Summary

2,6-Dimethyl-1,4-naphthoquinone does not react with certain reagents which easily add to the conjugated system of 2,6-dimethyl-3,4-naphthoquinone. Of the two isomeric quinones, on the other hand, only the α-quinone reacts with diazomethane, and this in an unusual manner. Both quinones, as well as other alkyl-substituted benzo- and naphthoquinones are capable of adding dienes, if somewhat slowly, making available an interesting type of compound containing bridge methyl groups between two cyclohexane rings.

Converse Memorial Laboratory
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[Contribution from the Research Laboratories of the Universal Oil Products Company]

Isomerization of Normal Butenes

By V. N. Ipatieff, Herman Pines and R. E. Schaad

The rearrangement of normal butenes in the presence of catalysts has not been studied quantitatively previously. Gillet[1] found that 1-butene changes into 2-butene when passed over heated aluminum sulfate. According to Hurd[2] such rearrangement also occurred during pyrolysis, with the ratio of the lower boiling 2-butene (0.5°) to the higher boiling 2-butene (2.5°) being 3/2. Runge and Mueller-Cunradi[3] patented a method of converting 1- into 2-butene by heating to 400–600° in an empty quartz tube or at 420° in contact with lime, aluminum phosphate, pumice or bauxite.

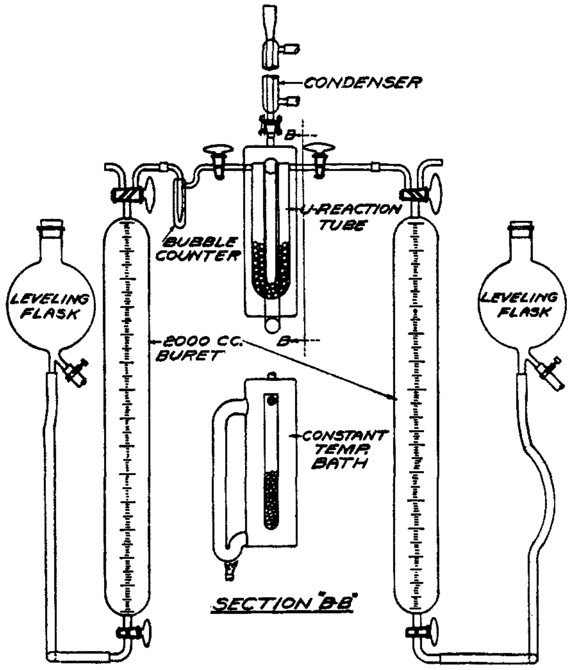
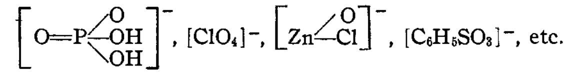
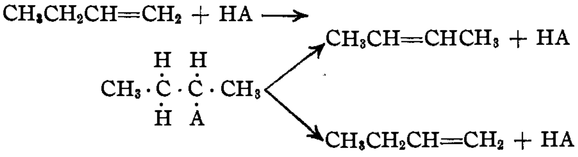


Fig. 1.

The present paper deals with rearrangements of normal butenes in the presence of catalysts. It is here assumed that the isomerization reaction consists of two steps: (1) formation of an addition product of the olefin with the catalyst and (2) the decomposition of such addition product whereby the same olefin or one with a different structure is split off and the catalyst is regenerated. In the following equations illustrating the isomerization, "A" represents groups such as



$$\left[O{=}P\begin{matrix}O\\OH\\OH\end{matrix}\right]^-,\ [ClO_4]^-,\ \left[Zn\begin{matrix}O\\Cl\end{matrix}\right]^-,\ [C_6H_5SO_3]^-,\ \text{etc.}$$



$$CH_3CH_2CH{=}CH_2 + HA \longrightarrow \begin{matrix}H & H\\ CH_3\cdot\dot{C}\cdot\dot{C}\cdot CH_3\\ \dot{H} & \dot{A}\end{matrix} \begin{matrix}\nearrow CH_3CH{=}CHCH_3 + HA\\ \searrow CH_3CH_2CH{=}CH_2 + HA\end{matrix}$$

