Summary

4-Nitrosalicylaldehyde has been prepared and two phenylhydrazones for its characterization have been described.

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

Conjugated Diolefins by Double Bond Displacement

BY ALBERT L. HENNE AND AMOS TURK

The reaction of methallyl chloride with magnesium in ether gives about 90% of the normally expected "dimethallyl" (2,5-dimethyl-1,5-hexadiene) and about 10% of "diisocrotyl" (2,5-dimethyl-2,4-hexadiene), depending on experimental conditions. When the crude product is distilled in steel equipment, a drift of physical properties occurs, which indicates that isomerization takes place. However, if the crude is washed free of acids and salts, and is distilled in glass, no drift occurs. This observation prompted an investigation of the conditions which would favor the displacement of the double bonds, a type of rearrangement which has been shown conclusively before, in various papers.[1a,b,c]

A systematic study of the effect of various reagents and of various experimental conditions on the rearrangements of dimethallyl and diallyl was first made.

Dimethallyl was treated unsuccessfully with iodine (five hours of reflux), oxalic acid (five hours of reflux); it rearranged very slightly after four hours of reflux with 50% hydrogen bromide, or six hours of reflux with 47% hydrogen iodide; it polymerized completely by heating with zinc chloride; alcoholic potassium hydroxide was without effect when refluxed, and of only slight value after five hours at 200°; fused potassium hydroxide was slightly better; ferric chloride caused much polymerization, but effected from 15 to 30% rearrangement at temperatures ranging from 150 to 230°; magnesium chloride caused 39% of rearrangement after six hours at 220°, and much polymerization; heat alone applied for twelve hours caused 27% rearrangement at 260° in iron and 41% in glass at the same temperature; alumina brought about a 25% yield at 250°, and 81% at 365.°

Diallyl resisted rearrangement when heated alone, with oxalic acid, alcoholic potassium hydroxide or magnesium chloride; in the latter case polymerization took place at temperatures higher than 140°. Alumina at 220° for four hours caused some rearrangement, and at 365° it gave a 34% yield; no polymerization occurred.

On the basis of these findings the following uniform procedure was adopted to study the rearrangement of some seven 1,5-dienes prepared by the condensations of various allylic chlorides.[1c] Each diene was passed through a vertical column of activated alumina 60 cm. long and 15 mm. in diameter, electrically heated to 365°. The rate was 60 ml. per hour. The reaction products were distilled through an analytical column, and the relative amounts of each were thereby determined. The portions corresponding to the various plateaus were identified by physical constants when possible, and by oxidation with ozone when needed. Crystalline derivatives were made in some cases. The physical constants obtained for the large reproducible samples of the diolefins thus prepared are listed in Table I.

The results of the rearrangements over heated alumina are listed in Table II.

In all cases 95% of material was recovered after the rearrangement reaction. The distillation gave the % indicated of pure compounds, and the balance was made up of low, intermediate and high boiling fractions.

Identifications of the rearranged products were made from literature data supplemented by the following experimental details.

I. Condensation of 2,4-hexadiene with maleic anhydride in benzene gave 3,6-dimethyl-1,2,3,6-tetrahydrophthalic anhydride, m. p. 94°.[2] The maleic anhydride adduct of the 1,3-hexadiene was 3-ethyl-1,2,3,6-tetrahydrophthalic anhydride, m. p. 52°; calcd. for $C_{10}H_{12}O_3$; C, 66.67; H, 6.67. Found: C, 66.60; H, 6.70.

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[1] (a) Cramer and Glasebrook, THIS JOURNAL, **61**, 230 (1939); (b) Levina and Kiryushov, *J. Gen. Chem.* (U. S. S. R.), **9**, 1834 (1939); (c) Henne, Chanan and Turk, THIS JOURNAL, **63**, 3474 (1941).

[2] Diels and Alder, *Ann.*, **470**, 62 (1929).

