SYNTHESIS AND PROPERTIES OF 1,3-BIS(4-NITROPHENYL)-1-BUTENE

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1,3-Bis(4-nitrophenyl)-1-butene was prepared by nitration of 1,3-diphenyl-1-butene (*I*) with fuming nitric acid in acetic acid. The double bond in *I* was protected by addition of bromine which was eliminated after the nitration. The UV, IR and ^{1}H-NMR spectra of the synthesized compounds are interpreted.

Photochemical properties, as well as the possible use in reproduction technique, represent interesting features of compounds, containing free double bond which can be activated by electron-accepting groups, such as carbonyl or nitro groups which have been studied most extensively.

In this paper we describe the synthesis of 1,3-bis-(4-nitrophenyl)-1-butene (*IV*) from 1,3-diphenyl-1-butene (*I*) prepared by dimerisation of styrene[1-6]. Direct nitration of the dimer *I* did not lead to the desired product and under the conditions employed, polymerisation invariably occurred. We chose therefore an indirect way, analogous to that used in the preparation of 4-nitrostyrene[7,8], consisting in protection of the double bond in the dimer *I* by addition of bromine[9]. Treatment of the obtained dibromide *II* with fuming nitric acid in acetic acid afforded *III* which was transformed into the alkene *IV* by elimination of bromine with potassium iodide in organic solvents. Highest yields (34%) were achieved when the elimination was carried out in dimethylformamide. During the reaction it was necessary to remove the arising iodine by addition of a saturated potassium sulfite solution. Elimination with zinc powder proved to be unsuccessful and the isolated material contained a great portion of the starting compound.

The two intermediates, *II* and *III*, can exist in several diastereoisomeric forms. It was not the aim of this work to separate or characterize these isomers and we studied only the configuration of the end product *IV* which can exist in two geometric isomers. According to the ^{1}H-NMR spectroscopy, the obtained product was practically pure *trans*-isomer. Its transformation into the *cis*-isomer was effected photochemically.

Introduction of nitro groups into the aromatic nuclei of *trans*-1,3-diphenyl-1-butene (*I*) results in a shift of the UV absorption maximum by 60 nm to higher wavelengths (Table I). A similar bathochromic shift can be observed also with the brominated dinitro derivative *III*. After photochemical isomerisation of *trans*-1,3-bis(4-nitrophenyl)-1-butene the UV maximum shifted towards shorter wavelengths by 20 nm. The IR spectra of *I* and *IV* exhibit medium absorption bands due to $\nu(C{=}C)$ vibrations in the region 1630–1675 cm^{-1}. The electron-accepting NO_2 groups cause a shift of these bands toward higher wavenumbers. Both the nitro derivatives *III* and *IV* display two bands due to $\nu(NO_2)$ at 1 347 and 1 530 cm^{-1}. Isomerisation of the *trans*-isomer *IV* to the *cis*-isomer is accompanied by marked changes in intensity of the out-of-plane CH-vibration bands in the region 700 to 1 000 cm^{-1} and by a shift of the $\nu(C{=}C)$ bands (1 630–1 675 cm^{-1}) toward lower wavenumbers. Spectrum of the *cis*-isomer contained a medium band at 1 219 cm^{-1} which can be due to deformation vibrations of this thermodynamically less advantageous isomer. ^{1}H-NMR spectra (Table II) confirmed that the end product *IV* is only the *para*-substituted derivative of *trans*-1,3-bis(4-nitrophenyl)-1-butene (the spectrum represented a typical AA'BB' spin system). Formation of the *cis*-isomer was not detected.

TABLE I

Properties of the Synthesized Compounds

Compound	M.p., °C (yield, %)	Formula (mol.w.)	Calculated/Found			λ_{max} (log ε)	$\nu(C{=}C)_{aliph}$ cm^{-1}	$\nu_s(NO_2)$ cm^{-1}	$\nu_{as}(NO_2)$ cm^{-1}
			% C	% H	% N				
II	100–101[a] (94·0)	$C_{16}H_{16}Br_2$ (367·9)	—	—	—	219 (4·410)	—	—	—
III	154–176 (87·5)	$C_{16}H_{14}Br_2N_2O_4$ (457·9)	41·8 43·92	3·09 3·42	6·12 5·50	272 (4·33)	—	1 358	1 542
IV trans	102–104 (34·3)	$C_{16}H_{14}N_2O_4$ (298·29)	64·42 64·61	4·73 4·47	9·39 9·28	313 (4·36)[b]	1 675[b]	1 347	1 530
IV cis	56–58 (73·8)	$C_{16}H_{14}N_2O_4$ (298·3)	64·42 64·43	4·73 4·65	9·39 9·25	293 (4·30)[b]	1 673[b]	1 347	1 530

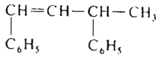
[a] Ref.[9] reports 100·7–101·7°C; [b] for the dimer *I* λ_{max} 253 nm (log ε = 4·30), see also[2,10]. $\nu(C{=}C)_{aliph}$ 1655 cm^{-1}.

