

## The Jacobsen Rearrangement. Behavior of Durennesulfonic Acid in Polyphosphoric Acid

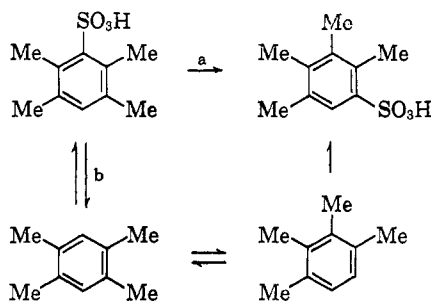
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Durennesulfonic acid rearranges in polyphosphoric acid to give prehnitenesulfonic acid in low yield. The rearrangement is accompanied by desulfonation. Analysis of the hydrocarbon and sulfonic acid phases separately showed only durenene and hexamethylbenzene in the hydrocarbon layer, while the sulfonic acids of durenene, prehnitene, and pseudocumene were identified. Isodurenene was absent from the hydrocarbon phase, but present in trace amounts as the sulfonic acid. Neither durenene nor prehnitene will rearrange in polyphosphoric acid alone or in the presence of *p*-toluenesulfonic acid. Arguments are presented to show that the Jacobsen rearrangement in this medium occurs *via* direct rearrangement of the sulfonic acid.

The Jacobsen rearrangement of polyalkylbenzenes<sup>2</sup> has received attention both because of its usefulness in the synthesis of some vicinally substituted tetraalkylbenzenes and because of the enigmatic character of its mechanism. Though most investigators have proposed ionic mechanisms,<sup>3</sup> none of which has proven completely satisfactory, the picture has been further confounded by the recent proposal<sup>4</sup> of a radical-ion mechanism. All of these proposals involve direct rearrangement of the sulfonic acid. A distinctly different proposal was put forward by Kilpatrick<sup>5</sup> based on his observation that of the three tetramethylbenzenes only prehnitene sulfonates irreversibly under the normal Jacobsen conditions. Thus, there are two contrasting paths proposed for the Jacobsen rearrangement: (a) direct reaction of the sulfonic acid; and (b) desul-



fonation, rearrangement of the hydrocarbon, and sulfonation of the vicinally substituted hydrocarbon irreversibly.

Smith<sup>6</sup> has stated that it is the sulfonic acid which rearranges. The evidence for this was that durennesulfonic acid rearranged in contact with phosphorus pentoxide while the hydrocarbon itself did not. Since the question of the actual entity undergoing rearrangement is a crucial one in terms of mechanism, it seems appropriate to submit it to a more searching examination. We were thus prompted to examine the behavior of durennesulfonic acid (DSA) in polyphosphoric acid (PPA).

(1) Participant in National Science Foundation Research Participation for College Teachers Program, summer 1964.

(2) For a review of the older literature, see L. I. Smith, *Org. Reactions*, **1**, 370 (1942).

(3) (a) R. T. Arnold and R. A. Barnes, *J. Am. Chem. Soc.*, **66**, 960 (1944); (b) E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 257; (c) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 665; (d) M. Suzuki, *Bull. Chem. Soc. Japan*, **36** (12), 1642 (1963).

(4) F. Bohlmann and J. Riemann, *Chem. Ber.*, **97**, 1515 (1964).

(5) M. Kilpatrick and M. W. Meyer, *J. Phys. Chem.*, **65**, 1312 (1961).

(6) L. I. Smith and O. W. Cass, *J. Am. Chem. Soc.*, **54**, 1614 (1932).

## Results

Durennesulfonic acid suspended in PPA at 80° rearranges slowly to give a low yield of prehnitenesulfonic acid (PSA). The reaction gives essentially the same mixture of products (see below) obtained in the Jacobsen rearrangement carried out normally.<sup>7</sup> Even the dark tarry material and sulfur dioxide are observed in both media. In PPA, however, the major reaction is desulfonation of the DSA. Analysis of the hydrocarbon fraction was made directly by gas chromatography. The sulfonic acids were desulfonated by flash distillation from phosphoric acid under conditions shown to lead to no rearrangement. The hydrocarbons isolated from the flash distillate were also analyzed by gas chromatography. The results of these analyses are shown in Table I.

Addition of prehnitene to the reaction mixture led to complete disappearance of the prehnitene from the hydrocarbon phase and an increased yield of PSA. Concomitantly the amount of durenene recovered as the hydrocarbon rose. When isodurenene was added to the reaction mixture in a similar manner, it essentially disappeared from the hydrocarbon fraction, but did not appear as isodurennesulfonic acid (ISA). The yield of PSA was not altered, but once again the amount of durenene recovered was increased.