Experimental Part

Apparatus and Procedure.—The apparatus used (Fig. 1) for studying isomerization of butenes at ordinary pressure consisted of two 2-liter gas burets, two leveling flasks, and a U-shaped reaction tube one-third full of glass spheres (3 to 5 mm. diameter) and surrounded by a jacket in which water and organic liquids were refluxed to maintain chosen, constant temperatures. The butene under investigation contained in the left buret was passed at a rate of 400–450 ml. per hour through a weighed quantity of the liquid isomerizing catalyst in the U-reaction tube and collected in the other buret which was always kept at approximately atmospheric pressure by manipulation of the leveling flasks.

For the experiments at superatmospheric pressure, the liquid butene under the desired nitrogen pressure in a steel charger provided with a gage glass, was passed through small copper tubing to the steel tube (13 mm. inside diameter) containing the solid catalyst. The speed of the butene flow was controlled by a needle valve at the exit end of the catalyst tube and a calibrated flowmeter

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[1] Gillet, *Bull. soc. chim. Belg.*, **29**, 192 (1920).

[2] Hurd, *Ind. Eng. Chem.*, **26**, 51 (1934); Hurd and Goldsby, This Journal, **56**, 1812 (1934).

[3] Runge and Mueller-Cunradi, U. S. Patent 1,914,674, June 20, 1933; *C. A.*, **27**, 4253 (1933).

through which the treated gas passed before collection over salt water in a calibrated gas holder, or, in some cases, liquefaction in a trap kept at −78° by solid carbon dioxide and acetone.

Method of Analysis.—The butene after subjection to the action of a catalyst under either atmospheric or higher pressure was analyzed by Podbielniak's[4] low-temperature fractional distillation method—the normal boiling points of the normal butenes being: 1-butene, −5.0°; *cis*-2-butene, +0.5° and *trans*-2-butene, +2.5°.

Preparation of the Butenes.—Dehydration of 1-butanol (0.5 mole per hour) over activated alumina at 427° gave 1-butene (100% pure), a result checking that of Pines.[5] However, after intermittent use in preparing several liters of liquefied butenes, the activated alumina then produced mixtures of 1- and 2-butene containing approximately 6% of the latter. Such partial isomerization is thought to be due to accumulation on the catalyst of small amounts of acidic materials resulting from oxidation by traces of air accidentally entering the catalyst chamber during shut-down periods.

The *trans*-2-butene was separated by low-temperature fractional distillation from a butene mixture (14.1% 1-C_4H_8, 8.2% *cis*- and 77.7% *trans*-2-butene) prepared by dehydrating 2-butanol at 300° over diatomaceous earth impregnated with phosphoric acid.

Other mixtures containing 65 to 88% of 2-butene were prepared similarly from 1-butanol, a result in agreement with that of Komarewsky and Johnstone[6] but contradicting that of King,[7] who reported the formation of 2-butene only by passing 1-butanol over pumice impregnated with glacial phosphoric acid.

Since exposure to sunlight is known to cause rearrangement of certain bromoalkenes (BrCH=CHBr and CH_3-CH=CHBr)[8] into equilibrium mixtures of the *cis* and *trans* isomers, it was desired to see whether *trans*-2-butene undergoes any such change. Accordingly the whole fraction, shown by analysis to be pure *trans*-2-butene, was then divided into three parts and stored as follows: (1) in a brown bottle kept in the dark at room temperature, (2) in a bottle of ordinary glass exposed to light and (3) in the liquid phase at −78°. After such storage for twelve days, all three samples were analyzed again and found to be pure *trans*-2-butene, which was saved for the experiment with phosphoric acid.

Discussion of Results

Isomerization of 1-Butene in the Presence of Phosphoric Acid.—As the temperature was raised, increasing amounts of 1-butene isomerized into 2-butene by passing through 36 g. of 100% orthophosphoric acid in the apparatus shown by Fig. 1. Between 3 and 6% by volume of butene was absorbed.

