BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 567—569 (1969)

Protonation of Allene. Evidence for the Formation of 1,1-Diphenyl-3,3-dibromoprop-1-ene

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(Received June 21, 1968)

It has been reported[1] that the action of phosphorus tribromide on 1,1-diphenylprop-2-yn-1-ol (I) in acetic acid affords 1,1-diphenyl-3,3-dibromoprop-1-ene (VIII) (mp 82°C) and that the reaction proceeds *via* the bromoallene intermediate II, as is shown in Scheme 1. Recently, Martinet and Doupeux[2] have reported the formation of 1,1-diphenyl-1,3-dibromoprop-2-ene (IX) (mp 81—82°C) by the reaction of hydrogen bromide and 1,1-diphenyl-3-bromopropa-1,2-diene (II), which had been isolated by the action of phosphorus tribromide on I in hexane.

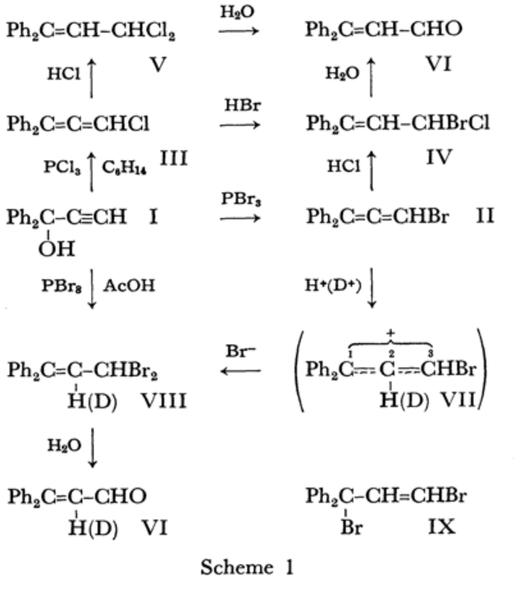
Our treatment of II with hydrogen bromide afforded crystals (mp 82°C) which were identical with those obtained previously.[2] However, some physical data (mp, infrared and NMR spectra) reported[2] for IX were identical with those of VIII. These ambiguous results prompted us to reinvestigate the structure of the dibromide and then the protonation of bromoallene II.

An evidence that the dibromide is allylic *gem*-dibromide (VIII) but not 1,3-dibromide (IX) was obtained by the following cross-addition reactions. 1,1-Diphenyl-3-bromo-3-chloroprop-1-ene (IV) (mp 50—52°C), derived from II and hydrogen chloride, was identical with that obtained from the chloro-analog of II (III) and hydrogen bromide, as is shown in Scheme 1. Since the treatment of II with a large excess of hydrogen bromide or of hydrogen chloride afforded VIII or dichloro-analog V, phosphorus trihalide in acetic acid was used as the source of hydrogen halide in order to avoid the presence of excess hydrogen halide. The bromochloro compound, IV, thus obtained was different from the dichloro-analog, V (mp 23.5—24°C), prepared by the addition of hydrogen chloride to III. The infrared spectra of IV and V were almost identical with that of VIII. The acid- or base-catalysed hydrolysis of IV and V gave 1,1-diphenylprop-1-en-3-al (VI), as in the case of VIII.[1] Finally, the structure of the dibromide reported in two previous articles[1,2] may be identified as allylic *gem*-dibromide VIII.

The above results led us to the following speculation. The cation in which the plus charge is located on C-3, $\rangle C{=}CH{-}\overset{+}{C}HBr$, may be more stable than that in which the charge is on C-1, $\rangle\overset{+}{C}{-}CH{=}CHBr$. The stability of the former may be due to a longer conjugate system for the delocalization of the positive charge.

The ultraviolet spectrum[1] of VIII, 242 (10200), 266 (14700), and 273 mμ (ε, 16500), shows the presence of a conjugate system corresponding to 1,1-diphenylethylene and supports the structure VIII. Martinet and Doupeux have assigned the structure IX to the dibromide on the basis of the infrared and NMR spectra, but not the ultraviolet spectrum. We have tried to identify the infrared and NMR spectral bands of VIII, by which they were misled to determine the structure of the dibromide to be IX.

The infrared spectrum of VIII showed a strong band at 880 cm^{-1}, as is shown in Fig. 1. In order to identify this band, VIII-2-d was prepared by the addition of deuterium bromide to II. In VIII-2-d, the 880 cm^{-1} band shifted to 735 cm^{-1}. Therefore, the band may be assigned to the out-of-plane deformation of $\overset{2}{C}$–H. This assignment is reasonable



Scheme 1

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[1] H. Tani and F. Toda, This Bulletin, **37**, 470 (1964).

