Usually no additional extraction was made. The toluene layer was separated and washed with a small amount of water, shaken clear with a little $Na_2SO_4$ (anhydrous) and then fractionated.

Examples of this procedure are listed in Table II.

Oxalic and tartaric acid fail to react in this method.

It will be apparent that the methods are not universally applicable, but the number of esters for which they can be expected to work is large and includes many of the common esters. The boiling points (uncorr.) of the esters prepared are listed in Table III.

TABLE III

Boiling Points of Organic Esters Prepared, °C.

| | 15 mm. Hg | 10 mm. Hg | 5 mm. Hg |
|---|---|---|---|
| Diethyl oxalate | 84 | 76 | 66 |
| Triethyl citrate | 183 | 177 | 164 |
| Diethyl adipate | 133 | 125 | 111 |
| Diethyl succinate | 106 | 99 | 88 |
| Ethyl furoate | 90 | | |
| Ethyl levulinate | 96 | 90 | 80 |
| Triethyl aconitate | 170 | 160 | 150 |
| Diethyl fumarate | 106 | 98 | 87 |
| Diethyl maleate | 106 | 99 | 86 |

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## Mechanism of the Thermal Isomerization of Bicyclo[2.2.1]heptadiene

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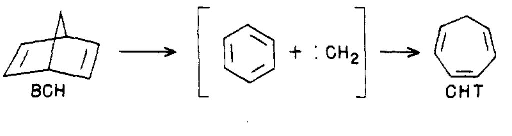
In a recent technical bulletin,[1] the thermal vapor phase isomerization of bicyclo[2.2.1]heptadiene (BCH) at 450–475° and atmospheric pressure was reported to yield about 45% cycloheptatriene (CHT). Toluene, acetylene, and cyclopentadiene (CPD) were identified as the principal side products. In order to elucidate the mechanism of this novel rearrangement, BCH was thermally isomerized and gas-liquid partition chromatography (GLPC) utilized to analyze the pyrolyzates. Product distribution data which show the effect of varying the residence time and the temperature are given in Table I.

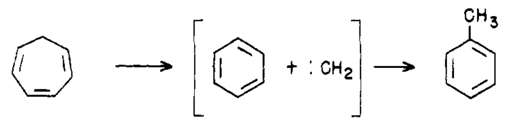
The data in Table I indicate that the yield of CHT rapidly decreased with increased residence time (decreased pass rate) at 475°. This effect is apparent from Column 9 which gives the toluene/CHT ratios. At 395° (Run 6) the yield of CHT is markedly higher and that of toluene lower than in the experiments at 475°. These results suggested that CHT was formed initially and subsequently rearranged to toluene. This formulation was verified when a sample of pure CHT was passed through the furnace at 478° (Run 7) and an almost quantitative conversion to toluene resulted. A small amount of benzene and a trace of ethylene were identified as side products (see Experimental, Table IV).

A series of experiments was carried out to test a mechanism involving methylene as an intermediate in the initial isomerization of BCH (Equation 1)



(1)

or in the subsequent rearrangement of CHT to toluene (Equation 2). These possibilities were



(2)

considered because of the observed benzene and ethylene side products, both in the isomerization of BCH (Run 3) and in the conversion of CHT to toluene (Run 7). Furthermore, photochemically generated methylene is known to add to benzene[2] and to benzene derivatives[3,4] to give cycloheptatrienes and their methylated aromatic isomers.

Pyrolysis of BCH in the presence of a large excess of *n*-butane (*e.g.*, Run 2) gave no trace of pentanes or benzene while the major products of isomerization and reverse Diels-Alder reaction were obtained in the expected proportions (Table I). In order to establish that methylene would actually react with butane under these conditions, diazomethane was passed through the furnace at 475° in the presence of excess butane. These conditions are comparable to those used by Rice and Glasebrook,[5] who established that methylene was formed at these temperatures in the presence of butane. In their experiments,[5] a tellurium mirror was removed and a red $(CH_2Te)_n$ polymer was formed, but the hydrocarbon products were not examined. Table II lists our data for the reaction of methylene with butane at 475°.

