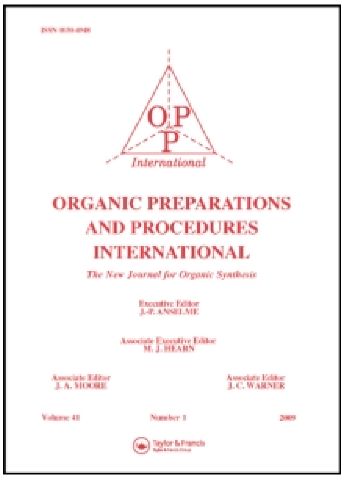

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SYNTHESIS OF 1-AZIDO-1,3-BUTADIENES.

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In connection with our study concerning vinyl azides and 1-azirines,[1-3] we have synthesized the title compounds, which are a new type of unsaturated azides. Five 1-azido-1,3-butadienes (IVa-IVe) were prepared by extension of the methods which were developed for the synthesis of terminal vinyl azides,[3] as shown in the following scheme; the results are summarized in Table I.

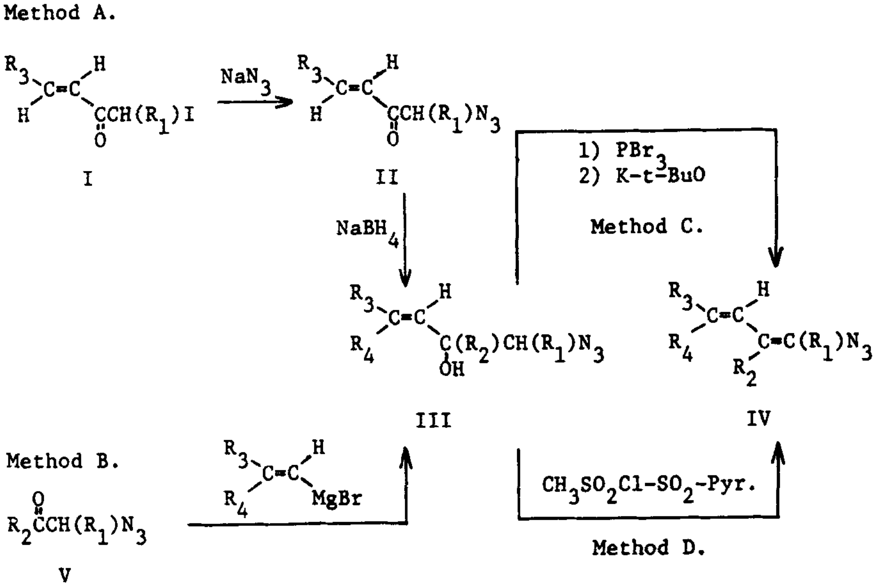
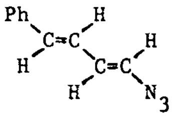


Table I.

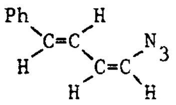
	IV				I (or V)$\rightarrow$III		III $\rightarrow$ V	
	R_1	R_2	R_3	R_4	Method	Yield (%)	Method	Yield (%)
a	H	H	Ph	H	A	76	C	67
b	Me	H	Ph	H	A	95	C	12
c	H	Ph	Ph	Ph	B	43	C	25
							D	65
d	Me	Ph	Ph	Ph	B	56	D	34
e	H	Ph	H	Me	B	16	D	30

Azidohydrins (III), which are the key intermediates of the syntheses, were prepared by two methods, A and B. Since the azidoketones (V) were easily prepared by the reaction of α-haloketones with sodium azide, method B was a more convenient path to prepare 2-substituted butadienylazides. However, this method was not applicable for the synthesis of 2-unsubstituted butadienylazides because α-azidoaldehydes are not readily available.

Bromination of IIIa and successive treatment of the resulting bromide with K-t-BuO in ether (method C) gave IVa in fairly good yield. The reaction product was found to be a mixture of two isomers of the azide by characteristic IR and nmr spectra of vinyl azides[3], and were separated into oily and crystalline compounds by recrystallization and column chromatography. The oily azide was assigned as the cis,trans-isomer



(IVa-t,t)



(IVa-c,t)

(IVa-c,t) by characteristic IR and nmr spectra; IR at 1400cm^{-1} (enhanced in-plane deformation of cis-olefin), nmr τ 4.45 (H_β, which is not deshielded by the azido group). The other crystalline isomer (mp. 49-51°C) should be (IVa-t,t), and IR and nmr spectra were consistent with this assignment.

