

method would be expected to depend primarily on the efficiency of the fractionating column.

Precaution.—Liquid anhydrous hydrogen fluoride produces severe burns on contact with the skin. Proper protective measures should be employed in handling this material.

Acknowledgment.—The samples of pure siloxanes and other silicones were made available for this research through the kindness of the Silicone Division, of the General Electric Co. and the Dow-Corning Company. The research was part of a project sponsored by the Office of Naval Research, U. S. Navy.

Summary

Methyl silicones, and other *n*-alkyl silicones

were found to be rapidly and completely converted to their equivalent alkylfluorosilanes by reaction with liquid, anhydrous hydrogen fluoride in the presence of anhydrous copper sulfate at atmospheric pressure. The reaction was developed into an analytical method for determining the silicone content and functional composition of methyl silicone products. The gaseous methyl fluorosilanes are first contacted with Drierite granules, to remove moisture, and then with sodium fluoride pellets, to remove residual hydrogen fluoride. Finally, the gases are condensed and separated into pure methylfluorosilane components by quantitative fractional distillation.

CLEVELAND, OHIO

RECEIVED OCTOBER 10, 1949

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Isomerization Accompanying Alkylation. VI. Reaction of Isobutylene and 2-Butene with Benzene^{1,2}

BY HERMAN PINES, J. D. LAZERTE^{3,4} AND V. N. IPATIEFF

The catalytic alkylation of benzene with butylenes at elevated temperatures and pressures has heretofore not been investigated with the purpose of establishing the structure of the compounds produced. The object of the present study was to determine whether such an alkylation is accompanied by a skeletal isomerization of the alkyl group. For that reason 2-butene and isobutylene was treated with benzene in the presence of catalysts such as silico-phosphoric acid, alumina-zinc chloride and silica-alumina. The reaction was carried out in a flow type apparatus, at a temperature ranging from 200–380°, and at a pressure of 40 atmospheres using about 2.5 moles of benzene per mole of olefins.

Silico-phosphoric acid catalyzed the reaction between benzene and 2-butene; 62–75 mole per cent. of monobutylbenzene was obtained, based on olefins reacted. The remainder of the 2-butene was converted to octylenes, di-butylbenzene and higher boiling hydrocarbons. The monobutylbenzene fraction contained besides *s*-butylbenzene, 12–21% *t*-butylbenzene. The quantitative composition of the monobutylbenzenes was determined by means of infrared spectral analysis. The presence of *t*-butylbenzene was further substantiated by the isolation of *t*-

butylbenzenesulfonamide, when the sulfonamides of monobutylated benzene were fractionally crystallized.

The reaction of benzene with isobutylene also yielded a mixture of *s*- and *t*-butylbenzene. In the experiment in which isobutylene was used, the degree of polymerization was more pronounced than in similar experiments carried out with 2-butene.

In the reaction between benzene and 2-butene, zinc chloride-alumina catalyst (25% by wt. zinc chloride and 75% aluminum oxide) caused only a small amount of isomerization to accompany alkylation, while silica-alumina catalyst produced a monobutylbenzene fraction free of *t*-butylbenzene. The experimental conditions and results obtained of the reaction of benzene with butylenes are summarized in Table I.

Since alkylation and dealkylation reactions are closely related, a study of the latter reaction was undertaken to ascertain if skeletal isomerization accompanied dealkylation. The dealkylation of di-*s*-butylbenzene or di-*t*-butylbenzene in the presence of benzene took place at temperatures of 300–350° to yield monobutylbenzenes consisting of both *s*- and *t*-butylbenzene. Catalysts used in these reactions were silicophosphoric acid and zinc chloride-alumina. The experimental data are summarized in Table II.

The use of orthophosphoric acid as a dealkylation catalyst was described previously by Ipatieff and Corson,⁵ who reported that di-*t*-butylbenzene and benzene at 300–325° under pressure was con-

(1) Presented before the Division of Petroleum Chemistry at the Meeting of the American Chemical Society, September, 1949, Atlantic City, N. J.

(2) For paper V of these series, see V. N. Ipatieff, E. E. Meisinger and H. Pines, *THIS JOURNAL*, **72**, 2772 (1950).