Mixtures containing 20 to 30% of 1-butene and 70–80% 2-butene resulted when either 1-butanol or 1-butene passed at a rate of 1 mole per hour through a Pyrex tube heated to 427° and packed with a 60 cc. gross volume of granular solid prepared from hydrate of alumina (1 mole) and orthophosphoric acid (1.6 moles).

TABLE I

ISOMERIZATION OF 1-BUTENE BY 100% ORTHOPHOSPHORIC ACID

Temp., °C.		26	78	100	135
% by volume	1-C_4H_8	96	88	66	40
	2-C_4H_8	4	12	34	60

Similar increase in isomerization with temperature rise (compare Table I) was observed under pressure in the presence of diatomaceous earth impregnated with phosphoric acid (Table II). At 249° this material converted 1-butene quantitatively into 2-butene without formation of polymers, but when the experiment was continued for a long time at 250 to 325°, this solid lost part of its activity as evidenced by the fact that isomerization to the 2-isomer was then 70 to 80% complete. Perhaps the decrease in isomerization activity was due to a slow partial dehydration of orthophosphoric acid through the pyro- and toward metaphosphoric acid.

With the second sample of the diatomaceous earth–phosphoric acid mixture, evidence of equilibrium was observed in that increasing the contact time about four-fold made no change in the percentage conversion of 1- into 2-butene. With contact times of 205 to 270 and 1020 seconds, from 72 to 79% of 2-butene was formed.

TABLE II

ISOMERIZATION OF 1-BUTENE UNDER PRESSURE IN THE PRESENCE OF DIATOMACEOUS EARTH IMPREGNATED WITH PHOSPHORIC ACID

Period no.	Temp., °C.	Press., atm.	Time, hrs.	C_4H_8 exit rate, 1/hr.	Exit C_4H_8, % by volume 1- C_4H_8	2- C_4H_8	Contact time, sec.
Sample No. 1, Catalyst "D"							
			Butene Charged		94	6	...
1	100	2.45	4.25	3.6	64	36	83
2	99	6.0	5.00	4.0	79	21	244
3	126	7.8	4.25	3.5	26	74	255
4	149	7.8	5.00	3.7	16	84	226
5	174	7.9	3.75	3.3	..	..	243
6	200	7.8	2.50	3.6	5.5	94.5	208
7	249	7.8	2.75	3.3	0.0	100.0	206

Isomerization of 1-Butene in the Presence of Other Substances.—Further experiments at atmospheric pressure (Fig. 1) showed formation of 2-butene to be: 21% at 21° in the presence of perchloric acid (70–72%); 13% at 76° in the presence of benzene sulfonic acid (75% aqueous

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(4) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 172 (1933).

(5) Pines, THIS JOURNAL, **55**, 3892 (1933).

(6) Komarewsky and Johnstone, private communication.

(7) King, *J. Chem. Soc.*, **115**, 1404 (1919).

(8) Van de Walle, *Bull. soc. chim. Belg.*, **27**, 209 (1913).

solution); 5% at 100° in the presence of an aqueous solution containing 75% of zinc chloride. Glacial acetic, mono- and dichloro acetic acids caused no isomerization at 100°.

Isomerization of *trans*-2-Butene by Phosphoric Acid.—Pure *trans*-2-butene (450 ml. per hour) on passage through 36 g. of 100% orthophosphoric acid at 100° (Fig. 1) underwent partial isomerization to a mixture containing 6.6% 1-butene, 6.0% *cis*- and 87.4% *trans*-2-butene.

Summary

1. Isomerization of 1- into 2-butene was slight in the presence of phosphoric acid at room temperature and increased with rising temperature. A similar increase in isomerization of 1- into 2-butene with temperature rise was observed under pressure in the presence of diatomaceous earth impregnated with phosphoric acid. At 249° isomerization was complete under 7.8 atmospheres pressure.

2. Pure *trans*-2-butene underwent partial isomerization into 1-butene (6.6%) and *cis*-2-butene (6.0%) during passage through 100% orthophosphoric acid at 100°.

