Studies on Fluorene Derivatives. XXI. The Radical Bromination of Dibiphenyleneethane and Its Derivatives by N-Bromosuccinimide*

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N-Bromosuccinimide (NBS) has been used as a brominating agent¹⁾ for a wide variety of organic compounds and as an oxidizing agent for some alcohols.

The present investigation is concerned with the reaction of NBS with dibiphenyleneethane and its bromoderivatives in order to introduce, selectively, a bromine atom on a methine group adjacent to an aromatic ring. These compounds were used further to prepare tribiphenylene-propane and its bromo derivatives by a halogen-metal interconversion reaction between 9-fluorenyl lithium and substituted 9-bromodibiphenyleneethane.²⁾

The bromination reaction was carried out readily by refluxing the hydrocarbons with equimolar quantites of NBS in absolute benzene for 4 hr. Fluorene,³⁾ 2-bromofluorene (70%)⁴⁾ and 2, 7-dibromofluorene (89%) react with NBS in benzene to give fairly good yields of the corresponding 9-bromosubstituted fluorenes. With dibiphenyleneethane it was possible, by selective bromination, to prepare mono or dibromosubstituted ethanes with high yields.

Two isomers were expected in the reaction of NBS with 2-bromodibiphenyleneethane. The structure of one, 2, 9′-dibromodibiphenyleneethane (see Table I, Run 6), was confirmed by synthesis from hydrogen bromide and 2-bromo-9′-hydroxydibiphenyleneethane. The reaction of 2, 7-dibromodibiphenyleneethane⁵⁾ with NBS also yielded two isomers, the structures of which were proved by independent syntheses.

The reaction of the symmetrical compounds, 2, 2′-,⁶⁾ 3, 3′-⁷⁾ and 4, 4′-dibromodibiphenyleneethanes,⁸⁾ with equimolar quantities of NBS gave the corresponding 2, 2′, 9-, 3, 3′, 9- and 4, 4′, 9-tribromodibiphenyleneethanes.

These results are summarized in Table I, which gives data on several preparations made under almost identical conditions.

It is very difficult to introduce a bromine atom on the 9-position of 1, 1′-dibromodibiphenyleneethane⁹⁾ with NBS. Both of the starting materials were recovered even after having been refluxed for 10 hr. periods, per-