(3) Universal Oil Products Company Predoctorate Fellow 1946–1949.

(4) This paper has been constructed from a portion of the thesis submitted in March, 1949, in partial fulfillment of the requirements for the degree of Ph.D. in Chemistry.

(5) V. N. Ipatieff and B. B. Corson, *THIS JOURNAL*, **59**, 1417 (1937).

TABLE I
 REACTION OF 2-BUTENE AND ISOBUTYLENE WITH BENZENE

Experiment no.	1	2	3	4	5	6
Catalyst, ^a kind	← Silico-phosphoric acid →				Zinc chloride- alumina	Silica- alumina
Hydrocarbons charged						
Benzene, moles	1.70	1.25	2.50	2.50	2.50	2.50
Olefins, kind	← 2-Butene →			Isobutylene	← 2-Butene →	
Olefins, moles	0.66	0.50	1.00	1.00	1.00	1.00
Experimental conditions ^b						
Temperature, °C.	200	255	300	250	200	250
Product formed ^c :						
Dimers (C ₈ H ₁₆), mole %	20	9	22	34	7	9
Butylbenzenes, mole %	62	75 ^e	67	31 ^e	43	56
Dibutylbenzene, mole %	8	8	3	2	32	18
Composition of the butylbenzenes ^d :						
<i>t</i> -Butylbenzene, %	12	13	21	87	2	0
<i>s</i> -Butylbenzene, %	88	87	79	13	98	100

^a In each experiment 50 ml. of catalyst (45–55 g.) was used. ^b The experiments were conducted at 40 atmospheres at an hourly liquid space velocity (ml. of hydrocarbons/ml. of catalyst/hour) of 1.0. ^c The yields were based on olefins used in the reaction. ^d The composition of the butylbenzenes was determined by infrared adsorption. ^e Sulfonamides were prepared according to E. H. Huntress and J. S. Autenrieth, THIS JOURNAL, 63, 3446 (1941). By fractional crystallization from a solution of benzene and hexane two compounds were separated: 1, m. p. 79–80°; 2, m. p. 135–136°; compound 1 corresponded to *p*-*s*- and compound 2 to *p*-*t*-butylsulfonamide. A mixed melting point with the respective pure compounds showed no depression.

 TABLE II
 DEALKYLATION OF DI-*s*-BUTYLBENZENE AND DI-*t*-BUTYLBENZENE

Experiment no.	7	8	9	10	11	12	13
Catalyst, ^a kind	← Silicophosphoric acid →				100% orthophos- phoric acid ^d	Zinc chloride- alumina	
Hydrocarbons charged:							
Dialkylbenzene, kind	← Di- <i>s</i> -butylbenzene →			Di- <i>t</i> -butylbenzene	Di- <i>s</i> -butyl- benzene	Di- <i>t</i> -butyl benzene	
Dialkylbenzene, moles	0.17	0.17	0.25	0.50	0.24	0.12	0.16
Benzene, moles	0.83	0.83	1.25	2.50	1.00	0.62	0.83
Experimental conditions ^b :							
Temperature, °C.	250	300	350	300	300–325	350	300
Products formed ^c :							
Monobutylbenzene, mole %	0	23	28	38	25	43	39
Dibutylbenzene, mole %	90	73	48	37	65	16	25
Composition of butylbenzene:							
<i>t</i> -Butylbenzene, %		14	17	85	80	10	91
<i>s</i> -Butylbenzene, %		86	83	15	20	90	9

^a Fifty ml. of catalyst (40–44 g.) were used in each experiment. ^b The experiments were conducted at 40 atm. pressure and at an hourly liquid space velocity of 1.0. ^c The yields were based on dibutylbenzene charged. Some condensable gases, polymers and polyalkylated benzene were formed. ^d The experiment was conducted in a rotating autoclave of 450 cc. capacity; 93.5 g. of acid was used. The duration of the experiment was six hours.

verted to *t*-butylbenzene. This experiment was repeated and it was found that the monobutylbenzene was composed of 80% *t*- and 20% of *s*-butylbenzene.

