The Friedel–Crafts Reaction of Butadiene with Benzene

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The aluminum chloride catalyzed reaction of butadiene with benzene yields a mixture of 1,1-, 1,2-, and 1,3-diphenylbutanes, together with *sec*- and *n*-butylbenzenes. The sulfuric acid catalyzed reaction gives the three isomeric diphenylbutanes in a ratio of 50–52:30–32:17–19. 1-Phenyl-2-butene was proved to be formed in the first step, and this intermediate gives the diphenylbutanes on further reactions. The formation of 1,1-diphenylbutane is explained by a mechanism involving a 1,2-hydride shift of 1-phenyl-2-butyl cation to form 1-phenyl-1-butyl cation.

The Friedel–Crafts reaction of 1,3-dienes with benzenes has been little studied although alkylation of aromatics with monoolefins has received extensive studies and applications.[1] In their early observations of the reaction of butadiene and benzene in the presence of sulfuric acid or of hydrofluoric acid at near room temperatures, Ipatieff, *et al.*,[2] found 1,2-diphenylbutane in the reaction products and explained its formation by 1,4 addition of benzene to butadiene followed by addition of another benzene molecule to the primary product 1-phenyl-2-butene. On the other hand, 1-phenyl-1-butene was one of the products from the reaction performed by passing a 4.5:1 molar mixture of benzene and butadiene through silicophosphoric acid catalyst at 216°.[3]

In a recent article[4] we briefly reported a casual finding of formation of an isomeric mixture of diphenylbutanes from butadiene and benzene in the presence of aluminum chloride. A closer study of the products from this reaction is described in the present article. A reinvestigation of the sulfuric acid catalyzed reaction is also reported.

Results and Discussion

Butadiene was allowed to diffuse slowly into a suspension of anhydrous aluminum chloride in benzene. Diphenylbutane fractions obtained (~15% yield) showed on gas–liquid partition chromatography (glpc) three peaks of identical retention times with those of authentic 1,1-, 1,2-, and 1,3-diphenylbutanes. 1,2- and 1,3-diphenylbutanes were isolated pure by preparative glpc and identified by comparison of their nmr spectra with those for the authentic samples. Although the 1,1 isomer, which elutes between the 1,2 and 1,3 isomers, could not be freed from the 1,3 isomer,[5] the nmr spectrum showed no extra absorption other than those ascribable to the two isomers. This allows us to assume that the product at least mainly consists of these three isomers.

The ratio of the isomers, determined by glpc peak area,[6] is listed in Table I. It should be mentioned that the ratio shown is not the true measure of the ratio of *formation* of the isomers because the diphenylbutanes formed by the reaction partly undergo degradation by the action of aluminum chloride during the reaction period. Thus, when a diphenylbutane mixture, 0.5 g, was treated with powdered aluminum chloride, 1.6 g, in benzene, 10 ml, at room temperatures for 3 hr, its amount decreased to one-fifth of the original, with complete disappearance of the 1,1 isomer, giving lower boiling materials. In fact, a considerable amount of the degradation products was obtained in expt 1 and 2. The main components of the degradation products were *sec*- and *n*-butylbenzenes. It is of interest to point out the detailed work by Roberts and collaborators[7] on aluminum chloride catalyzed degradation of related compounds, *i.e.*, 2,3- and 2,2-diphenylbutanes and 1,1- and 1,2-diphenyl-2-methylpropanes, which yielded isobutylbenzene consistently and *sec*-butylbenzene in some cases.[8] A detailed mechanistic study of the degradation of diphenylbutanes is beyond the scope of the present article and the formation of *sec*- and *n*-butylbenzenes is tentatively explained by the dealkylation and hydride abstraction mechanism as proposed by Roberts and collaborators.[9] Preponderance of *sec*-butylbenzene over *n*-butylbenzene in the degradation product would offer a difficulty, however, since it would require an importance of, for example, the reaction sequence 1 which involves an energetically unfavorable primary carbonium ion as compared with the more likely reaction sequence 2.

