A typical preparation of a stock solution of sodium n-propyl mercaptide is described below. This solution was diluted to approximately twice the initial concentration desired for the kinetic experiments and analyzed iodametrically immediately preceding each run. Initial concentrations under reaction conditions could then be calculated as for the esters. Specifically, these ranged from 0.0700M to 0.1070M for the reactions involving methyl mesitoate and methyl benzoate as substrates, and from 0.1280M to 0.1370M for neopentyl benzoate, while the initial mercaptide concentration ranged from 0.0800M to 0.1000M for the blanks which were run on the sodium n-propyl mercaptide solution alone.

A two-piece glass reaction vessel was used. The cap consisted of a 45/50 standard taper joint which was closed at the top, then fitted with inlet and outlet tubes for nitrogen both of which bore stopcocks. A short length of 14 mm. tubing with a 14/35 standard taper joint at the upper end projected vertically and served as a sample port. During kinetic runs this opening was closed by a 14/35 standard taper stopper held in place by a spring clamp. The other part consisted simply of a 45/50 standard taper joint which was closed off about 2 in. from the lower edge of the joint, thereby forming a flask of approximately 75 ml. capacity. Hooks were attached to both halves, which were held together by springs.

The reaction vessel was assembled and dried at 120° for 15 min. It was then fitted with a calcium chloride tube, and allowed to cool to room temperature. The vessel was placed in a thermostat, the outlet tube was attached to a mercury valve, and nitrogen was introduced through the inlet tube. After an inert atmosphere had been created, the nitrogen flow was stopped, except as the stopper was removed from the sample port during pipetting of samples. The vessel was then stoppered, flushed briefly with nitrogen as before, and the two stopcocks were close. When samples for analysis were removed the procedure used was the same as that described for the introduction of reactants.

All reaction rates were followed by analyzing for sodium n-propyl mercaptide. A 2-ml. sample was removed by pipette and added to 5 ml. of standard 0.1N iodine solution in 10 ml. of acetate buffer (0.05M in sodium acetate and in acetic acid). The excess iodine was titrated with 0.015N standard sodium thiosulfate.

Experiments were carried out on a qualitative basis which showed that sodium n-propyl mercaptide reacts with methyl mesitoate to yield methyl n-propyl sulfide and mesitoic acid, and with methyl benzoate to produce methyl n-propyl sulfide and benzoic acid.

Sodium propyl mercaptide in N,N-dimethylformamide. The salt was prepared in a nitrogen atmosphere from 2.22 g. (0.0967 g.-atom) of sodium and 11.5 ml. (0.127 mole) of propyl mercaptan in 80 ml. of dry xylene (distilled from calcium hydride).[35] After cooling in a nitrogen atmosphere, the mixture was poured into 400 ml. of dry ether, held at 0° for 0.5 hr., and filtered on a fritted glass funnel. The residue was washed well with dry ether and dried *in vacuo* over calcium chloride for 0.5 hr. The dry salt was then dissolved in 170 ml. of dry dimethylformamide, and the concentration was determined iodimetrically (0.4483M); yield 80%.

Acknowledgment. The authors wish to thank Mr. Richard Vogt for his assistance in obtaining the extent of reaction between neopentyl benzoate and benzyl mercaptide.

ANN ARBOR, MICH.

---

(35) H. Tilles, *J. Am. Chem. Soc.*, 81, 714 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Cyclopentene-3,5-dione. IV. Reaction with Brominating Agents and with Ethanol[1,2]

C. H. DEPUY, R. D. THURN, AND M. ISAKS

Received August 14, 1961

Cyclopentene-3,5-dione has been shown to react with a variety of halogenating agents, each one giving predominately a different halogenation product. Reaction with bromine in carbon tetrachloride proceeded by addition and substitution to give 2,4,5-tribromocyclopentane-1,3-dione while N-bromosuccinimide gave mainly 4,4-dibromocyclopentene-3,5-dione and 1,4,4-tribromocyclopentene-3,5-dione. Addition of the dione to a solution of bromine in aqueous sodium bicarbonate furnished 4,4-dibromocyclopentene-3,5-dione in satisfactory yields. The enedione also reacted smoothly with ethyl alcohol in the presence of boron trifluoride to form 3,4-diethoxycyclopent-2-enone. This compound could be reduced and hydrolyzed to 5-ethoxycyclopent-2-enone.