The data in Table II show that methylene reacts with *n*-butane at 475° to give a mixture of *n*-pentane and isopentane. Aside from Run 10, the aver-

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[1] Technical data supplied on request by the Shell Chemical Corp., New York, N. Y.

[2] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **72**, 2305 (1950).

[3] W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, **73**, 876 (1951).

[4] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **75**, 297 (1953).

[5] F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, **56**, 2381 (1934).

TABLE I

Thermal Isomerization of BCH

| Run No. | Pass Rate, Ml. Liq. BCH/Min. | Temp., °C. | Products, Mole %[a] BCH | CHT | Toluene | CPD | Benzene | Toluene/ CHT |
|---|---|---|---|---|---|---|---|---|
| 1 | 1.3 | 475 ± 5 | 0.55 | 23.0 | 33.9 | 42.0 | 0.59 | 1.5 |
| 2 | —[b] | 475 ± 5 | 0.0 | 10.6 | 48.5 | 40.9 | 0.0 | 4.6 |
| 3 | 0.7 | 482 ± 7 | 0.47 | 9.1 | 53.7 | (35.2)[c] | 1.58 | 5.9 |
| 4 | 0.5 | 475 ± 5 | 0.49 | 6.6 | 52.1 | 39.5 | 1.15 | 7.9 |
| 5 | 0.4 | 475 ± 5 | 0.36 | 6.5 | 58.6 | (33.2)[d] | 1.34 | 9.0 |
| 6 | 0.4 | 395 ± 5 | 8.17 | 44.8 | 8.4 | 38.3 | 0.30 | 0.19 |

[a] Determined by GLPC analysis on a type "B" column at 80°. [b] $n$-Butane used as a carrier gas. The residence time in the furnace was 10 sec. [c] Based on acetylene analysis. An infrared spectrum of the gaseous products (collected in a liquid nitrogen trap) revealed the presence of 0.3–1% ethylene. [d] Estimated. Some dimerization of the CPD had occurred before analysis.

age $n$-pentane/isopentane ratio was 1.13 ± 0.14. Based on the number of primary and secondary hydrogen atoms, the statistical ratio would be 1.50.[5a]

Consequently, methylene appears to show some discrimination for the secondary C–H bond of $n$-butane at 475°. However, methylene produced photochemically at −75° and +15° has been found[6] to be essentially indiscriminate in adding to the C–H bonds of $n$-pentane, 2,3-dimethylbutane, and cyclohexene in the liquid phase. This apparent difference in the selectivity of methylene between the vapor and liquid phase is similar to the situation in free radical chlorinations where vapor-phase substitution usually gives more selectivity than a liquid-phase reaction at the same temperature.[7]

TABLE II

Thermal Decomposition of Diazomethane in the Presence of $n$-Butane at 475°

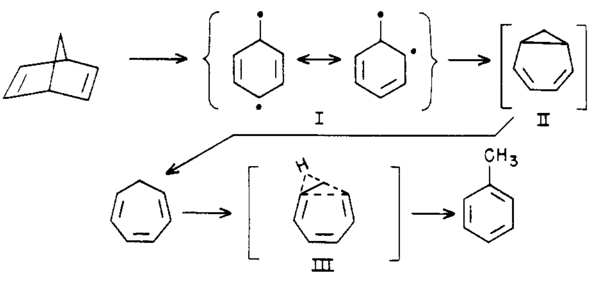
| Run No. | $n$-$C_5H_{12}$/$i$-$C_5H_{12}$[a] | $C_5H_{12}/C_4H_{10}$[a] | $C_7H_8/C_6H_6$[b] |
|---|---|---|---|
| 8 | 1.14 ± 0.04 | 0.011 | — |
| 9 | 1.15 ± 0.04 | 0.012 | — |
| 10[c,d] | 1.50 ± 0.05 | 0.013 | — |
| 11[c] | 1.05 ± 0.15 | 0.0029 | 0.004 |
| 12[c] | 1.17 ± 0.03 | 0.017 | 0.013 |

[a] By GLPC analysis at 30° on a type "A" column. [b] By GLPC analysis at 80° on a type "B" column. No trace of CHT was found. [c] The butane stream was passed through benzene at room temperature before pyrolysis. [d] Not analyzed at 80°.