The compound IVc was obtained in low yield by method C. This could be ascribed to spontaneous dehydrobromination immediately after formation of azidobromide and successive decomposition of the resulting butadienyl-azide by generated hydrogen bromide. Dehydration of azidohydrin (IIIc) (method D)[4,5] gave IVc in much better yield than method C. 2-Phenyl-butadienyl-azides (IVc,d,e) were prepared by method D in satisfactory yield.

EXPERIMENTAL

The synthesis of IVa and IVc are described in detail as representatives of method A-C and B-D. All reactions were carried out under nitrogen atmosphere. The crude butadienylazides were purified by passage through neutral alumina (Woelm, activity II) with hexane. Some of the azides were so labile that elemental analysis was precluded. The structures were determined by the IR and nmr spectra. All the spectral data are consistent with the assigned structures and showed characteristic spectra of unsaturated azides.[3] All melting points are uncorrected, IR spectra were recorded with a Shimazu IR-27, nuclear magnetic resonance spectra were obtained with either on a Varian A-60 or a JEOL MH-60.

1-Azido-4-phenyl-3-buten-2-on (IIa).—— To an ice bath cooled solution of 46.5g of 1-iodo-4-phenyl-3-buten-2-on (IIa) in 800ml of ethanol was added 22.5g of sodium azide in 150ml of water. After the reaction was allowed to stand overnight at 0°C, water was added until incipient turbidity, then cooled at -20°C for several hours. Filtration gave 33.4g (98%) of IIa as colorless needles, mp.49.0-50.5°C (dec.) from methanol, IR cm^{-1} (nujol) 2120 vs (N_3), 1640 vs (C=O), 960 vs (trans-CH=CH-); nmr τ (CCl_4) 2.26-2.75 (m, 6, $C_6H_5CH=$), 3.27 (d, 1, J=16Hz, =CHCO-), 5.95 (s, 2, CH_2).

<u>1-Azido-4-phenyl-3-buten-2-ol (IIIa)</u>.—— To an ice bath cooled solution of 33.4g of IIa in 250ml of ether was added 7.1g of $NaBH_4$ in 50ml of methanol. The solution was stirred overnight at room temperature. After the solvent was evaporated at reduced pressure, 2N AcOH was added until evolution of gas ceased. This was extracted with ether. The ether extract was washed with water and 2N $NaHCO_3$, then was dried with sodium sulfate. Removal of the solvent at reduced pressure gave 27.2g (78%) of pale yellow oil (IIIa), IR cm^{-1} (neat) 3400 s (OH), 2130 vs (N_3), 1665 w (C=C), 970 vs (<u>trans</u>-CH=CH-); nmr τ (CCl_4) 2.74 (s, 5, Ph), 3.41 (d, 1, J=16Hz, PhC<u>H</u>=), 3.90 (dd, 1, J=16Hz, J=6.5Hz, =C<u>H</u>CH(OH)-), 5.65 (q, 1, J=6.5Hz, -C<u>H</u>(OH)-), 6.57 (broad s, 1, O<u>H</u>), 6.76 (d, 2, J=6.5Hz, CH_2). Reaction of IIIa with benzoyl chloride by usual manner gave benzoate as white needle, mp. 27.0-28.0°C from <u>n</u>-hexane-ether.

<u>Anal</u>. of benzoate. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33.
Found: C, 69.50; H, 4.91; N, 14.12.

