[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

Substituted Styrenes. V. Reaction of Styrene and α-Methylstyrene with Dihalocarbenes

WESLEY J. DALE AND PAUL E. SWARTZENTRUBER

Received January 23, 1959

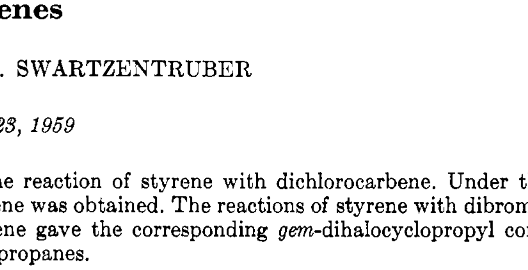
Optimum experimental conditions have been determined for the reaction of styrene with dichlorocarbene. Under the conditions described, a 76% yield of (2,2-dichlorocyclopropyl)benzene was obtained. The reactions of styrene with dibromocarbene and of α-methylstyrene with dichloro- and dibromocarbene gave the corresponding *gem*-dihalocyclopropyl compounds in yields of 72–81%. Reduction of the products yielded cyclopropanes.

In an effort to find confirmatory experimental evidence for the formation of dichlorocarbene as an intermediate in the alkaline hydrolysis of chloroform, Doering and Hoffmann[1] treated chloroform with cyclohexene in the presence of potassium *t*-butoxide and obtained 7,7-dichlorobicyclo[4.1.0]-heptane. Other olefins were found by these workers to react similarly with chloroform and bromoform in the presence of strong bases to give *gem*-dihalocyclopropanes and further examples of this reaction have been reported by Parham,[2] Skell,[3] and their co-workers.

In view of the ease with which dihalocarbenes can be generated in the presence of olefins, it would appear that the application of these reagents to the preparation of cyclopropane derivatives would be limited only by the availability of suitable olefins. Another aspect of the problem is encountered, however, when one considers the electrophilic character of carbenes. Olefins in which the nucleophilic character of the double bond has been reduced by electron-withdrawing groups should react less readily with carbenes than those in which the nucleophilic character has been increased by electron-donating groups. Some evidence in support of this view has been presented by Parham and Wright,[2c] Woodworth and Skell,[3c] and Doering and Henderson.[4]

Numerous investigations in our laboratory have been concerned with the effect of the nature and position of ring substituents on the chemistry of substituted styrenes.[5] The usual nucleophilic character of the double bond of styrene can be greatly diminished or even converted completely to one of electrophilic character, by placing a negative group, such as the nitro group, in the *ortho*- or *para*- position of the styrene nucleus. It is felt that a study of the reactions of dihalocarbenes with styrenes will throw additional light on the general reaction of carbenes with olefins, as well as in the formation of previously unreported cyclopropanes.

In the present study, dichloro- and dibromocarbene have been allowed to react with styrene (Ia) and α-methylstyrene (Ic) and the products have been reduced to phenylcyclopropanes by sodium and methanol.



a. R = H, X = Cl
b. R = H, X = Br
c. R = CH_3, X = Cl
d. R = CH_3, X = Br

Optimum conditions for the reaction of styrenes with carbenes were first determined by a study of the reaction of styrene itself with dichlorocarbene. The conditions were varied as to reaction time, temperature, solvent and ratio of styrene to dichlorocarbene. The best yields (71–76%) of (2,2-dichlorocyclopropyl)benzene (IIa) were obtained when an excess of styrene was used as the solvent for the reaction, the styrene being present in a molar ratio, to the dichlorocarbene, of from 4:1 – 6:1. Long reaction times (18–24 hr.) and low temperatures (−5 to −10°) were also found to increase the yields. These conditions were used to advantage in

---

(1) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(2) (a) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Am. Chem. Soc.*, **78**, 1437 (1956). (b) W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **22**, 730 (1957). (c) W. E. Parham and C. D. Wright, *J. Org. Chem.*, **22**, 1473 (1957).

(3) (a) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956). (b) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956). (c) R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **79**, 2542 (1957).

(4) W. von E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, **80**, 5274 (1958).

