

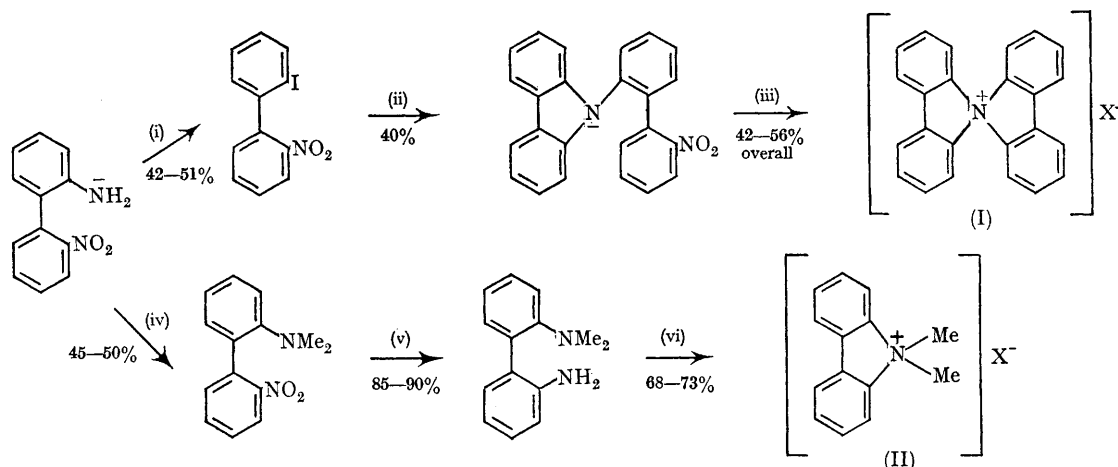
2,2'-Biphenyleneammonium Salts

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IN 1963, Nesmeyanov¹ synthesised the first, and until now the only known tetra-arylammonium salt containing the 2,2'-biphenylylenediphenylammonium cation. In connection with our work

on spiro-compounds of the main group elements,² we prepared the bis-2,2'-biphenyleneammonium cation (I) in a manner analogous to Nesmeyanov's (see Scheme).



(i) Diazotisation (KI) (42—51%); (ii) Carbazole-Cu; (iii) a, Reduction, b, Diazotisation (AcOH), c, heat; (iv) $\text{CH}_3\text{I}-\text{OH}^-$; (v) Reduction; (vi) Same as (iii) and then heat.

The following salts with cation (II) were obtained and analysed:

X	I	Br	Cl	I_3	BPh_4	$\text{BF}_4\text{H}_2\text{O}$	HgI_3	Picr.	PVI†
M.p.	285—288°	319—321	325—328	221—222	286—291	280—282	206—208	229—230	283—286

† PVI = tris-2,2'-biphenylenephosphate anion.

With the same starting material,³ an alternate carbazolum salt, the 2,2'-biphenylenedimethylammonium cation (II), was easily synthesised. The iodide of (II) is rather unstable; it decomposes rapidly at its m.p. (100—102°) and more slowly when heated in solution up to about 70°, yielding quantitatively *N*-methylcarbazole (and

methyl iodide).⁴ The corresponding tetraphenylborate (decomp. 188—191°) and tetrafluoroborate (decomp. 220—222°) are more stable. The n.m.r. spectrum of the latter shows methyl resonance at τ 5.92 and an aromatic multiplet at τ 1.4—2.3. Investigations with (II) as a methylation agent are in progress.

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¹ A. N. Nesmeyanov, T. P. Tolstaya, and A. V. Grib, *Doklady Akad. Nauk S.S.S.R.*, 1963, **153**, 608.

² G. Wittig and D. Hellwinkel, *Chem. Ber.*, 1964, **97**, 769; D. Hellwinkel, *Chem. Ber.*, 1965, **98**, 576; 1966, **99**, 3628; D. Hellwinkel and G. Kiltbau, *Annalen*, 1967, **705**, 86; *Chem. Ber.*, 1968, **101**, 121; D. Hellwinkel and G. Fahrback, *Annalen*, 1968, **712**, 1; 1968, **715**, 68.

³ J. A. Cade and A. Pilbeam, *J. Chem. Soc.*, 1964, 114.

⁴ The acyclic compound diphenyldimethylammonium iodide decomposes at ca. 160° (S. Gadowska and H. Decker, *Ber.*, 1903, **36**, 2487; E. D. Hughes and D. J. Whittingham, *J. Chem. Soc.*, 1960, 809).