Neither durenene nor prehnitene will rearrange in PPA alone, nor in the presence of a stable sulfonic acid (*p*-toluenesulfonic acid). Prehnitene does react with *p*-toluenesulfonic acid in PPA to give a nearly quantitative yield of sulfone. Reaction of DSA in PPA in the presence of an excess of *o*-xylene to act as a scavenger for the sulfonating agent released during desulfonation led to the formation of durenene and bis-*o*-xylyl sulfone but no PSA. An attempt to bring about rearrangement of DSA in a nonacidic medium (chloroform) failed. Only a small amount of desulfonation was observed.

## Discussion

It is important to ask first what connection exists between the Jacobsen rearrangement in sulfuric acid and the events observed in PPA. At present the only criterion for answering this question is the nature of the products obtained. On this basis the two reactions are the same since both give rise to the same products, even the dark tars and sulfur dioxide. Differences in the ratios of products found in the two media are

(7) O. Jacobsen, *Ber.*, **19**, 1209 (1886).

TABLE I  
 PRODUCTS FROM THE REACTION OF DURENESULFONIC ACID IN POLYPHOSPHORIC ACID AT 80°<sup>a</sup>

| Expt. | Time of reaction, hr. | Conditions                                     | Hydrocarbon extract, g. |                   | Steam distillate, <sup>b</sup> g. |                   |            |                   | Total yield of hydrocarbon, g. |
|-------|-----------------------|--|-------------------------|-------------------|-----------------------------------|-------------------|------------|-------------------|--------------------------------|
|       |                       |  | Durene                  | Hexamethylbenzene | Pseudo-cumene <sup>c</sup>        | Durene            | Prehnitene | Hexamethylbenzene |                                |
| 7     | 3                     |  | 1.48                    | 0.12              | 0.10                              | 1.24              | 0.002      | 0.003             | 3.0                            |
| 5     | 6                     |  | 1.30                    | 0.40              | 0.18                              | 0.51 <sup>d</sup> | 0.07       | 0.03              | 2.5                            |
| 11    | 7.5                   |  | 1.30                    | 0.30              | 0.06                              | 0.31 <sup>d</sup> | 0.07       | 0.07              | 2.1                            |
| 8     | 9                     |  | 1.10                    | 0.40              | 0.13                              | 0.01 <sup>d</sup> | 0.21       | 0.007             | 2.0                            |
| 3     | 12                    |  | 0.54                    | 0.26              | 0.15                              | 0.02 <sup>d</sup> | 0.21       | 0.01              | 1.2                            |
| 4     | 12                    | 1 g. of prehnitene added                       | 1.86                    | 0.26              | 0.06                              | 0.25 <sup>d</sup> | 0.58       | 0.02              | 3.0                            |
| 6     | 12                    | 1 g. of isodurene added                        | 1.55 <sup>d</sup>       | 0.35              | 0.10                              | 0.04 <sup>d</sup> | 0.21       | 0.04              | 2.3                            |
| 15    | 12                    | 10.2 g. of <i>o</i> -xylene added (0.096 mole) | 2.8                     |                   |                                   |                   |            |                   | 2.8                            |

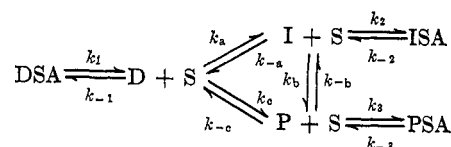
<sup>a</sup> All reactions used 6.0 g. (0.024 mole) of durenesulfonic acid dihydrate in 80 g. of polyphosphoric acid. <sup>b</sup> The hydrocarbons found in the steam distillate originated from the corresponding sulfonic acid. Hexamethylbenzene appeared in this extract to a small extent, presumably because of incomplete extraction by pentane in which it is only slightly soluble. <sup>c</sup> A trace of mesitylene was also present. <sup>d</sup> Small amounts of isodurene were indicated by shoulders on the g.p.c. peaks of durene using the PDEAS column.

readily explicable. In view of the similarities which exist, we will adopt the position that the two reactions proceed by the same routes, and that conclusions reached on the basis of observations in PPA are valid for the normal Jacobsen rearrangement.

It has long been known that in dilute sulfuric acid all isomeric tetramethylbenzenesulfonic acids desulfonate without rearrangement; *i.e.*, desulfonation is more rapid than is rearrangement by at least two orders of magnitude. A similar result pertains in PPA, since, when all sulfonating agents were removed by scavenging with *o*-xylene, desulfonation was the sole reaction observable. Clearly sulfonation is a necessary prerequisite for rearrangement, and one important function of the sulfuric acid used as a medium for the Jacobsen rearrangement is to reverse the desulfonation step.