(5) (a) W. J. Dale, *J. Am. Chem. Soc.*, **76**, 6172 (1954). (b) W. J. Dale and G. Buell, *J. Org. Chem.*, **21**, 45 (1956). (c) W. J. Dale and L. Levine, Abstracts of the Organic Division of the 128th Meeting of the American Chemical Society, Minneapolis, 1955. (d) W. J. Dale and H. E. Hennis, *J. Am. Chem. Soc.*, **80**, 3645 (1958). (e) W. J. Dale and H. E. Hennis, *J. Am. Chem. Soc.*, **81**, 2143 (1959). (f) W. J. Dale and G. W. Eigenmann, Abstracts of the Organic Division of the 132nd Meeting of the American Chemical Society, New York, 1957.

subsequent reactions to give good yields of products in every case. (2,2-Dibromocyclopropyl)benzene (IIb) was obtained in a 72% yield from the reaction of styrene with dibromocarbene. The reactions of α-methylstyrene (Ic) with dichlorocarbene and dibromocarbene gave (2,2-dichloro-1-methylcyclopropyl)benzene (IIc, 75%) and (2,2-dibromo-1-methylcyclopropyl)benzene (IId, 81%), respectively. It is evident from these results that the increased steric factor presented by the α-methyl group is not sufficiently great to cause a decrease in the yield of product. Rather, the increased yield of IId might be attributed to the increased nucleophilic character of the double bond due to the presence of the methyl group.

Each of the above *gem*-dihalocyclopropanes underwent reduction when allowed to react with sodium metal and wet methanol. Thus, (2,2-dichlorocyclopropyl)benzene (IIa) and (2,2-dibromocyclopropyl)benzene(IIb) yielded identical products (cyclopropylbenzene, IIIa), in 74% and 69% yields, respectively. Similarly, (2,2-dichloro-1-methylcyclopropyl)benzene (IIc) and (2,2-dibromo-1-methylcyclopropyl)benzene (IId) were reduced to the same product, (1-methylcyclopropyl)benzene (IIIc), in 54% and 40% yields, respectively.

An attempt was made to hydrolyze (2,2-dichlorocyclopropyl)benzene (IIa) using the method employed successfully by Schmerling[6] for the hydrolysis of *gem*-dichlorides to ketones. When the compound was heated with water in a sealed Pyrex tube at 200–205° for 4$^1/_2$ hr., however, only black polymeric material was obtained. Under less drastic conditions (105–110° for 4 hr.), only starting material was recovered, even in the presence of sodium carbonate.

EXPERIMENTAL

All boiling points and melting points are uncorrected.

The reaction of styrene, chloroform, and potassium t-butoxide. (2,2-Dichlorocyclopropyl)benzene (IIa). Potassium *t*-butoxide was prepared by the addition of 10.0 g. (0.256 g. atom) of clean potassium metal to an excess of refluxing anhydrous *t*-butyl alcohol. Following complete solution of the metal, the excess *t*-butyl alcohol was removed by distillation under reduced pressure. The solid cake of white salt which remained was broken into fine pieces by means of a glass rod. An atmosphere of nitrogen was maintained in the reaction flask during the preparation of the potassium *t*-butoxide and its subsequent reaction with the styrene and haloform.

The flask containing the potassium *t*-butoxide was cooled in an ice–salt bath (−5° to −10°) and 156 g. (1.50 moles) of freshly distilled styrene was added.[6] The bright green color which developed when the styrene came in contact with the potassium *t*-butoxide was due to the presence of 4-*t*-butylpyrocatechol, added to the styrene as an inhibitor. Dry, freshly distilled chloroform (29.9 g., 0.250 mole) was then added, dropwise, to the well stirred mixture over a period of 1 hour. When the addition of the chloroform was complete, the mixture was stirred in the ice–salt bath for an additional 3 hr. The flask was then stoppered and placed in a refrigerator at 10° for 18 hr.