TABLE I

ISOMER RATIO OF DIPHENYLBUTANES

Expt no.	Catalyst	Temp, °C	Isomer, %		
			1,1	1,2	1,3
1	$AlCl_3$	50	23	30	47
2	$AlCl_3$	20	25	29	46
3	H_2SO_4	0–5	50	31	19
4	H_2SO_4	0–5	53	30	17
5	H_2SO_4	0–5	50	32	18
6[a]	H_2SO_4	0–5	51	32	17
7[a]	H_2SO_4	0–5	48	31	21
8[b]	H_2SO_4	0–5	100	0	0

[a] Reaction of 1-phenyl-2-butene with benzene. [b] Reaction of 1-phenyl-1-butene with benzene.

The sulfuric acid catalyzed reaction was carried out in a similar manner, and the diphenylbutane fraction was tested by glpc and nmr to show that it consisted at least mainly of the three isomers. The ratio of

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(1) C. C. Price, *Org. Reactions*, **3**, 1 (1946); A. V. Topchiev, S. V. Zavgorodnii, and V. G. Kryuchkova, "Alkylation with Olefins," Elsevier Publishing Co., Amsterdam, 1964.

(2) V. N. Ipatieff, H. Pines, and R. E. Schaad, *J. Am. Chem. Soc.*, **66**, 816 (1944).

(3) V. N. Ipatieff, R. E. Schaad, H. Pines, and G. S. Monroe, *ibid.*, **67**, 1060 (1945).

(4) T. Inukai and M. Kasai, *J. Org. Chem.*, **30**, 3567 (1965).

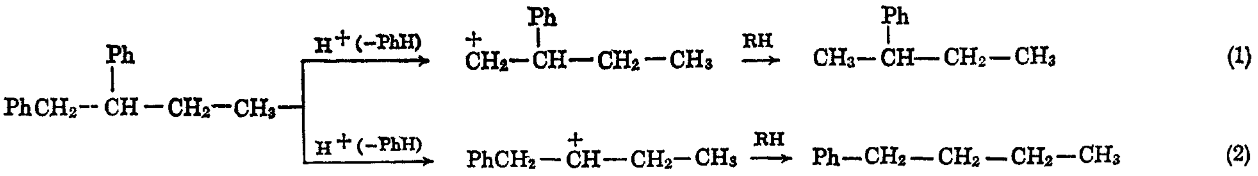
(5) Some overlapping of gas chromatographic peaks was inevitable with our preparative column, although with an analytical column an excellent separation was effected to warrant isomer ratio determinations.

(6) An artificial mixture of 1,1 (30.7%), 1,2 (32.1%), and 1,3 (37.1%) isomers exhibited a peak area ratio of 29.2:33.3:37.5.

(7) R. M. Roberts, A. A. Khalaf, and R. N. Greene, *J. Am. Chem. Soc.*, **86**, 2846 (1964).

(8) These workers submitted the compounds to more drastic conditions than ours, *i.e.*, heating at 100° for 3 hr without solvent and with water added as activator. Unfortunately 1,1-, 1,2-, and 1,3-diphenylbutanes appear not to have been studied by these workers.

(9) See Figure 1 of ref 7.



$$\mathrm{PhCH_2{-}\underset{}{\overset{Ph}{CH}}{-}CH_2{-}CH_3} \xrightarrow{H^+(-PhH)} \mathrm{\overset{+}{C}H_2{-}\overset{Ph}{CH}{-}CH_2{-}CH_3} \xrightarrow{RH} \mathrm{CH_3{-}\overset{Ph}{CH}{-}CH_2{-}CH_3} \quad (1)$$

$$\mathrm{PhCH_2{-}\overset{Ph}{CH}{-}CH_2{-}CH_3} \xrightarrow{H^+(-PhH)} \mathrm{PhCH_2{-}\overset{+}{C}H{-}CH_2{-}CH_3} \xrightarrow{RH} \mathrm{Ph{-}CH_2{-}CH_2{-}CH_2{-}CH_3} \quad (2)$$

isomers is listed in Table I (expt 3–5). In this reaction the degradation and isomerization of the diphenylbutanes should not have occurred seriously, since they remained essentially intact on treatment of each of the isomers, 0.5 g, with sulfuric acid, 3 g, in benzene, 10 g, at room temperature for as long as 18 hr.

