PYROLYSIS OF 7,7-DIBROMOBICYCLO [4.1.0] HEPTANE AND DERIVATIVES

A GENERAL 1,3,5-CYCLOHEPTATRIENE SYNTHESIS

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Abstract—Pyrolysis of 7,7-dibromobicyclo [4.1.0] heptane* in quinoline solution gives cycloheptatriene in good yield. 2- and 1-Bromocyclohepta-1,3-dienes have been isolated as intermediates. In the absence of base, toluene is the major product. Mixtures of 1-, 2- and 3-methyl- and methoxycycloheptatrienes are obtained from 3-methyl- and 1-methoxy-7,7-dibromonorcaranes respectively. The action of heat on 7,7-dibromonorcarene-2 and -3 has been studied. Some of the cycloheptadiene and cycloheptatriene derivatives described are thermally isomerizable.

THE value of halogenated cyclopropane derivatives as synthetic intermediates is now well recognized.¹ As part of our general interest in the properties and uses of dihalocarbene adducts of cyclic olefins, we wish to report the results of a study of the action of heat on 7,7-dibromonorcarane (I; X = Br) and some of its derivatives.

Winberg² showed that when 7,7-dichloronocarane (I; X = Cl) is pyrolysed at 500°, a 2:1 mixture of toluene and 1,3,5-cycloheptatriene (II) is obtained in 57% yield. This does not constitute a useful preparation of cycloheptatriene as the latter is difficult to separate from toluene. Very recently, Robinson³ improved this procedure: pyrolysis of 7,7-dichloronorcarane (I; X = Cl) on calcium oxide at 444° gives a 63% yield of cycloheptatriene, apparently uncontaminated with toluene.



* For convenience, in the remainder of the text, bicyclo [4.1.0] heptane is referred to as norcarane.

- ¹ W. Kirmse, Carbene Chemistry Chap. 8. Academic Press, New York (1964); W. E. Parham and E. E. Schweizer, Organic Reactions Vol. 13, pp. 55-90. J. Wiley, New York (1963).
- ^{*} H. E. Winberg, J. Org. Chem. 24, 264 (1959).
- * G. C. Robinson, J. Org. Chem. 29, 3433 (1964).

We have observed⁴ that, in general, dibromocarbene adducts of olefins are more thermolabile than their dichloro analogues. Thus, we found that when 7,7-dibromonorcarane⁵ (I; X = Br) is heated in quinoline solution at 220°, it rearranges with the loss of two molecules of hydrogen bromide to give cycloheptatriene, uncontaminated with toluene, in 66% yield. On a preparative scale, cycloheptatriene is obtained in 68% yield by heating a solution of I (X = Br) in boiling quinoline (b.p. 238°). Considering the ease both of preparation of the starting material and of conducting the reaction, this is likely to be the most convenient laboratory synthesis of the cycloheptatriene system so far reported.

When the pyrolysis is conducted under carefully controlled conditions in quinoline solution at 200°, a 38% yield of a mixture of 2- and 1-bromocyclohepta-1,3-dienes (respectively IV and V; X = Br) is obtained. Gas chromatography (glc) indicates the presence of two components in the approximate proportions of 2 : 1 and this was confirmed by the NMR spectrum of the mixture: integration of a triplet at 7·16 τ (J \sim 5·5 c/s), assigned to the C(7) protons of 1-bromocyclohepta-1,3-diene (V; X = Br) suggests that the latter isomer accounts for 36% of the mixture. That this material consists of a mixture of bromocycloheptadienes was confirmed by UV and NMR spectral data and by elemental analysis.

The allylic carbonium ion (III; X = Br) or a related species would be a likely intermediate in the thermal rearrangement of 7,7-dibromonocarane (I; X = Br). In the presence of base, this intermediate would be expected to lose a proton to give 2bromocyclohepta-1,3-diene (IV; X = Br). However, 1,5-hydrogen shifts have been shown to occur in the cycloheptadiene system⁶: thus at 150° the carboxylic acid (IV; $X = CO_{2}H$ isometizes to $V(X = CO_{2}H)$. It, therefore, seems likely that the initially formed IV(X = Br) is converted into V(X = Br) by such a mechanism. In support of this hypothesis, when the bromocycloheptadiene mixture is heated at 150° for 3 hr and the products distilled, a modest yield of a mixture containing ca. 60% of the 1-isomer (V; X = Br) is obtained. When the original bromocycloheptadiene mixture is heated in quinoline solution, cycloheptatriene (II) is obtained in 43% yield. Thus it appears that the conversion of 7,7-dibromonorcarane (I; X = Br) to cycloheptatriene proceeds via IV(X = Br) and V(X = Br), followed by another 1,5-hydrogen shift and then by elimination of a molecule of hydrogen bromide. The characterization of the bromocycloheptadiene intermediates and their conversion to cycloheptatriene adds support to the similar reaction sequence proposed by Robinson³ for the pyrolysis of 7,7-dichloronorcarane (I; X = Cl). However, the suggested isomerization of the latter to 2,3-dichlorocycloheptene would seem to be unlikely in the presence of base.



