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A STABLE 1,2-DIAZOCINE SYSTEM: 3,8-DIPHENYL-1,2-DIAZACYCLOOCTA-2,4,6,8-TETRAENES

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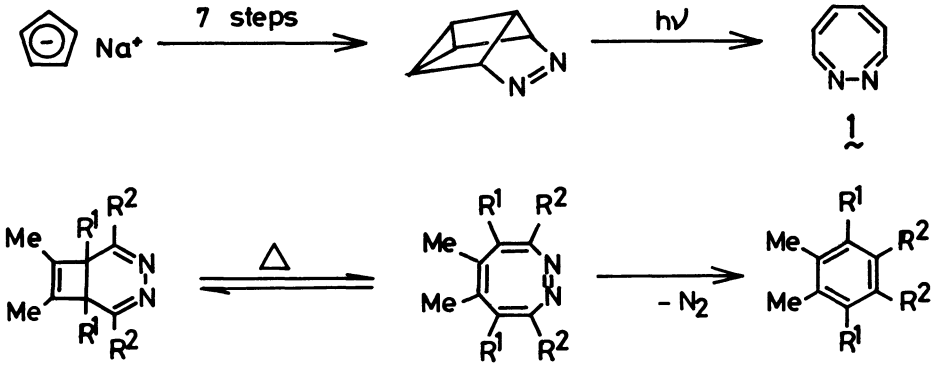
Stable 1,2-diazocines, 3,8-diphenyl-1,2-diazacycloocta-2,4,6,8-tetraenes, were prepared via halogenation-dehydrohalogenation sequences starting from readily available 3,8-diphenyl-1,2-diazacycloocta-2,8-diene. Thermolysis and photolysis of the 1,2-diazocines are also described.

In spite of rich chemistry of cyclooctatetraenes,[1] 1,2-diazacycloocta-2,4,6,8-tetraenes (1,2-diazocines) have not attracted much attention. Although dibenzo[c,g][1,2]diazocine[2] and substituted dibenzo[d,f][1,2]diazocines[3] have been prepared and found to be stable, 1,2-diazocines free of benzo groups have not been known until Trost et al.[4] succeeded in an elegant synthesis of parent 1,2-diazocine 1, which decomposes slowly in solution at room temperature and rapidly in the neat, by irradiation of diazatetracyclooctene. On the other hand, an attempt to isolate substituted 1,2-diazocines by thermal valence tautomerization of diazabicyclooctatrienes was unsuccessful, but instead substituted benzenes were obtained with the elimination of nitrogen[5] (Scheme 1). Thus, substituted monocyclic 1,2-diazocines have not been prepared up to date.



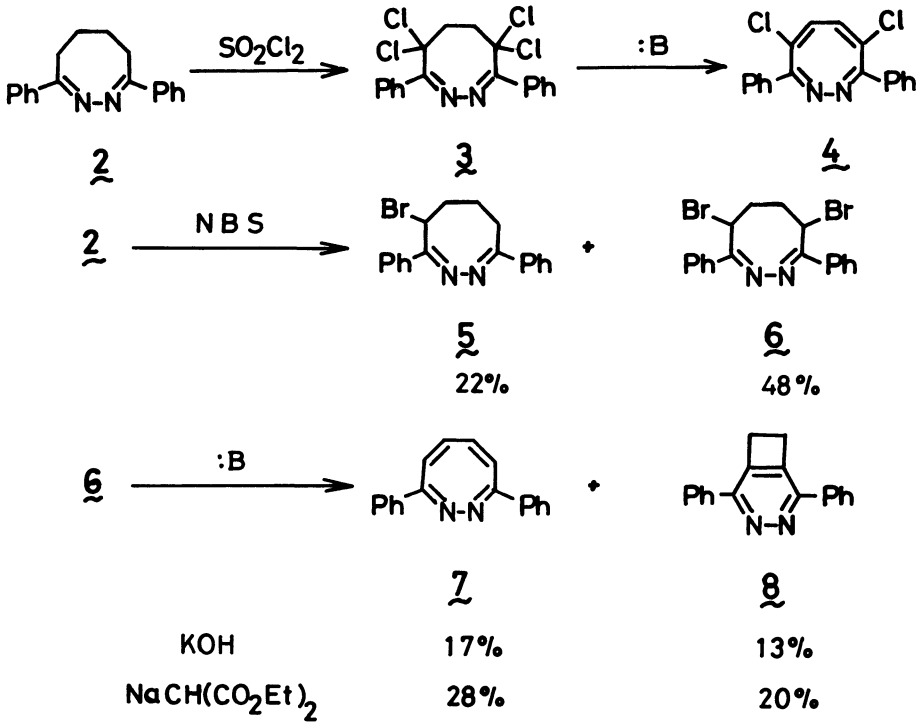
$R^1 = H, R^2 = Ph$; $R^1 = Me, R^2 = Ph$, $R^1 = R^2 = Me$

