

nitride by heating urea and boric acid appears implausible. However, when this BNO residue is heated in a stream of ammonia over the temperature range 500–950°, it is nitrified, with the simultaneous formation and removal of water, to give a relatively pure boron nitride (residue at 950°, 13.63% urea and boric acid reactants. *Anal.* B, 43.9; N, 54.2). This nitridation is significant in that the rate of nitridation progressively increases over the temperature range of 500–950°. This is in contrast to currently favored routes where a viscous boric oxide liquid on a preformed boron nitride or a calcium phosphate support shows slower rates of nitridation. This latter process is substantially unaffected by increasing temperatures over this temperature range. The final traces of oxide impurity may be removed from the boron nitride product by reaction with ammonia at higher temperatures or by heating in a nitrogen stream to 1650°, where the oxide impurity volatilizes (analysis B, 44.2; N, 56.0).

A wide range of nitrogenous materials may be substituted for urea in this reaction scheme, such as biuret, guanidine, cyanamide, dicyandiamide, thio-urea, ammeline, and melamine. The nitrogen contents of the solid intermediates and the final products show some variations, but the products obtained using cyanamide, dicyandiamide or guanidine are comparable or superior to that obtained using urea.

In cooperation with N. E. Weston and J. Thomas, Jr., in a paper to be published in the *J. Am. Chem. Soc.*, a turbostatic structure has been found for BN prepared from urea-boric acid and ammonia; a transformation of this structure to the ordered layer lattice occurs, a process which is unexpectedly promoted by boron oxide impurities.

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## THE CLAISEN REARRANGEMENT OF ALLYL ARYL SULFIDES

Sir:

Failure to produce Claisen rearrangement of allyl thiophenyl ether (I) under conditions<sup>1</sup> which can readily effect the rearrangement of the corresponding oxyethers at reasonable rates<sup>2,3</sup> has been noted recently.<sup>4</sup> The Russian authors of this report have stated that the principal product of the reaction studied earlier by Hurd and Greengard<sup>5</sup> was the

(1) For a full discussion of this reaction see D. S. Tarbell in R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1944, Chapter I.

(2) W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

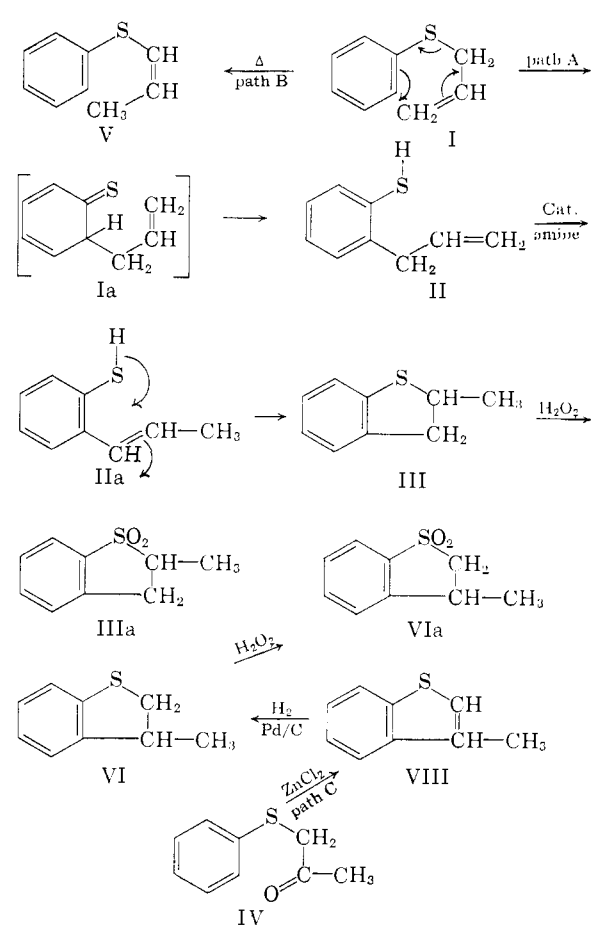
(3) H. I. Goering and R. R. Jackson, *ibid.*, **80**, 3277 (1958).

(4) E. N. Karaulova, D. Sh. Meilanova and G. D. Gal'pern, *Doklady Akad. Nauk S.S.S.R.*, **113**, 1280 (1957); *Zhur. Obshchei Khim.*, **27**, 3034 (1957).