A few years ago we developed a synthesis of the interesting and unusual compound cyclopentene-3,5-dione (I),[3] a stable, yellow solid which easily undergoes a large number of reactions, including condensations, reductions, derivatizations, and Diels-Alder additions. In general, it seems fair to say that there are almost no methods currently available for the synthesis of a vast number of simply substituted unsaturated cyclopentane derivatives, and we have been exploring the chemistry of cyclopentene-3,5-dione and of cyclopentenone,[4] as these molecules appear to be the most likely precursors for many other cyclopentane compounds. In this paper we report on the reactions of the dione with various brominating agents and with ethyl alcohol. All of these reactions lead to potentially useful synthetic intermediates, and some of them have interesting theoretical implications.

---

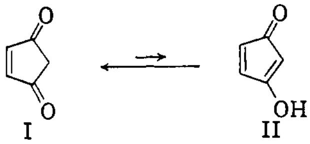
[1] Supported by a grant from the National Science Foundation.

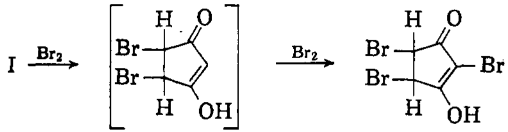
[2] Paper III in this series: C. H. DePuy and P. R. Wells, *J. Am. Chem. Soc.*, 82, 2909 (1960).

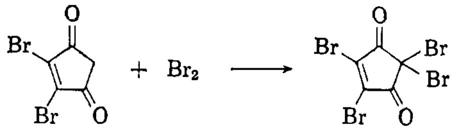
[3] C. H. DePuy and E. F. Zaweski, *J. Am. Chem. Soc.*, 81, 4920 (1959).

[4] C. H. DePuy, M. Isaks, and K. L. Eilers, *Chem. & Ind.*, 429 (1961).

We have pointed out previously[2,3] that the chemistry of cyclopentene-3,5-dione is made experimentally difficult, and at the same time theoretically interesting, by its close relationship, through its enol form, (II), to the unknown and highly unstable molecule cyclopentadienone.[4] Because of the instability of the enol form the compound exists solely as the diketone, despite the fact that dipolar repulsions between the carbonyl groups must be very large. As a consequence, I reacts extremely readily with a variety of reagents. When a solution of the dione was allowed to react with bromine in carbon tetrachloride or acetic acid solution, it took up two molar equivalents of bromine without a break, liberating hydrogen bromide. At the end of the reaction the characteristic yellow color of the dione had disappeared and removal of the solvent furnished a nearly quantitative yield of a white crystalline tribromide (III). This tribromide no longer exhibited the 5.82-μ infrared band characteristic of the enedione system, but instead showed a strong band at 6.27 μ and a medium band at 5.90 μ. This spectrum, together with its ultraviolet absorption λ_{max} 272, ϵ 17,600), its solubility in bicarbonate, and its enolic character suggested a mixture of cis and trans isomers of structure III. This could plausibly be imagined to arise through bromine addition followed by enolization and substitution. If bromine addition were stopped after one molar equivalent had been added, only the tribromide and starting material could be isolated. It seems likely then that the second step is faster than the first. This rapid addition of bromine to the double bond is to be contrasted with the results of Diels and Reinbeck,[5] who observed only substitution in the bromination of 1,2-dibromocyclopentene-3.5-dione, and with those of Koelsch and Wawzonek[6] who similarly observed only substitution on bromination of 1,2,4-triphenylcyclopentene-3,5-dione.