[2] P. Martinet and H. Doupeux, *Compt. rend.*, **261**, 2498 (1965).

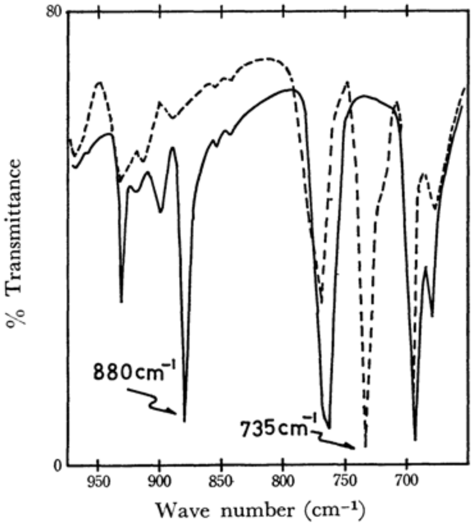

Fig. 1. The infrared spectra of VIII (——) and VIII-2-d (------).

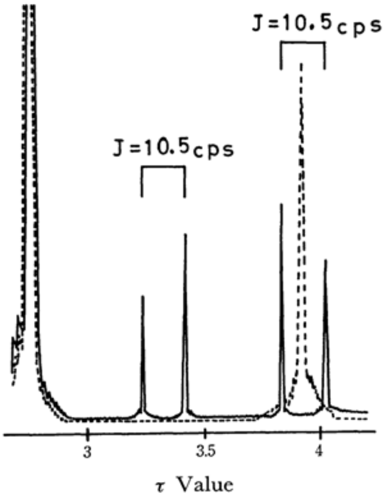

Fig. 2. The NMR spectra of VIII (——) and VIII-2-d (------).

since it is well known[3] that the general frequency for the CH out-of-plane deformation of trisubstituted ethylene, 840—800 cm^{-1}, varies with the change in substituents.

As is shown in Fig. 2, the NMR spectrum of VIII showed a multiplet (centered at 2.70, phenyl) and two doublets (centered at 3.35, J=10.5 cps and centered at 3.95τ, J=10.5 cps) in the integrated ratio of 10 : 1 : 1. Martient and Doupeux have identified the two doublets as two vinyl hydrogens of IX. However, since the structure VIII instead of IX was confirmed to be correct, the two doublets may be assinged to vinyl and allylic hydrogens. The doublet at the lower field, which disappeared in the spectrum of VIII-2-d (Fig. 2), may be attributed to the vinyl hydrogen. The remaining signal may be due to the allylic hydrogen. The observed value, 3.95τ, of the allylic methine hydrogen agrees fairly well with that calculated, 3.78τ, according to Shoolery's equation[4] using 2.33 and 1.32 ppm as the effective shielding constants of bromine and diphenylethylene respectively.

Experimental[5]

Instrumental Analyses. The infrared spectra were recorded in Nujol mull on a grating spectrophotometer, IR-G, of Japan Spectroscopic Co. The NMR spectra were recorded in carbon tetrachloride on a Japan Electron Optics Laboratory C-60 spectrometer, using TMS as the internal standard.

1,1-Diphenyl-3-bromopropadiene (II) and 1,1-Diphenyl-3-chloropropadiene (III). A solution of I (3.0 g, 15 mmol) in hexane (40 m*l*) was cooled to *ca.* −25°C with a dry ice-methanol bath. Into the solution, phosphorus tribromide (4.0 g, 15 mmol) was stirred over a 20-min period. The stirring was then continued for a further 2 hr at *ca.* −25°C. The crystalline solid recrystallized from hexane afforded II as colorless needles, 3.0 g (74%), mp 74.5—75°C (lit.[2] mp 67—69°C). IR: 1926 cm^{-1} ($\nu_{C=C=C}$).

Found: C, 66.07; H, 3.89%. Calcd for $C_{15}H_{11}Br$: C, 66.38; H, 4.06%.

The treatment of I with phosphorus trichloride in hexane under the conditions employed for the preparation of II afforded III as colorless needles in a 59% yield after recrystallization from hexane, mp 46.5—48.5°C. IR: 1930 cm^{-1} ($\nu_{C=C=C}$).

