adduct of acrylonitrile was placed in 135 ml. of methanol with 50 mg. of Adams catalyst and hydrogenated at room conditions. The platinum was removed by filtration and the filtrate was evaporated to dryness and gave 11.3 g. (93%) of crude amide, m. p. 149°. Treatment with charcoal in a 10% methanol solution gave a product melting sharply at 150°. A mixed melting point with the hexahydroamide prepared from VIII as reported previously showed no depression.

Attempted Ammonolyses of VIII.—All attempts to prepare IX by the action of ammonia on VIII failed. Treatment of VIII with aqueous ammonia or anhydrous ammonia in absolute ethanol with heating failed to give any solid product. Finally the procedure of Fellinger and Audrieth[4] was tried. A solution of 4.8 g. of VIII and 2 g. of ammonium chloride in 120 ml. of liquid ammonia was placed in a 500 ml. Parr bomb and heated at 80–100° for twenty-four hours. The ammonia was allowed to evaporate and the residue was dissolved in 10% methanol and treated with charcoal. After removing the charcoal by filtration and the methanol by evaporation, chilling the solution resulted in the formation of white crystals, 0.1 g. (5%), m. p. 120–122°. Hydrogenation of 52.6 mg. of the substance with 10 mg. of Adams catalyst absorbed slightly more than the theoretical amount of hydrogen which would have been taken up by a tetrahydrotoluamide. Recrystallization of the hydrogenated product gave a white solid, m. p. 141.5°. This does not correspond to the melting point of 155–156° reported for the only known form of hexahydro-*m*-toluamide,[9] and save for an analysis of the hydrogenated material these compounds were not investigated further.

Anal. Calcd. for $C_8H_{15}NO$: N, 9.91. Found: N, 9.70.

trans-**1,2,5,6-Tetrahydro-*o*-toluamide (X)**.—To 120 ml. of liquid ammonia were added 2 g. of sodium hydride and 4.8 g. of VIII. The mixture was heated as before in a Parr bomb, and then the ammonia was allowed to evaporate. The resulting powder was dissolved in water, neutralized with hydrochloric acid, and then ether extracted. Evaporation of the ether gave a gum which was dried on a porous plate and then treated with charcoal and recrystallized from 10% methanol; yield, 0.1 g. (5%), m. p. 166°.

Anal. Calcd. for $C_8H_{13}NO$: N, 10.06. Found: N, 9.75.

trans-**Hexahydro-*o*-toluamide (XII)**.—Twenty-six milligrams of XI was hydrogenated with Adams catalyst in methanol. Slightly more than the theoretical amount of hydrogen was absorbed. Evaporation of the methanol following removal of the catalyst gave a product melting at 178°. Recrystallization from hot water raised the melting point to 180°, reported m. p. for *trans*-hexahydro-*o*-toluamide is 180–181°.[3–8]

Two grams of *cis*-hexahydro-*o*-toluamide, 2 g. of sodium hydride and 100 ml. of liquid ammonia were heated under pressure at 90° for two hours. The material was worked up as in the preparation of XI and 0.3 g. (15%) of amide, m. p. 180°, was obtained. A mixed melting point with the product obtained by hydrogenating XI was not depressed. When 2 g. of X, 2 g. of sodium hydride and 100 ml. of liquid ammonia were allowed to stand together for several hours while the ammonia gradually evaporated, no *trans* amide was obtained.

Acknowledgment.—This work has been supported in part by a grant-in-aid from the Council of Research and Creative Work of the University of Colorado. The sodium hydride used in this work was a gift of the Electrochemical Division of E. I. du Pont de Nemours, Inc., and the thionyl chloride was a gift of the Hooker Electrochemical Company.

Summary

The condensation of piperylene with two negatively unsymmetrically substituted ethylenes, acrylonitrile and methyl acrylate, in the Diels–Alder reaction has been found to give in both cases chiefly the *cis*-ortho isomer. This is in agreement with predictions based upon electronic theories.

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[8] Zelinsky, *Ber.*, **41**, 2676 (1908).

[9] Markownikoff, *J. prakt. Chem.*, [2] **49**, 64 (1894).

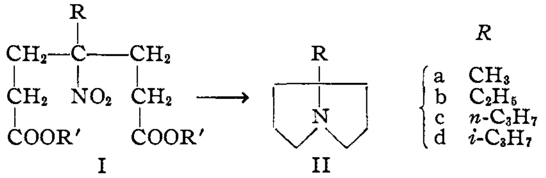
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of Pyrrolizidines. II. Basicities of 8-Alkylpyrrolizidines[1]

BY NELSON J. LEONARD AND KARL M. BECK[2]

The 8-alkylpyrrolizidines (II) offer an excellent opportunity for the detection of F-strain[3] in a bicyclic amine system, and the method of synthesis of 8-methylpyrrolizidine (IIa) reported from this Laboratory[1] shows promise of general application. Therefore, the preparation of homologous 8-alkylpyrrolizidines has been investigated so that the relative basicities of the products could be determined.

A favorable yield of 8-methylpyrrolizidine (IIa) had previously been realized in the hydrogenation of diethyl γ-methyl-γ-nitropimelate (Ia) in ethanol over copper chromite at 250–350 atm. and 275°.[1] In extending the method to 8-*n*-propyl-



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[1] For the first article in the series, see Leonard, Hruda and Long, THIS JOURNAL, **69**, 690 (1947).

[2] Present address: Abbott Laboratories, North Chicago, Illinois.

[3] Brown, THIS JOURNAL, **67**, 374 (1945).