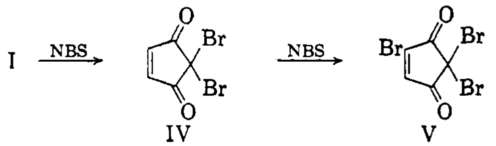

I II

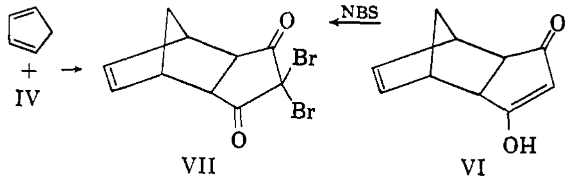

III



We next examined brominating conditions which we felt were more likely to preserve the enedione system. An attractive possibility appeared to be *N*-bromosuccinimide, (NBS), which can carry out substitution reactions adjacent to carbonyl groups. Cyclopentene-3,5-dione was therefore allowed to to react with NBS in refluxing carbon tetrachloride solution. Reaction was initiated by irradiation with ultraviolet light. When the reactants were present in equimolar amounts, much unchanged starting material could be successfully isolated. However, when two molar equivalents of NBS was used and the products distilled, a yellow, bromine-containing oil was obtained in good yield. On standing the oil partly crystallized to a yellow, solid dibromide (IV). The residual oil, after removal of unchanged dione by extraction with base, gave a yellow, solid tribromide (V). The tribromide was formed in higher yield than the dibromide, and the yield of IV varied from 0–18%.

The dibromide was a neutral compound, insoluble in base, but its spectral and chemical properties were virtually identical to those of cyclopentene-3,5-dione itself. We therefore suspected that it was the desired 4,4-dibromide and its structure was confirmed by treating it with cyclopentadiene to form a white, neutral Diels-Alder adduct. This adduct proved to be identical with one obtained by the reaction of adduct VI (obtained from cyclopentadiene and cyclopentene-3,5-dione) and NBS.[7] The NMR spectrum of IV was also consistent with its structure since it showed only a single, unsplit peak at $\delta = 7.33$ (in carbon tetrachloride relative to internal tetramethylsilane), approximately where the vinyl protons of cyclopentene-3,5-dione appear ($\delta = 7.31$).


IV V


VII VI

We have assigned structure V to the tribromide because it too is nonacidic and closely resembles the starting dione in its spectra properties. It can probably be obtained in quite good yield from three

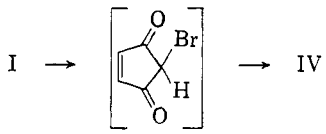
---

(5) O. Diels and M. Reinbeck, *Chem. Ber.*, 43, 1271 (1910).

(6) C. F. Koelsch and S. Wawzonek, *J. Org. Chem.*, 6, 684 (1941).

(7) L. Wolff and F. Rüdell *Ann.*, 294, 189 (1896), report the preparation of IV from dibromolevulinic acid. However, P. R. Wells (unpublished results, Iowa State University) has suggested that Wolff and Rüdel's compound was an isomeric lactone on the basis of its infrared spectrum.

or more moles of NBS but we have not attempted to work out conditions for maximum yields. In an attempt to follow the pathway of bromination we carried out a reaction with two molar equivalents of NBS and examined the NMR spectrum of aliquots from time to time. The starting dione and dibromide IV have singlets at $\delta = 7.31$ and 7.33, respectively. Initially the methylene singlet of the dione I decreases and after a time the singlet ($\delta = 7.50$) due to the tribromide V begins to appear. *No absorption which might be ascribed to the unique proton of the monobromide* VIII *could be detected at any time.* In the light of these results it appears probable that the initially formed monobromide either disproportionates readily to dibromide and dione by a route analogous to the disproportionation observed with bromoindandione[8]

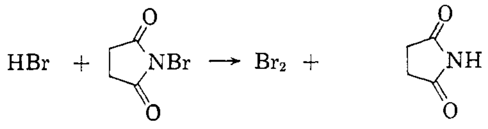


VIII

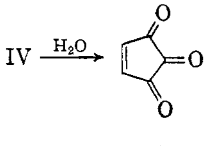
2VIII → I + IV

or that the bromination of the monobromide VIII with NBS is extremely fast compared with the rate of its formation. The origin of the tribromide V has also been studied briefly. Although IV contains positive bromine, as evidenced by reaction with potassium iodide, V is not formed by disproportionation of IV, as the latter is stable to refluxing carbon tetrachloride. But IV reacts further with NBS, by what is probably a nonradical chain reaction catalyzed by acid, involving molecular bromine. As the two bromines in IV prevent enolization of the dione, addition of bromine is followed by elimination of HBr to form V.

