The Isomerization of t-Butylphenols Using Zeolite Catalysts

A. P. BOLTON, M. A. LANEWALA, AND P. E. PICKERT

Union Carbide Corporation, Linde Division, Molecular Sieve Department, Tonawanda, New York 14152

Received March 14, 1968

Partially multivalent metal cation exchanged, partially decationized Type Y zeolites catalyze the isomerization of the tertiary butylphenols. Isomerization proceeds *via* a transalkylation mechanism, rather than through an intramolecular rearrangement, and is similar to the mechanism proposed for the isomerization of the diethylbenzenes. Equilibrium distributions of the monosubstituted isomers are derived from the dealkylation of the dialkylphenols. No isomerization occurs with zeolite catalysts in the absence of transalkylation. The equilibrium distributions at 200° are approximately 1% *ortho*, 72% *meta*, and 25% *para* in the monoalkyl fraction and 2% 2,6, 83% 3,5, 5% 2,4, and 10% 2,5 in the dialkyl fraction.

The alkylation of phenol with olefins as well as the rearrangement of alkylphenols using conventional Friedel–Crafts catalysts leads invariably to substitution in the *ortho* and *para* positions unless excessive, noncatalytic amounts of these materials are employed.[1] Catalytic amounts give kinetically controlled *ortho* and *para* substitution because of the strong directive influence of the hydroxyl group.[2] It has been pointed out that there is no *meta* substitution in phenol alkylation even with substituting groups which are extremely reactive by H. C. Brown's classification.[3] The alkylated product obtained with catalytic amounts of partially multivalent cation-exchanged, partially decationized Type Y Molecular Sieve contains high concentrations of the *meta*-substituted derivatives. The object of this study was to demonstrate that the formation of the *meta* derivatives is attributable to the transalkylation of the *ortho* and *para* derivatives and not to direct alkylation. Starting with pure samples of the three *t*-butylphenols it was possible to follow the reaction path of these transalkylation reactions and to identify the reaction intermediates. The isomerization of the diethylbenzenes using a zeolite catalyst has previously been shown to occur *via* a transalkylation mechanism and not through an intramolecular rearrangement.[4] In the case of the tertiary butylphenols, however, the relatively fewer number of polysubstituted isomers compared with the ethyl-substituted benzenes makes the system less complex and enables the role of transalkylation to be clearly demonstrated.

Discussion of Results

The isomerization of *o*-*t*-butylphenol is rapid, even at 100°. It can be seen from Table I that the monoalkyl fraction initially consisted almost entirely of the unchanged *ortho* isomer and the dialkyl fraction exclusively of the 2,4-dialkyl isomer. This is consistent with a transalkylation mechanism producing a kinetically controlled isomer distribution. The amount of *para* isomer steadily increased with time, and the *meta* isomer occurred only after most of the *ortho* isomer was converted into the *para* form. The appearance of the *meta* isomer coincided with that of the 2,5-dialkylphenol. Since isomerization was not found to occur in the absence of transalkylation, it can be assumed that transalkylation is an integral part of the isomerization reaction. That the *meta* isomer occurred after the formation of the *para* isomer discounts a simple 1,2 shift of the *t*-butyl group. If the isomer distribution in the dialkyl fraction is closely examined, however, a more complex mechanism is indicated. The preponderance of the 2,4 isomer in the dialkyl fraction in Table I shows that the transalkylation reaction is kinetically controlled, and the subsequent dealkylation of this isomer can reasonably account for the formation of the *para* isomer.

The isomerization of the *ortho* isomer at 200° (Table II) gives information on the reaction path at a later stage than the isomerization at 100° and closer to the equilibrium distribution. The main constituent in the monoalkyl fraction progressively changes from the *para* to the *meta* isomer. The concentration of the 2,5-dialkylphenol, initially zero, reaches a maximum of approximately 25% in 1 hr and then decreases to an equilibrium value of 9%. This indicates that the 2,5 isomer is a reaction intermediate for the formation of the 3,5 isomer.

The isomerization of *p*-*t*-butylphenol at 200° (Table III) is essentially the same as that of the *ortho* isomer since the latter was converted almost instantaneously into the former at 200° (Table II). Starting with both isomers, the final product distributions were the same. Again the 2,4 isomer was first formed and constituted 100% of the dialkyl fraction; the concentration of the 2,5 isomer gradually increased to a maximum of approximately 25% in 1 hr. The appearance of the 3,5 isomer occurred more slowly.