<u>1-Azido-4-phenyl-1,3-butadiene (IVa)</u>.—— To an ice bath cooled solution of 7.79g of IIIa and 2ml of pyridine in 180ml of ether was added 5.5g of phosphorous tribromide. After stirring for 2 hrs. the reaction mixture was poured into 200g of ice. The ether layer was separated, washed with cold water and cold 2N $NaHCO_3$ solution then dried over sodium sulfate. The solution was added dropwise into a suspension of 15g of K-t-BuO in 50ml of ether. After stirring for two days at room temperature, the reaction mixture was washed with water and dried over sodium sulfate. Removal of the solvent at reduced pressure gave black oil. This was extracted with <u>n</u>-hexane and the extract was passed through aluminum oxide with <u>n</u>-hexane and yielded after removal of the solvent, 4.4g (66.5% from IIIa) of yellow liquid. To this liquid was added 10ml of <u>n</u>-hexane and the solution was cooled at -20°C. Filtration of the precipitated yellow

crystal gave 1.9g of trans,trans-1-azido-4-phenyl-1,3-butadiene IVa-t,t, mp. 49.0-51.0°C, IR cm^{-1} (nujol) 2120 vs (N_3), 1640 s (C=C), 975 vs (trans-CH=CH-); nmr τ (CCl_4) 2.75 (s, 5, Ph), 3.10-3.95 (m, 4, olefinic protons). The mother liquor was poured through a column of 30g of aluminum oxide and was eluted with n-hexane. The first eluate (20ml) gave 0.8g of IVa-c,t as a yellow oil, IR cm^{-1} (neat) 2130 vs (N_3), 1640 s (C=C), 1400 vs (cis-CH=CH-), 970 vs (trans-CH=CH-); nmr τ (CCl_4) 2.75 (s, 5, Ph), 3.00-3.95 (m, 3, Hα Hγ and Hδ), 4.45 (dd, 1, J=7Hz, J=10Hz, Hβ). The following eluate (100ml) gave 1.5g of yellow liquid that proved to be the mixture of the two isomers by IR and nmr spectrum.

1-Azido-2,4,4-triphenyl-3-buten-2-ol (IIIc).—— To 17.1g of azidoacetophenone Va in 150ml of absolute ether was added dropwise ether solution of β-phenylstyryl magnesium bromide, which was prepared from 25.3g of β-phenylstyryl bromide and 2.4g of magnesium in 100ml of absolute ether, with vigorous stirring at 0°C. After stirred for 2 hrs., the solution was refluxed for 30 min. and cooled to room temperature. After 200ml of saturated aquous solution of NH_4Cl was added in portions, ether layer was treated in the usual manner. Removal of the solvent at reduced pressure gave a brown oil, which was chromatographed on aluminum oxide. Elution with benzene gave 22.1g (43%) of colorless crystal IIIc, mp. 90.5-92.0°C from n-hexane; IR cm^{-1} (nujol) 3550 s (OH), 2120 vs (N_3); nmr τ (CCl_4) 2.60-2.85 (m, 15, Ph), 3.36 (s, 1, -CH=), 6.61 (s, 3, CH_3), 7.86 (s, 1, OH).

Anal. Calcd for $C_{22}H_{19}N_3O$: C, 77.39; H, 5.61; N, 12.31.
Found: C, 77.56; H, 5.62; N, 12.32.

1-Azido-2,4,4-triphenyl-1,3-butadiene (IVc).—— The azidobutenol IIIc (3.41g, 10mmol) was treated with 3.5g of methanesulfonyl chloride containing sulfur dioxide in 20ml of dimethylformamide and 50ml of pyridine at room temperature, for 30 min.[4,5] The excess methanesulfonyl chloride was destroyed by the dropwise addition of 20ml of water with stirring (ice bath), then 200ml of water was added. The mixture was extracted with 200ml of ether, and the ethereal extract was washed with water then dried over Na_2SO_4. Removal of the solvent at reduced pressure gave brown oil. The hexane soluble portion of this liquid was chromatographed on alumina. The portion eluted with n-hexane gave 2.09g (43%) of yellow liquid IVc, IR cm^{-1} (neat) 2120 vs (N_3); 1600 s (C=C). The nmr spectrum τ (CCl_4) showed two pairs of doublet (olefinic protons, J=1.5Hz), one pair at 6.5 and 6.1 and the other at 6.74 and 6.20. The latter pair is about 10 times stronger than the former. Phenyl protons were observed at τ 2.69-2.93 as a multiplet having appropriate peak area for the mixture of isomeric azide. This indicated that the resulted azide was mixture of the geometric isomers of the expected azide. Separation of these two isomers was not performed.

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