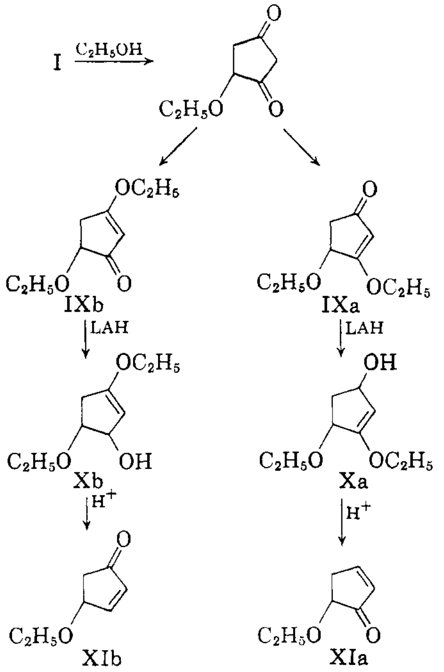
$$IV + Br_2 \longrightarrow V + HBr$$



The further reaction of 4,4-dibromocyclopentene-3,5-dione with NBS effectively prevented its isolation in more than small amounts, and an alternative route to this potentially useful intermediate was sought. The problem was complicated by the extremely rapid polymerization of the dione in basic solution,[2] and the rapid addition reactions in neutral and acidic solution. Nevertheless, we had previously shown that the anion of I could be trapped by a very reactive electrophile before it had a chance to polymerize by reaction with another molecule of dione.[2] And indeed it was found that an aqueous solution of the dione, when added to a bicarbonate solution of bromine in water, precipitated IV in 45% yield. The reaction is undoubtedly helped by the insolubility of the dibromide in water which slows down further reaction. By this method large amounts of this interesting compound can be prepared and it should prove useful for further elaboration into unusual cyclopentane derivatives. In particular we are investigating the hydrolysis of IV to cyclopentene-3,4,5-trione, the monocyclic analog of ninhydrin.



As normal monocarbonyl derivatives of I were formed so readily, it seemed probable that a monoketal could also be prepared, and with this end in view I was allowed to react with ethyl alcohol in the presence of boron trifluoride. Reaction readily took place and a compound $C_9H_{14}O_3$ (IX) was formed in good yield. This compound was neutral and showed infrared absorption at 6.27 μ. Acid hydrolysis regenerated some starting dione. The spectrum and analysis suggested that the compound was an ethoxy enol ether of cyclopentane-1,3-dione. Two isomers of this compound appeared possible, IXa and IXb.



When IX was reduced with lithium aluminum hydride, it was converted in high yield to a crystalline alcohol (Xa or Xb), suggesting that IX was not a mixture of isomers. This alcohol still exhibited enol ether absorption in the infrared and readily hydrolyzed in mild acid solution to form, in good yield, an ethoxycyclopentenone (XIa or XIb). No hydroxycyclopentenone could be detected among the products.

---

[8] L. Flatow, *Ber.*, **34**, 2146 (1901).

Structure XIa was confirmed for the ethoxycyclopentenone when a nuclear magnetic resonance spectrometer became available. The spectrum in deuterium oxide exhibited, in addition to the triplet and quartet for the ethyl group, a clean ABX system,[9] with the AB protons further split by coupling with both vinyl protons and the X proton (a quartet of equal intensities as expected) not further split. An extensive study of the NMR spectra of cyclopentenone compounds[10] has shown that protons adjacent to the carbonyl do not couple with the vinyl protons while those in the beta position do. Consequently, structures IXa, Xa, and XIa are assigned to the diethoxyenone, the alcohol and the ethoxycyclopentenone, respectively. All of these compounds can be prepared readily from cyclopentene-3,5-dione and should prove useful for further synthetic work in the cyclopentane system.

