reduced pressure left an oil, which slowly solidified upon standing. The resulting solid was triturated with ether and filtered under a dry nitrogen purge to give to a white solid (4.21 g, 97%): mp 73 °C; IR ($CHCl_3$) 2995 (m), 1750 (s), 1615 (m), 1597 (m), 1452 (s), 1350 (s), 1275 (s), 1225 (s), 1162 (m), 1028 (s) cm^{-1}; NMR ($CDCl_3$, 270 MHz) 7.90–7.20 (m, 10 H), 4.96 (s, 2 H), 4.33 (q, J = 7 Hz, 2 H), 3.95 (s, 3 H), 1.32 (t, J = 7 Hz, 3 H).

2-Carbethoxy-1-methyl-3,3-diphenylaziridine (5). 1-Carbethoxy-*N*-methyl-*N*-(diphenylmethylene)methanaminium trifluoromethanesulfonate (**2**) (138 mg, 0.32 mmol) was dissolved in tetrahydrofuran (3.2 mL) at room temperature and then cooled to −78 °C. To this homogenous solution was added potassium *tert*-butoxide (0.89 mL, 0.36 M in THF, 0.32 mmol) via syringe. The resultant deep red solution was stirred at −78 °C for 40 min and then added dropwise, via cannula, to a heated (102 °C) stirring solution of pyridine (0.10 mL, 1.24 mmol) in toluene (9.0 mL). The addition required approximately 8 min to complete, after which time the reaction was heated for an additional 30 min. The reaction mixture was cooled and the solvents were removed in vacuo. The residue was dissolved in ether and filtered through a glass wool plug. The ether was removed by rotary evaporation and the resultant orange oil was purified via column chromatograph [silica gel, hexanes/ethyl acetate, 4:1 (v/v)] to afford benzophenone (10 mg, 17%) and then the desired aziridine **5** as a clear oil (70 mg, 78%, R_f 0.2): IR ($CHCl_3$) 3020 (w), 2975 (m), 1740 (s), 1470 (m), 1450 (m), 1300 (m), 1270 (s), 1185 (s) cm^{-1}; NMR ($CDCl_3$, 270 MHz) 7.40–7.18 (m, 10 H), 4.00–3.85 (m, 2 H), 3.03 (s, 1 H), 2.28 (s, 3 H), 0.85 (t, 3 H, J = 7.1 Hz); MS (m/z) 281 (M^+), 55 (base); exact mass calcd for $C_{18}H_{19}NO_2$ 281.14157, obsd 281.1418 (0.8 ppm error).

2-Carbethoxy-3,4-dicarbomethoxy-1-methyl-5,5-diphenyl-3-pyrroline (7). Potassium *tert*-butoxide (1.90 mL, 0.53 M in THF, 1.00 mmol) was added to a suspension of iminium salt **2** (431 mg, 1.00 mmol) in THF (10 mL) at −78 °C. The resulting deep red solution was stirred for 5 min after which time dimethyl acetylenedicarboxylate (135 μL, 142 mg, 1.00 mmol) was added and the reaction was allowed to warm to room temperature over 1 h. The solvent was removed by rotary evaporation and the residue was subjected to silica plug filtration using ether as the eluent. Purification of the resultant oil by PTLC (silica gel, 20% ethyl acetate/hexane) afforded pyrroline **7** (360 mg, 87% R_f 0.23) as an oil: IR ($CHCl_3$) 3000 (m), 2945 (m), 1742 (s), 1736 (s), 1440 (m), 1285 (s), 901 (s) cm^{-1}; NMR ($CDCl_3$, 270 MHz) 7.68–7.08 (m, 10 H), 4.37 (s, 1 H), 4.24 (q, J = 7 Hz, 2 H), 3.76 (s, 3 H), 3.50 (s, 3 H), 1.99 (s, 3 H), 1.27 (t, J = 7 Hz, 3 H); MS (m/z) 423 (M^+), 350 (base); exact mass calcd for $C_{24}H_{25}NO_6$ 423.16816, obsd 423.1680 (−0.4 ppm error).

