lead to the 1,1 isomer. Isomerization of **21** to **22** is probably not important. (See Scheme IV.)

Experimental Section

Hydrogen Fluoride Alkylations.—These reactions were run in an all-copper vessel with a water-cooled copper tube as condenser. The bomb was charged with the dichloride, 100–200 *M* excess of liquid hydrogen fluoride, and an 11.3 *M* excess of benzene. The vessel was pressured to 75 psig with dry HCl. The magnetically stirred vessel was heated. A Grove loader at the top of the condenser maintained the pressure at 100 psig.

At the end of the reaction the contents were cooled. The benzene layer was separated from the catalyst layer and washed and neutralized.

Aluminum Chloride Reactions.—Aluminum chloride was added in small portions to 1 *M* solutions of the dichlorides in benzene. At the end of the reaction the catalyst was decomposed by cold, dilute hydrochloric acid. Water, dilute sodium bicarbonate, and water were used to wash the benzene solution. The solvent was dried over magnesium sulfate and removed under reduced pressure. Vapor phase chromatographic analysis was performed on a 10 ft × 0.25 in. Carbowax on Chromosorb W column, temperature programmed from 100 to 230° at 6°/min.

Preparation and Thermal Rearrangement of 5,5-Dichloro-5H-dibenzo[*a,d*]cycloheptene

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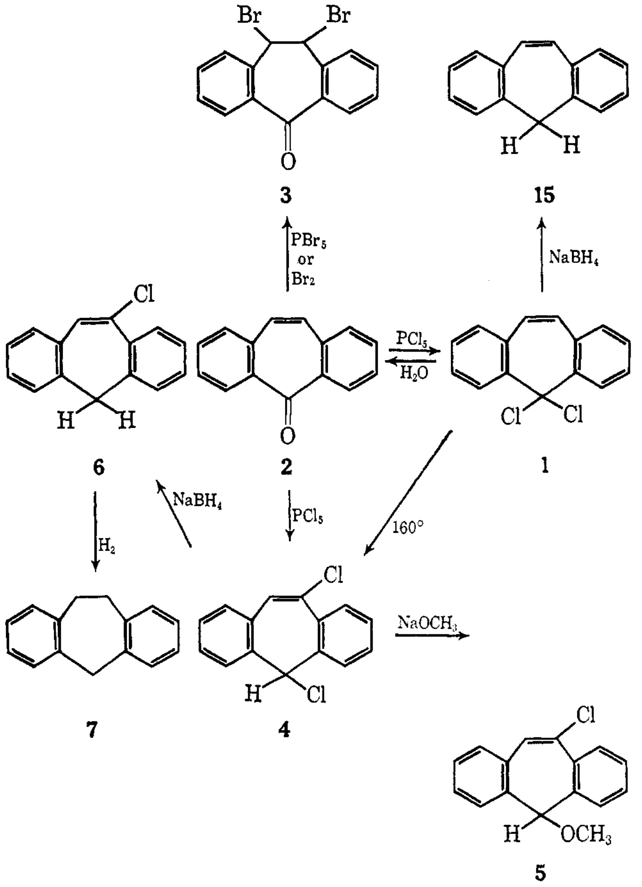
Reexamination of the method of preparation of the title compound has uncovered a thermal rearrangement which converted it into the 5,10-dichloro isomer. The structure of the isomer was established and a mechanism for the transformation is proposed. A convenient synthesis of the title compound has been found.

In connection with another problem, it was necessary to prepare 5,5-dichloro-5H-dibenzo[*a,d*]cycloheptene (**1**) or the dibromide. The route envisioned to the dihalide (Scheme I) was to treat ketone **2** with a phosphorus pentahalide. The only product obtained using phosphorus pentabromide was the bromine addition product (**3**) which was identical with material obtained by the use of bromine. Its formation is best explained by thermal dissociation of phosphorus pentabromide into bromine and phosphorus tribromide followed by addition of bromine to ketone **2**.

Treatment of ketone **2** with phosphorus pentachloride has been reported[1] to give dichloro compound **1**, but the product was used without characterization. The procedure was repeated, with molar equivalents of each reactant at 160°, instead of 2 molar equiv of halide per mole of ketone, and a dichloride was obtained. The product had only one reactive halogen atom, as demonstrated by its reaction with sodium methoxide and sodium borohydride; both products still contained one chlorine atom. The nmr spectrum of this dichloride showed one benzylic hydrogen atom (τ 3.91) with the remaining protons in the aromatic region. Structure **4** can be suggested as the most reasonable possibility from this information. The products from the reaction with sodium methoxide and sodium borohydride would be compounds **5** and **6**, respectively.

