

Hydrolysis of 0.5 g. with alcoholic sodium hydroxide gave 0.42 g. (93%) of the *cis* acid which was identified by a mixed melting point.

$\beta$ -(*p*-Bromobenzoyl)-butyric Acid (VIII).—*Cis*  $\beta$ -bromobenzoylcrotonic acid was dissolved in a warm solution of sodium carbonate and heated for a short time with a solution of a large excess of sodium hydrosulfite. On acidifying, the reduced acid was precipitated pure in practically quantitative yield.

$\beta$ -(*p*-Bromobenzoyl)-butyric Methyl Ester (VII).—A solution of 5 g. of the acid in 50 cc. of methanol containing 1 cc. of sulfuric acid was refluxed for two hours. The ester was isolated as a colorless oil of b. p. 193–194° at 20 mm., yield 3.9 g. (74%).

*Anal.* Calcd. for  $C_{12}H_{13}O_2Br$ : C, 50.50; H, 4.60. Found: C, 50.40; H, 4.33.

The silver salt preparation gave similar results but was less convenient because of the gelatinous nature of the silver salt.

Hydrolysis of the ester with alcoholic sodium hydroxide gave an almost quantitative yield of the acid.

$\beta$ -(*p*-Bromobenzoyl)-butyric Ethyl Ester (VII).—Prepared by esterification of the acid with absolute ethanol and sulfuric acid as above; yield 3.6 g. (71%); crystallized from ethanol; m. p. 34.5°.

*Anal.* Calcd. for  $C_{13}H_{15}O_2Br$ : C, 52.17; H, 5.06. Found: C, 52.10; H, 5.35.

Hydrolysis of 0.5 g. with alcoholic sodium hydroxide gave 0.41 g. (90%) of the acid which was identified by a mixed melting point.

### Summary

A study of the open chain and cyclic esters of *cis*  $\beta$ -bromobenzoylcrotonic acid is described and evidence for the structures is presented.

The reduction of the open chain esters gives  $\beta$ -bromobenzoylbutyric ester.

Cyclic structures for *cis*  $\beta$ -bromobenzoylcrotonic acid and its acid chloride are considered.

UNIVERSITY, VA.

RECEIVED SEPTEMBER 29, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## The Allyltoluenes<sup>1</sup>

BY CHARLES D. HURD<sup>2</sup> AND HARRY T. BOLLMAN<sup>3</sup>

Recently the pyrolysis of four unsaturated hydrocarbons,  $R-\beta-CH_2-\alpha-CH=CH_2$ , was reported.<sup>4</sup> The R was of low electron attraction (R = allyl, isopropyl, cyclohexyl, benzyl). The formation of much more propylene than ethylene indicated that the bond which was alpha to the unsaturation was stronger than the beta. The present paper deals with *o*- and *p*-allyltoluenes, compounds isomeric with the 4-phenyl-1-butene previously studied. The allyltoluenes are new compounds. They differ from 4-phenyl-1-butene in possessing a strongly electronegative R (tolyl).

*p*-Allyltoluene,  $CH_3-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}=\text{CH}_2$ , contains no beta bonds but only alpha bonds. These should be comparatively resistant to heat. The findings are in agreement with this viewpoint. Methane predominated in the gaseous products and more ethylene was formed than propylene. These facts suggest rupture at all three C-C positions in both side chains. Of course, some of the methane and ethylene are secondary products because of the high tempera-

tures involved. As would be expected, the allyltoluenes were somewhat more stable than 4-phenyl-1-butene.

The hydrocarbons were pyrolyzed as previously described.<sup>4</sup> An empty quartz tube was used, the heated volume of which was 17 cc. Data are summarized in Table I.