EXPERIMENTAL[11]

Cyclopentene-3,5-dione (I). The dione was prepared by the method of DePuy and Zaweski[3] as modified by House and Rassmussen.[12] Yields from 3,5-cyclopentene-diol averaged about 70%.

N-Bromosuccinimide. White label Matheson *N*-bromosuccinmide was used. Both aged and freshly recrystallized material was used. In general aged compound reacted more readily.

Formation of III *by bromination in carbon tetrachloride.* Bromine (17.2 ml. of 0.24 *M*) in carbon tetrachloride was added dropwise with stirring to a solution of dione (0.2 g.) in 15 ml. of ether. The yellow color of the dione disappeared and hydrogen bromide evolution was noticed. The solution was washed with water and dried over sodium sulfate. The white residue remaining after removal of solvent was recrystallized from ether-hexane to give 0.38 g. (59% yield) of tribromide which darkened at 150–160° and melted 173–175°. This compound also darkens slowly upon standing and in aqueous solutions.

Anal. Calcd. for $C_5H_3O_2Br_3$: C, 17.93; H, .903; Br, 71.60. Found: C, 18.40; H, 1.18; Br, 71.00.

Bromination in acetic acid. To 0.1 g. (0.001 mole) of cyclopentene-3,5-dione in glacial acetic acid was added 0.64 g. (0.002 mole) of pyridinium perbromide. After five minutes the solution was poured into ice water and extracted with ether. After drying and removal of solvent, a white solid was obtained, identical with that formed in carbon tetrachloride.

Bromination with N-bromosuccinimide. To 3.0 g. (0.031 mole) of cyclopentene-3,5-dione in 25 ml. of carbon tetrachloride was added 11.10 g. (0.062 mole) of *N*-bromosuccinimide. The reaction mixture was heated at reflux for 24 hours and irradiated at the beginning with a GE-RS sunlamp. After reflux the NBS had disappeared and succinimide was floating on the surface. The mixture was filtered and the succinimide washed with small portions of ether. The solvents were removed by distillation and the resulting oil chilled for 30 minutes, at which time a yellow precipitate had formed. This was filtered and sublimed to yield 1.5 g. (18% yield) of 4,4-dibromocyclopentene-3,5-dione (IV) which, after recrystallization from ether-hexane melted at 81–82°.

Anal. Calcd. for $C_5H_2Br_2O_2$: C, 23.65; H, 0.79; Br, 62.96. Found: C, 23.92; H, 1.09; Br, 62.78.

The reddish orange filtrate was distilled at 100–110°/4 mm. to yield 4.6 g. (58% yield) of a yellow oil. This oil was taken up in ether, the ether solution was washed with dilute sodium bicarbonate and the ether removed to furnish 1,4,4-tribromocyclopentene-3,5-dione (V), m.p. 60–61°.

Anal. Calcd. for $C_5HBr_3O_2$: C, 18.45; H, 0.24; Br, 72.04. Found: C, 18.22; H, 0.69; Br, 72.56.

4,4-Dibromocyclopentene-3,5-dione (IV). A solution of 6.4 g. (0.04 mole) of bromine and 3.36 g. (0.04 mole) of sodium bicarbonate in 80 ml. of water was chilled to 0° and added rapidly (5 min.) to a cold stirred solution of 1.92 g. (0.02 mole) of cyclopentene-3,5-dione dissolved in 40 ml. of water. The resulting solution was allowed to stand at room temperature for 5 min., then chilled and filtered, giving 2.08 g. of 4,4-dibromocyclopentene-3,5-dione m.p. 80–81°. The aqueous filtrate was extracted twice with ether, the ether dried, condensed, and pentane added. The resulting solution was cooled to Dry Ice temperature precipitating a further 0.2 g. of dibromide bringing the total yield to 2.28 g. (45%).

