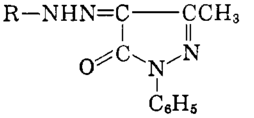
TABLE II

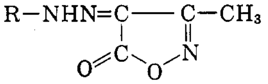
CHARACTERISTICS OF 1-PHENYL-3-METHYL-4-(SUBSTITUTED BENZENEAZO)-5-PYRAZOLONES



No.	R	Yield, %	M.P.	Color	Formula	Found	Calcd.
1	Phenyl	72	156°	Orange red	$C_{16}H_{14}N_4O$	N, 19.88	20.14
2	4-Chlorophenyl	78	142°	Orange red	$C_{16}H_{13}ClN_4O$	Cl, 10.98	11.36
3	2-Chlorophenyl	74	182°	Orange red	$C_{16}H_{13}ClN_4O$	Cl, 11.08	11.36
4	3-Nitrophenyl	79	180°	Orange red	$C_{16}H_{13}N_5O_3$	N, 21.42	21.67
5	2-Nitrophenyl	79	212°	Brownish red	$C_{16}H_{13}N_5O_3$	N, 21.36	21.67
6	2,5-Dichlorophenyl	79	224°	Orange red	$C_{16}H_{12}Cl_2N_4O$	Cl, 20.18	20.46
7	2-Chloro-4-nitrophenyl	80	223°	Deep red	$C_{16}H_{12}ClN_5O_3$	Cl, 9.62	9.93
8	2-Nitro-4-chlorophenyl	80	284°	Dull red	$C_{16}H_{12}ClN_5O_3$	Cl, 9.93	9.93

TABLE III

CHARACTERISTICS OF 3-METHYL-4-(SUBSTITUTED BENZENEAZO)-5-ISOXAZOLONES



No.	R	Yield, %	M.P.	Mixed M.P.	Color	Formula	Found	Calcd.
1	Phenyl	78	192°	192°	Pale yellow	$C_{10}H_9N_3O_2$	N, 20.42	20.68
2	4-Chlorophenyl	81	186°	186°	Yellow	$C_{10}H_8ClN_3O_2$	Cl, 14.68	14.94
3	2-Chlorophenyl	71	184°	183–184°	Pale yellow	$C_{10}H_8ClN_3O_2$	Cl, 14.52	14.94
4	3-Nitrophenyl	78	210°	210°	Light yellow	$C_{10}H_8N_4O_4$	N, 22.41	22.58
5	2,5-Dichlorophenyl	70	212°	212°	Yellow	$C_{10}H_7Cl_2N_3O_2$	Cl, 25.84	26.10
6	2-Chloro-4-nitrophenyl	72	210°	210°	Canary yellow	$C_{10}H_7ClN_4O_4$	Cl, 12.24	12.56
7	2-Nitro-4-chlorophenyl	73	184°	184°	Yellow	$C_{10}H_7ClN_4O_4$	Cl, 12.24	12.56

Characteristics of different isoxazolones prepared similarly are described in Table III.

Method B. The benzenediazonium salts were condensed with 3-methyl-5-isoxazolones in the manner described previously.[4]

Acknowledgment. The author's sincere thanks are due to Dr. S. S. Joshi of this College for his keen interest in this work and to the Ministry of Scientific Research and Cultural Affairs, Government of India, for a research scholarship.

DEPARTMENT OF CHEMISTRY
MEERUT COLLEGE
MEERUT, INDIA

A Study of the Anionotropic Rearrangement of 1,4-Hexadien-3-ol

JAMES M. SHACKELFORD[1] AND LOUIS H. SCHWARTZMAN[2]

Received March 30, 1961

The anionotropic rearrangement of 1,4-hexadien-3-ol (I) was studied in connection with a preparation for 1,3,5-hexatriene. The rearrangement gave a mixture containing 89% II and 11% III in quantitative yield. Each isomer was separated and chemically and physically characterized.

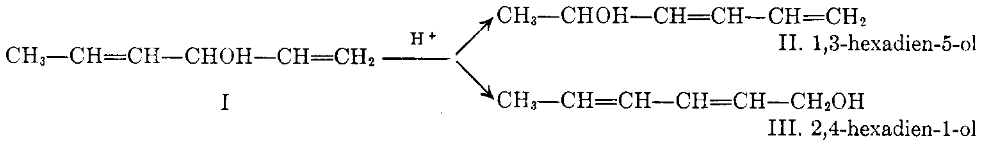
The anionotropic rearrangement of diolefinic alcohols, including I has been studied extensively.[3] Only the dienol II was obtained from I. However unsymmetrically substituted divinylcarbinols gave rearranged products corresponding to both II and III. A mechanism for the rearrangement reaction was postulated by Braude.[3b] It was suggested that an unsymmetrically substituted divinylcarbinol undergoes irreversible rearrangement, the hydroxyl group migrating to the more highly substituted γ-carbon and that the butadienylcarbinol formed thereby, undergoes a slow reversible five carbon oxotropic rearrangement. This suggested mechanism also postulated that the first reaction should be at least 10^3 times faster than the second with the result that no primary carbinol would be detected. The discrepancy between our findings and those reported

---

[1] Present address, Melpar Inc., Falls Church, Va.

[2] Deceased, November 1959.

(3) See the series of papers authored by Heilbron, Jones, McCombie, Weedon, and co-workers during the period of 1942–1950, *J. Chem. Soc.*, London, and (b) the series of papers by E. A. Braude and co-workers during the period of 1944–1953, *J. Chem. Soc.*, London.



earlier probably results from the analytical methods used for identification of products. We used mass spectrometry and vapor phase chromatography as aids in the determination of the previously undetected isomer. It is felt that had those instruments been used by the earlier workers they would have also found two rearrangement products from I.