An attempt was made to improve the yield of diphenylbutanes by using a smaller quantity of sulfuric acid so as to possibly lessen the polymerization of butadiene. It happened to reveal the intermediate formation of 1-phenyl-2-butene and 3-phenyl-1-butene in a ratio of 1:0.03. 1-Phenyl-1-butene, which was thought to be the precursor of 1,1-diphenylbutane, was not obtained; this was not due to its facile conversion to 1,1-diphenylbutane because this was not obtained in the expected amount either. Therefore, 1-phenyl-1-butene is not an intermediate of the reaction, and the three diphenylbutanes would have formed from 1-phenyl-2-butene. In keeping with this view, the reaction of pure 1-phenyl-2-butene (expt 6 and 7) gave the three diphenylbutanes in the exact same ratio as obtained from the butadiene–benzene reaction.

Consequently, the reaction scheme shown in Chart I is plausible.[10] Butenyl cation (I) reacts with benzene to give 1-phenyl-2-butene (II) (and 3-phenyl-1-butene in a small proportion), and II accepts proton to form 1-phenyl-3-butyl (III) and 1-phenyl-2-butyl cation (IV). III yields 1,3-diphenylbutane, and IV partly gives 1,2-diphenylbutane directly or partly undergoes 1,2-hydride shift to give 1-phenyl-1-butyl cation (V) which eventually yields 1,1-diphenylbutane. From the ratio of formation of 1,3-diphenylbutane to 1,1- plus 1,2-diphenylbutanes, the orientation of proton addition to II at the 2- and 3-positions may be estimated as 1:4, which is a reasonable ratio since IV is more stabilized by the presence of a phenyl group in proximity. It is of interest in this connection that 1-phenyl-1-butene yields only 1,1-diphenylbutane under the comparable conditions (expt 8). A strong stabilization of V by a phenyl group accounts for its exclusive formation from 1-phenyl-1-butene and for the ineffectiveness of the reverse 1,2-hydride shift ($\mathrm{V} \not\rightarrow \mathrm{IV}$).

The fate of 3-phenyl-1-butene, a minor product from I, could not be clarified. *meso-* and *dl*-2,3-diphenylbutanes are expected from its further reactions. The *meso* isomer was shown to be absent in the product (by glpc). Absence of the *dl* isomer was not confirmed but is suggested by the fact that 3-phenyl-1-butene does not give diphenylbutanes in a reasonable yield under comparable conditions.

Experimental Section

A 2.7-m PEG-6000 column was used at 190° for glpc analyses of isomeric composition of the diphenylbutanes. The determinations of the phenylbutanes and phenylbutenes were made at 150° with the same column and are semiquantitative since the peak area ratio was utilized without calibration. When identification of the materials must be based merely on their glpc retention times, a 2.7-m Silicone DC-550 column was also used to strengthen the identification. For the preparative glpc a PEG-6000 column (14 mm × 4 m) was used, at the same respective temperatures mentioned above. The nmr spectra (Table II) were determined with a Varian A-60 spectrometer on carbon tetrachloride solutions containing tetramethylsilane as internal standard.

TABLE II

NMR DATA[a]

Assignment	τ, ppm	Splitting or apparent multiplicity[b]	Relative peak area	J, cps
		$\mathrm{Ph_2CHCH_2CH_2CH_3}$		
Phenyl	2.884	1	10	
1-H	6.158	3	1	7.8
2-H	7.990	4	2	7.8
3-H	8.5–8.9	m[c]	5	
4-H	9.092	3		5.7
		$\mathrm{PhCH_2CHPhCH_2CH_3}$		
Phenyl	2.95	1	10	
1-H 2-H[d]	7.0–7.4	m	3	
3-H	8.372	5	2	7.0
4-H	9.250	3	3	7.0
		$\mathrm{PhCH_2CH_2CHPhCH_3}$		
Phenyl	2.925	1	5	
Phenyl	2.868	1	5	
1-H 3-H[d]	7.15–7.75	m	3	
2-H	7.9–8.4	m	2	
4-H	8.755	2	3	6.8
		$\mathrm{CH_3CHPhCHPhCH_3}$ *meso*[e]		
Phenyl	2.841	1	5	
1-H	8.985	2	3	6.3
2-H	7.00–7.50	m	1	
		$\mathrm{PhCH_2CH_2CH_2CH_3}$		
Phenyl	2.893	1	5	
1-H	7.420	3	2	7.0
2-H 3-H[d]	8.1–8.8	m	4	
4-H	9.075	3	3	6.0
		$\mathrm{CH_3CHPhCH_2CH_3}$		
Phenyl	2.885	1	5	
1-H	8.765	2	3	6.8
2-H	7.43	6?	1	7.0
3-H	8.405	5	2	7.2
4-H	9.168	3	3	7.2

[a] Of a 10% solution in carbon tetrachloride unless otherwise stated. [b] 1, 2, etc., stand for singlet, doublet, and so on, whereas m means an undefined multiplet. [c] Partially overlapped groups of peaklets. [d] Overlapped to a large extent. [e] Of a 5% carbon tetrachloride solution.