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TABLE I

Run	Compd.	g.	Brominating agent	g.	Solvent	ml.	Reaction condition time or temp.	Reaction product	Recryst. solvent	M. p. °C	Yield g.	Analyses and mixed m. p. Mol. Formula	Bromine, % Found	Bromine, % Calcd.
1	D	1.0	NBS	0.54	Benzene	20	4 hr.	9-Bromo-D[10]	Benzene	168∼170(d)	1.03	By mixed melting points and IR absorption spectrum		
2	D	1.0	NBS	0.7	Benzene	20	4 hr.	9, 9′-Dibromo-D[11]	Benzene	243(d)	1.12	By mixed melting points and IR absorption spectrum		
3	D	1.0	Br_2	0.5	$CHCl_3$	10	8 hr. 25°C	2-Bromo-D[12]	Alcohol	227∼229	0.39	By mixed melting points and IR absorption spectrum		
								9-Bromo-D	Benzene	166∼168(d)	0.05			
								9, 9′-Dibromo-D	Benzene	240∼242(d)	0.1			
								Oily product			0.3			
4	D	1.0	Br_2	0.5	CCl_4	100	9 hr. 25°C	Fluorenone[13]	Alcohol	83∼ 84	0.3	By mixed melting points and IR absorption spectrum		
								9, 9′-Dibromo-D	Benzene	240∼241(d)	0.65			
								10, 10-Diphenylene-9-phenanthrone	Benzene	256∼259(d)	0.02			
5	D	1.0	Br_2	0.5	CS_2	50	8 hr. 25°C	9-Bromo-D	Benzene	166∼167(d)	0.74	By mixed melting points and IR absorption spectrum		
								Dibiphenylene-ethylene[15]	Acetic ester	187	0.01			
								9, 9′-Dibromo-D	Benzene	241(d)	0.09			
6	2-Bromo-D	1.0	NBS	0.43	Benzene	20	4 hr.	2, 9-Dibromo-D[12]	Benzene	197∼199(d)	0.33	By mixed melting points and IR absorption spectrum		
								2, 9′-Dibromo-D	Cyclohexane	146∼148(d)	0.05	$C_{26}H_{16}Br_2$	32.51	32.74
7	2-Bromo-D	1.0	NBS	0.86	Benzene	20	4 hr.	2, 9, 9′-Tribromo-D	Benzene	198∼200(d)	0.5	$C_{26}H_{15}Br_3$	42.05	42.27
8	2, 2′-Dibromo-D	1.0	NBS	0.35	Benzene	20	4 hr.	2, 2′, 9-Tribromo-D	Acetic ester Benzene	195∼196(d)	0.41	$C_{26}H_{15}Br_3$	42.45	42.27
9	2, 2′-Dibromo-D	1.0	NBS	0.7	Benzene	20	5 hr.	2, 2′, 9, 9′-Tetrabromo-D	Acetic ester Benzene	214∼215(d)	0.3	$C_{26}H_{14}Br_4$	49.08	49.48
10	2, 7-Dibromo-D	1.0	NBS	0.35	Benzene	20	4 hr.	2, 7, 9-Tribromo-D	Acetic ester	216∼217(d)	0.01	$C_{26}H_{15}Br_3$	42.10	42.27
								2, 7, 9′-Tribromo-D	Benzene	206∼207(d)	0.43	$C_{26}H_{15}Br_3$	42.47	42.27
11	3, 3′-Dibromo-D	1.0	NBS	0.35	Benzene	20	4 hr.	3, 3′, 9-Tribromo-D	Cyclohexane Benzene	208∼210(d)	0.25	$C_{26}H_{15}Br_3$	41.70	42.27
12	4, 4′-Dibromo-D	1.0	NBS	0.35	Benzene	20	4 hr.	4, 4′, 9-Tribromo-D	Cyclohexane Benzene	201∼203(d)	0.28	$C_{26}H_{15}Br_3$	41.80	42.27

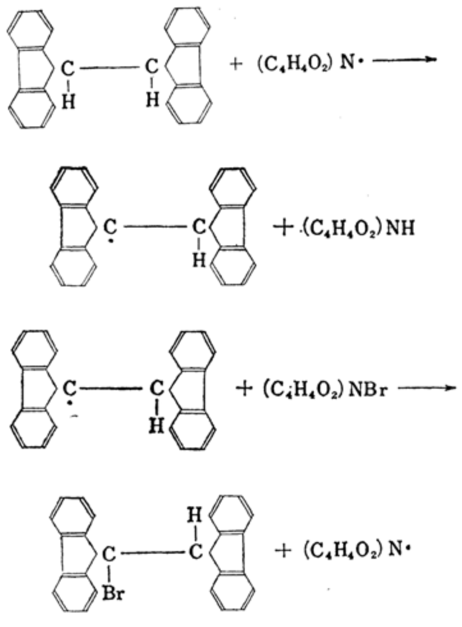
D: Dibiphenyleneethane

(d): Decomposition: These compounds were red colored because of the formation of dibiphenyleneethylenes at their melting points.

Run 5: Three products were separated by chromatography in benzene on alumina.

haps, because of the greater steric hindrance of the bromine atoms at the 1-positions.

These reactions proceed through a thermal, homolytic dissociation of the N–Br bond in NBS, followed by the abstraction of hydrogen from the methine groups by the free radical, and they involve chain termination accompanied by the formation of succinimide. The general mechanism acceptable for the bromination of dibiphenyleneethane derivatives may be visualized as follows:



However, it should be mentioned in connection with these results that, from the direct action of equimolar quantities of bromine on dibiphenyleneethane, small amounts of fluorenone and 10, 10-diphenylen-9-phenanthrone were isolated in carbon tetrachloride. In carbon disulfide, dibiphenylene-ethylene was formed. These compounds result from the formation of 9-bromo-substituted products followed by the evolution of hydrogen bromide. In addition, a small amount of nuclear-substituted 2-bromodibiphenyleneethane was obtained in the reaction carried out in chloroform. From these results, it seems likely, that the reactions with bromine proceed by an ionic mechanism.