One of the chlorine atoms was most certainly at position 5, as indicated by its reactivity. The position of the other atom could be a vinyl or aromatic position. The nmr spectrum was not helpful because the olefinic proton(s) is(are) shifted into the aromatic region. This indicates that the olefinic proton is deshielded, and the presence of a vinyl chlorine atom would explain this effect. Since nuclear chlorination can occur,[2] it was necessary to establish the position of the second halogen atom.

Scheme I



Catalytic hydrogenation of chloride **6** provided evidence for the position of the second halogen atom (Scheme I). If the inert chlorine atom were on an aromatic carbon atom, it would not be affected by reduction of the double bond. If it were on an olefinic carbon atom, it would become a benzyl halide, upon

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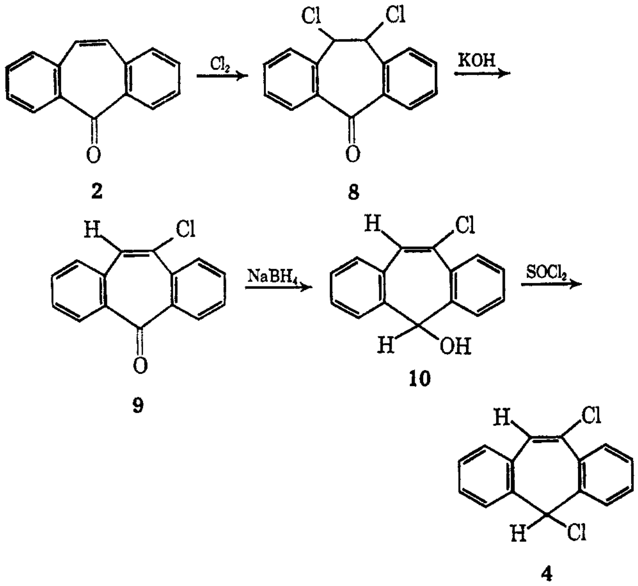
[1] E. D. Bergmann, D. Ginsburg, Y. Hirshberg, M. Mayot, A. Pullman, and B. Pullman, *Bull. Soc. Chim. France*, **18**, 697 (1951).

[2] E. D. Bergmann and J. Szmuszkovicz, *Bull. Res. Council Israel*, **1**, 90 (1952).

reduction, and would subsequently be replaced by a hydrogen atom. The product obtained, when the reduction was carried out with a palladium-on-charcoal catalyst, was the hydrocarbon **7**. This was strong evidence in support of structure **4**.

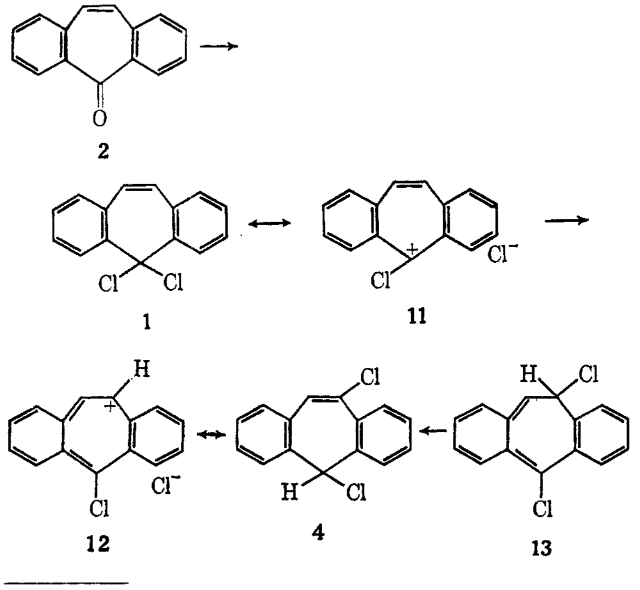
A synthesis of dichloride **4** was carried out as outlined in Scheme II, and the material obtained was identical with the phosphorus pentachloride product.

Scheme II



The formation of compound **4** from ketone **2** and phosphorus pentachloride requires comment, particularly because of the appearance of the hydrogen atom at C-5. The chlorine atom on the vinyl carbon atom can be explained by chlorination of the stilbene-like double bond of **2**, a recently observed reaction,[3] with subsequent thermal elimination of hydrogen chloride. Such a mechanism still requires an explanation for the hydrogen atom at position 5. A better proposal is outlined in Scheme III.