TABLE II

^{1}H-NMR Spectra of the Synthesized Compounds (δ, ppm)

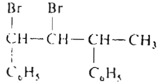
Compound	CH_3[a]	H_C[b]	H_B[a]	H_A[c]	C_6H_5			
II[c]	1·33	3·47	6·26 (*cis*)	—	7·13	—	—	—
	(*cis*, *trans*)	(*cis*, *trans*)	6·25 (*trans*)					
III	CH_3[a] 1·54, 1·49, 1·46, 1·43	—CH(Br)— 2·98	$—CH(C_2H_5)—CH_3$ 4·65	$—CH(Br)C_6H_5$ 5·16	C_6H_5 7·29	—	—	—
IV	1·57, 1·55, 1·44	3·07	4·56	5·13	7·61	—	—	—
V	CH_3[a]	H_C[b]	H_B[a]	H_A	H_{X_1}[a]	H_{X_2}[a]	H_{Y_1}[a]	H_{Y_2}[a]
cis[d]	1·513	4·04	6·07	6·61	7·41	7·38	8·16	8·13
trans[e]	1·44	3·72	6·47	6·43	7·38	7·34	8·11	8·05

[a] Doublet; [b] multiplet; [c] $J(H_C, CH_3) = 7·0$ Hz, $J(H_B, H_C) = 5·4$ Hz; [d] $J(H_C, CH_3) = 6·9$ Hz, $J(H_{X1}, H_{Y1}) = J(H_{X2}, H_{Y2}) = 9·0$ Hz, $J(H_A, H_B) = 10·2$ Hz; [e] $J(H_C. CH_3) = 7·0$ Hz, $J(H_{X1}, H_{Y1}) = J(H_{X2}, H_{Y2}) = 9·0$ Hz, $J(H_A, H_B) = 17·0$ Hz.



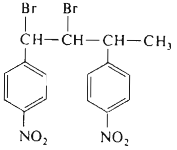
$\underset{C_6H_5}{CH}=CH-\underset{C_6H_5}{CH}-CH_3$

I

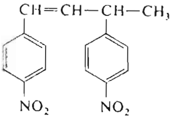


$\underset{C_6H_5}{\overset{Br}{CH}}-\overset{Br}{CH}-\underset{C_6H_5}{CH}-CH_3$

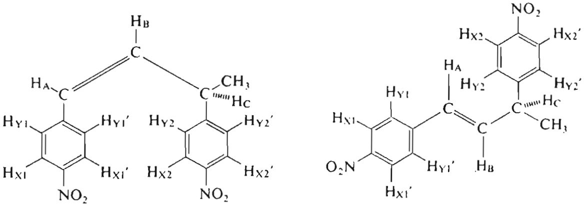
II



III



IV



cis *IV* *trans*

The dibromides *II* and *III* can exist as four racemates. According to the ^{1}H-NMR spectra, the obtained derivative *II* is composed of all the four epimers, in an approximate ratio 4 : 4 : 1 : 1 (from the intensity of methyl signals). On the other hand, the derivative *III* seems to be a mixture of only three racemic forms.

EXPERIMENTAL

The yields, melting points and analytical data of the prepared compounds are given in Table I. 1,3-Diphenyl-1-butene (*I*) was prepared by dimerisation of styrene in the presence of sulfuric acid[4], 1,2-dibromo-1,3-diphenylbutane (*II*) was obtained by addition of bromine to a solution of styrene oligomer[9]. IR spectra were taken on a UR-20 (Zeiss, Jena) spectrophotometer in the region 700—3800 cm^{-1} (saturated chloroform solution, 0·63 mm NaCl cells). Electronic absorption spectra were measured on a Specord UV VIS (Zeiss, Jena) spectrometer (4—6 . 10^{-5}M methanolic solutions, 1 cm cells). ^{1}H-NMR spectra were taken on a Tesla BS-487 C (80 MHz) instrument in deuteriochloroform at 25°C, using tetramethylsilane as internal standard.

1,2-Dibromo-1,3-bis(4-nitrophenyl)butane (*III*)

A suspension of 1,2-dibromo-1,3-diphenylbutane (*II*) (45·8 g; 0·1 mol) in acetic anhydride (about 250 ml) was added at −2° to +5°C during 3 h to a stirred mixture of fuming nitric acid ($h = 1.48$ kg m^{-3}; 32 ml), acetic acid (18 ml) and acetic anhydride (18 ml). After stirring for another 3 h the mixture was set aside for 24 h and then poured on ice (30 g). The separated crystals were filtered and washed with saturated sodium hydrogen carbonate solution and with water. After drying, the compound was crystallized from methanol; yield 50·03 g (87·5%).

Elimination of Bromine with Potassium Iodide

Potassium iodide (1·02 g; 0·006 mol) was added to a solution of the compound *III* (9·18 g; 0·025 mol) in dimethylformamide (50 ml). The stirred mixture was heated to 105—110°C and the liberated iodine was destroyed by addition of saturated potassium sulfite in the course of 3 h. The mixture was diluted with water, the product extracted with chloroform and chromatographed on an alumina column (Brockmann activity II). Crystallisation from diethyl ether (0°C) afforded 3·15 g (34·3%) of *trans*-1,3-bis(4-nitrophenyl)-1-butene (*IV*).

Photochemical isomerisation: A mercury lamp (RVK-125 W; Tesla) in a quartz tube was placed in the center of a reactor, filled with a solution of the elimination product (4·47 g; 0·015 mol) in acetonitrile (50 ml). The mixture was stirred by magnetic stirrer and by introduction of purified nitrogen. The reactor was cooled with water, the temperature of the reaction mixture being maintained at 25—28°C. After 4 hours' irradiation, acetonitrile was evaporated and the product was chromatographed on a column of neutral alumina (Brockmann activity II). Crystallisation from diethyl ether afforded 3·3 g (73·8%) of the *cis*-isomer.

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