Ring Closure of Heterocyclic Systems by Potassium-Graphite Intercalat – C_8K

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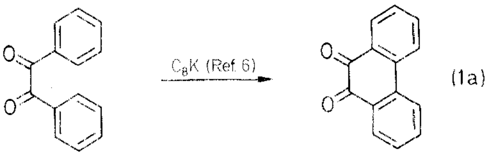
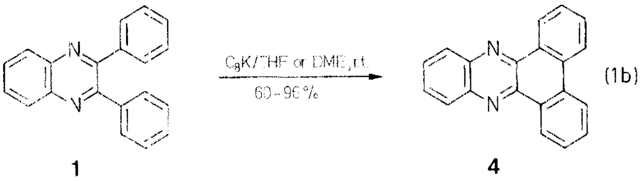
Potassium-graphite intercalate C_8K is the reagent of choice for the ring closure of the dianions of 2,3-diarylquinoxalines derivatives **1–3** to the dianions of dibenzo[*a*, *c*]phenazine derivatives **4–6** in high yields and high degree of purity. This process appears to occur *via* a thermal electrocyclic process of the dianions.

Potassium-graphite intercalate, C_8K, is a useful and efficient reducing agent.[1-3] Its highly ordered structure, combined with high reactivity, enables selective reduction processes such as reductive dimerization of ketones[4] and stereospecific debromination.[5]

Recently, we have reported the reaction of benzil with C_8K to form phenanthrenequinone in good yields and high purity[6] (eq. 1 a). In that reaction C_8K reacts with the carbonyl groups of the benzil to form a dianion, which in turn undergoes ring closure followed by aromatization of the biphenyl skeleton.

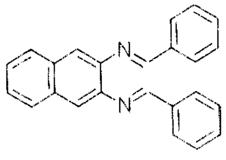




1 **4**

DME = dimethoxyethane

We now wish to report the use of C_8K in a ring closure reaction leading to heterocyclic systems (eq. 1 b). This reagent is convenient and leads to an easy preparation of nitrogen containing systems. The presence of two adjacent heteroatoms is common to both reactions presented in equations 1 a and 1 b. As presented in the Table, three substrates, 2,3-diphenylquinoxaline (**1**), 2,3-diphenylbenzo[*g*]-quinoxaline (**2**), and 2,3-di-*p*-tolylquinoxaline (**3**) were reacted with C_8K to form dibenzo[*a*, *c*]phenazine (**4**), tribenzo[*a*, *c*, *i*]phenazine (**5**), and 3,6-dimethyldibenzo[*a*, *c*]phenazine (**6**), respectively.



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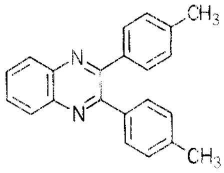

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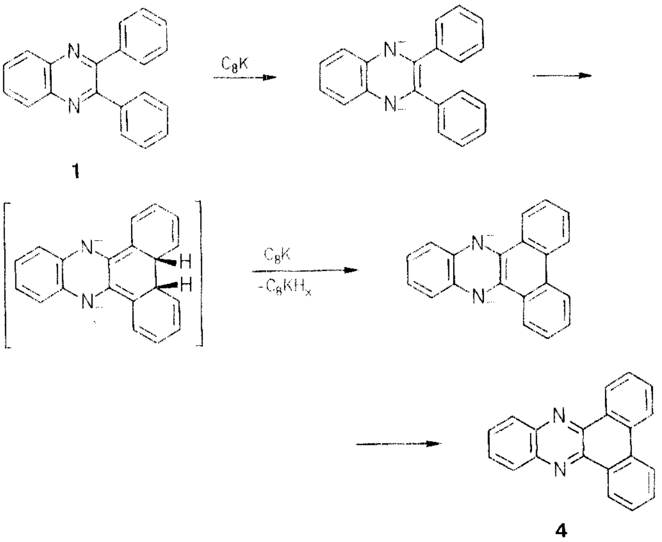
Attempts to react the substrates with dispersed potassium under similar conditions resulted only with decomposition products. We found that sodium metal reacts in the same manner, but at a much slower rate. The reduction process of **1** with sodium wire (in tetrahydrofuran-d_8) in an evacuated NMR tube was followed successively. In this experiment we could detect the formation of $\mathbf{1}^{2-}$ and after several weeks the spectrum of $\mathbf{4}^{2-}$ appeared, followed by disappearance of that of $\mathbf{1}^{2-}$. No spectrum of any other intermediate was observed.