Pyrolysis of 7,7-dibromonorcarane (I; X = Br) at 200° in the *absence* of base also gives a hydrocarbon fraction in good yield (61%). However, this material was shown

- ⁴ D. G. Lindsay and C. B. Reese, unpublished results.
- ⁶ W. von E. Doering and A. K. Hoffmann, J. Amer. Chem. Soc. 76, 6162 (1954).
- ⁴ A. P. ter Borg and A. F. Bickel, Rec. Trav. Chim. 80, 1229 (1961).

by NMR spectroscopy and glc to be a mixture of toluene (ca. 60%) and cycloheptatriene (II; ca. 40%). It is likely that the mechanism of toluene formation is distinct from that suggested above for cycloheptatriene; it probably involves acid-catalysed fission of the cyclopropane ring to give an intermediate such as VI(X = Br), which then undergoes a series of eliminations and prototropic shifts leading to toluene. Thus it seems that in the pyrolysis of 7,7-dichloronorcarane (I; X = Cl), Robinson³ avoided toluene formation² by removing hydrogen chloride as it was formed.



In order to demonstrate the generality of this approach to cycloheptatriene synthesis, 3-methyl-7,7-dibromonorcarane (VII) was heated at 200° in quinoline solution to give a mixture of 1-, 2- and 3-methylcycloheptatrienes (VIII, IX and X respectively), isolated in 66% yield. This approach may be compared with another general method⁷ of cycloheptatriene synthesis, which involves the cuprous bromide catalysed decomposition of diazomethane in hot aromatic hydrocarbon solutions. Although comparable yields, as based on diazomethane, were reported, the cycloheptatriene derivatives were obtained as 1-4% solutions in the starting materials and were presumably not so readily isolable. Invariably, mixtures of 1-, 2- and 3-substituted cycloheptatrienes were obtained.⁷

When 3-methyl-7,7-dibromonorcarane (VII) is heated at 200° in lepidine solution, a mixture of four methylbromocycloheptadienes (as indicated by glc) can be isolated in modest yield. There are only three possible initial ring expansion products, but clearly a more complex mixture can result from subsequent 1,5-hydrogen shifts.^{8.9}

It was of interest to examine the effect of heat on the methylcycloheptatriene mixture, obtained from VII. Analysis of the original products by glc indicates three components in the approximate proportions of 2:1:1. After this material had been heated in a sealed tube at 160° for 24 hr, a partially isomerized mixture was recovered in 90% yield; it was shown by glc to contain the original components in the approximate proportions of 1:1.5:4. The NMR spectrum of the resultant mixture has a strong doublet at 7.73 τ (J \sim 7c/s), which may be assigned⁹ to the resonance of the C(7) protons of 1-methylcycloheptatriene (VIII); this spectrum further indicates that the latter is the major constituent of the mixture. If, by analogy with methoxycycloheptatrienes,⁹ it is assumed that the 3-isomer (X) is thermodynamically more stable than the 2-isomer (IX), then it would seem that the original mixture is composed of the 1-, 2- and 3isomers in the relative proportions of 1:2:1, and the heat treated mixture is composed of these isomers in the proportions of 4:1:1.5. It should be emphasized that, unless one isomer is thermodynamically more stable than the others, the only

7 E. Müller, H. Kessler, H. Fricke and W. Kiedaisch, Liebigs Ann. 675, 63 (1964).

- ⁸ A. P. ter Borg, H. Kloosterziel and N. van Meurs, *Rec. Trav. Chim.* 82, 717 (1963); A. P. ter Borg and H. Kloosterziel, *Ibid.* 82, 741 (1963).
- * E. Weth and A. S. Dreiding, Proc. Chem. Soc. 59 (1964).

method of preparing a pure specimen of a substituted cycloheptatriene from the corresponding dibromonorcarane derivative would be by fractionation of a mixture of isomers by, for example, preparative glc. Furthermore, essentially the same cycloheptatriene mixture would be expected to result from the pyrolysis of a 1-, 2- or 3substituted derivative of 7,7-dibromonorcarane.