Experimental*

The General Reaction Procedure of Dibiphenyleneethanes with *N*-Bromosuccinimide.—To dibiphenyleneethane (1 g., 0.003 mol.) in dry benzene (20 ml.) *N*-bromosuccinimide (0.54 g., 0.003 mol.) was added, and the mixture was refluxed for 4 hr. The orange solution turned red. After this solution had cooled, the succinimide (0.3 g., m. p. 123°C) formed was filtered, and the benzene was removed in vacuo. The crystal mass was digested with water, then recrystallized from cyclohexane after it had been dried. When it had been cooled, a first crop of 0.91 g. of 9-bromodibiphenyleneethane was obtained. The concentration of the mother liquor gave a second crop of 0.12 g. of almost colorless hexagonal crystals. The yield was 84.4%; m. p. 168∼170°C. The structure was proved by a mixed melting point determination with an authentic sample of 9-bromodibiphenyleneethane, with had been prepared by the reaction of 9-hydroxydibiphenyleneethane and hydrogen bromide in acetic acid.

The Reaction of 2-Bromofluorene or 2, 7-Dibromofluorene with *N*-Bromosuccinimide.—A mixture of *N*-bromosuccinimide (3.6 g., 0.02 mol. or 5.5 g., 0.03 mol.) and 2-bromofluorene (5.0 g., 0.02 mol.) or 2, 7-dibromofluorene (10.0 g., 0.03 mol.) respectively in dry benzene (20 ml. or 50 ml.) was refluxed for 4 or 5 hr. After the mixture had been cooled, the succinimide was filtered off. Evaporation of the solvent, and recrystallization of the residue from dry cyclohexane or dry benzene, resulted in 4.5 g. (70.3%) of 2, 9-dibromofluorene (m. p. 118∼120°C) and 11.0 g. (88.6%) of 2, 7, 9-tribromofluorene (m. p. 190∼192°C). These products were identified by a comparison of mixed melting points and infrared absorption spectrum with authentic samples.

The General Reaction Procedure for the Bromination of Dibiphenyleneethane. — To a stirred solution of 1.0 g. (0.003 mol.) of dibiphenyleneethane in 20 ml. of chloroform, there was added very slowly, over an 8 hr. period, 0.5 g. (0.003 mol.) of bromine in 10 ml. of a chloroform solution at 25°C, followed by an additional hour of stirring. Shortly after the addition had begun, hydrogen bromide was evolved. The orange-red reaction mixture was washed with water and dried over anhydrous calcium chloride, and the chloroform was evaporated to a small volume at reduced pressure; when this had been cooled, the deposited material was filtered and recrystallized from benzene to give 9, 9′-dibromodibiphenyleneethane (m. p. 238∼242°C (decomp.)) (0.1 g.).

The first chloroform mother liquor was evaporated to one-half its original volume, and the precipitate was digested with hot cyclohexane. 2-Bromodibiphenyleneethane was obtained in the form of colorless needles, which recrystallized from alcohol to give 0.39 g. (m. p. 227∼229°C).

The second chloroform mother liquor was evaporated to dryness, and the oily solid was recrystal-

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* All the melting points are uncorrected.

lized from benzene, giving 0.05 g. of 9-bromodibiphenyleneethane (m. p. 166~168°C (decomp.)). These three compounds were identified by a comparison of melting points, mixed melting points and infrared absorption spectrum with authentic samples.

Syntheses of 2-Bromo-9′-hydroxydibiphenyleneethane and 2, 9′-Dibromodibiphenyleneethane.— Over a period of 2 hr., in an atmosphere of dry and oxygen-free nitrogen, 40 ml. of an ether solution containing 8.6 g. (0.062 mol.) of *n*-butyl bromide was added to a rapidly stirred mixture of 40 ml. of sodium-dried ether and 0.86 g. (0.12 g. atom) of freshly-cut lithium metal pieces. To this dark, *n*-butyl lithium solution, there was added, drop by drop, over a 45-min. period, a solution of 15.0 g. (0.061 mol.) of 2-bromofluorene in 100 ml. of an anhydrous xylene solution (exothermic reaction). The dark yellow-green color turned orange-red upon being heated. The ether was distilled off until a temperature of 120°C was reached, the solution turned dark-red, and a greenish-yellow solid deposited. Heating was continued for 30 min. at this temperature.