Suggested mechanism for the conversion of **1** to **4**

Table. Ring Closure Products of Phenyl-Substituted Nitrogen Heterocyclic Substrates.

Substrate	Product	Yield (%) (solvent)	m.p. (°C)	MS (70 eV)[a] m/e	^{1}H-NMR (THF-d_8)[b] δ (ppm)	Ref. for Lit. Data
1	**4**	70 (THF) 85 (DME)	223–224	226	9.37 (dd, 2H, J = 8.3 Hz); 8.53 (dd, J = 7.7 Hz, 1,5 Hz); 8.38, 7.84 (AA′ BB′, 4H); 7.75 (m, 4H)	10,7
2	**5**	60 THF) 65 (DME)	292–294	330	9.52 (d, 2H, J = 6.6 Hz); 9.05 (s, 2H); 8.75 (2H, J = 8.1 Hz); 8.33, 7.69 (AA′ BB′, 4H); 7.83 (m, 4H)	11
3	**6**	90 (THF) 96 (DME)	250–251	308	9.32 (d, J = 8.1 Hz, 2H); 8.55 (s, 2H); 8.35, 7.93 (AA′ BB′, 4H); 7.63 (dd, 2H, J = 8.5 Hz, 1.4 Hz); 2.71 (s, 6H).	12

[a] Recorded on a Varian MAT 311 spectrometer.

[b] NMR spectra were obtained on Bruker WH-300 pulsed FT spectrometer operating at 300.133 MHz for ^{1}H-NMR. The field/frequency regulations were maintained by ^{2}H locking and digitalized on an Aspect 2000 computer (32 K).

On the basis of the ^{1}H-NMR spectrum we suggest that the ring closure occurs *via* the dianion. Aromatization then occurs, although no hydrogen evolution could be detected, presumably due to adsorption of hydrogen on the metal intercalate.[9]

This ring closure process using C_8K affords an entry into a variety of polyheterocyclic compounds. Further investigations on the mechanism as well as on the synthetic applications of this reaction are under way.

All starting materials were prepared according to literature procedure by the reaction of benzil or 4,4′-dimethylbenzil with the appropriate diamine.[7] Their physical properties were identical to literature values.[7]

Potassium-Graphite Intercalate, C_8K:
Graphite powder (BDH, synthetic; 2.4 g) is placed in a 100 ml three-necked round-bottomed flask at 150 °C, magnetically stirred and kept under argon atmosphere. After 15 min, potassium (1 g, 25 mmol) is added in slices, and bronze colored C_8K (ca. 25 mmol) is formed. The reagent is cooled to r.t. and kept under argon.[13]

Dibenzo[*a*, *c*]phenazine Derivatives 4–6; General Procedure:
Freshly prepared C_8K (25 mmol) is covered with dry solvent (tetrahydrofuran or dimethoxyethane; 20 ml). Substrate **1**, **2**, or **3** (2 mmol) in solvent (30 ml) is added, and the reaction mixture is stirred at r.t., until starting material disappears (TLC: silica gel, petroleum ether/chloroform, 2:1). The reaction mixture is quenched with ethanol (10 ml), and filtered through a cintered glass funnel. Dichloromethane (20 ml) is passed through the funnel to wash traces of product. The filtrate is washed with water (3 × 20 ml), and the organic phase is dried with magnesium sulfate. Evaporation of the solvent followed by recrystallization from ethanol affords the cyclized product (Table).

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