Materials.—Butadiene, benzene, and anhydrous aluminum chloride were the same as those described in the previous paper.[4]

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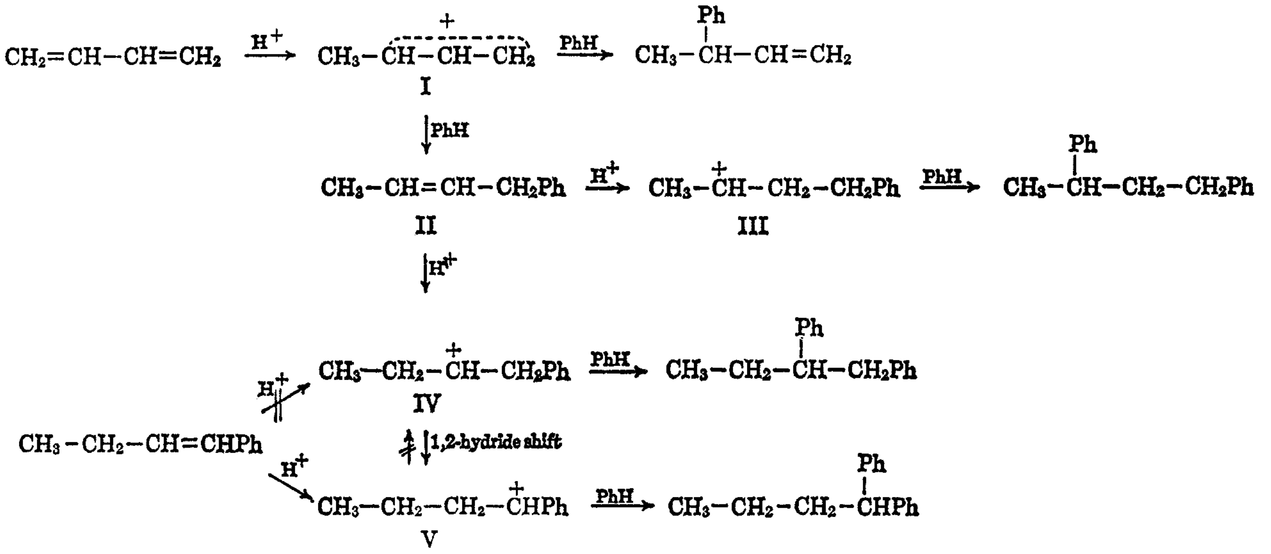
(10) It should be understood that the yields and ratios of isolated products might well be more a function of the chemical stability of their precursors under the reaction conditions than the thermodynamic stability or reactivity of the corresponding carbonium ion intermediates, because yields of diphenylbutanes are far from quantitative.

CHART I



Guaranteed reagent concentrated sulfuric acid, sp gr 1.84, was used as received.

Diphenylbutanes.—1,1-,[11] 1,2-,[2] 1,3-,[11] and *meso*-2,3-diphenylbutanes[11] were synthesized by the published procedures with slight modifications. Dehydrations of the intermediate carbinols were performed by heating with potassium bisulfate at 160–170°, 30 min, and hydrogenations of the olefins were performed by catalysis with W-7 Raney nickel at atmospheric pressure of hydrogen and at room temperature. All these diphenylbutanes were pure by glpc, had correct refractive indices,[11] and gave rise to nmr spectra consistent with the structures. 1,1-Diphenylbutane showed an infrared absorption spectrum identical with the published one.[12]

1-Phenyl-2-butene and 3-Phenyl-1-butene.—A mixture of these isomers was prepared according to the method of Wilson, *et al.*,[13] *i.e.*, by action of phenylmagnesium bromide on the butenyl chloride mixture.[14] Pure specimens were obtained by fractional distillation and preparative glpc: 1-phenyl-2-butene, bp 95.5–96° (50 mm) [lit.[13] bp 95° (50 mm)] and 3-phenyl-1-butene, bp 85–86.5° (50 mm) [lit.[13] bp 85° (50 mm)]. Their purity was checked by glpc and infrared spectra.[15]