TABLE I

PHYSICAL CONSTANTS

Compound	B. p., °C.	F. p., °C.	$n^{20°}\mathrm{D}$	d^2_4	MR. obs.	MR. calcd.	MR. exalt.
$CH_3CH{=}CHCH{=}CHCH_3$	82.0		1.4535	0.7242	30.69	28.97	1.72
$CH_2{=}CHCH{=}CHC_2H_5$	72.9		1.4402	.7070	30.63	28.97	1.66
$CH_3CH{=}CHCH{=}CHC_2H_5$	109.6		1.4578	.7384	35.52	33.59	1.93
$(CH_3)_2C{=}CHCH{=}CHCH_3$	111.5	−74.6	1.4680	.7449	35.89	33.59	2.30
$C_2H_5CH_3C{=}CHCH{=}CH_2$[a]	111		1.463				
$C_2H_5CH_3C{=}CHCH{=}CHCH_3$	135.2		1.4693	.7652	40.12	38.21	1.91
$(CH_3)_2C{=}CHCH{=}C(CH_3)_2$	134.5	+13.94	1.4781	.7615	40.97	38.21	2.76

[a] Probable structure.

TABLE II

EXPERIMENTAL RESULTS

Experiment	Original diene	% Unchanged	Rearranged products	%
I	C=C—C—C—C=C	44	C—C=C—C=C—C	39
			C=C—C=C—C—C	3
II	C=C(C)—C—C—C(C)=C	1	C—C(C)=C—C=C(C)C	81
III	C=C(C)—C—C—C=C	0	C—C(C)=C—C=C—C	58
IV	C=C—C(C)—C—C=C	0	C=C—C=C(C)—C	14
V	C=C—C—C—C=C—C	58	C=C—C(C)—C—C=C	8
			C—C=C—C=C—C—C	6
VI	C=C—C(C)—C—C=C—C	70	C—C=C—C=C(C)—C=C	4
VII	C—C=C—C—C—C=C—C	72	C—C—C=C—C=C—C—C	0.5

II. Reaction of the 2,5-dimethyl-2,4-hexadiene with maleic anhydride yielded only an amorphous, high melting product. This may be correlated with other observations reported in the literature which indicate that dienes with doubly substituted carbon atoms in the terminal (1,4) positions of a conjugated system RRC=C—C=CRR do not tend to give crystalline maleic anhydride addition products.[3]

III. 2-Methyl-2,4-hexadiene gave only an amorphous polymeric addition product when treated in the cold with maleic anhydride.[3]

IV. The rearranged diolefin was probably 4-methyl-1,3-hexadiene; it was condensed with maleic anhydride to yield an amorphous product. In contrast, an authentic sample of 3-methyl-2,4-hexadiene[4] (the other possible conjugated rearrangement product) was condensed with maleic anhydride under the same conditions, to give a crystalline substance, 3,4,6-trimethyl-1,2,3,6-tetrahydrophthalic anhydride, m. p. 76°; calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27; found: C, 68.21; H, 7.27. These Diels–Alder reactions (as well as all others carried out in this work) support the generalization cited above concerning crystalline and polymeric diene adducts; *e. g.*, C—C=C(C)—C=C—C gives a crystalline adduct while C—C—C(C)=C—C=C gives a polymeric adduct.

V. The maleic anhydride adduct of 2,4-heptadiene was 3-methyl-6-ethyl-1,2,3,6-tetrahydrophthalic anhydride, m. p. 70.5°; calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27; found: C, 68.07; H, 7.27.

VI. Ozonolysis of the 5-methyl-2,4-heptadiene yielded methyl ethyl ketone, acetic acid and oxalic acid, and no other fragments, thereby fixing the place of the double bonds. The maleic anhydride adduct of the 5-methyl-2,4-heptadiene was a polymer.

Discussion of the Isomerization

(a) It appears from Table II that rearrangements of double bonds under the conditions used occur most easily from the terminal position inward toward the center of the molecule; the shift toward a conjugated position becomes more difficult when one of the double bonds of the isolated diene is buried in the chain, and most difficult when both double bonds of the isolated diene are buried. This generalization is illustrated by the comparable sets of experiments, I > V > VII and IV > VI.

Experiment number:	I, V and VII
% Rearrangement:	39, 6 and < 1
Experiment number:	IV and VI
% Rearrangement:	14 and 4

(b) The rearrangement of a terminal double

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[3] Farmer and Warren, *J. Chem. Soc.*, 3221 (1931); Bacon and Farmer, *ibid.*, 1065 (1937).