In Runs 10, 11 and 12, a small amount of benzene was introduced into the butane stream. The last two columns of Table II show that the molar ratios of total pentanes to butane and of toluene to benzene are about equal. Consequently, butane and benzene are both about equally reactive toward methylene at this temperature.

Based on the above experiments, reactions (1) and (2) were eliminated as unimportant.

The mechanism proposed for the over-all conversion of BCH to toluene is given in Fig. 1. Rupture of the $C_1$-$C_7$ bond of BCH leads to the mesomeric diradical I. Such diradicals are well known in terpene pyrolyses; *e.g.*, in the thermal rearrangement of $d$-limonene[8] and $\alpha$- and $\beta$-pinene.[9] Diradical I can react to give CHT, possibly involving norcaradiene (II) as a transient intermediate.



$$2C_7H_8 \longrightarrow 2C_6H_6 + C_2H_4 \qquad (3)$$

Figure 1

One possibility for the conversion of CHT to toluene is a transition state (III) in which the hydrogen at $C_2$ migrates with concomitant breaking of the $C_1$—$C_7$ bond and formation of a $C_2$—$C_7$ bond. A similar type of rearrangement has been observed by van Aardt.[10] When phenylcycloheptatrienylmethanol was passed over alumina at 350°, 4-phenylstyrene was obtained in unspecified yield. A concerted intramolecular rearrangement would require 4-($\beta$-hydroxyethyl)biphenyl as an intermediate which would be subsequently dehydrated to give the styrene. Both in the latter isomerization and in the conversion of CHT to toluene, a carbon-

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(5a) Added in Proof: Recent results of J. H. Knox and A. F. Trotman-Dickenson [*Chem. and Ind.*, 731 (1957)] on the addition of photochemically generated methylene to alkanes in the gas phase from −80° to +200° predict a value of 0.7 for this ratio at 475°.

(6) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(7) C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., New York, N. Y., 1957, p. 357.

(8) H. Pines and J. Ryer, *J. Am. Chem. Soc.*, **77**, 4370 (1955).

(9) R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **73**, 4461 (1951).

(10) J. H. P. van Aardt, *J. Chem. Soc.*, 2965 (1954).

ium ion process cannot be ruled out, particularly in view of Rylander's[11] recent demonstration of the existence and stability of the tropylium ion in the gas phase.

Equation 3 accounts for the observed small amounts of benzene and ethylene. The absence of benzene in Run 2 (Table I), where a large excess of butane was present, is consistent with such a bimolecular process.

## EXPERIMENTAL

Bicyclo[2.2.1]heptadiene was generously supplied by the Shell Chemical Corp. and was distilled before use.

*Apparatus.* A 1.8 cm. o.d. by 50 cm. long horizontal Pyrex furnace with a volume of 85.5 ml. and fitted with a concentric thermocouple well was used in the pyrolyses. Liquid reactants were introduced through a vertically attached tube by means of a graduated dropping funnel. The gas streams were passed in through a flow meter which was calibrated against pure *n*-butane and could be adjusted to give a residence time of 10 sec. in the furnace.

*Method.* In the diazomethane-*n*-butane experiments, a 500-ml. flask was used as a diazomethane generator. After flushing the system with *n*-butane, the diazomethane generator (containing 2 g. of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and 50 ml. of cold 50% potassium hydroxide solution) was slowly warmed to 70° with a water bath. When the bath reached 50° the Dry Ice trap was attached. At the peak of diazomethane generation, a minor explosion was usually observed in the generating flask.