Scheme 1

We have now prepared stable monocyclic 1,2-diazocines via a classical halogenation-dehydrohalogenation sequence starting from readily available 3,8-diphenyl-1,2-diazacycloocta-2,8-diene 2[6]: This is in contrast to an unsuccessful attempt to prepare 1 via a halogenation-dehydrohalogenation sequence through 1,2-bis(t-butoxycarbonyl)-1,2-diazacyclooct-5-ene.[7] In this communication we wish to report the preparation of 3,8-diphenyl-1,2-diazocines, their thermolysis, and photolysis.

We have first investigated the preparation of a 1,2-diazocine via a chlorination-dehydrochlorination sequence starting from 2. After several attempted chlorinations under various conditions, it has been found that the 4,4,7,7-tetrachloride 3 was obtained in 83% yield on chlorination of 2

with four equivalents of sulfuryl chloride in methylene chloride at room temperature for 1 h. Dehydrochlorinations of 3 were investigated using various bases. Treatment of 3 with three equivalents of sodium hydroxide, sodium ethoxide, DBU or ethyl sodiomalonate in refluxing ethanol gave the expected 4,7-dichloro-3,8-diphenyl-1,2-diazocine 4, mp 158-159°C (dec), in 76, 79, 61 or 81% yield, respectively. On a similar treatment with triethylamine, however, 3 was unchanged. Structural elucidation of 3 and 4 was accomplished on the basis of spectral data.[8]



Scheme 2

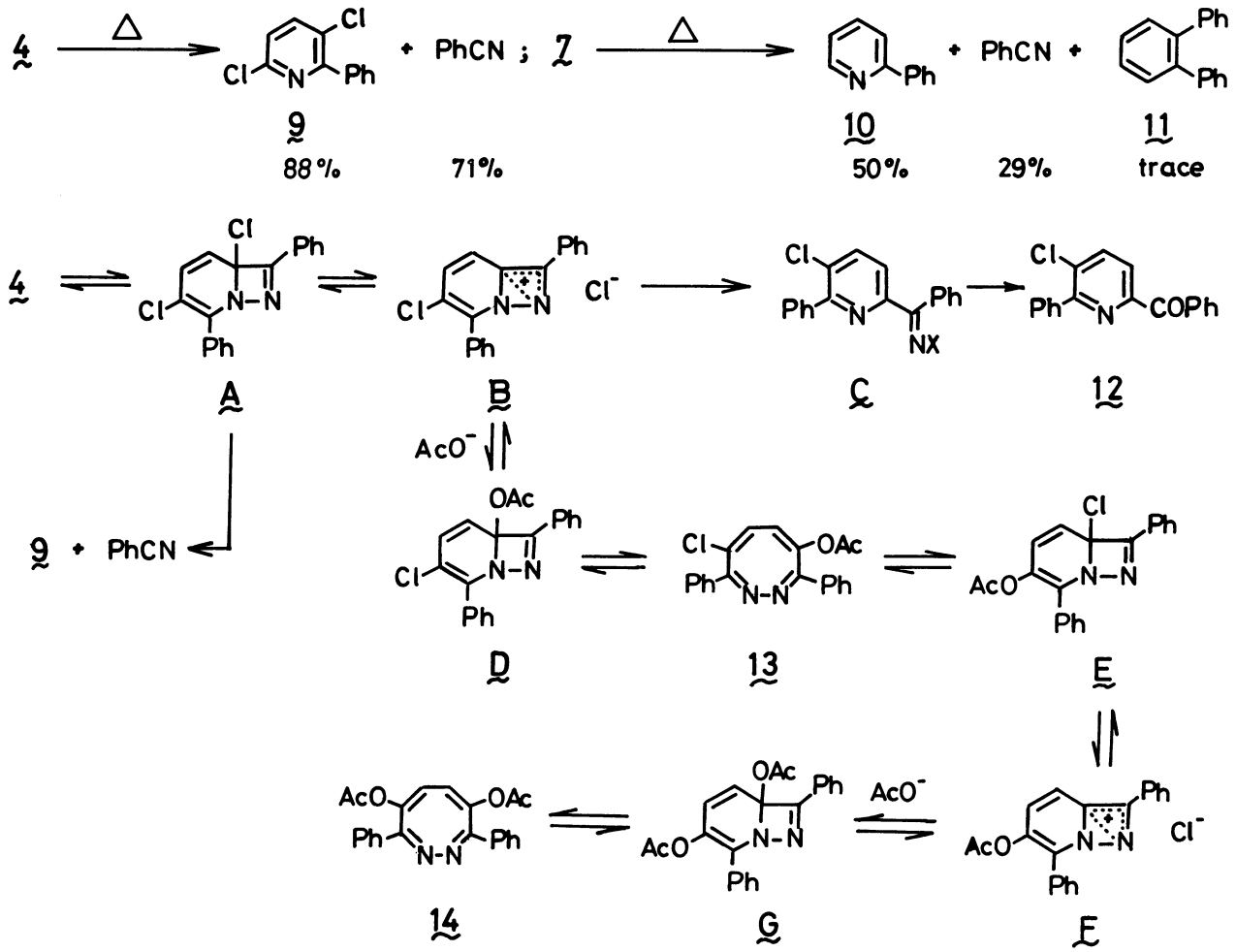
Next, a bromination-dehydrobromination sequence was investigated. Bromination of 2 with three equivalents of N-bromosuccinimide in the presence of benzoyl peroxide in refluxing carbon tetrachloride for 10 h gave a mixture of 4-bromo 5 and 4,7-dibromo derivative 6. Dehydrobromination of 6 with sodium hydroxide or ethyl sodiomalonate in refluxing ethanol afforded a mixture of 3,8-diphenyl-1,2-diazocine 7, mp 181-182°C, and cyclobutapyridazine 8, mp 195°C (lit.[9] mp 194°C).[10] The yields of 5, 6, 7 and 8 are shown in Scheme 2. Structural elucidation of 5, 6 and 7 was again accomplished on the basis of spectral data.[11]