(5) (a) C. D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, **72**, 3356 (1930). (b) See also, H. D. Hartough and S. L. Meisel, "Compounds with Condensed Thiophene Rings," Interscience Publishers, Inc., New York, N. Y., 1954, p. 35, and W. H. Taylor, *J. Am. Chem. Soc.*, **58**, 2649 (1936).

consequence of thermally induced prototropic isomerization to the propenyl thiophenyl ether (V) and no more than a trace of *o*-allylthiophenol (II) was found. This result has been attributed to the (assumed) inability to form the dienone intermediate (IA), analogous to that which has been established<sup>6,7</sup> for the Claisen oxyether rearrangement (path A) because of the recognized

weakness of the  $\pi$  bond in  $\text{C}=\text{S}$  and the instability of  $\pi$  links composed of other than *L* valence electrons<sup>8</sup>.



We have also observed the formation of (V), the thermal isomerization product, but we have been unable to detect any product resembling (II) under all the reaction conditions previously tried. However, we have now ascertained that on subjecting solutions of allyl thiophenyl ethers containing *N,N'*-diethylaniline or quinoline to distillation at atmospheric pressures entirely different results are observed. Under these conditions a new product is obtained which is isomeric with (I) and (V) and is not identical with either of the geometric isomers of (V). Furthermore, the new product occurs in 15–20% conversion from a single distillation, alongside of mostly the unreacted allyl thiophenyl

(6) H. Conroy and R. A. Firestone, *ibid.*, **75**, 2530 (1953); cf. also F. Kalberer and H. Schmid, *Helv. Chim. Acta*, **40**, 13, 253, 779 (1957).

(7) D. Y. Curtin and H. W. Johnson, Jr., *ibid.*, **96**, 2276 (1954).

(8) N. Lozac'h, *Record of Chem. Prog.*, **20**, 23 (1959).

ether, a small amount of the propenyl ether, and a trace amount of the thiol resulting from cleavage (rather than rearrangement) of the thiophenyl ethers. We have identified this substance as 2-methyl-2,3-dihydrothionaphthene<sup>9</sup> (III) by means of both synthetic and analytical procedures.

The identification of (III) is based on this evidence: Oxidation with 30% H<sub>2</sub>O<sub>2</sub> gives a sulfone (IIIA), m.p. 116.5–117.5° (calcd. for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>S: C, 59.4; H, 5.5. Found: C, 59.60; H, 5.51). The n.m.r. spectrum is in full agreement with the suggested structure showing (in deuteriochloroform) a sharp methyl proton doublet centered on  $\tau = 8.54$ , approximately 24 poorly resolved peaks grouped around  $\tau = 6.6$  (—C-H and CH<sub>2</sub> protons in the sulfone ring), and a group of sharp lines in the region of  $\tau = 2.5$  protons). Furthermore, the n.m.r. spectrum is very similar but not superimposable ( $\tau_{\text{CH}_3} = 8.62$ ) on that of the isomeric (VIA) which we prepared according to path C, proceeding through (VIII) and (VI) as previously described.<sup>10,11</sup> The sulfones, (IIIA) and (VIA), also differ decidedly in physical properties and in the important fingerprint region of their infrared spectra.

The fact that the propenyl thiophenyl ether (V) is quantitatively recovered from reaction conditions which can effect the conversion of (I) to (III) is a good indication that (V) is not an intermediate or a precursor of (III). The absence of any Claisen thiol product (II) suggests that the ring closure reaction proceeds very rapidly under the conditions of formation of (II). The formation of 2-methylcoumaran as a minor product of rearrangement of the oxyether<sup>1</sup> obviously occurs much less easily. The amine medium might also be expected to greatly facilitate the prototropic shift which competitively (and, to all intents and purposes, irreversibly) removes allyl thiophenyl ether from the reaction with formation of (V). Since the amount of (V) formed is significantly reduced from what was formerly experienced<sup>4</sup> (under conditions which do not produce (III)), we can perceive the full magnitude of the "catalytic effect" induced by the use of these high boiling amines. This is to say that while the accelerating influence of dimethylaniline solvent on the rate of rearrangement of the oxyether is negligible<sup>12,13</sup> it can serve as an indispensable medium for bringing about rearrangement of (I), which under (other) normal Claisen conditions is merely tautomerized. It is not clear, as yet, whether the influence of certain amines can be correlated with empirical solvent parameters such as Kosower's<sup>14</sup> "Z" value or others which have been shown to be applicable in

(9) This was once mistakenly assumed by Hurd and Greengard<sup>5</sup> to be the side product of the reaction conditions which have been shown<sup>4</sup> to lead to (V). Both in our experience and in ref. (4) (III) never has been identified previously as a product of the pyrolysis of allyl thiophenyl ether.

