

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Conjugated Diolefins by Double Bond Displacement. II

BY ALBERT L. HENNE AND HENRY H. CHANAN

The preceding paper¹ has described the rearrangement of seven 1,5-diolefins to conjugated dienes by passage over alumina heated to 365°. A new series of rearrangements has now been carried out at lower temperatures with a more efficient catalyst made of chromia deposited on alumina.

The use of chromia was proposed by Levina.² As chromia is a fine powder which packs and channels easily, it proved more convenient to use a mixed catalyst consisting of 5 mole per cent. of chromia on alumina, prepared by the method of Grosse and Ipatieff.³ The equipment and the rearrangement procedure were substantially as described in our preceding paper, with refinements in temperature control to ensure uniform regulation within 2°, and increase in dimensions of the catalyst column to a width of 2 cm. and a length of 120 cm. The optimum temperature for rearrangement was determined in pilot experiments by passing 1,5-hexadiene (diallyl) over the catalyst at the rate of one drop in three seconds, at temperatures varied in 25° intervals, and separating the resulting 2,4-hexadiene (dipropenyl) by fractional distillation. As the tem-

perature increased simultaneously from 7% to 9%, 12% and 14%. Consequently, a temperature of 250° was adopted as a standard for the whole study.

The progress of the rearrangement was followed by hourly readings of the refractive index. These readings which rose rapidly to a constant level due to the formation of the conjugated dienes, began in time to drop off markedly, showing that the catalyst was losing its efficacy. To regenerate the catalyst, the resinous deposit was first burned out by means of a stream of air at 450°. This treatment changed the color from the original blue-green to a bright orange, and at this stage a test for chromate ions was positive. After displacing the air with nitrogen, a stream of hydrogen was passed through at the same temperature for four hours; the catalyst, now green again, was then allowed to cool in a hydrogen atmosphere. This treatment restored the original efficacy, but became needed at increasingly shorter intervals.

All rearrangements were performed on freshly prepared or freshly regenerated catalysts. The diolefins tested were all of the 1,5-diene type; their synthesis was reported in another paper.⁴

TABLE I
TABLE OF EXPERIMENTAL RESULTS

Original diene	Low boiling, %	Intermediates, %	Polymers, %	Orig. diene recov., %	Rearrangement Products					
					Chief product	Yield, %	F. p., °C.	B. p., °C.	<i>d</i> ₂₀ ⁴	<i>n</i> _D ²⁰
CH ₂ =CHCH ₂ CH ₂ CH=CH ₂	...	17.2	6.1	...	CH ₂ CH=CHCH=CH ₂ ^{a,b}	76.7	...	82.0	0.7242	1.4535
CH ₂ =C(CH ₃)CH ₂ CH ₂ C(CH ₃)=CH ₂	0.9	7.9	5.5	...	(CH ₃) ₂ C=CHCH=C(CH ₃) ₂	85.5	-13.9	134.5	.7615	1.4781
CH ₂ =CHCH(CH ₃)CH ₂ CH=CHCH ₃	4.2	15.9	6.8	...	CH ₃ CH=CHCH=C(CH ₃)C ₂ H ₅ ^c	73.1	Glass	136.9	.7621	1.4703
CH ₂ =CHCH ₂ CH(CH ₃)CH=CHCH ₃	5.7	31.9	15.0	8.1	CH ₂ CH=CHC(CH ₃)=CHC ₂ H ₅ ^d	37.1	Glass	135.9	.7653	1.4670
CH ₂ =CHCH(CH ₃)CH(CH ₃)CH=CHCH ₃	4.4	51.5	11.5	9.9	CH ₃ CH=CHC(CH ₃)=C(CH ₃)C ₂ H ₅ ^e	22.6	Glass	156.5	.7855	1.4768
CH ₂ =CHCH ₂ CH ₂ CH=CHC(CH ₃) ₂	5.6	27.7	5.4	6.7	(CH ₃) ₂ C=CHCH=CHCH ₂ CH ₃ ^f	54.4	-96.4	135.8	.7559	1.4692
CH ₂ =CHCH(CH ₃)CH ₂ CH=CHC(CH ₃) ₂	9.8	25.8	5.9	9.5	(CH ₃) ₂ C=CHCH=C(CH ₃)C ₂ H ₅ ^g	48.9	-63.1	156.9	.7732	1.4792

^a The intermediate was a mixture of original and rearranged materials, in which it proved impossible to detect the presence of 1,4- or 1,3-hexadiene. ^b Much better than the 39% yield reported by rearrangement over alumina. ^c Gave acetic acid, identified by Duclaux number and methyl ethyl ketone with a 2,4-dinitrophenylhydrazone, m. p. 115°. ^d Gave acetic acid identified by Duclaux number and propionic acid with a *p*-toluide m. p. 123.5°. ^e Gave methyl ethyl ketone with a 2,4-dinitrophenylhydrazone m. p. 115°, and acetic acid identified by Duclaux number. ^f Gave acetone with a 2,4-dinitrophenylhydrazone m. p. 125°; the sample in which the expected propionic acid was being worked up was accidentally lost. ^g Gave acetone and methyl ethyl ketone, with 2,4-dinitrophenylhydrazones m. p. 125 and 116°, respectively.

perature rose, the yield of dipropenyl went from 49% at 200° to 64% at 250°, 65% at 275° and 64% at 300°, but the amount of polymerization

(1) Henne and Turk, *THIS JOURNAL*, **64**, 826 (1942).