An example of the cycloheptatriene synthesis under discussion was recently reported¹⁰ by Parham et al., who heated 1-ethoxy-7,7-dichloronorcarane (XI; R = Et, X = Cl) in quinoline solution and obtained a 37% yield of a product which they formulated as 1-ethoxycycloheptatriene (XIII; R = Et). That this rearrangement proceeds at a temperature far below that required² for the parent 7,7-dichloronorcarane (I: X = CI) can be rationalized in terms of enhanced stabilization of an intermediate such as XII(R = Et) by the ethoxy group. As the corresponding methoxycycloheptatrienes had been characterized by Weth and Dreiding,9 we prepared 1-methoxy-7,7dibromonorcarane (XI; R = Me, X = Br) and examined the effect of heat on it. This material is too labile to be characterized fully but when a solution in 2,6-lutidine is heated at 135°, a mixture of methoxybromocycloheptadienes is obtained in 70% vield. However, the expected methoxycycloheptatriene mixture is produced in only 33% yield by heating XI(R = Me, X = Br) at 150° in quinoline solution; it was shown by glc to contain three components in the approximate proportions of 1:10:3. The principal constituent, which accounted for ca. 70% of the mixture, was identified as 1-methoxycycloheptatriene (XIII; R = Me) by virtue of a characteristic doublet in its NMR spectrum⁹ at 7.55 τ (J ~ 7.2 c/s), attributable to the resonance of its C(7) protons. Two less intense, partially superposed triplets at 7.71τ and 7.76τ (J \sim 7.2 c/s for each) could be assigned to the resonances of the C(7) protons of 2- and 3-methoxycycloheptatrienes respectively. From the relative intensities of these triplets, it was deduced that the 3-isomer is the second most abundant constituent of the mixture.



The double-bond in 7,7-dibromonorcarene-2 (XIV) appears, like the methoxyl group in 1-methoxy-7,7-dibromonorcarane (XI; R = Me, X = Br), to facilitate its thermal rearrangement. A possible intermediate such as XV would be expected to be

¹⁰ W. E. Parham, R. W. Soeder and R. M. Dodson, J. Amer. Chem. Soc. 84, 1755 (1962).

of lower energy than III(X = Br). When XIV is heated in quinoline solution at 150°, it is converted into the expected mixture of 2- and 3-bromocycloheptatrienes (XVI and XVII respectively), but only in 37% yield. The two components were shown by glc to be present in the approximate proportions of 4:1, and NMR evidence suggests that the 2-isomer (XVI) predominates. After this material has been heated at 125° for 7 hr, the distillable products consist mainly of benzyl bromide, together with smaller quantities of 1-, 2- and 3-bromocycloheptatrienes. The origin of the benzyl bromide has not been established, but clearly 1,5-hydrogen shifts occur. An attempt was made to oxidize the original mixture of XVI and XVII with selenium dioxide¹¹ and obtain 2- and 3-bromotropones. However, tropone itself, isolated in 33% yield, is the only characterized product of this reaction.



Finally, the pyrolysis of the isomeric 7,7-dibromonorcarene-3 (XVIII) was studied. When this substance¹² is heated alone at 205°, the sole distillable product is benzyl bromide, obtained in 50% yield. This corresponds with the acid-catalysed conversion of 7,7-dibromonorcarane (I; X = Br) to toluene, discussed above. However, when XVIII is heated in the presence of quinoline, no volatile product can be detected.

EXPERIMENTAL

IR spectra were measured on a Perkin-Elmer Infracord or a Perkin-Elmer model 21 spectrophotometer. UV spectra were measured on a Cary model 14 M-50 recording spectrophotometer. NMR spectra of 10% solutions in CCl₄ were run at 60 Mc/s (on a Perkin-Elmer instrument) with tetramethylsilane as internal standard. The principal materials used in glc were polyethylene glycol cross-linked with pentaerythritol (L.A.C.) on Celite, and 10% Bentone in diisodecyl phthalate on Diatoport S.

