

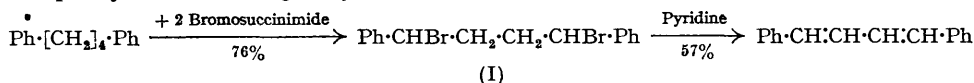
218. *The Reaction of 1:4-Diphenyl- and 1:1:4-Triphenyl-butane with N-Bromosuccinimide.*

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Just as 1:2-diphenylethane is dehydrogenated to stilbene by *N*-bromosuccinimide, so 1:4-diphenylbutane is converted into 1:4-diphenylbutadiene *via* a crystalline dibromide. Under the same conditions 1:1:4-triphenylbutane gives a monobromo-1:1:4-triphenylbutadiene, containing bromine in the chain. An isomeric monobromo-derivative is obtained by interaction of 1:1:4-triphenylbutadiene with elementary bromine. The mechanism of these reactions is discussed.

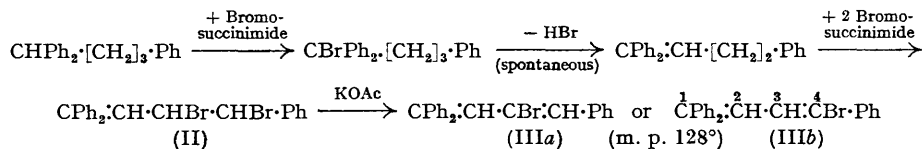
N-BROMOSUCCINIMIDE has been shown to replace an α -hydrogen atom in the benzyl group by bromine (Schmid and Karrer, *Helv. Chim. Acta*, 1946, 29, 573). In suitable cases this reaction can be used for dehydrogenation of saturated aliphatic bonds, Barnes (*J. Amer. Chem. Soc.*, 1948, 70, 145) having converted 1:2-diphenylethane into stilbene. When we treated 1:4-diphenylbutane with *N*-bromosuccinimide in carbon tetrachloride in the presence of benzoyl peroxide, we obtained a crystalline dibromide, to which formula (I) is ascribed, since upon being refluxed with pyridine (Ruzicka, Plattner, and

Heusser, *Helv. Chim. Acta*, 1946, 29, 473) it loses two moles of hydrogen bromide to give 1 : 4-diphenylbutadiene in good yield :



The yield of succinimide in the first step is quantitative, and the dibromide was isolated in 76% yield.

Application of this method to 1 : 1 : 4-triphenylbutane led to direct evolution of hydrogen bromide. After removal of the succinimide a viscous oil remained, which upon dehydrobromination with potassium acetate yielded a monobromo-1 : 1 : 4-triphenylbutadiene, m. p. 128° (IIIa or b). The probable explanation of this result is that a diphenylmethyl group reacts faster with N-bromosuccinimide than does a benzyl group (Buu-Hoï, *Annalen*, 1944, 556, 1). The tertiary bromide thus formed easily loses hydrogen bromide to give a butene, which now contains two active sites for attack : one allylic and one benzylic position. Thus the dibromide (II) can be formed, which is converted by acetate into a monobromo-derivative. The course of the reaction can be depicted as follows :



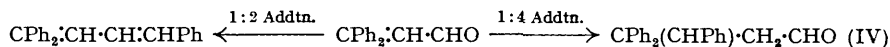
When, however, 1 : 1 : 4-triphenylbutadiene was treated with bromine in carbon tetrachloride, a different monobromo-derivative, m. p. 151°, was obtained. In view of the fact that the double bond C₍₃₎-C₍₄₎ in triphenylbutadiene is more reactive towards bromine than is C₍₁₎-C₍₂₎ (see IIIb), it appears probable that the primary product is again a dibromide of structure (II). It can thus be assumed that the two monobromo-derivatives are geometrical isomers (although positional isomerism as in IIIa and IIIb cannot be excluded). The spectra of the two bromination products (see Table) show a close similarity to each other and to that of 1 : 1 : 4-triphenylbutadiene.

Absorption spectra of 1 : 1 : 4-triphenylbutadiene and its isomeric monobromo-derivatives (in 95% alcohol).

	Min.,		Max.,		Min.,		Max.,	
	λ (Å)	log ε	λ (Å)	log ε	λ (Å)	log ε	λ (Å)	log ε
1 : 1 : 4-Triphenylbutadiene	2200	4.1	2410	4.2	2680	3.7	3360	4.6
Monobromo-derivative, m. p. 151°	2190	4.0	2420	4.2	2720	3.7	3330	4.5
Monobromo-derivative, m. p. 128°	2210	4.1	2410	4.2	2720	3.7	3340	4.5

Oxidation of both monobromides with permanganate in acetone gave benzophenone, thus excluding the possibility of nuclear bromination in one of the *gem*-phenyl rings. It therefore seems probable that the third ring also remained unsubstituted and that elementary bromine, like N-bromosuccinimide, effects substitution in the chain.

1 : 1 : 4-Triphenylbutadiene was synthesized from phenylacetic acid and ββ-diphenylacetaldehyde as described by F. Bergmann, Israelashvili, and Gottlieb (*J.*, 1952, 2522). When the aldehyde was condensed with benzylmagnesium chloride, the desired hydro-



carbon could be isolated only in 7.5% yield, the main product (28%) being a saturated aldehyde (IV), as shown by comparison of its absorption spectrum with that of ββ-diphenylacetaldehyde and by formation of characteristic carbonyl derivatives.