The important observation that neither durene nor prehnitene will rearrange in contact with PPA is in accord with the findings reported by Smith and Cass.<sup>6</sup> The addition of a stable sulfonic acid does not alter that result. However, sulfur trioxide must be formed by desulfonation and will be present in the reaction mixture as such or in the form of sulfuric acid or a mixed polyacid. We cannot ascertain whether the hydrocarbon will rearrange in the presence of this agent. However, it does not seem likely that the addition of a small amount of sulfuric acid would alter the proton-donating power of the medium sufficiently to permit rearrangement. If the hydrocarbon does not rearrange, it seems surprising that the sulfonic acid which must certainly be less basic than the hydrocarbon should undergo an acid-catalyzed reaction in a medium which leaves the hydrocarbon unaffected. Perhaps the observation may be due solely to the lack of solubility of the hydrocarbon in the medium, since both the hydrocarbons and the sulfonic acids are of limited but unknown solubility in PPA.

Despite the inaccessibility of the rearrangement under nonsulfonating conditions, the results reported here permit certain conclusions to be drawn *vis-à-vis* the Kilpatrick mechanism. Assuming for the sake of argument that the sole route to rearrangement is *via* the hydrocarbon, the set of equations shown will define the mechanism. All but one of the reactions shown are known to occur. Smith and Cass<sup>6</sup> have



D = durene  
 I = isodurene  
 P = prehnitene  
 S = SO<sub>3</sub> or its equivalent

shown that all three hydrocarbons sulfonate without rearrangement. We have confirmed these reports. In dilute acid media all three sulfonic acids desulfonate without rearrangement. Kilpatrick,<sup>8</sup> *et al.*, have shown that both durene and prehnitene rearrange in liquid hydrogen fluoride to give isodurene. The reaction *c* which converts durene directly to prehnitene has not been observed, and the above authors termed it unlikely. Isodurene has been shown theoretically<sup>9</sup> and found experimentally<sup>10</sup> to be at least 50 times as basic as either durene or prehnitene. It is the only hydrocarbon which accumulates when any of the three tetramethylbenzenes is treated with hydrofluoric acid.<sup>11</sup> Therefore, isodurene would be expected to accumulate in the hydrocarbon phase in the reaction in PPA. This does not happen. Such a result could be explained without abandoning the mechanism if durene were to rearrange directly to prehnitene which would then have to sulfonate rapidly and irreversibly. If this were correct, isodurene would not appear in the hydrocarbon phase. Since both  $k_a$  and  $k_{-b}$  are measurably slow in liquid hydrofluoric acid, and isodurene is the most stable of the tetramethylbenzenes, the rates of reaction of isodurene to form either durene ( $k_{-a}$ ) or prehnitene ( $k_b$ ) must be quite slow. Therefore, added isodurene would have no escape route except *via* one of these slow processes. Our results show that isodurene can disappear rapidly from the hydrocarbon phase, presumably *via* sulfonation and rearrangement. Thus we

(8) M. Kilpatrick, J. A. S. Bett, and M. L. Kilpatrick, *J. Am. Chem. Soc.*, **85**, 1038 (1963).

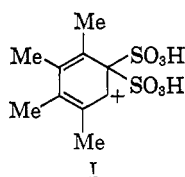
(9) S. Ehrenson, *ibid.*, **83**, 4493 (1961), **84**, 2681 (1962); R. L. Flurry, Jr., and P. G. Lykos, *ibid.*, **85**, 1033 (1963).

(10) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951); M. Kilpatrick and F. E. Luborsky, *ibid.*, **75**, 577 (1953).

(11) D. A. McCaulay and A. P. Lien, *ibid.*, **74**, 6246 (1952).

conclude that the sulfonic acid itself must be capable of rearranging.

Support for this conclusion can be adduced from the work of Bohlmann and Riemann.<sup>4</sup> They report that PSA obtained from ring-labeled durene contained 13% of the original C<sup>14</sup> at the carbon bearing the sulfonic acid and 17% at the neighboring unsubstituted carbon. Were the Kilpatrick mechanism alone operative, these two positions would necessarily be equivalently labeled. They also report<sup>4</sup> that PSA undergoes a rapid and complete exchange of its sulfonic acid moiety with S<sup>35</sup>-labeled sulfuric acid. If this exchange proceeds *via* desulfonation and resulfonation, it renders the meaning of the above experiment uncertain. However, it then eliminates the cornerstone of Kilpatrick's mechanism, *viz.*, the irreversible nature of the sulfonation of prehnitene. Possibly exchange may involve the symmetrical ion I. In any case, the results support



the conclusion that the Kilpatrick mechanism cannot be the only route for the Jacobsen rearrangement.