Pyrolysis of 7,7-dibromobicyclo [4.1.0] heptane (I; X = Br) in quinoline solution

(a) A solution of 7,7-dibromobicyclo [4.1.0] heptane⁵ (8.6 g) in quinoline (21.5 g), contained in a distillation apparatus fitted with a 9 cm Vigreux column, was heated at 200° in a stream of N_a and under slightly red. press. After intervals of 20 min, the press. was reduced to ca. 16 mm and products with b.p. below 90° were allowed to distil. The total distillate obtained during 2 hr was redistilled and a fraction b.p. 82-83°/16 mm (2 g, 38%) consisting of a mixture of bromocycloheptadienes was obtained. (Found: C, 48.2; H, 5.4; Br, 45.8. Calc. for C₇H₉Br: C, 48.6; H, 5.2; Br, 46.2%.) The mixture was resolved by glc into two components in the proportion of ca. 1:2. λ_{max}^{BtoH} 253 mµ (log ε 3.43); NMR spectrum: 3.7 τ , a multiplet; 4.3 τ , a multiplet; 7.16 τ , a triplet (J ~ 5.5 c/s); 7.7 τ , a multiplet; 8.1 τ , a multiplet. Ratio of wt. of aliphatic to wt. of olefinic protons: 2.0. Ratio of wt. of 7.16 τ to wt. of other aliphatic protons: 0.12.

(b) A solution of I (X = Br; 5 g) in quinoline (25 g) was heated under N₂ in a distillation apparatus at atm. press. and at 220° for 1 hr. The distillate was redistilled and had b.p. 110°/760 mm; it was identified as cycloheptatriene (1·2 g, 66%) by comparison of its UV, IR and NMR spectra with those of authentic material. Analysis by glc showed it to be free from toluene. (Found: C, 90·9; H, 8·9. Calc. for C₇H₃: C, 91·2; H, 8·8%.)

(c) A solution of I (X = Br; 30 g) in quinoline (150 g), contained in a distillation apparatus fitted with a 25 cm Vigreux column, was heated under reflux and a fraction, b.p. 110–114° was collected

¹¹ G. Sunagawa, N. Soma and H. Nakao, Chem. Abstr. 55, 15376 (1961).

¹² K. Hoffmann, S. F. Orochena, S. M. Sax and G. A. Jeffrey, J. Amer. Chem. Soc. 81, 992 (1959).

over a period of 2 hr. This material was confirmed by glc and NMR spectroscopy to be pure cycloheptatriene (7.4 g, 68 %).

Pyrolysis of bromocycloheptadiene mixture

(a) In quinoline solution. A solution of bromocycloheptadiene mixture (5 g) see (a) above in quinoline (25 g) was heated at 220° for 1 hr, and the products were distilled to give cycloheptatriene (1·1 g, 43%), b.p. $110-112^{\circ}/760$ mm.

(b) In the absence of quinoline. The bromocycloheptadiene mixture (2.0 g) was heated at 150° for 3 hr. The products were distilled and a fraction (0.3 g, 15%), b.p. 78-80°/16 mm was collected. (Found: C, 48.0; H, 5.1%), $\lambda_{\text{max}}^{\text{ROH}}$ 254 m μ (log ε 3.83). Glc showed that the material consisted of two components in the ratio of ca. 3:1 (the ratio of the same components in the starting material was ca. 1:2). The NMR spectrum of the new mixture of bromocycloheptadienes showed a relatively more intense triplet at 7.16 τ . Ratio of wt. of 7.16 τ protons to wt. of other aliphatic protons: 0.20.

Pyrolysis of 7,7-dibromobicyclo [4.1.0] heptane (I; X - Br) in the absence of quinoline

7,7-Dibromobicyclo [4.1.0] heptane (9.5 g) was heated at 200° for 2 hr under slightly red. press. in a stream of N₂. Distillation of the products gave a fraction (2.1 g, 61%), b.p. 110°/760 mm, which was shown by glc and NMR spectroscopy to be a mixture of toluene (ca. 60%) and cycloheptatriene (ca. 40%).