**Liquid Products.**—The liquid products from *o*-allyltoluene gave toluene, *o*-xylene and unchanged *o*-allyltoluene between 110–190°. The fraction boiling above 190°, which made up one-third of the recovered material, yielded a solid which was distilled at reduced pressure. Naphthalene was the major product in this solid. Bromination of the 110–190° fraction in carbon tetrachloride removed the allyltoluene, allylbenzene and other unsaturates from the toluene and xylene. The last two, separated by fractional distillation, were confirmed by formation of dinitrotoluene (m. p. 68°) and the sulfonamide derivative of *o*-xylene (m. p. 141°).

Similarly, *p*-allyltoluene yielded toluene and *p*-xylene in the condensed liquids; derivative, trinitro-*p*-xylene, m. p. 135°. The liquid products from the 575° experiment gave these fractions: (°C., g.,  $n_D^{20}$ ) 110–140, 2.8, 1.501; 140–176, 2.3, 1.517; 176–181, 8.0, 1.521; 181–189, 11.7, 1.527; 116–120 at 70 mm., 1.9, 1.538; and 10.0 g. of residue. The quantity of benzene from *o*- or *p*-allyltoluene was always negligible.

**Non-Rearrangement of 4-Phenyl-1-butene into *o*-Allyltoluene.**—To ascertain whether or not 4-phenyl-1-butene (allylphenylmethane) would rearrange into *o*-allyltoluene,

(1) A part of this investigation was financed from funds donated to the American Petroleum Institute by the Universal Oil Products Company. The investigation was listed as Project No. 18.

(2) Director, Project No. 18.

(3) American Petroleum Institute Research Fellow.

(4) Hurd and Bollman, THIS JOURNAL, 55, 699 (1933).

TABLE I  
 PYROLYSIS OF *o*- AND *p*-ALLYLTOLUENE

Temp., °C.	Time, min.	Liq., g.	Products condensed by ice, g.	Contact time, sec.	Decomp., %	Gas, cc.	Gaseous products, % by vol.				
							C <sub>3</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	H <sub>2</sub>	C <sub>n</sub> H <sub>2n+2</sub>	$\frac{n}{n}$ in C <sub>n</sub> H <sub>2n+2</sub>
<i>o</i> -Allyltoluene											
650	78	42.2	35.9	3.3	75	3650	7.8	14.8	30.2	47.2	1.06
700	82	25.7	19.5	5.4	80	2780	6.9	13.9	31.8	47.4	1.06
<i>p</i> -Allyltoluene											
575	93	39.6	36.7	4.5	51	500	16.2	17.4	16.4	49.9	0.89
650	99	45.4	39.1	3.9	76	4250	7.9	11.4	28.7	51.9	1.04

analogously to allyl phenyl ether into *o*-allylphenol, 25 cc. of the hydrocarbon (b. p. 175–178°) was distilled from a flask into a reaction tube at 400°, then condensed and recycled for a period of ninety-seven hours. Glass seal connections were used throughout. During the run the liquid darkened slightly and a moderate coating of hard carbonaceous matter covered the inner walls of the reaction tube. Distillation of the product gave evidence of considerable change. Twelve cc. was collected between 165–176.5°, 8 cc. at 176.5–178°, and 4 cc. at 178–180°. The 4-cc. fraction, which would have contained any of the *o*-allyltoluene (b. p. 181–182°), was oxidized by alkaline permanganate. It contained none for the resulting acid was benzoic, not *o*-toluic, as evidenced by its m. p. of 121.5–122°. The m. p. of benzoic acid is appreciably lowered by even a 1% admixture of toluic acid, hence this

drolsis and separation of the ether layer gave a yield of 30 g. of *o*-allyltoluene after drying and distilling; yield, 70% or better.

The odor of this hydrocarbon was rather flat and was in decided contrast to the aromatic odor of its isomers, *p*-allyltoluene and 4-phenyl-1-butene. The liquid was colorless when freshly distilled but colored on standing. After a month it assumed a yellow-green tint. The constants for this substance and others mentioned in this paper are listed in Table II.

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>, C, 90.9; H, 9.09. Found, C, 90.2, 90.4; H, 9.19, 9.49.