To ascertain if the monoalkylated products from the benzene-butylene reactions were themselves isomerized under the conditions employed, experiments were conducted passing either *s*- or *t*-butylbenzene with benzene at a pressure of 40 atm. over silicophosphoric acid catalyst. Isomerization did not take place at 250°. At 350°, however, *s*-butylbenzene was isomerized to give a 74% yield of monobutylbenzene fraction containing 10% *t*-butylbenzene. Under similar

conditions *t*-butylbenzene and benzene resulted in a 53% yield of butylbenzene containing 31% of *s*-butylbenzene. When these last two reactions were carried out in the absence of benzene the extent of isomerization was greatly reduced. The reactions made in the presence of zinc chloride-alumina catalyst and benzene at a temperature of 350° gave almost identical results with those obtained when silicophosphoric acid catalyst was used under the same conditions. The results are given in Table III.

In many cases it was necessary to remove the small amount of olefins admixed with butylbenzenes, before the latter were submitted to an

TABLE III
 ISOMERIZATION OF *s*-BUTYL BENZENE AND *t*-BUTYL BENZENE

Experiment no. Catalyst, ^a kind	14	15	16	17	18	19	20	21	22	
	← Silicophosphoric acid →						← Zinc chloride-alumina →			
Hydrocarbons charged: Butylbenzene, kind	← <i>s</i> -Butylbenzene →				← <i>t</i> -Butylbenzene →				<i>s</i> -Butylbenzene	<i>t</i> -Butylbenzene
Butylbenzene, moles	0.25	0.25	0.25	0.32	0.25	0.25	0.33	0.25	0.25	
Benzene, moles	0.62	0.62	0.62	0.00	0.62	0.62	0.00	0.62	0.62	
Experimental conditions ^b										
Temperature, °C.	250	300	350	350	250	350	350	350	350	
Butylbenzene recovered, ^c mole %	92	91	74	72	83	53 ^d	42	52	42	
Composition of butylbenzene:										
<i>t</i> -Butylbenzene, %	0	11	10	3	100	69	2	10	68	
<i>s</i> -Butylbenzene, %	100	89	90	97	0	31	818	90	32	

^a Fifty ml. (40–42 g.) of catalyst was used in each experiment. ^b The experiments were conducted at 40 atm. of pressure at an hourly liquid space velocity of 0.33. ^c Some condensable gases, polymers and polyalkylated benzene were formed. ^d Sulfonamides were prepared, from which were separated by fractional crystallization *p*-*s*-butylbenzenesulfonamide melting at 79–80° and *p*-*t*-butylbenzenesulfonamide melting at 133–134°. Mixed melting point with the corresponding pure sulfonamides did not show any depression.

infrared spectral analysis. To achieve it two procedures were used: (1) The hydrocarbons were selectively hydrogenated in the presence of copper-alumina catalyst to the corresponding paraffins without hydrogenating the aromatic ring.⁶ The paraffins were then separated from the aromatics chromatographically, using silica gel as the adsorbent.⁷ (2) The second method for the removal of olefins consisted in treating the butylbenzene fraction with benzene in the presence of hydrogen fluoride at 0°. Thus benzene and the olefins condensed to yield alkylbenzenes which, owing to their high boiling point, were separated from the butylbenzenes by fractional distillation. Butylbenzenes under these conditions did not undergo any reaction.

Experimental Part

Hydrocarbons.—2-Butene and isobutylene were of C. p. grade and according to mass spectrographic analysis they were over 99% pure.

s-Butyl- and *t*-butylbenzene were according to infrared analysis over 99% pure.

Di-*s*-butylbenzene was prepared by treating benzene with 2-butene in the presence of 96% sulfuric acid⁸ using 3.2 moles of benzene and 6.9 moles of 2-butene and 175 g. of 96% sulfuric acid. A yield of 38% (224 g.) of a mixture of di-*s*-butylbenzenes was obtained, boiling at 235° (751 mm.), n_D^{20} 1.4879.

p-Di-*t*-butylbenzene was prepared⁹; it melted at 78°.

Catalysts.—Silicophosphoric acid was a commercial grade Universal Oil Products Company Polymerization, Catalyst.⁹ The extruded pills were ground and screened to conform to 8–12 mesh size.