3-Methyl-7,7-dibromobicyclo [4.1.0] heptane (VII)

4-Methylcyclohexene (24 g) was treated with dibromocarbene generated from potassium t-butoxide (1.04 M solution in t-butanol, 450 ml) and bromoform (75 g) according to the procedure of Skell and Garner,¹³ and the products were worked up in the manner described for cyclohexene. The required 3-*methyl*-7,7-*dibromobicyclo* [4.1.0] *heptane* (VII) (20.8 g, 31 %) was isolated by distillation and had b.p. 68-70°/0.5 mm. (Found: C, 36.3; H, 4.7; Br, 60.3. C₈H₁₂Br₂ requires: C, 35.8; H, 4.5; Br, 59.6%.) NMR spectrum: multiplets centred at 8.1 τ , 8.7 τ and 9.1 τ .

Pyrolysis of 3-methyl-7,7-dibromobicyclo [4.1.0] heptane (VII) in lepidine

(a) A solution of 3-methyl-7,7-dibromobicyclo [4.1.0] heptane (5 g) in lepidine (20 g) was heated under N₂ in a distillation apparatus at 200° at a press. high enough to limit the distillation of starting material and lepidine. The distillate collected during 2 hr was redistilled and a fraction consisting of a pale yellow, unstable liquid (0.8 g, 23%), b.p. 42-43°/0.7 mm was obtained. This material consisted of a mixture of methylbromocycloheptadienes. (Found: C, 50.9; H, 5.6. Calc. for C₈H₁₁Br: C, 51.4; H, 5.9%), $\lambda_{max}^{E10R} 252 m\mu (\log \varepsilon 3.79)$. Glc indicated four principal constituents in approximate proportions of 1:5:2:3 in order of increasing retention times. NMR spectrum: broad multiplet centred at 4.2 τ , weight ca. 1, assigned to olefinic protons; broad multiplet centred at 7.9 τ , weight ca. 3, assigned to methylene protons; A multiplet centred at 9.0 τ (probably consisting of four singlets at 8.88 τ , 9.00 τ , 9.02 τ and 9.06 τ), wt. ca. 1, assigned to methyl protons.

(b) A solution of VII (5 g) in quinoline (20 g) was heated in a distillation apparatus under N₂ at 200° and at slightly below atm. press. The distillate collected after 1½ hr was redistilled to give a fraction (1.3 g, 66%), b.p. 56-58°/50 mm consisting of a mixture of methylcycloheptatrienes. (Found: C, 90.7; H, 10.1. Calc. for C₈H₁₀: C, 90.5; H, 9.5%). $\lambda_{\text{max}}^{\text{BUOH}}$ 260 m μ (log ε 3.54). The mixture was resolved by glc into three components in the approximate proportions of 2:1:1 in order of increasing retention times. NMR spectrum: 3.6 τ , a multiplet assigned to C(3) and C(4) protons; 4.0 τ , a multiplet, assigned to C(2) and C(5) protons; 8.1 τ , a multiplet (probably consisting of singlets at 8.0 τ and 8.2 τ and a doublet at 8.1 τ), assigned to methyl protons.

Thermal equilibration of methylcycloheptatriene mixture

The methylcycloheptatriene mixture (2.0 g), described in experiment (b) above was heated in a sealed tube at 160° for 24 hr and redistilled. The distillate (1.8 g), b.p. 56-58°/50 mm had λ_{max}^{EtoH} 263 (log ε 3.51), λ_{min} 226 m μ (log ε 3.01). (Found: C, 89.8; H, 9.4%.) This material was resolved by glc into three components with the approximate proportions of 1:1.5:4 (with retention times corresponding to those of the components of the starting material, in which the relative abundances were

18 P. S. Skell and A. Y. Garner, J. Amer. Chem. Soc. 78, 5430 (1956).

approximately 2:1:1). NMR spectrum: 3.63τ , a multiplet, assigned to C(3) and C(4) protons; 4.0τ , a multiplet, assigned to C(2) and C(5) protons; 4.78τ , a quartet (double-triplet), assigned to C(1) and C(6) protons; 7.75τ , a multiplet consisting largely of a doublet at 7.73τ (J = 7 c/s), assigned to C(7) protons of 1-methylcycloheptatriene; three singlets at 8.00τ , 8.07τ and 8.17τ , assigned to methyl protons (the most intense signal at 8.07τ is assigned to the methyl protons of 1-methylcycloheptatriene).