(10) E. G. G. Werner, *Rec. Trav. Chim.*, **68**, 509 (1949).

(11) F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **73**, 2251 (1951).

(12) J. F. Kincaid and D. S. Tarbell, *ibid.*, **61**, 3085 (1939).

(13) D. S. Tarbell and J. F. Kincaid, *ibid.*, **62**, 728 (1940).

(14) E. M. Kosower, *ibid.*, **80**, 3253, 3261, 3267 (1958).

the Diels–Alder reaction<sup>15</sup> or to catalytic activity of the type recently identified for the Diels–Alder by other workers.<sup>16,17</sup> The close similarity of the Claisen, the Diels–Alder and a host of others now classified as four-center reactions often has been pointed out.<sup>18</sup> We are presently studying such relationships in terms of the rate response to changes in reaction medium and temperature, as well as photochemical catalysis.

**Acknowledgment.**—We are obliged to Mr. Francis Scalzi and Mr. R. W. Body for some very timely assistance and discussions.

(15) J. A. Berson, Z. Hamlet and W. A. Mueller, *ibid.*, **84**, 297 (1962).

(16) P. Yates and P. Eaton, *ibid.*, **82**, 4436 (1960).

(17) G. I. Fray and R. Robinson, *ibid.*, **83**, 249 (1961).

(18) See, for example, E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 646.

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### A CONVENIENT SYNTHESIS OF 3,5-CYCLOHEPTADIENONE

Sir:

Cycloheptadienones and alkoxy- and acyloxy-cycloheptatrienes have proved to be valuable intermediates for the synthesis of tropone and tropolones.<sup>1,2</sup> Here, we wish to report the synthesis of 3,5-cycloheptadienone (IV) by a method which is not only operationally simple but which also may be useful for the synthesis of other unconjugated cycloalkadienones. 3,5-Cycloheptadienone has been prepared previously by Meinwald, *et al.*,<sup>3</sup> by the base degradation of tropinone methiodide.

Reaction of 1-ethoxycyclohexene (I), prepared from cyclohexanone *via* the diethyl ketal,<sup>4</sup> with dichlorocarbene<sup>5</sup> gave 1-ethoxy-7,7-dichloronorcarane (II), b.p. 64–64.5° (1.0 mm.), in 87% yield (found: C, 51.86; H, 6.99). Rearrangement of this material in hot quinoline resulted in the elimination of *both* atoms of chlorine and the formation of 1-ethoxy-1,3,5-cycloheptatriene (III),<sup>6</sup> b.p. 52–53° (4.0 mm.) in 37% yield;  $\lambda_{\text{max}}^{\text{neat}}$ : 6.18, 6.50, 7.00, 7.23, 7.42, 7.69, 7.89, 8.31, 8.59, 8.93, 9.54, 12.40, and 14.07 $\mu$ ;  $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ : 290 m $\mu$  (3,840),<sup>7</sup> 207 m $\mu$  (17,050), (calcd: C, 79.37; H, 8.88; found: C, 79.25; H, 8.23). Hydrolysis of III with a very small quantity of hydrochloric acid in methanol–water produced 3,5-cycloheptadienone (IV), b.p. 43.5–45° (4.6 mm.), in 91% yield.

(1) E. E. van Tamelen and G. T. Hildahl, *J. Am. Chem. Soc.*, **78**, 4405 (1956).

(2) O. L. Chapman and P. Fitton, *ibid.*, **83**, 1005 (1961).

(3) J. Meinwald, S. L. Emerman, N. C. Yang and G. Büchi, *ibid.*, **77**, 4401 (1955).

(4) A. Johannissian and E. Akunian, *Bull. univ. état R. S. S. Arménie*, No. **5**, 235, 245 (1930); *C. A.*, **25**, 921, 922 (1931).

(5) W. E. Parham and E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

(6) This structure, rather than one of the other two possible structures or a mixture of all three, was assigned to III because of the excellent yield of 3,5-cycloheptadienone (IV) obtained on mild acid hydrolysis. It is probable that the conditions for hydrolysis were drastic enough to hydrolyze the enol ether, but mild enough to prevent isomerization of the double bonds; *e.g.*, see F. B. Colton, I. N. Nysted, B. Riegel and A. L. Raymond, *J. Am. Chem. Soc.*, **79**, 1123 (1957). The structure of this product will be investigated in greater detail in the future.