1-(Carbethoxymethyl)-3,4-dicarbomethoxy-2,2-diphenyl-3-pyrroline (12). Carbethoxymethyl trifluoromethanesulfonate (95 μL, 130 mg, 0.55 mmol) was added to a solution of imine **8** (250 mg, 0.55 mmol) in methylene chloride (600 μL). After 24 h, the solvent was removed under a dry stream of nitrogen and replaced with acetonitrile (4 mL). Dimethyl acetylenedicarboxylate (68 μL, 78 mg, 0.55 mmol) was added to this solution, which was then transferred by cannula into a flask containing anhydrous cesium fluoride (662 mg, 4.36 mmol). After stirring at ambient temperature for 23 h, the solvent was removed by rotary evaporation and the residue was subjected to a silica pork workup. The crude product was purified by PTLC (silica gel, 20% ethyl acetate/hexane) to give cycloadducts **12** (117 mg, 52%, R_f 0.22) and **7** (19 mg, 8%, R_f 0.14). Cycloadduct **12**: IR ($CHCl_3$) 3025 (m), 3000 (m), 2955 (m), 2900 (w), 2850 (w), 2790 (w), 1730 (s), 1670 (m), 1490 (m), 1445 (s), 1370 (m), 1272 (s), 1210 (s), 1192 (s), 1110 (m), 1080 (m), 1030 (m), 970 (m), 905 (w), 855 (w), 790 (w), 695 (m) cm^{-1}; NMR ($CDCl_3$, 270 MHz) 7.40 (m, 10 H), 4.10 (q, J = 7 Hz, 2 H), 4.06 (s, 2 H), 3.80 (s, 3 H), 3.52 (s, 3 H), 2.91 (s, 2 H), 1.20 (t, J = 7 Hz, 3 H); MS (m/z) 423 (M^+); exact mass calcd for $C_{24}H_{25}NO_6$ 423.16815, obsd 423.1680 (−0.4 ppm error).

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Registry No. **1**, 13280-16-5; **2**, 108795-80-8; **3**, 108795-81-9; **5**, 108795-82-0; **6**, 108795-83-1; **7**, 108795-84-2; **8**, 51411-41-7; **9**, 108795-86-4; **11**, 108795-87-5; **12**, 108795-88-6; DMAD, 762-42-5; $CF_3SO_3CH_2CO_2Et$, 61836-02-0.

Hyper-Acyloin Condensation, from Simple Aromatic Esters to Phenanthrenequinones: A New Reaction of C_8K

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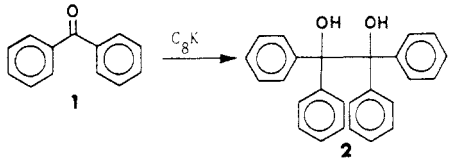
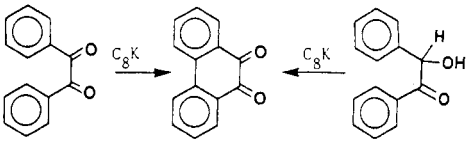
Introduction

Potassium–graphite intercalation compound, C_8K, is a useful and efficient reducing agent. In this compound potassium atoms are located in a highly ordered mode between the carbon layers of graphite. This structural feature enables a selective reactivity of C_8K, in comparison to nonintercalated dispersed potassium.[1] For example, benzophenone (**1**) undergoes a bimolecular reduction process with C_8K to form the corresponding pincaol (**2**). A "layer edgel mechanism" has been suggested to explain this specific behavior[2] (eq 1).



(1)



(2)

Recently, we reported a unique ring-closure process that occurs in the reaction of C_8K with benzil (**3**) to yield phenanthrenequinone (**4**)[3] (eq 2). In this reaction, formation of the benzil dianion (3^{2-}) is followed by a pericyclic cyclization. The resulting dianion 4^{2-} is quenched by water, and upon air oxidation phenanthrenequinone (**4**) is obtained. The same product is obtained when C_8K is reacted with benzoin (**5**). In this case, the first step is deprotonatin followed by enolization to form benzil dianion (3^{2-}), and following the sequence mentioned above phenanthrenequinone is produced[4] (eq 2). The high efficiency of this ring-closure reaction can be rationalized by the positioning of 3^{2-} in a syn conformation. This conformation can be achieved by a linkage of the dianion to the intercalate layer edge[2] (Figure 1).

Aromatic acid esters, e.g., methyl benzoate, undergo an acyloin condensation reaction with alkali metals to form a benzoin derivative.[5] However, this condensation usually gives low yields and generally is not considered an attractive synthetic method. Furthermore, the mechanism is not well established, although it is usually assumed that an α-diketone is an intermediate.