Silica-alumina catalyst was Universal Oil Products type A cracking catalyst in the form of cylinders $1/8" \times 1/16"$.

(6) V. N. Ipatieff, H. Pines, V. Dvorkovitz and R. C. Olberg, *J. Org. Chem.*, **12**, 34 (1947).

(7) B. J. Mair and A. F. Forziati, *J. Research Nat. Bur. Standards*, **58**, 151, 165 (1944).

(8) V. N. Ipatieff, B. B. Corson and H. Pines, *THIS JOURNAL*, **58**, 919 (1936).

(9) V. N. Ipatieff, U. S. Patents 1,993,512 and 1,993,513 (March 5, 1935), 2,018,085 and 2,018,086 (Oct. 22, 1935), 2,020,649 (Nov. 12, 1935), 2,057,433 (Oct. 13, 1936), 2,050,871 (Nov. 17, 1936).

This catalyst contained 90% by weight of silica and 10% by weight of alumina.¹⁰

Zinc chloride-alumina catalyst¹¹ was prepared by mixing 80 g. of activated alumina, 10–12 mesh size, with 20 g. of zinc chloride in 125 ml. of water. The water was evaporated and the catalyst was dried in an oven for twelve hours at 160°.

Apparatus.—A flow type pressure apparatus was used in the continuous experiments. The catalyst tube was provided with a spiral preheater and a supporting rod (spacer); the catalyst was placed in the center of the reaction tube. The function of the preheater was to permit the reactants to be preheated to the temperature at which the catalyst was maintained; the spacer had a dual function, to support the catalyst and to decrease the free space in the tube.

Infrared Spectral Analysis.—The percentages of *t*- and *s*-butylbenzene in the butylbenzene fraction were determined on a Beckman infrared spectrophotometer, model IR-2, using rock-salt cells of 0.1 mm. widths. The spectra of pure *s*- and *t*-butylbenzene were determined in the wave length ranging from 7.5 to 13.0 microns; these spectra were identical with those reported by the American Petroleum Institute Project 44. Wave lengths of 8.00 and 10.51 microns were used for the quantitative determination of the butylbenzenes. The absorption coefficients of pure *s*- and *t*-butylbenzene are given in Table IV.

 TABLE IV
 ABSORPTION COEFFICIENTS OF PURE BUTYL BENZENES
 (0.1 MM. CELL)

Wave length, microns	<i>t</i> -Butyl	<i>s</i> -Butyl
8.00	0.945	0.09
10.51	.01	.349

Summary

The catalytic reaction of 2-butene and isobutylene with benzene under pressure and at elevated temperatures has been studied.

Silicophosphoric acid and alumina-zinc chloride catalyst cause skeletal isomerization to accompany the alkylation reaction.

The dealkylation of di-*t*-butylbenzene and di-

(10) C. L. Thomas, J. Hoekstra and J. T. Pinkston, *THIS JOURNAL*, **66**, 1694 (1944).

(11) L. Schmerling and V. N. Ipatieff unpublished results.

s-butylbenzene, respectively, in the presence of benzene and catalysts yields a mixture of *t*- and *s*-butylbenzene.

In the presence of silicophosphoric acid and

zinc chloride-alumina catalyst *s*-butylbenzene isomerizes partly to *t*-butylbenzene and *t*-butylbenzene to *s*-butylbenzene.

EVANSTON, ILLINOIS

RECEIVED OCTOBER 31, 1949

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF MCGILL UNIVERSITY, MIDDLEBURY COLLEGE, AND THE JOHNS HOPKINS UNIVERSITY]

The Sulfuric Acid Condensation Products of Symmetrical Dialkylacetonedicarboxylic Esters

BY EVANS B. REID¹

The observation by Schroeter² that the solid dimer of methyl ketene (III)^{3,4} results from saponification and decarboxylation of either the methyl or ethyl ester of 1,3-dimethylcyclobutane-2,4-dione carboxylic acid (I), is the main evidence in favor of a cyclobutane structure for the latter compounds. Beyond this, remarkably thorough investigations of the properties of these compounds,^{2,5} failed to uncover any facts which could not be accommodated by the cyclobutane structure (I).