The isomerization of *m*-*t*-butylphenol at 100° (Table IV) proceeded at a slower rate than that of the *ortho* isomer. Neither transalkylation nor isomerization occurred before a reaction time of 4 hr. The 2,5 and the 3,5 isomers appeared simultaneously. The results obtained at 200° (Table V) showed the transalkylation reaction to proceed faster than at 100°, producing a significant conversion in 4 min. Again, the 2,5 and the 3,5 isomers initially constituted most of the dialkyl fraction. This reaction required over 50 hr to reach equilibrium, presumably because of the greater stability of the *m*- and 3,5-alkylphenols. The final equilibrium mixture at 200°, starting with any of the three alkylphenol isomers contained ~1% *ortho*, 72% *meta*, and 28% *para* in the monoalkyl fraction and 2% 2,6, 83% 3,5, 5% 2,4, and 10% 2,5 in the dialkyl fraction. The extent of transalkylation is about 23% phenol, 54% monoalkylphenol, and 23% dialkylphenol.

(1) R. D. Wysong, Ph.D. Thesis, Vanderbilt University 1967, part I, p 40.

(2) J. H. Patinkin and B. S. Friedman, "Friedel-Crafts and Related Reactions," Vol. II, part I, G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1964, pp 75–77.

(3) J. Blackwell and W. J. Hickingbottom, *Chem. Ind.* (London), 1569 (1961).

(4) A. P. Bolton, M. A. Lanewala, and P. E. Pickert, *J. Org. Chem.*, **33**, 1513 (1968).

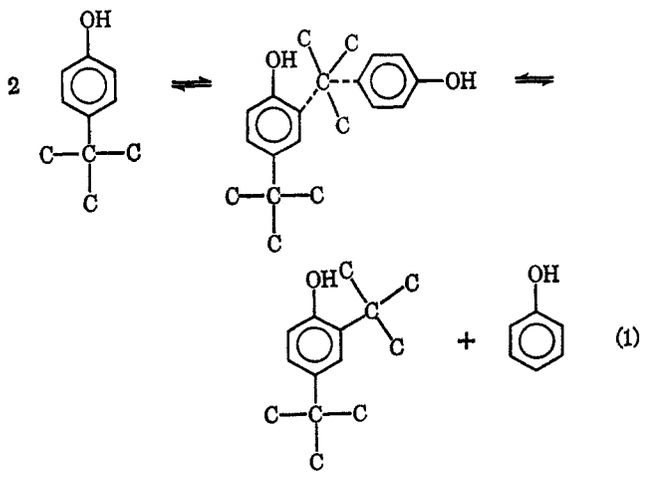
TABLE I

THE ISOMERIZATION OF *o*-*t*-BUTYLPHENOL AT 100°

	Products, mol %			Isomer distribution (normalized), mol %					
Time	Phenol	*t*-Butylphenol	Di-*t*-butylphenol	*o*	*m*	*p*	2,6	3,5	2,4	2,5
0 min	0	100	0	99.2	0.3	0.5				
0.5 min	9.1	84.3	6.6	97.7	0.4	1.9			100	
1.5 min	10.8	80.8	8.4	92.8	0.4	6.8			100	
2.5 min	9.5	80.6	9.9	90.7	0.5	8.8			100	
10 min	13.0	23.0	14.0	79.2	0.6	20.2			100	
20 min	18.1	66.3	15.6	68.9	0.4	30.7			100	
30 min	20.0	62.0	18.0	61.1	0.5	38.4			100	
1 hr	20.4	60.2	19.4	50.8	0.3	48.9			100	
2 hr	22.9	56.0	21.1	37.8	0.4	61.8			100	
4 hr	22.7	53.7	23.6	23.4	0.6	76.0			100	
5 hr	22.8	53.6	23.6	18.3	0.4	81.3			100	
22 hr	22.7	53.6	23.7	3.3	1.0	95.7			99.8	0.2
30 hr	22.5	53.6	23.9	1.4	2.3	96.3			99.8	0.2