1-Phenyl-1-butene.—Attempted isomerization of 1-phenyl-2-butene to 1-phenyl-1-butene according to the literature procedure[16] led to only slight isomerization. Under more drastic conditions, *i.e.*, by heating 1-phenyl-2-butene (9 g) with 0.5 ml of 90% ethanol and 2 g of potassium hydroxide for 24 hr with stirring, isomerization occurred, yet not completely; a 1:4 mixture of 2-butene:1-butene was obtained. Pure 1-phenyl-1-butene was isolated by preparative glpc and had bp 90.5–92° (25 mm) [lit.[17] bp 91.0–92.0° (23 mm) for *trans* and bp 84.0–85.0° (23 mm) for *cis*], n^{20}_{D} 1.5417 (lit. n^{20}_{D} 1.5420,[18] n^{23}_{D} 1.5428[17] for *trans*; n^{20}_{D} 1.5284,[18] n^{23}_{D} 1.5282[17] for *cis*).

Aluminum Chloride Catalyzed Reaction of Butadiene and Benzene (Expt 1).—About 11 l. of butadiene (0.49 mole) was slowly introduced into a stirred suspension of 10.6 g of anhydrous aluminum chloride in 300 ml of benzene over a period of 3.3 hr at 50°. The butadiene was allowed to diffuse into the suspension through an opening in the side arm of the reaction flask. After the addition of butadiene was completed, the dark red mixture was cooled with iced water and the catalyst was decomposed by adding water. The benzene layer was washed with water, concentrated aqueous sodium hydroxide, then with water successively, and was dried with calcium chloride. The benzene was removed by distillation, and the residue was distilled at 9 mm to yield (i) bp <70° (3.1 g), (ii) bp 70–143° (4.2 g), (iii) bp 143–148° (12.1 g), and a dark red residue (31.4 g). Fraction i consisted of *sec*-butylbenzene (50%), *n*-butylbenzene (35%), and 1-phenyl-2-butene (15%) (see below). Fraction ii contained 1,1-diphenylbutane (19%), 1,2-diphenylbutane (28%), and 1,3-diphenylbutane (33%), besides lower boiling materials (20%). The isomeric ratio of 1,1-, 1,2-, and 1,3-diphenylbutanes in fraction iii was 23:28:49. Calculated for the total product, the ratio is 23:30:47 and the yield of diphenylbutanes is 15% based on butadiene used.

Anal. Calcd for $C_{16}H_{18}$: C, 91.4; H, 8.6. Found (fraction iii): C, 91.6; H, 8.6.

sec-Butylbenzene and *n*-butylbenzene were isolated by preparative glpc and identified as such. ***sec*-Butylbenzene** (*Anal.* Calcd for $C_{10}H_{14}$: C, 89.6; H, 10.4. Found: C, 89.6; H, 10.4.) had n^{30}_{D} 1.4848 (lit.[19] n^{30}_{D} 1.48537). ***n*-Butylbenzene** (*Anal.* Calcd for $C_{10}H_{14}$: C, 89.6; H, 10.4. Found: C, 89.4; H, 10.4.) had n^{30}_{D} 1.4849 (lit.[19] n^{30}_{D} 1.48502). Their infrared absorption spectra were identical with the published ones,[20] and nmr spectra were in accord with the assigned structures.

Sulfuric Acid Catalyzed Reaction of Butadiene with Benzene (Expt 3).—About 10.5 l. of butadiene (0.47 mole) was slowly introduced into a stirred suspension of 50 g of concentrated sulfuric acid in 150 g of benzene during 1 hr at 0–5°. After the addition of butadiene was completed, the mixture was stirred at the same temperature for 1 hr and was made alkaline by adding aqueous sodium hydroxide. All the volatile materials were exhaustively steam distilled from the mixture, leaving a large volume of yellow gum of, presumably, butadiene polymers. The aqueous condensate (10 l.) was extracted with benzene, and the combined benzene layer was dried with calcium chloride. The benzene was removed by distillation, and the residue was distilled at 10 mm to yield (i) bp ≤127° (0.3 g), (ii) bp 127–153° (19.4 g), (iii) bp 153° (1.4 g), and (iv) brown residue (1.7 g). Fraction i showed glpc peaks attributable to *sec*-butylbenzene (75%) and *n*-butylbenzene (25%) and was free from 1-phenyl-2-butene and 1-phenyl-1-butene. Although fraction i may contain a trace of 3-phenyl-1-butene, its detection was not feasible since it is eluted very close to *n*-butylbenzene (with a PEG-6000 column) and very close to *sec*-butylbenzene (with a Silicone DC-550 column). Scantiness of the material prevented separation and identification of the components. Fractions ii and iii consisted of 1,1-, 1,2-, and 1,3-diphenylbutanes, and the ratio of the isomers was 50:31:19 for the total products (20% based on the butadiene used).