Trost et al.[4] demonstrated that when heated 1 decomposed to benzene and pyridine with comparable rates, and when irradiated with ultraviolet light 1 gave only benzene. Thus, we have investigated thermolysis and photolysis of stable 1,2-diazocines 4 and 7.

When heated in refluxing toluene for 4 h, 4 gave 3,6-dichloro-2-phenylpyridine 9 and benzonitrile. The 1,2-diazocine 7 was rather thermally stable than 4, and when heated in toluene under reflux for 24 h, 7 afforded a mixture of 2-phenylpyridine 10 and benzonitrile, together with a trace amount of o-terphenyl 11 and unchanged 7 (35%). In contrast with 1,[4] thermolysis of 4 and 7 exclusively gave the pyridines with the extrusion of benzonitrile.

The thermolysis of 4 or 7 can be regarded as proceeding via a valence isomer, 1,8-diazabicyclo[4.2.0]octatriene, with the extrusion of benzonitrile: This was proved by the following evidence. When 4 was heated in wet toluene under reflux for 2 h, 9 and 6-benzoyl-3-chloro-2-phenyl-

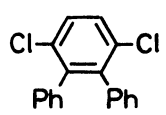
pyridine 12 were obtained in 10 and 20% yields, respectively. The 1,2-diazocine 4 was stable in refluxing benzene. However, 4 gave 4-acetoxy-7-chloro- 13, mp 138-139°C (dec), and 4,7-bis(acetoxy)-3,8-diphenyl-1,2-diazocine 14, mp 186-188°C (dec), in 6 and 53% yields respectively, when heated with six equivalents of silver acetate in benzene under reflux for 6 h. The structures 9—14 were identified on the basis of spectral data.[12]



Scheme 3

The pathways for the above thermal reactions are illustrated as shown in Scheme 3. In particular, the formation of 12, 13 and 14 strongly supports the intervention of 1,8-diazabicyclo[4.2.0]-octatrienes, A, D, E and G, and homocyclopropenium salts, B and F. In refluxing toluene A gives 9 with the extrusion of benzonitrile, whereas in wet toluene under reflux A is partially converted into 12 via B and then C (X=Cl or OH). The process 4 → A → B → C is closely similar to that of the rearrangement of bromocyclooctatetraene to trans-β-bromostyrene via a homocyclopropenium salt like B.[13] It is evident that the 1,2-diazocines 13 and 14 are formed via the processes B → D → 13 and 13 → E → F → G → 14, respectively.

On the other hand, irradiation of 4 in benzene or ethanol with Pyrex-filtered light from a 200-W high-pressure mercury lamp for 2 h afforded 1,4-dichloro-2,3-diphenyl-benzene 15 in a quantitative yield.[14] Under similar conditions, 7 gave o-terphenyl 11 in 43% yield together with unidentified oily products.



Thus, the 1,2-diazocine 4 is an useful synthon for other 1,2-diazocines bearing various substituents at 4- and 7-positions, which are convertible into pyridines and o-terphenyls; work along this line is in progress.