The reaction mixture was then allowed to come to room temperature and 200 ml. of water was added. The slightly basic mixture was carefully neutralized with dilute hydrochloric acid and the organic and aqueous layers were separated. The aqueous layer was extracted three times with light petroleum ether (b.p. 80–86°), the combined extracts and original organic layer were washed with two 100-ml. portions of water, and the solution was dried over Drierite. The solvent was removed by distillation at atmospheric pressure and the remaining material was fractionally distilled under vacuum. The product, (2,2-dichlorocyclopropyl)benzene (IIa), (35.7 g., 76%) was obtained as a colorless, sweet smelling liquid, b.p. 78–83° (2 mm.), n_D^{25} 1.5498–1.5500.

Refractionation through a Todd Precise Fractionation Assembly gave a pure sample boiling at 114° (13 mm.), n_D^{23} 1.5501. Infrared absorption maxima occur at 3.45 (m), 6.27(m), 6.66(s), 6.88(s), 7.00(s), 8.13(s), 8.38(m), 8.95(s), 9.26(s), 9.55(s), 9.75(s), 10.54(m), 10.74(m), 11.00(w), 11.46(w), 12.86–12.93(s), 13.32(s), 13.60–13.67(s), and 14.33–14.40(s)μ.

Anal. Calcd. for $C_9H_8Cl_2$: C, 57.78; H, 4.31. Found: C, 57.69; H, 4.62.

The procedure described above was found to give the best yield of IIa. Variations on this procedure gave the following results: (a) When the chloroform was added to the mixture of styrene and potassium *t*-butoxide over a period of 30 min. at 0°, and the reaction mixture was stirred for an additional 45 min., only a 50% yield of product was obtained. (b) When the temperature of the exothermic reaction was permitted to rise to 60–80°, the other conditions being similar to (a), a yield of only 26% was obtained. This low yield is probably due to the loss of chloroform by evaporation before the reaction can take place. (c) When the procedure was varied only by reducing the molar ratio of styrene to dichlorocarbene from 6:1 to 4:1, the yield was reduced from 76% to 71%. Reducing the ratio to a point (1:1.3) where another solvent (benzene) was necessary, reduced the yield of product to 15%.

The reaction of styrene, bromoform, and potassium t-butoxide. (2,2-Dibromocyclopropyl)benzene (IIb). The reaction was performed as described in detail above for (2,2-dichlorocyclopropyl)benzene, using potassium *t*-butoxide prepared from 10.0 g. (0.256 g. atom) of potassium metal, freshly distilled bromoform (63.2 g , 0 250 mole), and styrene (156 g., 1.50 moles) Fractional distillation of the reaction product yielded 49.9 g. (72%) of (2,2-dibromocyclopropyl)benzene (IIb) obtained as a colorless liquid, b.p. 88–98° (1 mm.), n_D^{22} 1.5982–1.5989. Refractionation through a 10-cm. Vigreux column yielded a middle fraction boiling at 97° (1 mm.), n_D^{22} 1.5988 (lit.,[3b] b.p. 94° (2 mm.), n_D^{25} 1.5963). The infrared spectrum exhibits bands at 3.20(m), 6.24(m), 6.67(s), 6.90(s), 7.04(m), 8.15(w), 8.98(s), 9.23(m), 9.58(s), 9.72(s), 10.66(m), 10.79(m), 13.01(s), 13.58(s), 14.27–14.35(s), and 14.63–14.77(s)μ.

Anal. Calcd. for $C_9H_8Br_2$: C, 39.17; H, 2.92. Found: C, 39.30; H, 3.16.

The reaction of α-methylstyrene, chloroform, and potassium t-butoxide. (2,2-Dichloro-1-methylcyclopropyl)benzene (IIc). In the manner described for the analogous reaction of styrene, 29.9 g. (0.250 mole) of chloroform was added dropwise to a cold (about −5°), well stirred mixture of α-methylstyrene (Ic) (177 g., 1.50 moles) and potassium *t*-butoxide, prepared from 10.0 g. (0.256 g. atom) of potassium. Following the addition of the chloroform (about 45 min.), the mixture was stirred an additional 4 hr. at −5° and then placed in a refrigerator at 10° for 38 hr. The product was isolated as described above. The yellow liquid obtained was fractionated under reduced pressure to give 37.9 g. (75%) of (2,2-dichloro-1-methylcyclopropyl)benzene (IIc) as a colorless liquid, b.p. 77–81° (5 mm.), n_D^{22} 1.5404–1.5406. Redistillation through a 15-cm. Vigreux column yielded a middle fraction boiling at 75–77° (1 mm.), n_D^{22} 1.5406. Absorption maxima occur in the infrared at 3.25(m), 3.29(m), 3.33(m), 3.40(m), 3.47(m), 6.24(m), 6.69(s), 6.93(s), 7.03(m), 7.24(m),

---

(6) L. Schmerling, *J. Am. Chem. Soc.*, 68, 1650 (1946).