(2) Levina, *J. Gen. Chem. (U. S. S. R.)*, **7**, 1587 (1937); **9**, 1834 (1939).

(3) Grosse and Ipatieff, *Ind. Eng. Chem.*, **32**, 268 (1940).

Experimental Results

The results of the rearrangements are listed in the table, together with the observed physical properties of the rearranged dienes. These physical measurements are equal to those reported

(4) Henne and Chanana, *THIS JOURNAL*, **66**, 392 (1944).

before¹ for the first three lines of the table and more precise than those in the literature for the third⁵ and the fourth⁶ line of the table.

Since the carbon skeleton of the molecules is not altered during the rearrangements, as shown before¹ by hydrogenation to known paraffins, the problem of identification is merely one of locating the double bonds. This was done by oxidation with ozone, using experimental procedures described previously.^{7,8} The ozonization results are listed in the notes of the table.

Comments

For double bond displacement chromia-coated

- (5) Bjelouss, *Ber.*, **43**, 2332 (1910).
 (6) v. Auwers and Westermann, *ibid.*, **54**, 2993 (1921).
 (7) Henne and Hill, *THIS JOURNAL*, **65**, 752 (1943).
 (8) Henne and Perilstein, *ibid.*, **65**, 2183 (1943).

alumina proved considerably more efficient than plain alumina. It permitted operation at 250° instead of 365° and reduced polymer formation.

The ease of rearrangement was found contradictory. In agreement with our first experiments, terminal bonds shifted inwards with ease, particularly well over a methyl group in *iso*-position; yet two compounds so constructed failed to rearrange.

Summary

Twelve dienes of the 1,5-type were subjected to double bond shift at 250° over a catalyst made of chromia and alumina. Seven were transformed to conjugated diolefins, while five failed to rearrange to any appreciable extent.

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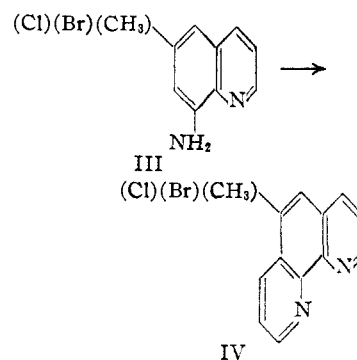
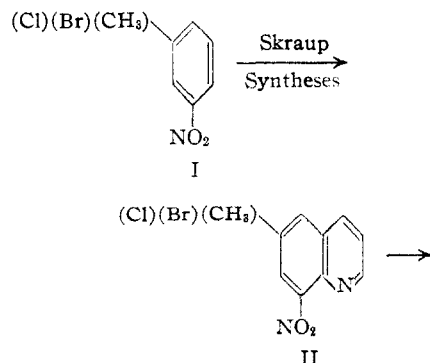
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Derivatives of 1,10-Phenanthroline¹

BY FREDERIC RICHTER² AND G. FREDERICK SMITH

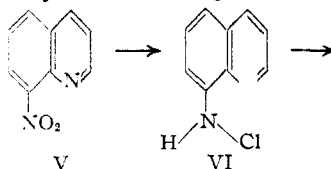
Although the application of the Skraup synthesis to 1,2-phenylenediamines suitably substituted in either the 4- and/or 5-positions might appear to be the most direct approach to the synthesis of 5 (6)-substituted (1,10)-phenanthrolines the side reactions encountered practically preclude the isolation of the desired products.³

Application of the method of Skraup to suitably substituted 2-nitroanilines (I) followed by reduction of the resulting 8-nitroquinolines (II) and application of a second Skraup synthesis to the 8-aminoquinolines so formed (III) is the basis for the present series of syntheses



From the standpoint of orientation, at least, 2-nitroanilines substituted in either the 4- or 5-positions could be employed because these positions later become equivalent in 1,10-phenanthroline. In the present series only 4-substituted 2-nitroanilines were employed.

The 5(6)-chloro(1,10)-phenanthroline obtained by the above scheme agreed in melting point and other properties with that obtained by Kuczynski and Sucharda⁴ who heated a mixture of 8-nitroquinoline, glycerol and hydrochloric acid under pressure. It is of interest to note that the chloro-phenanthroline obtained by this method is probably formed through 8-amino-5-chloroquinoline



(1) This contribution contains material from a dissertation presented by Frederic Richter to the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

(2) Aeration Processes Corporation Fellow in chemistry during the years 1939-1941. Present address: United States Rubber Company, Hogansville, Georgia.

(3) C. R. Smith, *THIS JOURNAL*, **52**, 397 (1930).

(4) Kuczynski and Sucharda, *Roczniki Chem.*, **16**, 513 (1936).