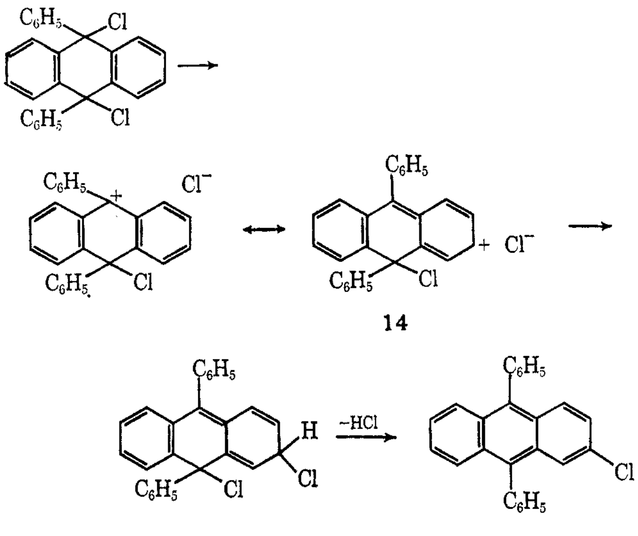
Scheme III



The steps are (a) initial formation of the 5,5-dichloride (**1**), (b) thermal anionotropic rearrangement (**11** → **12**), and (c) aromatization by a 1,5-hydride shift (**13** → **4**). These steps have all been observed in similar systems.

The anionotropic rearrangement is analogous to the transformation in the anthracene series[4,5] shown in Scheme IV.

Scheme IV



In the present example, formation of a more stable carbonium ion, tropylium ion **12**, is possible and the allylic cation analogous to **14** is not observed. The result is formation of a vinyl instead of an aromatic chloride.

The last step is an aromatization which can proceed intramolecularly by a 1,5-hydride shift, a well-established mechanism in cycloheptatriene systems.[6]

If the thermal anionotropic rearrangement is responsible for the failure to obtain dichloride **1**, then it should be isolatable under milder conditions, which will permit its formation but not its rearrangement. When phosphorus oxychloride was the solvent at reflux temperature (105°), dichloride **1** was readily obtained (Scheme I). The infrared spectrum of the unstable product showed that neither rearranged dichloride nor starting ketone was present. Evidence for the structure of the product was provided by its rapid hydrolysis to ketone **2**, and reduction with sodium borohydride to hydrocarbon **15**. Upon heating to 160°, the 5,5-dichloride rearranged in good yield to the 5,10-dihalide (**1** → **4**), thus confirming the suspected path.

The original procedure[1] for chlorination of ketone **2** with phosphorus pentachloride involved 2 molar equiv of halide per 1 equiv of ketone. On using these conditions, several products were isolated, in addition to dichloride **4**, which contained three chlorine atoms and had the composition $C_{15}H_9Cl_3$. Because of low yields and the inconsistent nature of the reaction, it was not further investigated.

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(3) D. P. Wyman, J. Y. C. Wang, and W. R. Freeman, *J. Org. Chem.*, **28**, 3173 (1963).

(4) E. D. Bergmann and O. Blum-Bergmann, *J. Am. Chem. Soc.*, **59**, 1439 (1937).

(5) G. M. Badger and M. E. Mitchell, *Australian J. Chem.*, **18**, 919 (1965).

(6) A. P. terBorg, H. Kloosterziel, and N. van Muers, *Rec. Trav. Chim.*, **82**, 717 (1963).

Experimental Section

Melting points and boiling points are uncorrected. The nmr spectra were measured on a Varian Associates A-60 instrument in deuteriochloroform, with TMS as an internal standard.

Reaction of 5H-Dibenzo[*a,d*]cyclohepten-5-one (2) with Phosphorus Pentabromide.—A mixture of 10 g (0.050 mole) of ketone[7] **2**, 21.5 g (0.050 mole) of phosphorus pentabromide, and 150 ml of benzene was heated at 65° for 4 hr. The solid which separated was collected and recrystallized from benzene to give 8.3 g (46%) of dibromo ketone **3**, mp 214° dec. A mixture melting point with an authentic sample[8] was not depressed.

Reaction of 5H-Dibenzo[*a,d*]cyclohepten-5-one (2) with Phosphorus Pentachloride.—A mixture of 10 g (0.049 mole) of each reactant was heated at 160° for 2 hr. The volatile material was removed with an aspirator, and the residue was distilled, bp 164–170° (0.10 mm). The distillate solidified and was recrystallized from ligroin to give 9.3 g (73%) of dichloride **4**, mp 118–120°.