The dienol III was found in the higher boiling fraction of the rearranged product from I and was characterized by its ultraviolet spectrum, melting point, and reduction to *n*-hexyl alcohol. A kinetic study of the rearrangement of I was also carried out. Under similar, but not quite identical conditions of acid strength and solvent, the reaction rate constant was found to be 1.94×10^{-4} min.$^{-1}$ compared to 1.75×10^{-4} min.$^{-1}$ as determined by Braude.

The mechanism proposed by Braude for the anionotropic rearrangement of diolefinic alcohols such as I involved a consecutive reaction. We believe that in the rearrangement of I that the products are formed by a concurrent reaction. This conclusion is based on the fact that II, which would be an intermediate in the formation of III according to the Braude mechanism could not be readily converted to III. The consecutive reaction proposes the irreversible rapid three carbon oxotropic rearrangement of I to II which subsequently through a slow reversible five carbon oxotropic rearrangement forms III. The isomerization of II to III has been reported to proceed slowly, only a few per cent being obtained after ten hours.[4] We also tried this rearrangement and obtained similar results. When II in 20% ethanol-water was admixed with 1*N* hydrochloric acid, no III could be detected after seventy-two hours, whereas, the isomerization of I gave *ca.* 10% of III in five minutes. This would indicate that this rearrangement does not proceed through the intermediate of II.

EXPERIMENTAL[5]

Rearrangement of 1,4-hexadien-3-ol (I)—*heterogeneous.* I (118 g.) in 900 ml. of 0.1*N* hydrochloric acid was vigorously shaken for 5 min. Potassium carbonate (0.15 mole) was added at once, and the mixture was stirred for 1 min. The solution was saturated with salt and extracted with ether (3 × 150 ml.). The ether extracts were washed with saturated potassium carbonate solution (100 ml.), dried over magnesium sulfate, concentrated, and distilled through a Todd column (12:1 reflux ratio). There were obtained II (107 g.), b.p. 75–76°/30 mm., n^{25}_D 1.4778 and III (10 g.), b.p. 78–80°/10 mm., solidified in the receiver, m.p. 28–29°. Total material balance, 99+%. Analysis by means of mass spectrometry indicated that the mixture, before distillation, contained 11% III, 89% II, and no I.

III was identified by means of its m.p. 28–29°,[6,7] ultraviolet spectrum, (ϵ 24,400 at 227 mμ), and by reduction to *n*-hexyl alcohol over platinum.

Rearrangement of I—*homogeneous.* I (120 g.) was added to 880 ml. of 50% ethanol-water containing 3.65 g. hydrogen chloride and was allowed to stand at 25° for 35 min. Sodium bicarbonate (0.15 mole) was added, and then the solution was saturated with salt. The organic layer was separated, the aqueous layer was extracted with ether, and the organic solutions were combined, dried over magnesium sulfate, concentrated, and distilled through a Todd column (12:1 reflux ratio). There was obtained a mixture, (103 g., 85%) b.p. 72–75°/40 mm., which was analyzed by means of mass spectrometry and found to contain II (87%), III (10%), unchanged I (2%), and traces of another unknown product of mass 112.

Attempted acid-catalyzed rearrangement of II. One milliliter of II was diluted with ethanol (19 ml.), and the resulting solution was made up to 99 ml. with distilled water. One milliliter of 1*N* hydrochloric acid was added, the solution thoroughly mixed and placed in a Cary ultraviolet recording spectrophotometer at 227 mμ. There was no detectable change in absorption after 20 min. There was also no change of absorption at 223 mμ after 30 min. After 72 hr. only a very slight shift (*ca.* 1%) was observed in the region 220–240 mμ from the standard absorption curve for II.

Rearrangement of I—*kinetic study.* These kinetic experiments were carried out in a constant temperature room maintained at 25° ± 0.5° with the use of a Cary ultraviolet recording spectrophotometer, Model No. 11 with matched silica cells (1 cm.). I dissolved in 50% (by volume) ethanol-water was mixed with the desired amount of hydrochloric acid. After being shaken for 30 sec., the solution was poured into one of the matched cells and then inserted in the spectrophotometer. Zero time was arbitrarily taken as the time when all of the acid was added, but before the solution was shaken. The absorption was measured at 223 mμ during the experiments and in each case the recording of the optical density *vs.* time gave a straight line. The absorption at 223 mμ was characteristic of II, the predominant isomer in the rearranged product. We found, as did Braude, the reaction to be first order and the rate constants to be directly proportional to the concentration of acid and independent of the initial carbinol concentration. The I concentration (moles/l.), acid concentration, and corresponding reaction rate constant were: 8.4×10^{-5}, $10^{-2}N$, 196.0×10^{-4} min.$^{-1}$; 8.4×10^{-4}, $10^{-3}N$, 19.1×10^{-4} min.$^{-1}$; 8.4×10^{-5}, $10^{-4}N$, 1.94x 10^{-4} min.$^{-1}$

Koppers Co., Inc.
Monroeville Research Center
Box 128
Monroeville, Pa.

---

[4] I. N. Nazarov and L. B. Fisher, *Izvest. Akad. Nauk. S.S.S.R., Otel. Khim. Nauk.*, 427 (1948).

[5] Melting points and boiling points are uncorrected.

[6] T. Reichstein, C. Ammann, and G. Trivelli, *Helv. Chim. Acta*, **15**, 261 (1932) reported m.p. 30.5°.

[7] G. E. Woods, N. C. Bolgiano, and D. E. Duggan, *J. Am. Chem. Soc.*, **77**, 1800 (1955), reported m.p. 29°.