7.95(w), 8.97(m), 9.16(m), 9.28(s), 9.54(s), 9.67(s), 10.68(m), 10.95(w), 11.28(m), 12.86–12.98(s), 13.25(s), and 14.20–14.33(s)μ.

Anal. Calcd. for $C_{10}H_{10}Cl_2$: C, 59.72; H, 5.01. Found: C, 59.85; H, 5.28.

The reaction of α-methylstyrene, bromoform, and potassium t-butoxide. (2,2-Dibromo-1-methylcyclopropyl)benzene (IId). α-Methylstyrene (177 g., 1.50 moles) was reacted with 63.2 g. (0.250 mole) of bromoform and potassium *t*-butoxide, from 10.0 g. (0.256 g. atom) of potassium, in the manner described for the reaction of α-methylstyrene and chloroform. The reaction product, (2,2-dibromo-1-methylcyclopropyl)benzene (IId) (58.9 g., 81%) was obtained as a colorless liquid, b.p 94–100° (2 mm.), n_D^{22} 1.5831–1.5848. A refractionation of the product through a 15-cm. Vigreux column yielded a middle fraction boiling at 91–92° (1 mm.), n_D^{22} 1.5842. The product solidified upon cooling, m.p. 35.5–36°. The infrared spectrum exhibits absorption maxima at 3.28(m), 3.31(m), 3.38(s), 3.43(m), 3.50(m), 6.24(m), 6.32(w), 6.69(s), 6.94(s), 7.00(s), 7.24(m), 7.57(w), 7.66(w), 7.98(w), 8.71(m), 8.99(m), 9.32(s), 9.42(s), 9.80(s), 10.73(m), 10.97(m), 11.59(m), 11.79(m), 13.10(s), and 14.30–14.41 (s)μ.

Anal. Calcd. for $C_{10}H_{10}Br_2$: C, 41.41; H, 3.48. Found: C, 41.55; H, 3.55.

The reduction of (2,2-Dichlorocyclopropyl)benzene with sodium and methanol. Cyclopropylbenzene (IIIa). The method described by Doering and Hoffmann[1] for the reduction of 7,7-dibromobicyclo[4.1.0] heptane was employed with only slight modification. Following the complete reaction of the sodium metal (46 g., 2.0 g. atoms) with the wet methanol (10 ml. of water to 300 ml. of methanol), 200 ml. of water was added, the layers were separated, and the aqueous layer was neutralized with hydrochloric acid before being extracted with ether. From 18.7 g. (0.100 mole) of (2,2-dichlorocyclopropyl)benzene (IIa) there was obtained 8.7 g. (74%) of cyclopropylbenzene as a colorless liquid, b.p. 64–70° (18 mm.). A redistillation of the product through a Todd Precise Fractionation Assembly yielded a middle fraction boiling at 69° (12 mm.), n_D^{22} 1.5316, d_4^{20} 0.936; M_D calcd. 38.8, M_D found 39.1 (lit., b.p. 60–63° (11 mm.), 7 n_D^{20} 1.5320,[7] d_D^{25} 0.9374[8]). Absorption maxima were observed in the infrared at 3.24(s), 6.22(s), 6.64(s), 6.80(s), 6.89(m), 6.97(m), 8.18(m), 8.49(w), 9.05(w), 9.22(s), 9.53(s), 9.74(s), 10.03(w), 11.11(s), 12.28(s), 13.26–13.37(s), and 14.30–14.39(s)μ.

Anal. Calcd. for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.21; H, 8.51.