Reaction Mechanism

The results from the isomerization of the *t*-butylphenols indicate that adjacent *t*-butyl groups cannot readily exist on the aromatic nucleus presumably because of the steric limitations. An intramolecular rearrangement by a 1,2-shift mechanism has to be discounted because the *para* isomer is formed before the *meta* isomer during the isomerization of *o*-*t*-butylphenol. Isomerization *via* a transalkylation mechanism, similar to that proposed for the diethylbenzenes,[4] satisfactorily explains the experimental results. A mechanism for the transalkylation step involving a bimolecular intermediate, formed by the condensation of two monoalkylphenols which subsequently yields a molecule of phenol and a molecule of a dialkylphenol, imposes limitations on the possible isomers that may be derived from the transalkylation reactions. Since adjacent *t*-butyl groups are not readily formed, there is but one dialkylphenol isomer that can be derived from the transalkylation of two *p*-*t*-butylphenol molecules, namely, the 2,4 isomer as indicated by eq 1. With a similar intermediate, it is possible to obtain the 2,6-, 2,4-, and 2,5-di-*t*-butylphenols from the *ortho* isomer but only the 2,5 and 3,5 isomers from *m*-*t*-butylphenol. In a similar way, the monoalkylphenol isomers, derived from the transalkylation of a dialkylphenol and phenol, are dependent on the particular disubstituted phenol isomer.



(1)

The loss of one *t*-butyl group from the 3,5 isomer through transalkylation with an unsubstituted phenol invariably results in a molecule of the *meta* isomer. However, because of the strong directive influence of the hydroxyl group, the isomers formed by the transfer of the *t*-butyl group to the unsubstituted phenol molecule are invariably *ortho* and *para*. This is substantiated by the monoalkyl isomer distribution shown in Table I.

Using the limitations imposed on the products from the transalkylation reactions, the reaction in Scheme I can be derived. The experimental results obtained in this study are in close agreement with such a reaction scheme.

The directive influence of the hydroxyl group on the phenol to *ortho* and *para* substitution results in the preferential formation of some isomers over other possible isomers. The transalkylation of the *meta* isomer

TABLE II

THE ISOMERIZATION OF *o*-*t*-BUTYLPHENOL AT 200°

	t-Butylphenol fraction (normalized), mol %			Di-*t*-butylphenol fraction (normalized), mol %			
Time	*o*	*m*	*p*	2,6	3,5	2,4	2,5
0 min	99.2	<0.3	0.5				
2.5 min	4.3	8.1	87.6	1.9	1.4	93.7	3.0
10 min	3.3	21.1	75.6	3.2	6.7	70.0	20.1
23 min	2.6	32.8	64.6	2.9	15.7	60.2	21.2
40 min	2.0	41.3	56.7	3.3	26.2	47.8	22.7
1 hr	1.5	48.2	50.3	2.3	34.7	37.4	25.6
2 hr	1.3	58.8	33.9	2.2	53.0	22.4	22.4
4 hr	0.6	66.6	32.8	1.6	69.8	10.6	18.0
22 hr	0.4	71.0	28.6	1.9	82.8	6.1	9.2

TABLE III

THE ISOMERIZATION OF *p*-*t*-BUTYLPHENOL AT 200°

	t-Butylphenol fraction (normalized), mol %			Di-*t*-butylphenol fraction (normalized), mol %			
Time	*o*	*m*	*p*	2,6	3,5	2,4	2,5
0 min	<0.3	<0.3	99.4				
1.5 min	2.7	2.1	95.2	4.9	0.4	90.3	4.4
3.5 min	3.0	5.0	92.0	3.9	1.6	87.9	7.2
10 min	3.0	12.5	84.5	3.8	4.1	79.5	12.6
15 min	2.8	18.0	79.2	3.2	6.8	70.5	19.5
20 min	2.0	23.0	75.0	3.9	9.1	71.3	15.7
31 min	2.1	29.9	68.0	3.7	15.3	62.2	18.8
40 min	2.0	34.4	63.6	4.4	20.9	55.1	19.5
50 min	1.4	40.3	58.3	3.8	24.6	47.0	24.6
1.40 hr	1.2	50.2	48.6	3.3	40.9	32.4	23.4
3.00 hr	0.5	59.6	39.9	2.6	60.4	18.2	18.8
5.30 hr	0.5	65.0	34.5	2.7	73.3	10.3	13.7
27.00 hr	0.5	71.3	28.2	1.6	81.3	7.0	10.5
46.00 hr	0.2	72.5	27.3	1.6	82.9	5.3	10.2