1-Methoxycyclohexene

Trimethyl orthoformate (260 g) was added to a solution of mesitylenesulphonic acid (1.5 g) in cyclohexanone (196 g) and anhydrous MeOH (320 ml). A vigorous reaction ensued which caused ebullition, after which the reaction solution was heated under reflux for a further 15 min. Then additional mesitylenesulphonic acid (1.0 g) was added and the products were fractionated through an efficient column. The required 1-methoxycyclohexene (100 g, 45%) distilled in the range 138-142°/760 mm (lit.,¹⁴ 40-41°/15 mm). (Found: C, 74.9; H, 10.95. Calc. for C₇H₁₄O: C, 74.9; H, 10.8%.) v_{max} 1675 cm⁻¹, NMR spectrum: 5.5 τ , a multiplet, wt. 1, assigned to olefinic proton; 6.58 τ , a singlet, wt. 3, assigned to methoxyl protons; 8.0 τ , a multiplet, wt. 4, assigned to allylic methylene protons; 8.43 τ , a multiplet, wt. 4, assigned to homoallylic methylene protons.

Attempted isolation of 1-methoxy-7,7-dibromobicyclo [4.1.0] heptane (XI; R = Me, X = Br)

1-Methoxycyclohexene (25 g) was allowed to react with dibromocarbene, generated from bromoform (75 g) and potassium t-butoxide¹³ (1.04 M solution in t-butanol, 450 ml). After the usual workup, the solvent (pet. ether, b.p. 40–60°) was carefully removed to yield *crude* 1-methoxy-7,7-dibromobicyclo [4.1.0] heptane (31 g, 49%). It was not possible to purify this material by distillation as it was thermally unstable above ca. 50°.

Methoxybromocycloheptadienes

A solution of the above material (XI; R = Me, X = Br; 10 g) in 2,6-lutidine (30 ml) was heated at 135° for 45 min. The products, which were partly solid, were distributed between water (100 ml) and pet. ether (b.p. 40-60°, 100 ml). The organic layer was washed with 1 N HCl (2 × 100 ml), water (100 ml), and then dried (MgSO₄). The solvent was removed by evaporation and the residue distilled (oil-bath temp, 100°). A straw-coloured fraction (5 g, 70%) consisting of methoxybromocycloheptadienes. (Found: C, 47·0; H, 5·9. C₈H₁₁BrO requires: C, 47·3; H, 5·5%) had b.p. $63-67^{\circ}/0.7 \text{ mm}$, v_{max} 1630, 1660 cm ⁻¹, λ_{max}^{Euga} 284 (log ϵ 3·24), λ_{min} 258 m μ (log ϵ 3·16). This material darkened on exposure to the atm. NMR spectrum: 3·84 τ , 4·37 τ and 5·25 τ , multiplets, combined weight ca. 1, assigned to olefinic protons; 6·46 τ , a multiplet, weight ca. 1, assigned to methoxyl protons; 7·0-8·5 τ , multiplets, combined weight ca. 2, assigned to protons attached to saturated carbon atoms.

Methoxycycloheptatrienes

A solution of XI (R = Me, X = Br; 12 g) in quinoline (36 g), contained in a distillation apparatus, was heated in a stream of N₂ at 150° under slightly red. press. Redistillation of the crude distillate, collected during 1 hr, gave a liquid (1.7 g, 33%), b.p. 49–50°/6 mm, composed of a mixture of methoxycycloheptatrienes. Glc resolved the mixture into three components in the approximate proportions of 1:10:3 in order of increasing retention times. NMR spectrum: 3.76τ and 3.98τ , multiplets, combined weight 3; 4.78τ , a multiplet, wt. 2; 6.50τ , a singlet, wt. 3, assigned to methoxyl protons; 7.56τ , a doublet (J ~ 7.2 c/s), assigned to C(7) protons of 1-methoxycycloheptatriene. Weaker signals included two triplets at 7.71τ and 7.76τ , the latter being more intense. λ_{max}^{EtoH} 287 m μ .

7,7-Dibromobicyclo [4.1.0] heptene-2 (XIV)

1,3-Cyclohexadiene (23.3 g) was treated with dibromocarbene generated¹³ from bromoform (75 g) and potassium t-butoxide (1.04 M in t-butanol, 450 ml). The products were worked up as before and 7,7-*dibromobicyclo* [4.1.0] *heptene*-2 (42.1 g, 58%), b.p. 68-70°/0.8 mm was isolated by distillation. (Found: C, 33.4; H, 3.3; Br, 60.6. C,H₈Br₃ requires: C, 33.4; H, 3.2; Br, 63.4%). NMR

¹⁴ A. Johannissian and E. Akunian, Bull. Univ. État R.S.S.-Arménie 5, 235, 245 (1930); Chem. Abstr. 25, 921 (1931).