Intermediate Formation of 1-Phenyl-2-butene and 3-Phenyl-1-butene.—About 12 l. of butadiene was introduced into a stirred suspension of 5.0 g of concentrated sulfuric acid in 300 ml of benzene at 5° during 1.5 hr. The mixture was stirred for a

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[11] K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.*, **74**, 365 (1952).

[12] "Sadtler Standard Infrared Spectra," Midget Edition, Sadtler Research Laboratories, Philadelphia, Pa., 1959, Spectrum No. 9980.

[13] K. W. Wilson, J. D. Roberts, and W. G. Young, *J. Am. Chem. Soc.*, **71**, 2019 (1949).

[14] L. F. Hatch and S. S. Nesbitt, *ibid.*, **72**, 727 (1950).

[15] Reference 12, 1962, Spectrum No. 7852; 1959, Spectrum No. 1616.

[16] R. T. Arnold and S. Searles, Jr., *J. Am. Chem. Soc.*, **71**, 2021 (1949).

[17] C. F. Hauser, T. W. Brooks, M. L. Miles, M. A. Raymond, and G. B. Butler, *J. Org. Chem.*, **28**, 372 (1963).

[18] A. L. Henne and A. H. Matuszak, *J. Am. Chem. Soc.*, **66**, 1649 (1944).

[19] A. F. Forziati and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **43**, 473 (1949).

[20] Reference 12, 1962, Spectra No. 247 and 6318.

further 30 min at the same temperature, and the resulting solution was worked up as above. Distillation at 10 mm yielded (i) bp 40–60° (6.6 g), (ii) bp 60–69° (3.7 g), (iii) bp 69–120° (1.7 g), and (iv) bp 120° (1.8 g). Fractions i and ii were 1-phenyl-2-butene contaminated with a few per cent of 3-phenyl-1-butene. Fraction iii also contained 1-phenyl-2-butene (24%). Fractions iii and iv gave rise to several overlapping glpc peaks which were not subjected to further examination. The total yield of 1-phenyl-2-butene was about 10.2 g and that of 3-phenyl-1-butene was 0.3 g (from glpc peak area). 1-Phenyl-1-butene was absent in all of these fractions.

Sulfuric Acid Catalyzed Reaction of Phenylbutenes with Benzene. General Procedures.—To a stirred suspension of 5 g of concentrated sulfuric acid in 150 ml of benzene at 0–5° was added 3 g of the phenylbutene dissolved in 30 ml of benzene in 5 min, and the mixture was stirred for 1.5 hr. The reaction mixture was made alkaline by adding aqueous potassium carbonate and was steam distilled. The product was collected by extraction with benzene, vacuum distilled, and analyzed by glpc. **1-Phenyl-2-butene** (expt 6 and 7) gave a mixture of diphenylbutanes (Table I) in a 40% yield. **1-Phenyl-1-butene** (expt 8) gave only 1,1-diphenylbutane, n^{20}_{D} 1.5568 (lit.[11] n^{20}_{D} 1.5568) in 52% yield. **3-Phenyl-1-butene** was 60% recovered; the residue of distillation contained a trace of materials whose glpc retention times coincide with those of diphenylbutanes.