SCHEME I

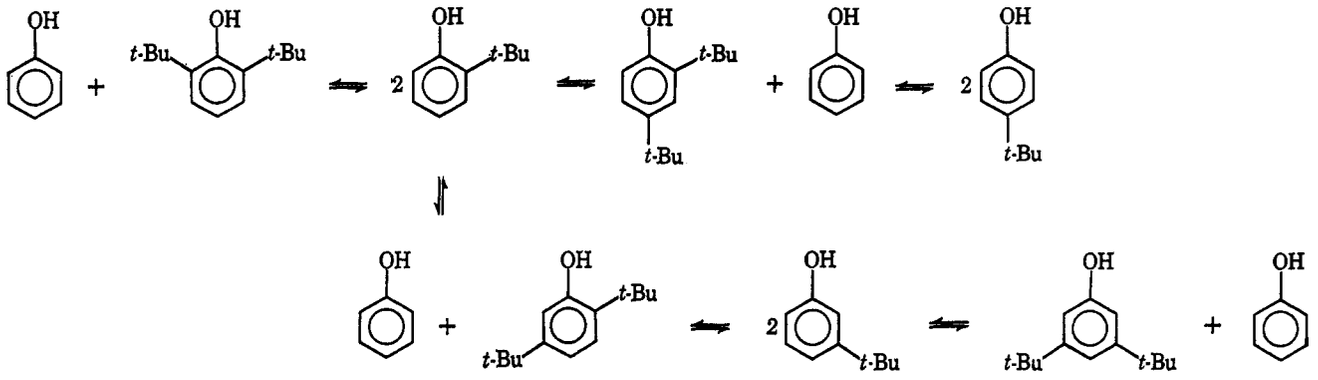


TABLE IV

THE ISOMERIZATION OF *m*-*t*-BUTYLPHENOL AT 100°

Time	Products, mol %			Isomer distribution (normalized), mol %						
	Phenol	*t*-Butylphenol	Di-*t*-butylphenol	*o*	*m*	*p*	2,6	3,5	2,4	2,5
0 min		100		0.5	98.1	1.4				
2 min		100		0.5	97.9	1.6				
5 min		100		0.6	97.9	1.5				
10 min		100		0.4	98.2	1.4				
20 min		100		0.4	98.0	1.6				
1 hr		100		0.4	98.0	1.6				
2.00 hr	0.0	100	0.0	0.5	98.2	1.3				
3.53 hr	0.6	99.2	0.2	0.5	97.8	1.7	0	~50		~50
24.00 hr	3.5	94.9	2.6	0.4	98.3	1.3	0	57	0	43
32.0 hr	4.1	92.2	3.7	0.5	98.3	1.2	0	63	0	37
48.0 hr	4.4	91.6	4.0	0.6	97.9	1.5	0	63	0	37
72.0 hr	4.8	91.0	4.2	0.4	98.1	1.5	0	72	0	28

TABLE V

THE ISOMERIZATION OF *m*-*t*-BUTYLPHENOL AT 200°

Time	Product, mol %			Isomer distribution (normalized), mol %						
	Phenol	*t*-Butylphenol	Di-*t*-butylphenol	*o*	*m*	*p*	2,6	3,5	2,4	2,5
2 min	2.7	94.5	2.8	0.2	97.9	1.7	1.1	58.2	1.1	39.6
4 min	3.8	91.9	4.3	0.2	97.2	2.6	0.6	64.5	1.2	33.7
6 min	6.5	87.5	6.0	0.2	95.4	4.4	0.6	69.2	1.4	28.8
10 min	8.8	82.9	8.3	0.2	93.3	6.5	0.9	71.6	0.9	27.0
20 min	10.0	77.8	12.2	0.2	90.2	9.6	0.3	79.8	0.6	19.3
1 hr	16.3	64.2	19.5	0.2	83.5	16.3	0.3	90.0	1.0	8.7
4 hr	19.1	58.7	22.2	0.5	79.6	19.9	0.3	95.2	1.3	3.2
6 hr	22.2	55.1	22.7	0.6	78.0	21.4	0.3	95.6	1.1	3.0
24 hr	20.2	57.4	22.4	0.7	78.0	21.3	0.2	97.1	1.2	1.5
50 hr	22.4	54.8	22.8	0.6	74.2	25.2	1.0	89.3	3.4	6.3
100 hr	22.6	54.6	22.8	0.6	71.5	27.9	1.5	83.5	5.2	9.8

results in the formation of the 2,5 and the 3,5 isomers simultaneously. The relatively rapid increase of the 3,5 isomer compared with the 2,5 isomer at 200° (Table V) may be explained not by the rapid formation of the former but by the further conversion of the latter into the *ortho* isomer as pictured in the proposed reaction (Scheme I).