3. 1-Butene isomerized partially into the 2-isomer in the presence of perchloric acid and aqueous solutions of zinc chloride and benzene sulfonic acid.

RIVERSIDE, ILLINOIS RECEIVED SEPTEMBER 10, 1934

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 147]

Di-(*p*-bromophenyl)-furans and 1,4-Diketones

BY ROBERT E. LUTZ AND W. M. EISNER

This paper deals with the preparation of some new compounds of this series and some further studies of typical reactions.[1]

The nitric–acetic acid oxidation[1i] of 2,5-di-(*p*-bromophenyl)-3,4-dichloro and dibromofurans (I) gives in good yields the corresponding *cis* di-(bromobenzoyl)-dihalogenoethylenes III. The configurations are based on the fact that these compounds are the labile forms and are converted by the action of sunlight on a chloroform solution containing iodine into the stable and therefore *trans* isomers.[1d] The synthesis of the *trans* dibromo isomer IV from dibromofumaryl chloride II by the Friedel–Crafts reaction confirms these configurations (see Diagram 1). All four of these dihalogenoethylenes are reduced with ease by means of zinc and glacial acetic acid to di-(bromobenzoyl)-ethane V (known[2]).

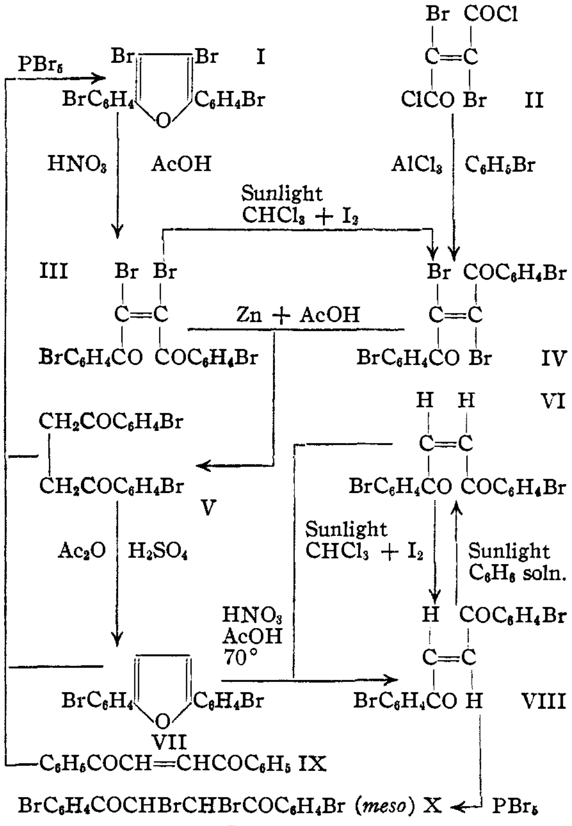

DIAGRAM 1.

2,5-Di-(bromophenyl)-furan VII, prepared by the action of acetic anhydride and sulfuric acid on di-(bromobenzoyl)-ethane V, is easily oxidized by the nitric–acetic acid method, giving however the *trans* di-(bromobenzoyl)-ethylene VIII. The *cis* isomer VI[3] is undoubtedly first formed in the oxidation; it may be prepared by exposing a benzene solution of the *trans* isomer to the sunlight, and is very easily rearranged back into the *trans* isomer, either by the nitric–glacial acetic

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[1] *Cf.* (a) Conant and Lutz, THIS JOURNAL, **47**, 881 (1925); Lutz, *ibid.*, (b) **48**, 2905 (1926); (c) **51**, 3008 (1929); **52**, (d) 3405, (e) 3423 (1930); Lutz and Taylor, *ibid.*, **55**, (f) 1168, (g) 1585, (h) 1593 (1933); Lutz and Wilder, *ibid.*, **56** (i) 979, (j) 2145 (1934).

[2] Hale and Thorpe, *ibid.*, **35**, 272 (1913).

[3] We are indebted to Mr. P. A. Whitaker for the isolation of this compound.