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Fixation of an Enediol by Acetal Formation. Synthesis of a 1,3-Dioxole

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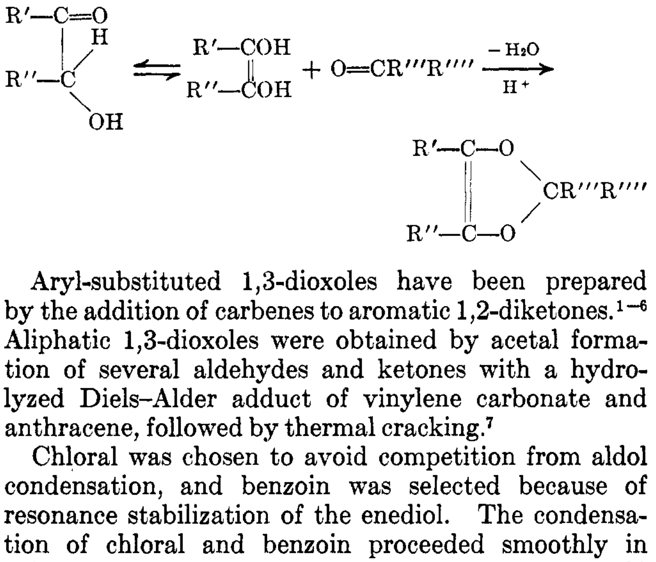
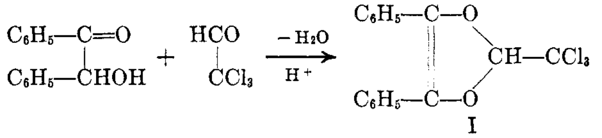
The first case of a fixation of an enediol (benzoin) by an aldehyde (chloral) is reported, yielding the new 2-trichloromethyl-4,5-diphenyl-1,3-dioxole. Acetoin cannot be condensed directly with chloral but requires base-catalyzed addition to give a 5-hydroxydioxolane from which the corresponding dioxole can be prepared. The reactions of chloral with several other hydroxycarbonyls and of other aldehydes with benzoin result in structures other than dioxoles.

The usual methods of stabilizing the enolic form of aldehydes or ketones consist in the direct esterification or etherification of the carbonyl group in an enolizing medium. The fixation of an enol by acetal formation with another carbonyl compound has not been discussed in previous literature. It was thought that ring formation from an α-hydroxy carbonyl and an aldehyde or ketone should favor condensation to a 1,3-dioxole.



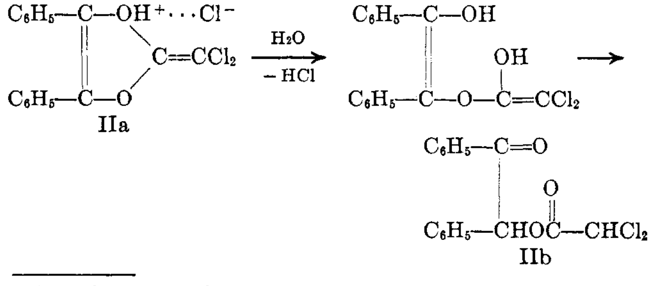
Aryl-substituted 1,3-dioxoles have been prepared by the addition of carbenes to aromatic 1,2-diketones.[1–6] Aliphatic 1,3-dioxoles were obtained by acetal formation of several aldehydes and ketones with a hydrolyzed Diels–Alder adduct of vinylene carbonate and anthracene, followed by thermal cracking.[7]

Chloral was chosen to avoid competition from aldol condensation, and benzoin was selected because of resonance stabilization of the enediol. The condensation of chloral and benzoin proceeded smoothly in refluxing benzene with acidic catalysts to give an 85% yield of crude 2-trichloromethyl-4,5-diphenyl-1,3-dioxole (I).



I

Small amounts of benzil and tetraphenylfuran were isolated from the reaction mixture. These by-products were apparently formed by disproportionation and condensation of benzoin and have been obtained in higher yield from benzoin and sulfuric acid.[8,9] Compound I is hydrolyzed by concentrated hydrochloric acid in ethanol to benzoin and chloral. It is easily oxidized by air to benzil, chloral, and acidic products. Acids catalyze the autoxidation while amines or hydroquinones inhibit it. This was demonstrated by comparing induction periods and rates of oxygen absorption of a neutral solution of I in methanol with an acidic, basic, and neutral hydroquinone-containing solution. It was also observed that thermal degradation during distillation is accelerated by hydrogen chloride gas formed by partial pyrolysis of the chloral acetal. It was therefore necessary to carry out all purification steps including distillation in basic medium. A gradual pyrolysis of I was observed also at room temperature after extended bulk storage in a closed container. An assumed intermediate diene hydrochloride (IIa) was



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