83. *A New Reagent for Primary and Secondary Aliphatic Amines.*

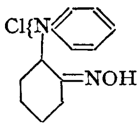
By Arthur J. Birch.

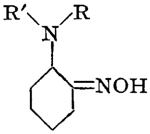
2-*iso*Nitroso*cyclo*hexane-1 : 1′-pyridinium chloride (I) reacts with primary and secondary aliphatic amines in aqueous solution to give the corresponding 2-*iso*nitroso*cyclo*hexylamine (II), and these derivatives can often be used to characterise the amine.

It is well known that nitrosochlorides react with primary and secondary amines to give " nitrolamides," which, being usually well crystallised and stable substances, might be used for the characterisation of such amines. This is particularly true of α-thujene nitrosochloride which gives well-crystallised, high-melting derivatives with a variety of amines, including ammonia, morpholine, diethylamine, di*iso*butylamine, benzylamine, and α-phenylethylamine (Birch; and Birch and Earl, *J. Proc. Roy. Soc. N.S.W.*, 1937, **71**, 334; 1938, **72**, 55); moreover, α-thujene is readily obtained from commercially available sources.

The chief drawback to the use of this and other nitrosochlorides (such as that from α-pinene) is their instability on keeping; also, in reaction with an amine they decompose to some extent with loss of hydrogen chloride to give an unsaturated compound (cf. Birch, *ibid.*, 1938, **72**, 106). On the other hand, *cyclo*hexene nitrosochloride is particularly stable, and Wallach (*Annalen*, 1906, **343**, 49) was unable to convert it into *cyclo*hexenone oxime by treatment with pyridine or quinoline. In the case of pyridine, at least, this is due to the formation of a *pyridinium chloride* (I), which can be kept indefinitely, is readily soluble in, and stable to water, and reacts immediately on warming with an aqueous solution of an aliphatic primary or secondary amine to give the *iso*nitroso*cyclo*hexylamine (II). Since the amines are, as a rule, stronger bases than pyridine, it is advisable to add 1 mol. of sodium carbonate to ensure complete reaction. Amine salts may also be used in the presence of excess aqueous sodium carbonate.

(I.)





(II; R = H, Alkyl; R′ = Alkyl.)

The products separate as oils, which usually crystallise in the presence of a little petrol, and can be recrystallised from benzene–petrol or aqueous alcohol. As derivatives, they are not altogether satisfactory, since those derived from the lower amines are rather soluble in water, and those from some of the higher amines crystallise slowly, unless seeded. Although the m. p.'s of isomeric and adjacent homologous compounds are sometimes rather close, the mixed m. p.'s show considerable depression.

The reagent has the advantage of stability, easy preparation, and suitability for use in aqueous solution. It is hoped to obtain a better reagent of the same type from some other nitrosochloride. The derivatives prepared are tabulated below.

Amine.	M. p. of deriv.	Formula.	Analysis. Found, N%.	Analysis. Required, N%.
Dimethylamine	120°	$C_8H_{16}ON_2$	17·9	18·0
n-Propylamine	72	$C_9H_{18}ON_2$	16·9	16·5
n-Butylamine	81	$C_{10}H_{20}ON_2$	15·8	15·2
*iso*Butylamine	73	,,	15·0	,,
tert.-Butylamine	91	,,	14·9	,,
Diethylamine	63	,,	15·7	,,
Morpholine	118	$C_{10}H_{18}O_2N_2$	14·0	14·1
Piperidine	116 *	$C_{11}H_{20}ON_2$	14·4	14·3
*cyclo*Hexylamine	145	$C_{12}H_{22}ON_2$	13·6	13·3
n-Heptylamine	66	$C_{13}H_{26}ON_2$	12·3	12·4

* Perrot (*Compt. rend.*, 1936, **203**, 329) gives m. p. 119°.

EXPERIMENTAL.

cyclo*Hexene Nitrosochloride.*—This was prepared by Wallach's method (*loc. cit.*), an equimolecular amount of amyl nitrite being substituted for ethyl nitrite; 12 g. were obtained from 40 c.c. of *cyclo*hexene.

2-iso*Nitroso*cyclo*hexane*-1 : 1′-*pyridinium Chloride.*—*cyclo*Hexene nitrosochloride (11 g.) and pyridine (20 c.c.) were mixed to a paste and cautiously warmed on the steam-bath until the strongly exothermic reaction began; the mixture was then cooled in water. Addition of alcohol (15 c.c.) containing water (4 c.c.) and heating on the steam-bath produced a clear yellow solution, which gave a cream-coloured, crystalline precipitate on cooling and addition of ethyl acetate (15 c.c.) On recrystallisation from alcohol–water (30 c.c.; 4 c.c.) the pure *chloride* (15 g.) was obtained as monohydrated, colourless, prismatic needles, m. p. 125° (Found : C, 53·8; H, 7·1. $C_{11}H_{17}O_2N_2Cl$ requires C, 54·0; H, 6·95%).

2-iso*Nitroso*-1-*dimethylamino*cyclo*hexane*.—The details of preparation of this *compound* are given as an example of the use of the reagent. A 10% aqueous solution of the reagent (5 c.c.) was added to 10% aqueous sodium carbonate (2·5 c.c.), mixed with an aqueous solution containing dimethylamine hydrochloride (0·2 g.; *ca.* 1 mol.) and 10% sodium carbonate solution (2·5 c.c.), and warmed on the steam-bath for 3 minutes; an oil separated, which crystallised on cooling. It recrystallised from benzene–petrol (b. p. 40—60°) as colourless, prismatic needles, m. p. 120° (Found: C, 61·9; H, 10·1; N, 17·9. $C_8H_{16}ON_2$ requires C, 61·6; H, 10·2; N, 18·0%).

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