Except in Runs 3 and 5, the products were stored at −80° until analyzed by GLPC. All GLPC analyses were performed with a Perkin Elmer Vapor Fractometer Model 154B. Low boiling materials were chromatographed at 30° on a 4-m. type "A" column packed with di-*n*-decyl phthalate on Celite. The analyses in Table I were obtained on a 2-m. type "B" column packed with ethyl hexyl sebacate on Celite at 80°. In order to show the sharpness of the separations attained, retention times at 30° and 80° for all the compounds studied are given in Table III. Comparative retention times were obtained on authentic specimens of all products and known mixtures were used for quantitative calibration. Areas were measured with a planimeter and only small corrections were necessary to convert area per cent to weight per cent.

TABLE III

GLPC RETENTION TIMES[a]

| Component | Type "A" Column, 30° | Type "B" Column, 80° |
|---|---|---|
| Air | 1.65 (1.75) | 0.65 (0.7) |
| *n*-Butane | 3.9 (4.05) | 0.9 (1.1) |
| Isopentane | 8.0 (8.6) | 1.7 (1.85) |
| *n*-Pentane | 10.4 (11.1) | 2.3 (2.5) |
| CPD | 21.9 (23.2) | 3.9 (4.25) |
| Benzene | — | 11.4 (12.2) |
| BCH | — | 13.3 (14.1) |
| Toluene | — | 26.4 (29.3) |
| CHT | — | 30.5 (32.0) |

[a] In minutes. Helium was used as the carrier gas at a flow rate of about 120 ml./min. The first number denotes the appearance of the initial rise of the peak. The retention time for the peak maximum is given in parentheses. Deviations from these average values occurred when very large or very small amounts of the component were present.

A high purity specimen of CHT was obtained by distillation of the pyrolyzate from Run 6 through a spinning band Podbielniak column. GLPC analysis of a fraction boiling at 117° is given in Table IV along with the product analysis for its pyrolysis at 478° (Run 7).

TABLE IV

DATA ON THE PURITY AND PYROLYSIS OF CHT

| Component | Mole %, CHT[a] | Mole %, Run 7[a,b] |
|---|---|---|
| CHT | 98.67 | 0.87 |
| Toluene | 0.0 | 96.48 |
| CPD | 0.43[c] | 0.89 |
| Benzene | 0.89[c] | 1.76 |

[a] Analyses at 80° on a type "B" column. [b] A trace of ethylene was identified by mass spectrometry in the material collected in a liquid nitrogen trap. [c] Carried over during fractionation because of a vapor pocket in the top of the Podbielniak column.

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[11] P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

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## Condensation of Rhodanine with Pyridine and Quinoline Aldehydes

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5-Substituted rhodanines (I), which contain the toxiphoric dithiocarbamate chromophore —NCSS— have been the subject of scrutiny as fungicides and mildew-proofing agents.[3–9] Among the most effective were those obtained by condensation of rhodanine with the heterocyclic aldehydes of the furan and thiophen series.[8] Since carbonyl derivatives of

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[1] Present Address; Electrochemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

[2] Present Address; Royal College of Science and Technology, Glasgow, Scotland.

[3] National Processes Ltd., French Patent **813,863**, June 10, 1937.

[4] National Processes Ltd., and W. J. Carter, Brit. Patent **484,576**, May 5, 1938.

[5] National Processes Ltd., and W. J. Carter, Brit. Patent **471,415**, Dec. 1, 1946.

[6] A. A. Somerville, to R. T. Vanderbilt Co. Inc., U.S. Patent **2,776,922**, Jan. 8, 1957.

[7] E. B. Alvord, to Grasselli Chemical Co., U.S. Patent **1,962,109**, June 5, 1934.

[8] F. C. Brown, C. K. Bradsher, and E. N. Lawton, *Ind. Eng. Chem.*, **45**, 1027 (1953).

[9] F. C. Brown, C. K. Bradsher, S. M. Bond, and R. J. Grantham, *Ind. Eng. Chem.*, **46**, 1503 (1954) and previous references therein cited.