The reduction of (2,2-dibromomocyclopropyl)benzene with sodium and methanol. Cyclopropylbenzene (IIIa). (2,2-Dibromocyclopropyl)-benzene (IIb) (27.6 g., 0.100 mole) was reduced with 46 g. (2.0 g. atoms) of sodium and 300 ml. of wet methanol in the above manner. The product obtained (8.1 g., 69%) was identical with that obtained from the dichloro compound as evidenced by both boiling point (65° at 17 mm.) and refractive index (n_D^{22} 1.5315).

The reduction of (2,2-dichloro-1-methylcyclopropyl)benzene and (2,2-dibromo-1-methylcyclopropyl)benzene with sodium and methanol. (1-Methylcyclopropyl)benzene (IIIc). By the method described above, 10.1 g. (0.050 mole) of (2,2-dichloro-1-methylcyclopropyl)benzene (IIc) was reduced with 23 g. (1.0 g. atom) of sodium and 200 ml. of wet methanol to give 3.5 g. (54%) of colorless (1-methylcyclopropyl)-benzene (IIIc), b.p. 72–77° (22 mm.), n_D^{21} 1.5146–1.5150. Refractionation of the product through a 10-cm. Vigreux column yielded a middle fraction boiling at 69° (18 mm.), n_D^{21} 1.5151. The reduction of 21.8 g. (0.075 mole) of (2,2-dibromo-1-methylcyclopropyl)benzene (IId) by 32 g. (1.4 g. atoms) of sodium and 300 ml. of wet methanol yielded 4.0 g. (40%) of (1-methylcyclopropyl)benzene (IIIc), b.p. 70–74° (22 mm.), n_D^{21} 1.5152–1.5157. Redistillation of the product through a 10-cm. Vigreux column yielded a middle fraction boiling at 71° (20 mm.), n_D^{21} 1.5152. The infrared absorption spectrum of the product exhibits maxima at 3.22(s), 3.29(s), 3.35(s), 3.45(m), 6.22(s), 6.31(w), 6.66(s), 6.86(s), 6.92(s), 7.00 (m), 7.23(m), 7.42(w), 8.93(s), 9.24(w), 9.33(m), 9.71(s), 9.86(s), 10.72(m), 11.07(w), 11.61(w), 11.81(s), 12.73(w), 13.13–13.23(s), and 14.24–14.35(s)μ.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.56; H, 9.04.

COLUMBIA, MO.

---

(7) G. S. Hammond and R. W. Todd, *J. Am. Chem. Soc.*, **76**, 4081 (1954).

(8) M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Preparation of Polymers Containing Pyridine Units from Polyvinyl Ketones

C. S. MARVEL AND DONALD J. CASEY[1]

Received January 19, 1959

Poly(methyl vinyl ketone) was converted to the polyoxime and this polymer, under the conditions of the Knoevenagel 1,5-dioxime ring closure, gave a copolymer of methyl vinyl ketone with some 2,6-dimethylpyridine units which consisted of 76.2 mole % of the latter. Similarly a copolymer of phenyl vinyl ketone and phenyl vinyl ketoxime containing 70.2 mole % ketoxime units was converted to a copolymer of phenyl vinyl ketone and 2,6-diphenylpyridine units which consisted of 50.3 mole % of the latter. Neither copolymer was thermally stable.

The marked thermal and chemical stability of the pyridine nucleus prompted an investigation of the heat resistance of polymers which incorporate a pyridine ring as a structural feature of the polymer chain. A promising approach to the desired polymers was suggested by the work of Marvel and Levesque[2] on the structure of low molecular weight poly(methyl vinyl ketone). During this

---

(1) The work discussed herein was supported by Contracts AF 33(616)-3772 and -5486 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. Reproduction of this paper in whole or in part is permitted for any purpose of the United States Government. This paper is based on portions of a thesis submitted by Donald J. Casey to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) (a) C. S. Marvel and C. L. Levesque, *J. Am. Chem. Soc.*, **60**, 280 (1938). (b) C. S. Marvel and C. L. Levesque, *J. Am. Chem. Soc.*, **61**, 3234 (1939).