The validity of the proposed reaction scheme is supported by data obtained from the isomerization of 2,6-di-*t*-butylphenol at 100° (Table VI). As predicted, the *ortho* isomer was initially formed exclusively. The *para* isomer did not appear, even though a significant quantity of the *ortho* isomer was present, until a substantial amount of the 2,4 isomer was formed. The appearance of the 2,5 isomer preceded that of the *meta* isomer as required by the reaction scheme and finally the 3,5 isomer was formed.

TABLE VI

THE ISOMERIZATION OF 2,6-DI-*t*-BUTYLPHENOL AT 100°

Time	*t*-Butylphenol fraction (normalized), mol %			Di-*t*-butylphenol fraction (normalized), mol %			
	o	*m*	*p*	2,6	3,5	2,4	2,5
0 min				100			
0.5 min	100	0	0	100	0	0	0
1 min	100	0	0	99.0	0	1.0	0
3 min	100	0	0	98.5	0	1.5	0
30 min	88.7	0	11.3	93.5	0	6.4	0.1
1 hr	85.7	0	14.3	93.2	0	6.6	0.1
4 hr	80.5	0	19.5	72.6	0	27.1	0.3
6 hr	67.6	0	32.4	66.8	0	32.5	0.7
24 hr	47.7	0.8	51.5	40.2	0	59.0	0.8
31 hr	45.8	0.7	53.5	38.0	0	61.0	1.0
46 hr	39.0	1.2	59.8	28.0	0	71.0	1.0
52 hr	9.0	6.4	84.6	4.3	1.3	91.2	2.2
70 hr	3.6	11.8	84.6	1.2	6.5	84.1	8.2
78 hr	2.8	13.8	83.4	1.7	7.8	80.9	9.6

Experimental Section

The alkylphenols were obtained from the Aldrich Chemical Co., Milwaukee, and had the following purities in mole per cent: *o*-alkylphenol, 99.2% *ortho*, <0.3% *meta*, and 0.5% *para*; *m*-alkylphenol, <0.5% *ortho*, 98.1% *meta*, and 1.4% *para*; *p*-alkylphenol, <0.3% *ortho*, <0.3% *meta*, and 99.4% *para*.

The isomerization reactions were carried out in a sealed magnetically stirred 100-ml flask immersed in a constant-temperature bath. The catalyst, 45% rare earth cation-exchanged–45% decationized Type Y Molecular Sieve with a SiO_2–Al_2O_3 molar ratio of 5.0, was prepared by repeatedly contacting NaY with a 10% aqueous solution of ammonium chloride until the sodium cation-exchange level was reduced to 10% of the total base exchange capacity. This zeolite was then ion exchanged with the theoretical amount of rare earth chloride required to effect a 45% rare earth cation exchange. The catalyst was decationized by calcination at 550° in an air purge for 2 hr. A 1-g sample of catalyst was used with 50 g of monoalkylphenol. Samples of the reaction mixture were removed periodically and analyzed by glpc. Isomer distributions in the tables are given in normalized mole per cent. The similar boiling points and polarities of the alkylphenols make the effective separation of the isomers difficult to achieve by normal chromatographic techniques. However, when these isomers are converted into their silyl ethers, an effective separation[5] is obtained. Component identification and distribution was verified by ir analyses. The analyses of the silyl ether derivatives of the alkylphenols were carried out on a Perkin-Elmer 154 vapor fractometer fitted with a 100-ft squalene column and operated at 65° with a He carrier gas pressure of 30 psi. The dialkylphenol isomers were separated on 150-ft SE-30 column, programmed at 7°/min from 50° with a He carrier gas pressure of 5 psi.

Registry No.—*o*-*t*-Butylphenol, 88-18-6; *m*-*t*-butylphenol, 585-34-2; *p*-*t*-butylphenol, 98-54-4; 2,6-di-*t*-butylphenol, 128-39-2.

(5) R. W. Martin, *J. Amer. Chem. Soc.*, **74**, 3024 (1952).

