

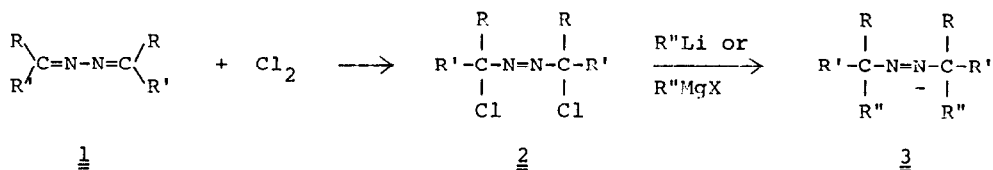
A NEW SYNTHESIS OF t-AZOALKANES

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(Received in UK 22 November 1973; accepted for publication 6 December 1973)

t-Azoalkanes 3 have been widely used as radical generators for the investigation of the mechanisms of homolytic reactions¹⁾ and they are potential high temperature initiators in applied chemistry. Most procedures for their preparation are oxidations of primary t-alkylamines by one of several known oxidation pathways²⁻³⁾. An exception to this principle is the synthesis by chlorination of ketazines 1 and the successive alkylation of the chloro azoalkanes 2 by Grignard reagents or lithium alkyls⁴⁾. The yields in this process are, however, generally poor.



None of the known preparative procedures are suited to general large scale syntheses for t-azoalkanes 3.

A general synthesis adaptable for this purpose is reported here in the reaction of chloro azoalkanes 2 with excess trialkyl- or triphenyl aluminum in petrolether at -70° - 0°C. In simple systems yields between 80 and 100% are obtained and even highly sterically hindered azoalkanes can be prepared conveniently in good yields. Competitive side reactions are the formation of ketazines 1 and of secondary azoalkanes by hydride transfer in the hindered systems. The reaction can be performed on a molar or larger scale. This makes t-azoalkanes available for the investigation of their thermal and catalytic decomposition as well as their use as initiators or intermediates in syntheses.

Preparation of Ketazines 1

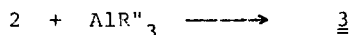
1.1 Mole ketone, 0.5 mole 85% hydrazine hydrate and a few drops conc. HCl are refluxed for 3 hs. For hindered ketones reaction periods of up to 100 hs and the use of 100% hydrazine are recommended. For solid ketones such as 2-adamantanone petroleum ether solutions are used. The cooled reaction mixture is extracted with ether and the ketazines 1 are isolated from the neutral and dry organic phase by distillation.

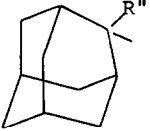
Preparation of Chloro Azoalkanes 2 ⁵⁾

A dilute petroleum ether solution of the ketazine 1 is cooled to -60° and saturated with chlorine until the yellow colour persists. The excess chlorine is then rapidly removed by brief evacuation. During this procedure the chloro azoalkane 2 usually precipitates as colorless crystals, which are collected by filtration and recrystallized from petroleum ether or methylene chloride, if required. The yields are between 65 and 80%.

Preparation of t-Azoalkanes 3

A petroleum ether solution of 0.2 mole trialkyl-⁶⁾ or triphenyl-⁷⁾ aluminum in a 1-L three-necked flask under nitrogen is treated between -70° and 0°C with 0.1 mole 2 in 300 ml petroleum ether. The reaction is usually over after two hours at 25° and only for highly hindered ketones are longer reaction times of 12 - 14 hours required. The excess aluminum organic compound is destroyed by careful addition of 4:1 benzene-ethanol with external cooling to 0° and the hydrolysis is completed by the addition of an excess of 2 n sulfuric acid. After washing and drying the organic phase, the t-azoalkanes 3 are isolated by distillation in vacuo or by chromatography on neutral alumina. The azocompounds were characterized by elemental analysis, uv-, nmr- and mass spectrometry. All compounds 3 showing the characteristic uv-absorption between 364 and 382 nm with $\epsilon=15 - 40$ and the M/2-14 peak in the mass spectra. Selected results are recorded in table 1.

Table 1. Preparation of t-Azoalkanes 3

R	R'	R''	% <u>3</u>	bp/mm O _C	λ_{max} (ε) nm	a)
CH ₃	CH ₃	C ₂ H ₅	100	55/14	364 (21)	H
CH ₃	CH ₃	i-C ₄ H ₉	73	94/13	372 (16)	H
CH ₃	CH ₃	1-C ₈ H ₁₇	80	- -	368 (18)	H
CH ₃	C ₂ H ₅	C ₂ H ₅	96	88/13	376 (15)	H
CH ₃	i-C ₃ H ₇	CH ₃	76	85/13	376 (16)	H
CH ₃	t-C ₄ H ₉	C ₂ H ₅	64	58/.01	378 (17)	H
CH ₃	t-C ₄ H ₉	C ₆ H ₅	50 ^{b)}	56 ^{c)}	368 (40)	H
CH ₃	neo-C ₅ H ₁₁	C ₂ H ₅	59	98/.01	378 (19)	H
i-C ₃ H ₇	i-C ₃ H ₇	CH ₃	80	91/.01	376 (18)	I
-(CH ₂) ₆ -		C ₂ H ₅	74	98/.01	380 (22)	II
		CH ₃ ⁸⁾	86	166-167, 5 ^{c)}	387 (14)	B
		C ₂ H ₅ ⁸⁾	71	78, 5-80 ^{c)}	394 (15)	B
		1-C ₈ H ₁₇ ⁸⁾	83	54-56 ^{c)}	397 (19)	B

a) H = in hexane; I = in isooctane; B = in benzene

b) in benzene

c) Fp.

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