At present the experimental evidence available will not suffice to define one unique mechanism for the Jacobsen rearrangement. All of the evidence can be accommodated by a generalized mechanism involving three basic steps: (a) protonation of the sulfonic acid; (b) a series of reversible 1,2 shifts; and (c) deprotonation. The product at equilibrium would be the most stable sulfonic acid. Since the relative thermodynamic stabilities of the sulfonic acids need bear no direct relation to those of the corresponding hydrocarbons, the formation of PSA should evoke no surprise.

### Experimental Section

**Reaction of DSA in PPA.**—Six grams (0.024 mole) of DSA (as the dihydrate)<sup>12</sup> was placed in a 200-ml. round-bottomed flask and 80 g. of commercial PPA was added. The tightly stoppered reaction flask was immersed completely in an oil bath maintained at 80°. The mixture was stirred continuously during the reaction time which varied from 3 to 12 hr. The dark reaction mixture was poured into ice-water, and the solution was extracted with three 75-ml. portions of pentane. The pentane extracts were combined and dried over calcium chloride, and the pentane was removed by evaporation. The crude hydrocarbon obtained was weighed.

(12) L. I. Smith and O. W. Cass, *ibid.*, **54**, 1612 (1932).

In a three-necked flask was placed 75 ml. of 85% phosphoric acid. The acid was heated to 140–150° and superheated steam was passed through the hot acid. To this was added dropwise the aqueous portion of the reaction mixture. About 1200 ml. of distillate was collected over a 3-hr. period. The distillate was extracted twice with 100-ml. portions of pentane. The extracts were combined and dried, and after removal of the pentane, the crude hydrocarbon was weighed. Desulfonation of DSA or ISA by this process was found to lead to no rearrangement.

Analysis of the hydrocarbons obtained by direct extraction or by desulfonation was made by gas chromatography.

**Attempted Rearrangement of Hydrocarbons.**—A mixture of 2 g. (0.015 mole) of durene and 50 g. of PPA was heated at 85° while being stirred continuously for 12 hr. The reaction mixture was worked up according to the procedure given above. Analysis by gas chromatography showed that durene alone was present in the product. No trace of isodurene could be identified. Similar treatment of prehnitene led only to recovered prehnitene with no trace of durene or isodurene in the recovered hydrocarbon.

A sample of *p*-toluenesulfonic acid heated under the conditions of the above reaction proved to be stable and no toluene could be isolated from the reaction. A mixture of 0.8 g. (0.006 mole) of durene, 2.3 g. (0.012 mole) of *p*-toluenesulfonic acid, and 40 g. of PPA was stirred and heated at 80° for 9 hr. Recovered hydrocarbon was shown by gas chromatographic analysis to be pure durene.

A mixture of prehnitene, *p*-toluenesulfonic acid, and PPA heated for a similar period gave a quantitative yield of solid, m.p. 166°,  $\bar{\nu}$  1140 and 1300 cm.<sup>-1</sup>, which was presumed to be 2,3,5,6-tetramethyldiphenyl sulfone.

**Reaction of DSA and PPA in the Presence of *o*-Xylene.**—A mixture of 6 g. (0.024 mole) of DSA dihydrate, 10.2 g. (0.096 mole) of *o*-xylene, and 80 g. of PPA was stirred and heated for 12 hr. at 80°. No black tar was formed and no sulfur dioxide was evolved. When the reaction mixture was poured into ice-water, a voluminous precipitate was formed which was isolated by filtration. The yield of dry solid was 5.6 g.,  $\bar{\nu}$  1140 and 1300 cm.<sup>-1</sup>, and, after recrystallization from ethanol, it melted at 162.5–163.5°. A melting point of 162° has been reported<sup>13</sup> for 3,3',4,4'-tetramethyldiphenyl sulfone. Both durene (2.8 g., 0.021 mole) and *o*-xylene (3.8 g.) were recovered, but no PSA was found in the solution.

**Gas Chromatographic Analysis.**—Analyses were run on a Perkin-Elmer 154B gas chromatograph using either a 6 ft. × 0.25 in. column containing 15% of Ucon Polar on Chromosorb at 145°, or a 10 ft. × 0.25 in. column containing 15% PDEAS on Chromosorb at 135°. Helium was employed as carrier gas. The first column was effective in separating all of the hydrocarbons except durene and isodurene. Separation of the latter was achieved with the second column. Representative retention times are shown in Table II.

TABLE II

|                   | Time, min. |       |
|-------------------|------------|-------|
|                   | Ucon Polar | PDEAS |
| Pseudocumene      | 3.4        | 9.4   |
| Durene            | 6.5        | 17.4  |
| Isodurene         | 6.5        | 18.3  |
| Prehnitene        | 8.1        | 21.7  |
| Hexamethylbenzene | 15.5       | 43.0  |

(13) H. Drews, A. Meyerson, and E. K. Fields, *ibid.*, **63**, 3871 (1961).