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NOVEL AND CONVENIENT SYNTHESES OF SUBSTITUTED 1,4-DIAZOCINES AND 1,4-DIAZONINES

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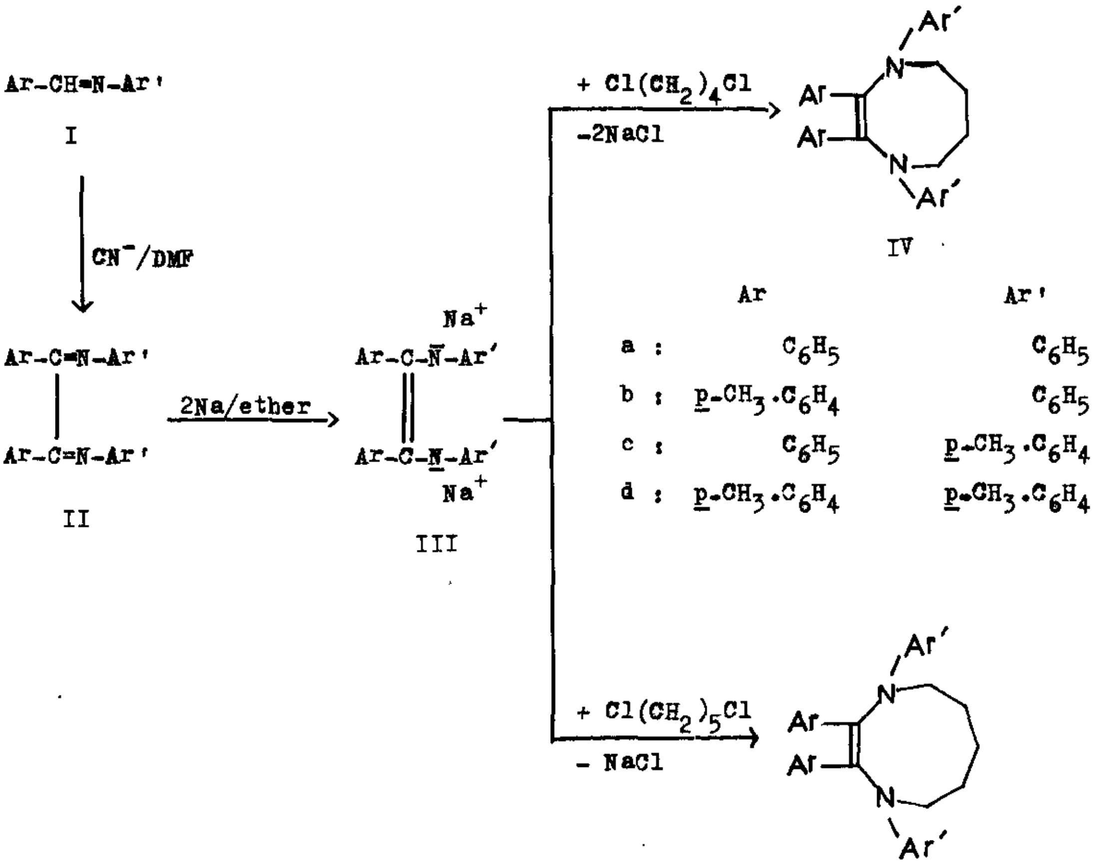
Treatment of dianils with sodium in dry ether followed by addition of 1,4-dichlorobutane and 1,5-dichloropentane gave 1,2,3,4-tetraaryl-1,4,5,6,7,8-hexahydro-1,4-diazocines and 1,2,3,4-tetraaryl-4,5,6,7,8,9-hexahydro-1H-1,4-diazonines respectively.

A few derivatives of diazocines and diazonines have been reported earlier in literature.1) No method of direct syntheses of these compounds is available. We now report a new and convenient procedure for preparing 1,2,3,4-tetraaryl-1,4,5,6,7,8-hexahydro-1,4-diazocines and 1,2,3,4-tetraaryl-4,5,6,7,8,9-hexahydro-1H-1,4-diazonines. These compounds, being homologues of diazepines, are potential biologically active agents.