Anal. Calcd for $C_{15}H_{10}Cl_2$: C, 69.0; H, 3.9; Cl, 27.1. Found: C, 68.8; H, 4.1; Cl, 27.1.

The nmr spectrum had peaks at τ 2.0–2.8 (m, aromatic and olefinic) and 3.91 (s, benzylic) in an area ratio of 9:1.

In another experiment the dichloride was isolated without distillation. After removal of the volatile material, as before, the residue was dissolved in hot ligroin and filtered. Upon cooling, 5.2 g (40%) of product was obtained, mp 118–120°.

10-Chloro-5H-dibenzo[*a,d*]cycloheptene (6).—A 7.5-g (0.029 mole) portion of dichloride **4** was added slowly to a suspension of 3 g (0.08 mole) of sodium borohydride in 40 ml of diglyme. When the addition was complete and all of the solid had dissolved, the solution was allowed to stand for 15 min. Water was added and the mixture was extracted with ether. The organic layer was washed with water, dried, and distilled to give 6.0 g (91%) of chloride **6**, bp 140° (0.10 mm). The product gave a negative test with methanolic silver nitrate and a positive test with potassium permanganate.

Anal. Calcd for $C_{15}H_{11}Cl$: C, 79.4; H, 4.9; Cl, 15.6. Found: C, 79.7; H, 4.8; Cl, 15.6.

The nmr spectrum had peaks at τ 2.2–2.9 (m, aromatic and olefinic) and 6.35 (s, benzylic) in an area ratio of 9:2.

5-Methoxy-10-chloro-5H-dibenzo[*a,d*]cycloheptene (5).—A solution of 1.1 g (0.020 mole) of sodium methoxide in 20 ml of methanol was added to a solution of 2.6 g (0.010 mole) of dichloride **4** in 30 ml of methanol. After standing for 3 hr at room temperature, the solution was concentrated. Water was added and the mixture was extracted with benzene. The organic layer was washed with water, dried, and distilled to give 1.9 g (75%) of ether **5**, bp 150° (0.10 mm). The product was also obtained by letting the dichloride stand in methanol overnight. It gave no precipitate with methanolic silver nitrate.

Anal. Calcd for $C_{16}H_{13}ClO$: C, 74.6; H, 5.1; Cl, 13.8. Found: C, 75.0; H, 5.3; Cl, 13.6.

The nmr spectrum had peaks at τ 2.1–2.9 (m, aromatic and olefinic), 5.25 (s, benzylic), and 6.57 (s, methoxyl) in an area ratio of 9:1:3.

Catalytic Reduction of 10-Chloro-5H-dibenzo[*a,d*]cycloheptene (6).—A solution of 1.0 g (0.0044 mole) of chloride **6** in 50 ml of ethyl acetate was reduced in a Parr shaker with 10% palladium-on-charcoal catalyst under 48 psi of hydrogen at room temperature. The course of the reaction was followed by vapor phase chromatography, and was complete after 16 hr. Isolation in the usual manner gave, after recrystallization from ethanol, 0.48 g (57%) of solid, mp 74–75°. A mixture melting point with 10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene[7] (**7**) was not depressed.

10,11-Dichloro-10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-one (8).—Chlorine was passed through a solution of 6.0 g (0.029 mole) of ketone **2** in 25 ml of carbon tetrachloride for 30 min. The solution was kept at room temperature with an ice bath. The solid was collected and recrystallized from carbon tetrachloride to give 3.4 g (42%) of chloro ketone **8**, mp 184–185°.

Anal. Calcd for $C_{15}H_{10}Cl_2O$: C, 65.0; H, 3.6; Cl, 25.6. Found: C, 64.6; H, 3.8; Cl, 26.0.

The nmr spectrum had peaks at τ 1.8–2.8 (m, aromatic) and 4.41 (s, benzylic) in an area ratio of 8:2.

10-Chloro-5H-dibenzo[*a,d*]cyclohepten-5-one (9).—A mixture of 3.4 g (0.012 mole) of dichloro ketone **8**, 4.0 g (0.010 mole) of sodium hydroxide, and 200 ml of methanol was heated at reflux for 1 hr and concentrated. Upon addition of water, a solid separated which was collected and recrystallized from ethanol, yield 2.3 g (80%), mp 125–126°.