Diels-Alder adduct of 4,4-dibromocyclopentene-3,5-dione and cyclopentadiene (VII). 4,4-Dibromocyclopentene-3,5-dione (0.32 g.) was dissolved in an excess of freshly distilled cyclopentadiene and allowed to stand at 4° for one hour. The resultant solid was filtered and recrystallized from hexane to yield 0.24 g. (51%) of product. An analytical sample, after two additional recrystallizations from hexane, melted at 137–138°.

Anal. Calcd. for $C_{10}H_8Br_2O_2$: C, 37.53; H, 2.52. Found: C, 37.73; H, 2.87.

Bromination of the cyclopentadiene-cyclopentenedione adduct. The cyclopentadiene-cyclopentene-3,5-dione adduct[3] (VI) (0.9 g., 0.0055 mole) was dissolved in 15 ml. of carbon tetrachloride, *N*-bromosuccinimide (2 g. 0.011 mole) was added and the mixture was heated at reflux for four hours. The succinimide was removed by filtration and the solvent removed from the filtrate leaving a white residue which, after three recrystallizations from hexane, melted at 137–138°. This dibromide was identical to the dibromide (VII) prepared above as shown by mixed melting point and infrared spectrum.

3,4-Diethoxycyclopent-2-enone (IXa). Cyclopentene-3,5-dione (12.4 g., 0.13 mole) was dissolved in 50 ml. of absolute ethanol and to this was added ethyl orthoformate (20 g., 0.0135 mole) and boron trifluoride etherate (20 ml.). The mixture was stirred at room temperature for 12 hours and then poured into 200 ml. of saturated sodium carbonate solution. Enough additional water was added to dissolve the inorganic salts and the aqueous solution was extracted with three 50-ml. portions of ether; the ether layers were combined, dried, and the solvent removed. Distillation of the residue gave 3,4-diethoxycyclopent-2-enone (12.1 g., 56% yield), b.p. 91–99°/1 mm. The compound had an ultraviolet max at 227.5 $m\mu$, log ϵ, 3.52 (in methylcyclohexane).

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.64; H, 8.11.

Preparation of 3,4-diethoxycyclopent-2-ene-1-ol (Xa). 3,4-Diethoxycyclopent-2-enone (8.4 g., 0.05 mole) was dissolved in 50 ml. of dry ether and added dropwise with stirring to lithium aluminum hydride (1 g. 0.1 equivalent) in 50 ml. of ether. After the addition was complete the solution was heated at reflux for 15 min. and hydrolyzed with a slurry of sodium sulfate and water. The ether layer was removed, dried, and removed by distillation. The residual oil was distilled at 82–85°/1 mm. to yield 5.4 g. (63% yield) of an oil which solidified on standing at 0°. Recrystallization from pentane gave 4.8 g. of pure alcohol, m.p. 46–47°.

---

(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, McGraw Hill, New York, 1959, p. 132.

(10) C. H. DePuy and C. E. Lyons, unpublished work.

(11) All melting points are uncorrected. Analyses were performed by Weiler and Strauss, Microanalytical Laboratory, 164 Banbury Road, Oxford, England, and Midwest Microlab Inc., 7838 Forest Lane, Indianapolis 20, Ind.

(12) H. House, G. Rassmussen, C. H. DePuy, and E. F. Zaweski, *Org. Syntheses, in press.*

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 63.07; H. 9.36.

5-Ethoxycyclopent-2-enone (XIa). 3,4-Diethoxycyclopent-2-ene-ol (2 g., 0.01 mole) was dissolved in 10 ml. of water and 10 ml. of 3 *M* hydrochloric acid solution was added. After standing for 15 min. the solution was extracted with ether, the ether layers were combined, dried, and distilled. The ketone boiled at 81–82°/15 mm. and weighed 1 g. (67% yield), λ_{max} 219 mμ (log ϵ 3.77).

Anal. Calcd. for $C_7H_{14}O_2$: C, 66.64; H, 7.99. Found: C, 66.49; H, 8.21.

A 2,4-dinitrophenylhydrazone was prepared in the usual way, m.p. 154.5–155.5 (dec.).

