

Organic Azides. 3.* Ultrasound Synthesis of Propargyl Azide, Azidoacetonitrile and Primary Allylic Azides

HANNO PRIEBE

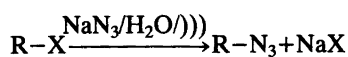
Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, 0315 Oslo 3, Norway

The title azides were prepared from the corresponding activated primary halides and aqueous sodium azide under ultrasonic irradiation.

Various applications of ultrasound in heterogeneous reactions have been published.² This paper describes the direct formation of azides from activated primary organic halides and aqueous sodium azide solution under ultrasonic irradiation (])).

A mixture of the alkyl halide and saturated aqueous sodium azide is irradiated in an Erlenmeyer flask using a commercial ultrasonic cleaner. After 1–4 h, the corresponding alkyl azide can be easily condensed or extracted from the water phase.

The advantage of the new method is the direct use of sodium azide as a cheap, available azide ion source. Additional reaction steps to generate another azide group-transfer reagent like hydrazoic acid,³ trimethylsilyl azide⁴ or tetramethylguanidinium azide⁵ are not necessary. The use of co-solvents⁶ like ethanol often leads to separation problems, especially from low boiling organic azides as in this case. Water as sole solvent can easily be separated by decantation and usual drying operations. The use of phase-transfer catalyst⁷ is not necessary, because ultrasound works as an effective “non-chemical phase-transfer agent”. If the alkyl halide and the saturated aqueous sodium azide solution are left 1–4 h at 60 °C without ultrasonic irradiation, nearly no conversion was observed. Ultrasonic irradiation is decisive for good conversion in this liquid



R	RN ₃	RX X=Cl	X=Br
HC≡C-CH ₂ -	1	1a	1b
N≡C-CH ₂ -	2	2a	
H ₂ C=CH-CH ₂ -	3	3a	3b
H ₂ C=CCl-CH ₂ -	4	4a	
H ₂ C=CBr-CH ₂ -	5		5b

Scheme 1.

biphasic system. Reaction conditions and yields of the isolated products are given in Table 1.

Also the influence of sodium iodide on the reaction has been investigated. Only in the case of 3a and 5b did an equimolar amount of sodium iodide increase the rate of conversion to the azide. A greater sodium azide excess increases the rate of conversion as expected. It is most advantageous to prepare 1 and 3 from the corresponding bromides. Chlorides in general require longer reaction times. Shorter reaction times lead to mixtures of alkyl azide and unreacted alkyl halide. Longer reaction times increase the conversion but decrease the isolated yield due to decomposition or cycloaddition dimerisation of the azide. The density-difference between halide and the corresponding azide influences the conversion. In the case density_{halide} > 1.18 > density_{azide} the water phase separates product and educt and the conversion is high. A 30 % aqueous solution of sodium azide has a density of 1.18. In all other cases, where

* Part 2, see Ref. 1.

Table 1. Reaction conditions and yields.

RN ₃	RX	Molar ratio RX/NaN ₃ /NaI	Reaction time (h)	Isolation method ^a	Yield (%)	Lit. Yield (%)
1	1a	1:4:0	3.0	A	60	Not reported ⁸
1	1a	1:4:1	3.0	A	35	
1	1b	1:4:0	1.5	A	88	
1	1b	1:2:1	1.5	A	72	
2	2a	1:4:0	3.0	B	64	64 ^{10a} , 65 ⁴ 83.5 ^{10b}
2	2a	1:4:1	3.0	B	61	
3	3a	1:4:1	3.0	A	88	30 ^{9a}
3	3a	1:4:0	3.0	A	56	
3	3b	1:4:0	1.5	A	91	100 ⁴
3	3b	1:4:1	1.5	A	57	
4	4a	1:4:0	4.0	B	81	—
4	4a	1:4:1	2.0	B	41	
5	5b	1:4:1	1.0	B	52	—
5	5b	1:4:0	2.0	B	48	

^a A=Condensation; B=Extraction.

halide and azide remain dissolved in each other, the conversion is lower.

The reaction of 1-bromopropane with two equivalents sodium azide solution yields only 20 % propyl azide after 3 h ultrasonic irradiation at 60 °C. The method seems to require propargylic or allylic activation or a neighbouring cyano group. The spectroscopic and physical data are given in Table 2.

EXPERIMENTAL

Warning. All these compounds are known to be potentially explosive and appropriate caution should be applied!

Synthesis of the described azides; General procedure: The alkyl halide (0.04 mol) is added to a 30 % aqueous solution of sodium azide (0.16 mol) in an Erlenmeyer flask with reflux condenser. Sodium iodide (0.04 mol) is added to the solution only in the cases 3a and 5b, where it is advantageous. The flask is immersed 1–2 cm under the water surface in an ultrasonic cleaner (Bandelin, Sonorex RK 255, 500 W/35 kHz) at 50 °C. During the reaction time the temperature is allowed to rise up to 65 °C.