Oxidation of *o*-allyltoluene by refluxing with alkaline permanganate until no more oil was visible yielded *o*-toluic acid, m. p. 102°; neutral equivalent, 135.7 (calculated value, 136.1).

 TABLE II  
 PHYSICAL CONSTANTS

	The allyltoluenes		The allyltoluene dibromides	
	ortho	para	ortho	para
B. p., °C. (mm.)	181–181.6 (750) 93–95 (30) 88–90 (25)	180–181 <sup>a</sup> (750) 58–60 <sup>b</sup> (1.65)	166–168 (15)	186 (34) 159–161 <sup>b</sup> (16–17) 110–112 <sup>b</sup> (0.7–0.9)
$n_D$	1.5255 (6°) 1.5209 (14°) 1.5171 (24°)	1.5210 <sup>b</sup> (10°)	1.5910 (9°) 1.5850 (21°) 1.5808 (31°)	1.5930 <sup>b</sup> (5.6°) 1.5855 <sup>b</sup> (23°)
$d_4$	0.9110 (7°) .8970 (24.5°) .8890 (35°)	0.9157 <sup>b</sup> (6.8°) .9043 <sup>b</sup> (26.2°)	1.6224 (12°) 1.6087 (24°) 1.6010 (30°)	1.614 <sup>b</sup> (5.6°) 1.595 <sup>b</sup> (21°)

<sup>a</sup> The isomeric *p*-propenylytoluene, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH=CHCH<sub>3</sub>, boils at 195–197°, according to Kunckell, *Ber.*, **36**, 2235 (1903). <sup>b</sup> These data were obtained by Charles I. Parrish.

must have been absent. Also, the neutral equivalent value of 122.7 was satisfactory for benzoic acid.

In the same apparatus and also at 400°, 25 cc. of *o*-allyltoluene was heated continuously for forty-eight hours. That it was more stable than 4-phenyl-1-butene was evident because distillation of the product yielded only the unchanged allyltoluene. There was no change in b. p.

#### Synthesis of Reagents

*o*-Allyltoluene.—*o*-Tolylmagnesium bromide was made from 56 g. of *o*-bromotoluene, 8 g. of magnesium and 200 cc. of dry ether. A little allyl bromide was added to start the reaction, after which the *o*-bromotoluene reacted readily. A solution of 40 g. of allyl bromide made up to 50 cc. in dry ether was added to the Grignard reagent. Heat was generated during this addition and refluxing was maintained for a half hour after all was added. Hy-

*p*-Allyltoluene was prepared similarly from *p*-bromotoluene. In a run thrice the size of the one described with the ortho isomer, 4 g. of di-*p*-tolyl and 97 g. (75% yield) of *p*-allyltoluene were formed. The odor of this allyltoluene resembled that of *p*-cymene. It was colorless and on long standing assumed a slight green tint. For analysis, the *p*-allyltoluene was converted into its dibromide.

*o*- and *p*-Allyltoluene Dibromides, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CHBr-CH<sub>2</sub>Br.—These bromides, prepared by addition of the calculated amount of bromine to each of the allyltoluenes in ice-cold carbon tetrachloride, were viscous, colorless and almost odorless oils. Purification was by vacuum distillation.

*Anal.* (ortho) Calcd. for C<sub>10</sub>H<sub>12</sub>Br<sub>2</sub>: Br, 54.75. Found: Br, 54.33, 54.31. *Anal.* (para) Found: Br, 54.86, 54.69.

### Summary

*o*-Allyltoluene and *p*-allyltoluene and their dibromides were synthesized. Study was made of the pyrolysis of the allyltoluenes. They provided a contrast to previously studied unsaturated hydrocarbons in possessing somewhat greater

stability and in giving rise to more ethylene than propylene in the gas. The significance of these facts is discussed. Prolonged heating of 4-phenyl-1-butene failed to effect any rearrangement into *o*-allyltoluene.