References

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2) W. W. Paudler and A. G. Zeiler, J. Org. Chem., 34, 3237 (1969). However, they gave the erroneous nomenclature, dibenzo[b,f][1,2]diazocine, for dibenzo[c,g][1,2]diazocine.
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6) C. G. Overberger and I. Tashlick, J. Am. Chem. Soc., 81, 217 (1959).
7) L. A. Carpino and J. P. Masaracchia, J. Org. Chem., 37, 1851 (1972).
8) All new compounds reported here gave satisfactory elemental analyses.
3: Mp 150-151°C; ^{1}H NMR ($CDCl_3$) δ 3.10 (4H, s), 7.30-7.80 (10H, m); MS m/e 398, 400, 402, 404, 406 (M^+). 4: ^{1}H NMR ($CDCl_3$) δ 6.53 (2H, s), 7.25-7.90 (10H, m); ^{13}C NMR ($CDCl_3$) δ 127.9 (d), 128.5 (d), 128.8 (s), 130.5 (d), 131.6 (d), 132.7 (s), 150.4 (s, C=N); MS m/e 326, 328, 330 (M^+). The ^{1}H NMR spectrum of 1 shows one sharp singlet at δ 6.04 (4H), which a europium shift reagent ($Eu(fod)_3$) splits into an AB quartet (J=11 Hz), and one broad singlet at δ 6.93 (2H)[4] (see ^{1}H NMR data of 7[11]).
9) G. Maier, Chem. Ber., 99, 1229 (1966).
10) Treatment of 5 with ethanolic potassium hydroxide afforded a cyclooctatriene in low yield. The 5,6-dichlorodiazocine, an isomer of 4, was obtained via a chlorination-dehydrochlorination sequence starting from the cyclooctatriene.
11) 5: Mp 112-113°C; ^{1}H NMR ($CDCl_3$) δ 1.40-3.10 (6H, m), 4.70-5.05 (1H, m), 7.25-8.15 (10H, m); MS m/e 340, 342 (M^+). 6: Mp 141-142°C; ^{1}H NMR ($CDCl_3$) δ 2.20-2.45 (4H, m), 5.30-5.62 (2H, m), 7.35-7.95 (10H, m); MS m/e 418, 420, 422 (M^+). 7: ^{1}H NMR ($CDCl_3$) δ 6.49 (4H, s), 7.30-7.90 (10H, m); ^{1}H NMR (DMSO-d_6) δ 6.45, 6.58 (each 2H, d, J=11.2 Hz), 7.05-7.60 (10H, m); ^{13}C NMR ($CDCl_3$) δ 127.2, 128.3, 129.2, 129.8, 135.7, 153.1 (C=N); MS m/e 258 (M^+).
12) 9: Mp 100-101°C; ^{1}H NMR ($CDCl_3$) δ 7.10, 7.59 (each 1H, d, J=8.0 Hz), 7.30-7.85 (5H, m); MS m/e 298, 300, 302 (M^+). 12: Mp 119-120°C; IR (KBr) 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.20-8.25 (m); MS m/e 293, 295 (M^+). 13: IR (KBr) 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.97 (3H, s), 6.20, 6.80 (each 1H, d, J=4.5 Hz), 7.21-7.48 (6H, m), 7.50-7.80 (4H, m); ^{13}C NMR ($CDCl_3$) δ 20.4 (q, CH_3), 119.6 (d, CH=), 127.6, 128.0, 128.4, 128.5 (each d), 128.9 (s, =C(Cl)), 132.9, 133.2 (each s), 144.4 (s, =C(OAc)), 149.2, 150.0 (each s, C=N), 166.9 (s, C=O); MS m/e 350, 352 (M^+). 14: IR (KBr) 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.98 (6H, s), 6.22 (2H, s), 7.25-7.42 (6H, m), 7.45-7.76 (4H, m); ^{13}C NMR ($CDCl_3$) δ 20.5 (q, CH_3), 118.3, 127.8, 128.4, 130.0 (each d), 133.5 (s), 145.1 (s, =C(OAc)), 149.0 (s, C=N), 167.0 (s, C=O); MS m/e 374 (M^+). IR spectra of the compounds 10 and 11 were identical with those of authentic samples, respectively.
13) R. Huisgen and W. E. Konz, J. Am. Chem. Soc., 92, 4102 (1970); W. E. Konz, W. Hechtl, and R. Huisgen, ibid., 92, 4104 (1970).
14) 15: Mp 169-170°C; ^{1}H NMR ($CDCl_3$) δ 6.90-7.30 (10H, m), 7.37 (2H, s); MS m/e 298, 300, 302 (M^+).

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