EXPERIMENTAL

Bromination of 1 : 4-Diphenylbutane.—A mixture of 1 : 4-diphenylbutane (2.1 g.), N-bromosuccinimide (3.6 g.), and benzoyl peroxide (50 mg.) in carbon tetrachloride (50 c.c.) was refluxed

for 30 minutes. The precipitated succinimide (2 g.) was filtered off, and the filtrate evaporated to dryness. The residue solidified upon trituration with ethanol. Recrystallization from this solvent gave the *dibromide* (I) (2.8 g.) as needles, m. p. 119° (Found: C, 52.5; H, 4.2. $C_{16}H_{16}Br_2$ requires C, 52.2; H, 4.3%).

A solution of this dibromide (1.2 g.) in pyridine (15 c.c.) was refluxed for 45 minutes. The solvent was removed *in vacuo*, and the residue steam-distilled. Plates appeared in the distillate, and after crystallization from alcohol these had m. p. 151°, not depressed by admixture of an authentic sample of 1 : 4-diphenylbutadiene; the yield was 400 mg. (57%).

Reaction between $\beta\beta$ -Diphenylacetaldehyde and Benzylmagnesium Chloride.—To a Grignard solution [from benzyl chloride (7 g.) and magnesium (1.5 g.) in dry ether] was added dropwise (1 hour) at 0° an ethereal solution of $\beta\beta$ -diphenylacetaldehyde (10.8 g.). After being refluxed for 2 hours, the mixture was decomposed with ammonium chloride. The oily organic residue slowly deposited crystals (1 g.). After two crystallizations from butanol $\beta\beta\gamma$ -triphenylbutaldehyde (IV) was obtained in colourless prisms, m. p. 157—159°, stable towards boiling 20% sulphuric acid (Found: C, 88.0; H, 6.6. $C_{22}H_{20}O$ requires C, 88.0; H, 6.7%); the *semi-carbazone* crystallized from toluene–ligroin in long needles, m. p. 138° (Found: C, 77.1; H, 6.4; N, 11.6. $C_{23}H_{23}ON_3$ requires C, 77.3; H, 6.4; N, 11.8%), and the 2 : 4-dinitrophenylhydrazone from butanol in yellow prisms, m. p. 187—188° (Found: N, 12.3. $C_{28}H_{24}O_4N_4$ requires N, 11.7%).

The yellow oil, remaining after separation of the aldehyde, was fractionated *in vacuo*. The fraction of b. p. 210°/3 mm. (2 g.) was triturated with ethanol, and the solid so obtained was recrystallized from the same solvent. 1 : 1 : 4-Triphenylbutadiene formed needles, m. p. 101°, identical with the hydrocarbon described previously (Staudinger, *Ber.*, 1909, **42**, 4258; F. Bergmann, Israelashvili, and Gottlieb, *loc. cit.*).

Reactions of 1 : 1 : 4-Triphenylbutadiene.—*With bromine.* A solution of triphenylbutadiene (0.25 g.) in carbon tetrachloride (10 c.c.) was treated at 0° with a solution of bromine (400 mg.) in the same solvent and left in the dark for 24 hours. Copious evolution of hydrogen bromide occurred. The residue was triturated with methanol and recrystallized from light petroleum. The *monobromide* (IIIa or b) formed prisms, m. p. 151° (230 mg.) (Found: C, 73.5; H, 4.5; Br, 21.8. $C_{22}H_{17}Br$ requires C, 73.1; H, 4.7; Br, 22.2%).

With maleic anhydride. A mixture of triphenylbutadiene (1 g.) and maleic anhydride (4 g.) was heated at 180° during 2 hours, ethanol added, and the mixture left overnight. The *adduct* (1.2 g.), recrystallized from butyl acetate–acetic acid, had m. p. 171° (Found: C, 77.0; H, 5.2. $C_{26}H_{22}O_4 \cdot \frac{1}{2}H_2O$ requires C, 76.7; H, 5.6%).

Bromination of 1 : 1 : 4-Triphenylbutane.—A mixture of 1 : 1 : 4-triphenylbutane (1.3 g.), *N*-bromosuccinimide (1.6 g.), benzoyl peroxide (40 mg.), and carbon tetrachloride (25 c.c.) was refluxed for 30 minutes, hydrogen bromide being eliminated especially towards the end of the time. The precipitated succinimide (0.87 g.) was filtered off, the solvent evaporated, and the residual, viscous, yellow-brown oil (1.6 g.) dissolved in benzene (15 c.c.). Potassium acetate (7 g.) and glacial acetic acid (12 c.c.) were added, and the mixture was refluxed for 30 minutes. The solution was then poured into ice-cold sodium hydroxide solution, and the product extracted with ether. The ether residue crystallized upon treatment with cold ethanol. Recrystallization from the same solvent gave the *monobromide* (IIIa or b) as light yellow rods, m. p. 128° (Found: C, 73.2; H, 4.5. $C_{22}H_{17}Br$ requires C, 73.1; H, 4.7%).

Oxidation of Monobromides.—(i) The monobromide of m. p. 151° (1 g.) was treated with a solution of potassium permanganate (3 g.) in acetone (100 c.c.) at room temperature for 36 hours. The mixture was worked up in the usual way and gave as neutral reaction product benzophenone (100 mg.), identified as its 2 : 4-dinitrophenylhydrazone, m. p. 238°, by comparison with an authentic sample. (ii) Oxidation of the monobromide of m. p. 128° similarly afforded benzophenone as the sole neutral reaction product.

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