Isolation method A (for low-boiling azides). The product is condensed under low pressure into a trap, cooled with liquid nitrogen. The product is recondensed and dried by condensa-

tion through a U-shaped tube, filled with phosphorus pentoxide desiccant. If necessary, the product can be distilled under low pressure.

Isolation method B. The product is extracted four times with ether (4×100 ml). After drying the solution with calcium chloride the ether is removed in water-pump vacuum. The residue is pure enough for most purposes. If necessary, the product can be distilled under low pressure.

Acknowledgements. Financial support from the Royal Norwegian Council for Scientific and Industrial Research is gratefully acknowledged.

REFERENCES

- Priebe, H. *Acta Chem. Scand. B* 38 (1984) 623.
- a. Boudjouk, P. *Nachr. Chem. Tech. Lab.* 31 (1983) 798 and references therein; b. Raucher, S. and Klein, P. *J. Org. Chem.* 46 (1981) 3558.
- Ben Cheik, R., Chaabouni, R., Laurent, A., Mison, P. and Nafti, A. *Synthesis* (1983) 685.
- a. Nishijama, K. and Karigomi, H. *Chem. Lett.* (1982) 1477; b. Weber, W. P. *Silicon Reagents for Organic Synthesis*, Springer, Berlin, Heidelberg 1983, Chapter 4; c. Kirchmeyer, S., Mertens, A. and Olah, G. A. *Synthesis* (1983) 500.

Table 2. Physical and spectroscopic data of azides.

RN ₃	B.p. °C/Torr	n _D ²⁰	UV(CH ₃ CN) λ _{max} (log ε)	IR ν (cm ⁻¹)	¹³ C NMR (50.3 MHz, CDCl ₃), δ	¹ H NMR (200 MHz, CDCl ₃), δ
1	72.6/760	1.4520	215(2.510)	≡C-H (3296) N ₃ (2100,1335)	75.35 (dt, C-2) 75.08 (d, C-1) 39.00 (t, C-3)	3.94 (d, 2H, J=2.52) 2.64 (t, 1H, J=2.52)
2	46/10	1.4532	221(2.494)	N ₃ (2110,1260)	114.22 (s, C-2) 37.81 (d, C-1)	4.09 (s, 2H)
3	76.5/760 ^{9a}	1.4345	213(2.790)	C=C(1648) N ₃ (2100,1250) ^{9b}	131.56 (d, C-2) 119.07 (t, C-1) 53.39 (t, C-3)	5.89 (ddt, 1H, J=17.1;10.0;6.1) 5.34 (dm, 1H, J=1.4) 5.27 (m, 1H) 3.76 (d, 2H, J=5.88)
4 ^a	36/30	1.4724	221(2.446)	C=C (1635) N ₃ (2100,1280)	136.36 (s, C-2) 115.27 (t, C-1) 56.49 (t, C-3)	5.47 (dt, 1H, J=1.8;1.2) 5.42 (dt, 1H, J=0.7) 3.92 (s, 2H)
5 ^b	32/12	1.5076	221(2.723)	C=C(1628) N ₃ (2100,1278)	126.48 (s, C-2) 119.51 (t, C-1) 58.16 (t, C-3)	5.92 (dt, 1H, J=2.3;1.2) 5.67 (dt, 1H, J=0.6) 4.00 (s, 2H)

^a Found: C 30.67; H 3.52; N 35.84. Calc. for C₃H₄CIN₃: C 30.65; H 3.43; N 35.74. MS Mol. wt., obs. 117.0087, calc. for C₃H₄CIN₃ 117.0094.

^b Found: C 22.30; H 2.44; N 25.88. Calc. for C₃H₄BrN₃: C 22.24; H 2.48; N 25.93. MS Mol. wt., obs. 160.9579, calc. for C₃H₄BrN₃ 160.9589.

5. Papa, A. J. *J. Org. Chem.* 31 (1966) 1426.
6. Biffin, M. E. L., Miller, J. and Paul, D. B. In Patai, S. *The Chemistry of the Azido Group*, Interscience, London, New York 1971, Chapter 2.
7. a. Reeves, W. P. and Bahr, M. L. *Synthesis* (1976) 823; b. Lehmkuhl, H., Rabet, F. and Hauschild, K. *Synthesis* (1977) 184.
8. Baldwin, M. G., Johnson, K. E., Lovinger, J. A. and Parker, C. O. *J. Polym. Sci. Part B* 5 (1967) 803.
9. a. Foster, M. O. and Fierz, H. E. *J. Chem. Soc.* 93 (1908) 1174; b. Sheinker, Y. N., SenYavina, L. B. and Zheltova, V. N. *Dokl. Akad. Nauk* 160 (1965) 1339.
10. a. Freudenberg, K., Eichel, H. and Leutert, F. *Ber. Dtsch. Chem. Ges.* 65 (1932) 1138; b. Grundmann, C. In Müller, E., Ed., *Houben-Weyl, Methoden der Organischen Chemie*, Thieme, Stuttgart 1965, Vol. 10/3, p. 796.

Received February 13, 1984.