Treatment of dianils (IIa-d) with sodium in dry ether and subsequent addition of dry 1,4-dichlorobutane gave 1,2,3,4-tetraaryl-1,4,5,6,7,8-hexahydro-1,4-diazocines (IVa-d) which were crystallised from benzene-ethanol mixture. Similar treatment of dianils IIa and IIc with sodium in dry ether and subsequent addition of dry 1,5-dichloropentane gave 1,2,3,4-tetraaryl-4,5,6,7,8,9-hexahydro-1H-1,4-diazonines (Va,c) which were crystallised from benzene-ethanol mixture. The structures of these compounds were confirmed by the satisfactory spectral data and elemental analyses.2)

The formation of the products IVa-d and Va,c from the dianils is depicted in the following scheme :



	Ar	Ar'
a :	C_6H_5	C_6H_5
b :	p-$CH_3.C_6H_4$	C_6H_5
c :	C_6H_5	p-$CH_3.C_6H_4$
d :	p-$CH_3.C_6H_4$	p-$CH_3.C_6H_4$

V

	Ar	Ar'
a :	C_6H_5	C_6H_5
c :	C_6H_5	p-$CH_3.C_6H_4$

This synthesis involves the initial formation of dianion III3), by the electron transfer from sodium to dianil, which attacks 1,4-dichlorobutane and 1,5-dichloropentane with elimination of chloride ions (detected by the formation of silver chloride with aq. silver nitrate) to give rise to 1,2,3,4-tetraaryl-1,4,5,6,7,8-hexahydro-1,4-diazocine and 1,2,3,4-tetraaryl-4,5,6,7,8,9-hexahydro-1H -1,4-diazonine, respectively.

Table: 1,4-Diazocines IV and 1,4-diazonines V obtained from dianils

Starting materials	Products[a]	mp (°C)	Yield %
IIa	IVa	205-207	65
IIb	IVb	199-200	50
IIc	IVc	249-250	70
IId	IVd	194-195	60
IIa	Va	212	57
IIc	Vc	223-224	40

a Recrystallised from benzene-ethanol mixture.

EXPERIMENTAL

The starting materials (IIa-d) were prepared by stirring an equimolar mixture of Schiff bases (Ia-d) and sodium cyanide in dry DMF for 72 hr at room temperature (20°) following the reported method[4)].

1,2,3,4-Tetraaryl-1,4,5,6,7,8-hexahydro-1,4-diazocines (IVa-d).

Sodium pieces (1g, 0.044g atom) were slowly added to dry ether (60 ml) with stirring under a nitrogen atmosphere and a solution of dianil (0.005mole) in dry ether (10 ml) was added dropwise; stirring at reflux temperature was continued for 4 hr and the contents were allowed to cool. Unreacted sodium pieces were removed. Dry 1,4-dichlorobutane (0.01 mole) was slowly added and the mixture was heated to reflux. The ethereal suspension was washed 2-3 times with water and dried over anhydrous sodium sulphate. The solvent was removed on a rotary evaporator and the residual material was crystallised from benzene-ethanol mixture.

1,2,3,4-Tetraaryl-4,5,6,7,8,9-hexahydro-1H-1,4-diazonines (Va-b).

In place of 1,4-dichlorobutane in the above procedure dry 1,5-dichloropentane was slowly added.

The yield and mp of the products have been given in Table.

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REFERENCES AND NOTES

1. H. Grinberg, S. Lamdan and C.H. Gaozza, J.Heterocyclic Chem., 1975, 12, 763.
2. For example the spectral data for compounds IVa and Va are as follows:
   IVa: IR ν_{max}^{Nujol} cm^{-1}: 1600 (C=C), UV λ_{max}^{EtOH} nm: 288, 380, NMR ($CDCl_3$) δ : 1.75 (m,4H,C-CH_2), 4.00 (m,4H,N-CH_2), 7.10 (m,20H,arom.).
   Va : IR ν_{max}^{Nujol} cm^{-1}: 1600 (C=C), UV λ_{max}^{EtOH} nm: 290, 380, NMR ($CDCl_3$) δ : 1.66 (m,6H,C-CH_2), 4.00 (m,4H,N-CH_2), 6.91 (m,20H,arom.).
3. K.N. Mehrotra and G. Singh, Synthesis, 1980, 1001.
4. J.S. Walia, L. Guillot, J. Singh, M.S. Chattha and M. Satyanarayana J.Org.Chem., 1972, 37, 135.

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