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AZA-TRANSFER REACTIONS

A NOVEL METHOD FOR THE CONVERSION OF MONOSUBSTITUTED HYDRAZINO COMPOUNDS INTO HYDROCARBONS

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The monosubstituted hydrazines usually are converted to hydrocarbons by treatment with aqueous cupric acetate, ferric chloride, potassium chromate, mercuric(II)oxide, silver(II)oxide, silver(II)acetate or by decomposition of arylsulphonylhydrazides in the presence of an alkali[1].

There are several examples, which could be explained as aza-transfer reactions, known in the literature[2,3,4]. However, the generality of this principle has been recognized in the last decade[5]. Recently, aza-transfer reactions have been successfully employed for the preparation of tetrazolo- and azidoazines[6,7], thiatriazoles[8], heterocyclic amines from the corresponding azides[9], and participation of diazo or azido groups in the construction of several bicyclic and polycyclic systems has been demonstrated[10].

In continuation of our studies of the utilization of aza-transfer reactions for synthetic purposes, we now report a simple and selective method which has been devised for the transformation of monosubstituted hydrazines into hydrocarbons with p-toluensulphonylazide under the phase-transfer catalysis reaction conditions[11], according to the Scheme

$$R{-}NHNH_2 + Tos{-}N_3 \xrightarrow[\substack{NaOH \\ H_2O/ArH}]{TEAB} R{-}H + 2N_2 + Tos{-}NH_2$$

Scheme

The method represents a more selective alternative in comparison to catalytic dehalogenation, since by catalytic dehalogenation, especially of bicyclic and polycyclic heterocyclic systems, partial hydrogenation of the ring system could also take place[12].

General procedure. - To an aqueous solution of sodium hydroxide (50%, 10 ml) was added tetraethylammonium bromide (TEAB) (0,1 g), hydrazino compound (0,002 mole), and a solution of p-toluensulphonylazide (0,002 mole) in benzene or xylene (10 ml). The reaction mixture was refluxed until all p-toluensulphonylazide had reacted (2-10 hours). The organic layer was separated, the water layer extracted with benzene (3 times, 10 ml) and dried over sodium sulphate. Evaporation of the combined extracts in vacuo yielded the corresponding hydrocarbons. From the water phase p-toluensulphonamide has been isolated as by-product upon neutralization.

The hydrocarbons liquid at room temperature were isolated either by GLC (FFAP, 10% Chromosorb W 60/80), or as hydrochlorides. In the latter case the organic layer was extracted with aqueous solution of hydrochloric acid (2N, 2 times, 10 ml). Evaporation of the combined extracts in vacuo yielded the corresponding hydrochlorides.

The experimental details are summarized in the Table.

The presence of an ammonium salt as catalyst is essential. When experiments were carried out under the same conditions, but omitting the TEAB, only the traces (1-3%) of hydrocarbons were detected and isolated by T.L.C. (Merck DC-Fertigplatten Kieselgel 60-F254, chloroform:methanol 9:1 as solvent). Besides tetraethylammonium bromide, benzyltrimethylammonium chloride an benzyltriethylammonium chloride were used as catalysts affording the final products in approximately the same yields, while tetra-n-butylammonium bromide seems to be less satisfactory.

The yields of conversion in aromatic series are low to moderate, while the yields in heterocyclic series are good. The exceptions are those heterocyclic systems which are not stable in alkaline solution, as it has been demonstrated earlier for s-triazolo/4,3-b/pyridazine derivatives[13,14].

The investigations of the mechanism of this type of aza-transfer reaction with possible formation of either 1,5-disubstituted or 1,4-disubstituted pentazene intermediates are in progress.

Table Conversion of monosubstituted hydrazines into hydrocarbons with p-toluensulphonylazide in the presence of tetraethylammonium bromide as phase transfer catalyst.

Hydrazino Starting compound	Solvent[a]	Reaction time (hours)	Product	Yield (%)	Lit.ref.[b]
Phenylhydrazine	A	6	Benzene	40[c]	
4-Nitrophenylhydrazine	B	2	Nitrobenzene	8[c]	15
2,4-Dinitrophenylhydrazine	B	4	m-Dinitrobenzene	6	16
2-Hydrazinopyridine	B	6	Pyridine	98[d]	
3-Hydrazonopyridazine	B	8	Pyridazine	79[d]	17
6-Hydrazinoimidazo/1,2-b/pyridazine	B	5	Imidazo/1,2-b/pyridazine	68	18
6-Hydrazino-2-phenylimidazo/1,2-b/pyridazine	B	10	2-Phenylimidazo/1,2-b/pyridazine	35	19
6-Hydrazinoimidazo/1,2-b/pyrido/3,2-d/pyridazine	B	6	Imidazo/1,2-b/pyrido/3,2-d/pyridazine	40	20
6-Hydrazino-7-methyl-s-triazolo/4,3-b/pyridazine	B	6	7-Methyl-s-triazolo/4,3-b/pyridazine	11	21
6-Hydrazino-8-methyl-s-triazolo/4,3-b/pyridazine	B	6	8-Methyl-s-triazolo/4,3-b/pyridazine	7	21
6-Hydrazino-s-triazolo/1,5-b/pyridazine	B	3	s-Triazolo/1,5-b/pyridazine	85	22
6-Hydrazino-s-triazolo/4,3-b/pyrido/2,3-d/pyridazine	B	6	s-Triazolo/4,3-b/pyrido/2,3-d/pyridazine	28	20

[a] Solvent A: xylene/50%/ NaOH in water, 1:1; solvent B: benzene/50%/ NaOH in water, 1:1

[b] The products are in all respects (IR, NMR, MS and m.p.or b.p.) identical with the authentic samples prepared according to the procedures reported in the literature

[c] Separated by G.L.C.

[d] Isolated as hydrochloride salt

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