Found: C, 78.72; H, 4.58%. Calcd for $C_{15}H_{11}Cl$: C, 79.43; H, 4.91%.

1,1-Diphenyl-3,3-dibromoprop-1-ene (VIII) and 1,1-Diphenyl-3,3-dibromoprop-1-ene-2-d (VIII-2-d). The dibromide VIII was prepared by the reaction of I and phosphorus tribromide in acetic acid[1] or by that of II and hydrogen bromide in hexane,[2] mp 82°C (lit.[1] 82°C: lit.[2] 81—82°C). The mixed melting point of the dibromides prepared according to the methods of those two articles showed no depression.

The deuterated dibromide, VIII-2-d, was obtained by the reaction of II and deuterium bromide[6] in hexane; it consisted of colorless prisms, mp 82°C. IR: 2500 ($\nu_{=C-D}$) and 735 cm^{-1} ($\delta_{=C-D}$). NMR: 2.70 (multiplet, phenyl, 10 H) and 3.95τ (singlet, methine, 1H). The acid- or base-catalyzed hydrolysis of VIII-2-d afforded VI-2-d in a quantitative yield. For VI-2-d, the CH out-of-plane deformation of trisubstituted ethylene of VI, 880 cm^{-1}, was shifted to 755 cm^{-1}.

1,1-Diphenyl-3-bromo-3-chloroprop-1-ene (IV). *A*)

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[3] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London (1958), p. 31.

[4] B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

[5] All melting points are corrected.

[6] Deuterium bromide was prepared by the reaction of phosphorus tribromide and deuterium oxide, according to the reported procedure: H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964).

Into an ice-cooled mixture of II (2.58 g, 9 mmol) and acetic acid (5 m*l*), phosphorus trichloride (1.5 g, 10 mmol) was stirred over a 5-min period. The stirring was continued for a further 30 min, and the reaction mixture was decomposed with water and extracted with ether. The ether layer was washed with water and dried over sodium sulfate, and the solvent was evaporated to dryness to leave IV as colorless leaflets, 0.9 g (37%), mp 50—52°C,. IR: 875 cm^{-1} ($\delta_{=C-H}$).

Found:[*1] C, 56.96; H, 3.70%. Calcd for $C_{15}H_{12}BrCl$: C, 58.54; H, 3.90%.

B) Into an ice-cooled mixture of III (1.7 g, 7.5 mmol) and acetic acid (5 m*l*), phosphorus tribromide (1.0 g, 3.5 mmol)[*2] was stirred over a 5-min period. Crystalline solid 1.3 g (56%), mp 50—52°C. A mixed-melting-point determination with crystals obtained by the procedure A showed no depression. The infrared spectrum was identical with that of crystals obtained by the procedure A. The acid- or base-catalyzed hydrolysis of IV afforded VI in a quantitative yield, mp 44°C. A mixed-melting-point determination with an authentic specimen (lit.[7]) mp 44.5—45.5°C) showed no depression.

1,1-Diphenyl-3,3-dichloroprop-1-ene (V). Into an ice-cooled solution of I (3.0 g, 15 mmol) in acetic acid (5 m*l*), phosphorus trichloride (4.0 g, 30 mmol) was stirred over a 5-min period. After 2 days, the reaction mixture was decomposed with water and extracted with ether. The ether layer was washed with water and dried over sodium sulfate. The crude oil remaining after the evaporation of the solvent was distilled to afford V, 2.3 g (65%), bp 134°C/2 mmHg, mp 23.5—24°C. IR: 1617 ($\nu_{C=C}$) and 876 cm^{-1} ($\delta_{=C-H}$). The spectrum was similar to those of VIII and IV.

Found: C, 68.28; H, 4.31%. Calcd for $C_{15}H_{12}Cl_2$: C, 68.44; H, 4.56%.

The acid or base-catalyzed hydrolysis of V afforded VI in a quantitative yield, mp 44°C. A mixed-melting-point determination with an authentic sample (lit.[7]) mp 44.5—45.5°C) showed no depression.

The treatment of III with hydrogen chloride in hexane also afforded V in a quantitative yield.

[*1] Since the bromochloride IV was converted into dibromide VIII and dichloride V gradually by repeated recrystallizations from hexane, it was difficult to purify it further.

[*2] When a large excess of phosphorus tribromide was used, dibromide VIII was isolated as the sole product.

[7] H. Lorenz and R. Wizinger, *Helv. Chim. Acta*, **28**, 600 (1945).