[4] Emil G. Wiest, Ph.D. Dissertation, The Ohio State University, 1940.

bond is facilitated by the presence of a side methyl group in the 2-position. This is illustrated by the comparable results in experiments I >III >II.

Experiment number: I, III and II
% Rearrangement: 39, 58 and 81

It is also noteworthy that the rearrangement of dimethallyl occurred more easily than that of diallyl for all different sets of experimental conditions which were used.

The same observation concerning the effect of a side chain methyl group was made in the cases of 1-octene and 2-methyl-1-heptene, both prepared by magnesium condensations of allylic chlorides and reported in a previous paper.[1c] No isomerization of 1-octene occurred under the reaction conditions used, whereas the 2-methyl-1-heptene rearranged to 2-methyl-2-heptene whenever magnesium chloride was present and the temperature was allowed to rise.

(c) For symmetrical carbon skeletons, the direction of the shift is mainly toward the center of the molecule; only a small amount of diene with its conjugated system at one end of the molecule was found in the case of 1,3-hexadiene obtained from 1,5-hexadiene.

(d) In the cases where the tendencies of shifting toward the center and of shifting past a methyl group would conflict, the tendency to shift past the side chain predominates; *e. g.*, $\mathrm{C{=}C{-}C(C){-}C{-}C{=}C{-}C \rightarrow C{-}C{-}C(C){=}C{-}C{=}C{-}C}$ and $\mathrm{C{=}C{-}C(C){-}C{-}C{=}C \rightarrow C{-}C{-}C(C){=}C{-}C{=}C}$.

(e) Some pyrolysis or shift in the carbon structure is observed in all the cases of hot alumina treatment, and small amounts of low boiling hydrocarbons are obtained. In the case of 1,5-heptadiene, a carbon skeleton rearrangement product was isolated, namely, 3-methyl-1,5-hexadiene.

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Summary

The displacement of the double bonds in diolefins has been investigated. The diolefins dimethallyl and diallyl were first studied to determine various sets of conditions which would promote isomerization, and to establish a standard procedure for use with other hydrocarbons. After this a series of 1,5-diolefins was subjected to catalytic alumina treatment, and the products were separated, studied and identified. The characteristics of the isomerization reaction have been discussed.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, SCHOOL OF PHARMACY, UNIVERSITY OF MARYLAND]

Diazonium Borofluorides. III. Their Use in the Bart Reaction

BY A. WAYNE RUDDY,* EDGAR B. STARKEY AND WALTER H. HARTUNG

Of the various methods for preparing aromatic arsonic acids, that developed by Bart[1] has been most widely used. Solutions of diazonium chlorides or sulfates are added to sodium arsenite in alkaline or neutral solution in the presence of various metals or their salts. Subsequent investigators have introduced various modifications and improvements[2] so that now in many instances good yields are possible. However, Bart's original procedure and all subsequent modifications are handicapped by the use of unstable diazonium intermediates.

The use of the stable diazonium borofluorides in these Laboratories for the preparation of aromatic mercurials[3] and of aromatic nitro compounds[4] suggested their use also in the Bart reaction. Results justified the expectations.

The diazonium borofluorides of aromatic amines may be readily prepared in excellent yields by allowing the amine to react with fluoboric acid and sodium nitrite. Because of their increased stability they were observed to have less tendency to decompose or to form by-products when allowed to react with sodium arsenite; furthermore, the reactions could be carried out at room temperature.

This modification was introduced into the Bart

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* H. A. B. Dunning Fellow, 1938–1940.

[1] Bart, German Patents 250,264, 254,092, and 268,172.

[2] (a) Mouneyrat, British Patent 142,947; (b) Schmidt, *Ann.*, **421**, 159 (1920); (c) Doak, THIS JOURNAL, **62**, 167 (1940).

[3] Dunker, Starkey and Jenkins, *ibid.*, **58**, 2308 (1936); Dunker and Starkey, *ibid.*, **61**, 3005 (1939).

[4] Starkey, *ibid.*, **59**, 1479 (1937).