Bromocycloheptatrienes

A solution of 7,7-dibromobicyclo [4.1.0] heptene-2 (5.9 g) in quinoline (17.0 g), contained in a distillation apparatus fitted with a 9 cm Vigreux column, was heated in a stream of N₂ at 150° and under slightly red. press. The distillate, collected during 30 min, was redistilled and a pale yellow liquid (1.5 g, 37%), b.p. 76-78°/16 mm, containing a mixture of bromocycloheptatrienes was obtained. (Found: C, 49.2; H, 4.4; Br, 46.4. Calc. for C_7H_7Br : C, 49.2; H, 4.2; Br, 46.7%.) λ_{max}^{0} 265 m μ (log ε 3.56). The mixture was resolved by glc into two main components in the approximate proportion of 1:4, the more abundant component having the longer retention time. NMR spectrum: 3.5 τ , a multiplet, wt. 1.75, assigned to C(3) and C(4) protons; 3.9 τ , a multiplet, wt. 1.25, assigned to C(2) and C(5) protons; 4.5 τ , a multiplet, wt. 2, assigned to C(1) and C(6) protons; 7.70 τ and 7.76 τ , triplets (J = 7 c/s for both), combined wt. 2 (the 7.76 τ triplet predominates), assigned to the C(7) protons of 3- and 2-bromocycloheptatriene respectively.

Reaction between bromocycloheptatriene mixture and selenium dioxide

To a solution of the above bromocycloheptatriene mixture (4.6 g; consisting of the 2- and 3isomers in the respective proportions of ca. 4:1) in dry dioxane (20 ml) was added freshly sublimed SeO₂ (2.7 g) and the stirred mixture heated under reflux for 2 hr. The products were filtered through supercel, and the filtrate evaporated and then distilled. A fraction (0.95 g, 33%) with b.p. 76–78°/ 1 mm was identified as tropone (Found: C, 78.8; H, 5.9. Calc. for C₇H₆O: C, 79.2; H, 5.7%) by comparison of its IR, UV and NMR spectra with those of authentic material.

Thermal rearrangement of bromocycloheptatriene mixture

The above 4:1 mixture of 2- and 3-bromocycloheptatrienes was heated in a stoppered tube at 125° for 7 hr and the products distilled. NMR spectrum of distillate: principal signals— 2.72τ , a singlet, wt. 5; 5.60τ , a singlet, wt. 2—suggested that the material was mainly benzyl bromide (authentic material has singlets at 2.7τ and 5.65τ); weak signals in the 7-8 τ region— 7.16τ , a doublet (J = 7 c/s), assigned to C(7) protons of 1-bromocycloheptatriene; 7.70τ and 7.76τ , two triplets (J = 7 c/s for both), assigned to C(7) protons of 3- and 2-bromocycloheptatriene respectively—suggested presence of 1-, 2- and 3-bromocycloheptatrienes as minor constituents and furthermore that the 1- and 3- were both more abundant than the 2-isomer. These observations were confirmed by glc.

Pyrolysis of 7,7-dibromobicyclo [4.1.0] heptene-3 (XVIII)

(a) 7,7-Dibromobicyclo [4.1.0] heptene- 3^{12} (9.5 g) was heated in a 10 ml flask, fitted with an aircondenser and CaCl₂ tube at 205° for $1\frac{1}{2}$ hr, after which time glc analysis indicated that one material accounted for 95% of the volatile products. The total reaction mixture was dissolved in CHCl₃ (50 ml), washed with NaHCO₃aq (2 × 50 ml), water (50 ml), and the dried (MgSO₄) organic layer evaporated and then distilled. A colourless lachrymatory liquid (3.15 g, 50%), b.p. 89-90°/27 mm was collected and identified as benzyl bromide. (Found: C, 49.5; H, 4.2; Br, 46.3. Calc. for C₇H₇Br: C, 49.2; H, 4.2; Br, 46.3%) by comparison of its UV, IR and NMR spectra with those of authentic material.

(b) A solution of XVIII (3 g) in quinoline (8.5 g) was heated at 220°. Glc analysis of the reaction mixture after various intervals indicated the absence of volatile constituents other than starting material. After 3 hr, the reactants had been converted into a deep-red viscous oil.

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