EVANSTON, ILL.

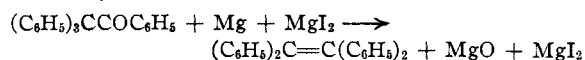
RECEIVED OCTOBER 2, 1933

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## Reduction by Magnesium + Magnesium Iodide. XII. The Reduction of Benzopinacolone

BY W. E. BACHMANN

Aromatic ketones are reduced by a mixture of magnesium and magnesium iodide;<sup>1</sup> intermediate ketyl radicals  $R_2COMgI$  are formed which double up to form a pinacolate  $R_2(OMgI)CC(OMgI)R_2$ . We have now tried the action of the reducing mixture on the mixed aliphatic-aromatic ketone benzopinacolone. This compound was found to react readily with the binary mixture in ether and benzene with the formation of an orange-red to red color. If the reaction is carried out at 80–85° tetraphenylethylene is formed in yields as high as 92%; indeed, the reaction constitutes an excellent method for preparing tetraphenylethylene.<sup>2</sup> It is clear that the reducing action is accompanied by an intramolecular rearrangement; and the reaction may be formulated as follows



The quantity of magnesium that reacts corresponds to 90% of that required by the equation and is equivalent to nearly one gram atom of metal for one gram mole of pinacolone. That the tetraphenylethylene is formed in the mixture prior to hydrolysis was proved by isolation of the ethylene before addition of water. Since the magnesium iodide is regenerated in the reaction, it follows that small amounts of the halide should suffice for complete reduction. Such was found to be the case; however, the reaction is much slower and practically it was found desirable to use from 0.4 to 1.0 gram mole of magnesium iodide for each mole of pinacolone.

In addition to tetraphenylethylene there is produced a small amount (8–10%) of by-product

(1) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236 (1927).

(2) Compare Steinkopf and Wolfram, *Ann.*, **430**, 114 (1922), who obtained tetraphenylethylene in 86% yield by reduction of benzopinacolone in alcohol solution by amalgamated zinc and hydrogen chloride.

in the form of an uncrystallizable yellow gum the composition of which is unknown. This gum is the principal product (70–80%) when the reaction is carried out at room temperature; the reactions leading to its formation require less magnesium, only 0.7 to 0.78 gram atom of magnesium per mole of pinacolone. It appears that the tetraphenylethylene and part of the gum come from the same intermediate reduction product since the yield of tetraphenylethylene is increased by continuing the reaction at 80° after interaction has been completed at room temperature. It is considered that reduction occurs through the addition of MgI groups to the carbonyl group but the actual nature of the intermediate reduction products is not known.

### Experimental

**Preparation of Tetraphenylethylene from Benzopinacolone.**—A mixture of 3 g. of iodine (equivalent to 0.4 gram mole of halide per mole of pinacolone) and 3 g. of magnesium powder is heated in a mixture of 5 cc. of ether and 20 cc. of benzene until the mixture is nearly colorless; 10.5 g. of benzopinacolone and 70 cc. of benzene are added and the resulting mixture is refluxed for twenty hours. The orange-red mixture is filtered from the excess of magnesium and poured into water; dilute acid is added in order to dissolve the magnesium hydroxide which is produced. The ether-benzene solution is concentrated to a small volume and cooled. Total yield of tetraphenylethylene, 9.2 g. (92%).

**Reaction under Various Conditions.**—Numerous experiments were carried out on 3.48 g. (0.01 gram mole) samples in order to determine the effect of various factors. No reaction took place when benzopinacolone was heated with magnesium in the absence of magnesium halide.

When only one hour was allowed for the reaction using 0.4 gram mole of magnesium halide in 2 cc. of ether and 30 cc. of benzene, a considerable amount of pinacolone remained unchanged; by using a full mole of halide an 85% yield of tetraphenylethylene was obtained in the same length of time. By employing weighed amounts of