Anal. Calcd. for $C_{13}H_{14}O_5N_4$: C, 50.98; H, 4.61; N, 18.29. Found: C, 50.55; H, 4.55; N, 18.36.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

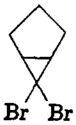
Rearrangement of 6,6-Dibromobicyclo[3.1.0]hexane[1]

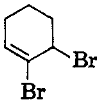
JOSEPH SONNENBERG AND S. WINSTEIN

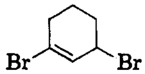
Received September 18, 1961

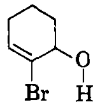
The product of addition of dibromocarbene to cyclopentene, 6,6-dibromobicyclo[3.1.0]hexane, rearranges readily to the allylic dibromide, 2,3-dibromocyclohexene. For this reason, it is isolable as a pure unrearranged material only with care. The 6,6-dibromobicyclo[3.1.0]hexane is converted to 2-bromo-2-cyclohexenol by aqueous silver nitrate or by boiling aqueous acetone. The rearranged allylic dibromide yields the same bromohydrin in aqueous acetone, but a considerable quantity of nitrate ester accompanies the bromohydrin from the silver nitrate treatment. Apparently, the two dibromides do not react by way of a truly common carbonium ion intermediate.

As is well known, the reaction of olefins with dihalocarbene[2] can give rise to dihalocyclopropane derivatives. During the development of synthetic approaches to bicyclo[3.1.0]hexyl systems[3] we investigated briefly the action of dibromocarbene on cyclopentene and found that the expected product, 6,6-dibromobicyclo[3.1.0]hexane (I), was isolable only with mild work-up procedures. Otherwise, the rearranged dibromide II was obtained. This and other observations made at that time are of obvious importance in connection with reported rearrangement reactions[4,5] of the 6,6-dibromide I. For this reason, it seems desirable to report the results of our brief study, and these are presented in the present article.


I


II


III


IV

2,3-Dibromocyclohexene. The initial attempts to obtain dibromide I gave a liquid boiling over a wide range with considerable variation in refractive index. After several redistillations, a constant boiling liquid was obtained whose physical properties agreed with those reported for the 6,6-dibromide I by Skell and Garner,[6,7] but which proved to be 2,3-dibromocyclohexene (II) instead.[8] This material had a correct analysis for $C_6H_8Br_2$, showed the presence of unsaturation in the infrared and yielded cyclohexene on reduction with sodium in moist methanol.[2]

In agreement with the structure assigned to dibromide II, only one bromine atom is reactive to silver nitrate and the proton magnetic resonance spectrum shows five proton signals. An alternative structure, 1,3-dibromocyclohexene (III), which also fits the available chemical information, was rejected because the product from hydrolysis of the rearranged dibromide, namely, 2-bromo-2-cyclohexenol[9] (IV), m.p. 38–40°, exhibited intramolecular hydrogen bonding. Only the bromohydrin from 2,3-dibromocyclohexene is capable of an intramolecular interaction between the hydroxyl and bromine groups.

Additional support for the structure of dibromide II is that methyllithium converts it to 2-bromo-3-methylcyclohexene. The latter was re-

---

[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] W. E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[3] (a) S. Winstein, J. Sonnenberg, and L. de Vries, *J. Am. Chem. Soc.*, **81**, 6523 (1959); (b) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

[4] P. S. Skell and S. R. Sandler, *J. Am. Chem. Soc.*, **80**, 2024 (1958).

[5] W. R. Moore and H. W. Ward, *Chem. & Ind.*, 594 (1961).

[6] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956).

[7] These authors have more recently recognized that the dibromide sample was very predominantly rearranged material. (P. S. Skell, private communication, March 1959).

[8] The 2,3-dibromocyclohexene is reported to be the product formed when 1,2,3-tribromocyclohexane is heated with potassium hydroxide. [W. G. Christiansen, U. S. Patent 2,146,720 (1939).]

[9] The acetoxybromocyclohexene from treatment of 1,2,3-tribromocyclohexane with potassium acetate in acetic acid gives rise to a bromohydrin,[10] m.p. 39–40°, probably identical to bromohydrin IV.

[10] R. Cornubert, A. Rio, and P. Senechal, *Bull. soc. chim. France*, **22**, 46 (1955).