These weakly acidic substances were, at first, considered the only products resulting from the action of cold sulfuric acid upon symmetrical dimethylacetonedicarboxylic esters.⁶ Later, basic compounds were isolated,² to which were assigned 2,6-dialkoxy- γ -pyrone structures (II, where R equals methyl or ethyl).

In the present work both the acidic and the basic substances arising from the sulfuric acid condensation of ethyl α, α' -dimethylacetonedicarboxylate have been examined critically. This has resulted in the conclusions that, whereas the base is correctly represented by the diethoxy- γ -pyrone structure (II), the properties of the acidic body are incompatible with the cyclobutanic formulation (I), and clearly favor the 2-hydroxy-6-ethoxy- γ -pyrone expression (IV), though they do not exclude the 4-hydroxy isomeride (VI).

The Basic Compound.—This substance proved exceptionally stable. It was inert to phenylhydrazine, and after having been refluxed with distilled water for eight hours was recovered

(1) Some of this work is taken from the doctoral dissertation of the author, McGill University, Montreal, 1940. Certain evidence was there presented which tended to show that the cyclobutane structure assigned to the acidic condensation product by Schroeter [*Ber.*, **49**, 2697 (1916)] was not completely satisfactory. An α -alkoxy- γ -pyrone structure (IV, of the present paper), was considered, but was rejected on the basis of experimental evidence then at hand. Part of this earlier work was repeated and extended at Middlebury College, Vermont, in subsequent years. Between 1946-1949, at The Johns Hopkins University, conclusive evidence was obtained in favor of the pyrone structure.

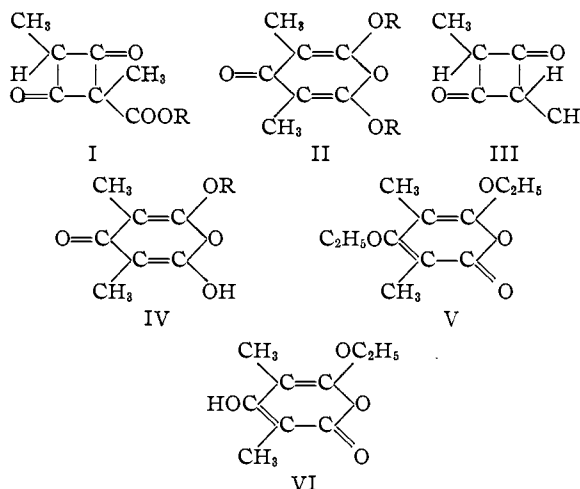
(2) Schroeter, *Ber.*, **49**, 2697 (1916).

(3) Staudinger, *ibid.*, **44**, 533 (1911).

(4) The chemistry of the lower aldoketenes is under investigation in these laboratories, and will form the subject of a later communication.

(5) Schroeter, *ibid.*, **59**, 973 (1926).

(6) Schroeter and Stassen, *ibid.*, **40**, 1604 (1907).



unchanged. Ozone at -30° scarcely attacked it, and on exhaustive treatment at room temperature a true ozonide failed to form. The presence of two ethoxy groups was demonstrated. While typical unsaturation tests were obtained with bromine and neutral permanganate, evidence of oxidation under acidic conditions could only be secured on heating. On the other hand it was susceptible to hydrolysis under weakly basic conditions furnishing pentanone-3. These facts, together with its solubility in acids and insolubility in bases, are rationalized only by the expression 3,5-dimethyl-2,6-diethoxy- γ -pyrone (II).⁷

The Acidic Compound.—In contrast with the basic substance, the so-called ethyl 1,3-dimethylcyclobutane-2,4-dionecarboxylate was exceedingly unstable. The most carefully purified material showed definite signs of decomposition within two weeks. Yet it proved completely inert to hydrogen and Adams catalyst under ordinary conditions. This inertia is difficult to reconcile with the relatively strained cyclobutanedione structure, since ethyl cyclopentanone-1-carboxylate was readily reduced to the corresponding alcohol under the same circumstances.⁸

A peculiar result emerged from hydrolysis studies. Thus, while the substance was readily

(7) Compare Willstätter and Pummerer, *ibid.*, **38**, 1461 (1905).

(8) Reid and Parker, unpublished results from these laboratories.