Into this resultant solution there was stirred, drop by drop, a solution of anhydrous xylene containing 11.0 g. (0.061 mol.) of fluorenone. The reaction mixture, which changed brown, was then heated to 100°C over a 90-min. period. The brown precipitate was filtered, hydrolyzed with a dilute ammonium chloride solution, and then recrystallized from cyclohexane to give 11.9 g. (m. p. 123~125°C) of 2-bromo-9′-hydroxydibiphenyleneethane.

Found: Br, 18.26. Calcd. for $C_{26}H_{17}OBr$: Br, 18.79%.

IR: 3270 (ν_{O-H}), 1155 (ν_{C-O}) cm^{-1} (KBr-disk).

The xylene mother liquor was also hydrolyzed with the same solution and dried over anhydrous sodium sulfate. Evaporation in vacuo gave a residual product which was chromatographed in benzene on alumina. 2-Bromo-9′-hydroxydibiphenyleneethane (m. p. 123~125°C) (2.6 g., total 58%) and 2-bromofluorene (0.5 g.) were obtained from the column.

2, 9′-Dibromodibiphenyleneethane.—A solution of 1.0 g. of 2-bromo-9′-hydroxydibiphenyleneethane in 10 ml. of acetic acid was saturated with dry hydrogen bromide. The product was filtered off and recrystallized from cyclohexane to give 2,9′-dibromodibiphenyleneethane (m. p. 146~148°C (decomp.)) (0.6 g.), identical in melting point, mixed melting point and infrared absorption spectrum with the compound obtained by the reaction of 2-bromodibiphenyleneethane and *N*-bromosuccinimide.

Found: Br, 32.51. Calcd. for $C_{26}H_{16}Br_2$: Br, 32.74%.

Syntheses of 2, 7-Dibromo-9′-hydroxydibiphenyleneethane and 2,7,9′-Tribromodibiphenyleneethane. —The former compound was prepared by the same procedure as was 2-bromo-9′-hydroxydibiphenyleneethane. Yield, 20.4% (m. p. 198~200°C).

Found: Br, 31.54. Calcd. for $C_{26}H_{16}OBr_2$: Br, 31.70%.

IR: 3260 (ν_{O-H}), 1154 (ν_{C-O}) cm^{-1} (KBr-disk).

2, 7, 9′-Tribromodibiphenyleneethane. — A solution of 1.0 g. of 2, 7-dibromo-9′-hydroxydibiphenyleneethane in 40 ml. of acetic acid was saturated with dry hydrogen bromide. The solid which was thus formed was recrystallized from benzene to give 2, 7, 9′-tribromodibiphenyleneethane; m. p. 206~207°C (decomp.); 0.8 g. (70%).

Found: Br, 42.10. Calcd. for $C_{26}H_{15}Br_3$: Br, 42.27%.

This product was identical in mixed melting point and infrared absorption spectrum with that obtained by the reaction of 2, 7-dibromodibiphenyleneethane and *N*-bromosuccinimide.

The Syntheses of 2, 7-Dibromo-9-hydroxydibiphenyleneethane and 2, 7, 9-Tribromodibiphenyleneethane.—The former compound was prepared by a method similar to that used for 2, 7-dibromo-9′-hydroxydibiphenyleneethane. Yield, 73%, m. p. 225~226°C.

Found: Br, 31.58. Calcd. for $C_{26}H_{16}OBr_2$: Br, 31.70%.

IR: 3230 (ν_{O-H}), 1155 (ν_{C-O}) cm^{-1} (KBr-disk).

2, 7, 9-Tribromodibiphenyleneethane.—2, 7-Dibromo-9-hydroxydibiphenyleneethane (1.5 g.) was dissolved in 60 ml. of acetic acid, which was then saturated with dry hydrogen bromide. The product deposited was recrystallized from benzene; (1.4 g., 83.3%) m. p. 216~217°C (decomp.). This product was identical in mixed melting point and infrared absorption spectrum with the product obtained by the reaction of 2, 7-dibromodibiphenyleneethane and *N*-bromosuccinimide.

Found: Br, 42.44. Calcd. for $C_{26}H_{15}Br_3$: Br, 42.27%.

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