The Photolysis and Pyrolysis of *trans*-β-Azidovinyl *p*-Tolyl Sulfone

JOHN S. MEEK AND JOANNA S. FOWLER[1]

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

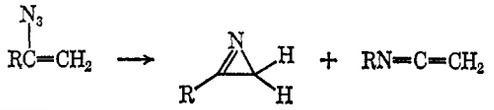
Received November 2, 1967

The pyrolysis and photolysis of a terminal vinyl azide, *trans*-β-azidovinyl *p*-tolyl sulfone (**1**), was studied in an effort to learn about possible intermediates in these decompositions. When pyrolysis of **1** was carried out in aqueous ethanol and other solvents, *p*-toluenesulfonylacetonitrile (**2**) was formed. When photolysis in aqueous ethanol or other moist solvents was used, 2,3-di-*p*-toluenesulfonylaziridine (**3**) was formed. No **3** was found in the pyrolysis and no **1** was detected in the irradiation (at about 0°) observations which indicate that different pathways are involved. Irradiation of 4(5)-*p*-toluenesulfonyltriazole, isomeric with **1**, did not give rise to **2** or **3**. The photolysis is believed to give 3-*p*-toluenesulfonyl-3H-azirine (**4**) some of which is hydrolyzed to give *p*-toluenesulfinic acid which then condenses with remaining **4** to give **3**. When the photolysis was carried out in the presence of benzenesulfinic acid, 2-benzenesulfonyl-3-*p*-toluenesulfonylaziridine was formed. This new reaction of the 3H-azirine system was also shown by the addition of *p*-toluenesulfinic acid to 2,3-diphenyl-3H-azirine and to 2-phenyl-3-methyl-3H-azirine. Attempts to isolate **4** gave material having absorption in the infrared spectrum, characteristic of the 3H-azirine system, but the material rapidly gave polymeric material behaving similarly to other 3H-azirines lacking a substituent in the 2 position.

The production of different intermediates in the photolytic and pyrolitic loss of nitrogen from organic azides is of current interest and has been discussed recently.[2] Although the photolysis and pyrolysis of triarylmethyl azides gives qualitatively the same products, the migratory aptitudes of phenyl and substituted phenyl groups are markedly different.[2] Lewis and Saunders suggested that a discrete nitrene intermediate is involved in the photochemical process but probably not in the thermal process, and they have discussed the possible multiplicity of the nitrene involved in the photochemical process.[3]

In other recent work it is believed that neither singlet nor triplet pivaloyl nitrene is an intermediate in the thermal or in the photoinduced Curtius rearrangement of pivaloyl azide. Both arrangements are most likely concerted processes.[4]

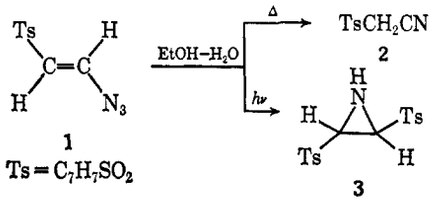
The pyrolysis of vinyl azides has been investigated by Smolinsky[5] who has isolated 3H-azirines and observed



(1) National Institutes of Health Predoctoral Fellow, 1966–1967.
(2) W. H. Saunders, Jr., and E. A. Caress, *J. Amer. Chem. Soc.*, **86**, 861 (1964).
(3) F. D. Lewis and W. H. Saunders, Jr., *ibid.*, **89**, 645 (1967).
(4) S. Linke, G. T. Tisue, and W. Lwowski, *ibid.*, **89**, 6308 (1967).
(5) G. Smolinsky, *ibid.*, **83**, 4483 (1961); G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).

N-alkyl ketenimines from this reaction. Hassner and Fowler[6] have developed a general synthesis of 3H-azirines from the photolysis of vinyl azides obtainable from olefins. Others[7,8] have also observed the formation of 3H-azirines and unstable ketenimines from the photolysis and pyrolysis of vinyl azides. Boyer[9] has reported that the photolysis and pyrolysis of β-styryl azide yield phenylacetonitrile. In no case has it previously been shown that the photolysis and pyrolysis of a given vinyl azide proceed along different pathways to the observed products.

At this point it is stressed that in the photolysis and pyrolysis of β-azidovinyl *p*-tolyl sulfone (**1**) the products are different and exclusive; that is, no *p*-toluenesulfonylacetonitrile (**2**) is detected in the photolysis of **1** and no 2,3-di-*p*-toluenesulfonylaziridine (**3**) is produced in the pyrolysis of **1**. This is evidence that different



1
Ts = $C_7H_7SO_2$

2

3

(6) A. Hassner and F. W. Fowler, *Tetrahedron Lett.*, 1545 (1967).
(7) R. Harvey and K. W. Ratts, *J. Org. Chem.*, **31**, 3907 (1966).
(8) C. S. Cleaver and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 3716 (1965).
(9) J. H. Boyer, W. E. Krueger, and G. J. Mikol, *ibid.*, **89**, 5505 (1967).