Anal. Calcd for $C_{15}H_9ClO$: C, 74.7; H, 3.8; Cl, 14.7. Found: C, 74.9; H, 4.1; Cl, 14.5.

The nmr spectrum showed peaks at τ 1.8–2.6 (m, aromatic and olefinic).

10-Chloro-5-hydroxy-5H-dibenzo[*a,d*]cycloheptene (10).—A 1.37-g (0.0057 mole) portion of chloro ketone **9** was added in portions to 0.5 g (0.013 mole) of sodium borohydride in 50 ml of methanol and, after 30 min, the solvent was removed. The residue was extracted with benzene, and the organic layer was washed with water, dried, and concentrated. The solid obtained was recrystallized from benzene–ligroin to give 1.3 g (94%) of alcohol **10**, mp 108–109°.

Anal. Calcd for $C_{15}H_{11}ClO$: C, 74.0; H, 4.7; Cl, 14.6. Found: C, 74.1; H, 4.8; Cl, 14.3.

The nmr spectrum showed peaks at τ 2.1–2.9 (m, aromatic and olefinic), 4.70 (s, benzylic), and 6.62 (s, hydroxyl, peak disappeared when shaken with D_2O) in an area ratio of 9:1:1.

5,10-Dichloro-5H-dibenzo[*a,d*]cycloheptene (4).—A 0.50-g (0.0020 mole) portion of alcohol **10** was dissolved in 2 ml of thionyl chloride and heated for 5 min on a steam bath. Upon concentration and recrystallization from ligroin, 0.35 g (67%) of solid was obtained, mp 119–120°. A mixture melting point with the solid obtained from the reaction of phosphorus pentachloride with ketone **2** was not depressed.

5,5-Dichloro-5H-dibenzo[*a,d*]cycloheptene (1).—A mixture of 10 g (0.050 mole) of ketone **2**, 10 g (0.050 mole) of phosphorus pentachloride, and 50 ml of phosphorus oxychloride was heated at reflux for 2 hr, cooled, and concentrated. The infrared spectrum of the oil showed neither carbonyl absorption nor peaks for dichloride **4**. On standing, the oil solidified, mp 110–112°, and could be recrystallized slowly from ligroin, mp 112–113°.

Anal. Calcd for $C_{15}H_{10}Cl_2$: C, 69.0; H, 3.9; Cl, 27.1. Found: C, 69.3; H, 4.1; Cl, 27.3.

The nmr spectrum had peaks at τ 1.65–1.85 (m), 2.60–2.70 (m), and 2.80 (s) in an area ratio of 2:8:2.

This material was best handled without purification because of the ease with which it reverted to the ketone. Hydrolysis of the crude dichloride from 10 g of ketone **2** in 1,2-dimethoxyethane–dilute hydrochloric acid (1 hr on a steam bath) gave, after recrystallization from ethanol, 9.0 g (90%) of starting ketone, mp 86–88°, which was identified by its infrared spectrum.

Treatment of 5,5-Dichloro-5H-dibenzo[*a,d*]cycloheptene with Sodium Borohydride.—A 1.0-g (0.0038 mole) portion of dichloride **1** was added to a solution of 1.0 g (0.026 mole) of sodium borohydride in 25 ml of diglyme. After standing overnight, the mixture was concentrated and extracted with benzene. The extract was chromatographed on alumina with 1:1 benzene–ligroin. The first fraction was collected and gave 0.34 g (47%) of 5H-dibenzo[*a,d*]cycloheptene (**15**), mp 130–131°. A mixture melting point with authentic material was not depressed.

Thermal Rearrangement of 5,5-Dichloro-5H-dibenzo[*a,d*]cycloheptene.—A 2.0-g (0.0010 mole) portion of ketone **2** was converted to the 5,5-dichloro compound **1**, as just described, and heated to 160° in an oil bath. Examination of the infrared spectrum of the reaction mixture at various time intervals showed that dichloride **1** was converted to dichloride **4**, and that the rearrangement was essentially complete after 4 hr. The melt crystallized on cooling and, after two recrystallizations from ligroin, gave 1.4 g (70%) of 5,10-dichloro-5H-dibenzo[*a,d*]cycloheptene (**4**), mp 118–120°. A mixture melting point with the independently synthesized material was not depressed.

Acknowledgment.—The author is grateful to Dr. T. H. Regan for the nmr spectra and for helpful suggestions concerning their interpretation.

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(8) W. Treibs and H. J. Klinkhammer, *Chem. Ber.*, **84**, 671 (1951).