Results and Discussion

In view of the above-mentioned reactions of benzo-

(1) General reviews: (a) Boersma, M. A. M. *Catal. Rev.—Sci. Eng.* **1974**, *10*, 243. (b) Bergbreiter, D. E.; Killough, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2126. (c) McKillop, A.; Young, D. W. *Synthesis* **1979**, *401*, 81. (d) Setton, R.; Beguin, F. *Synth.* **1982**, *4*, 299.
(2) Tamarkin, D.; Rabinovitz, M. *Synth. Met.* **1982**, *4*, 299.
(3) Tamarkin, D.; Benny, D.; Rabinovitz, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 642.
(4) Tamarkin, D.; Rabinovitz, M., unpublished results.
(5) General references on the acyloin condensation: Finley, K. T. *Chem. Rev.* **1964**, *64*, 573. Smith, B. H. *Bridged Aromatic Compounds*; Academic: New York, 1964; p 27. Bloomfield, J. J.; Nelke, J. M. *Org. React. (N.Y.)* **1976**, *23*, 250.

0022-3263/87/1952-3472$01.50/0

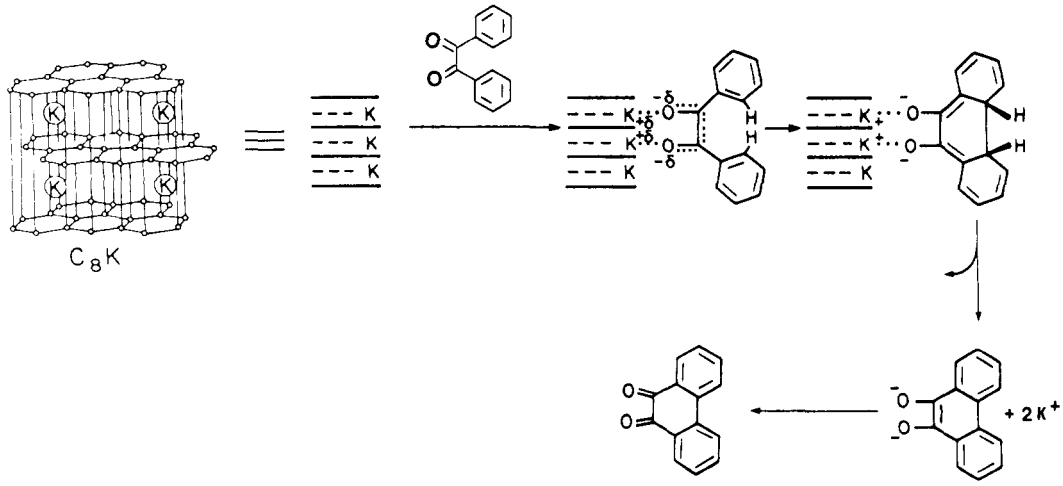


Figure 1. Layer edge mechanism of the reaction of C_8K with α-diketones.

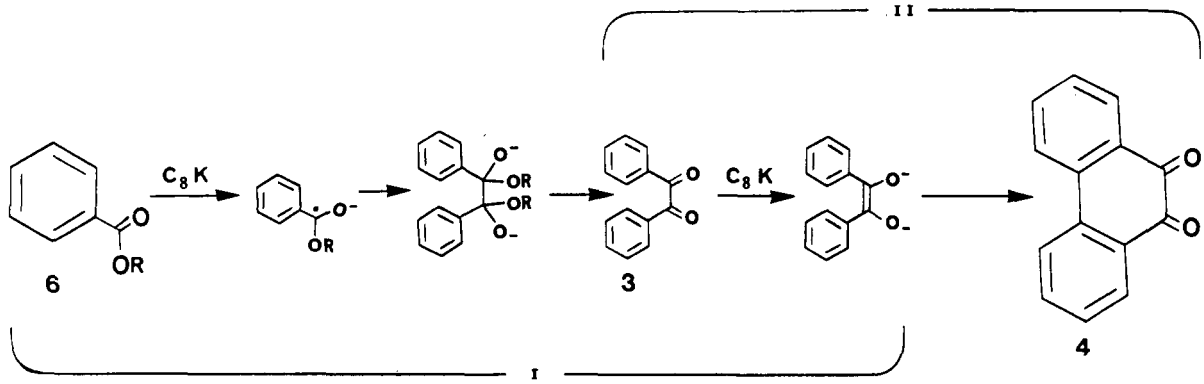


Figure 2. The stepwise reaction of C_8K with aromatic acid esters.

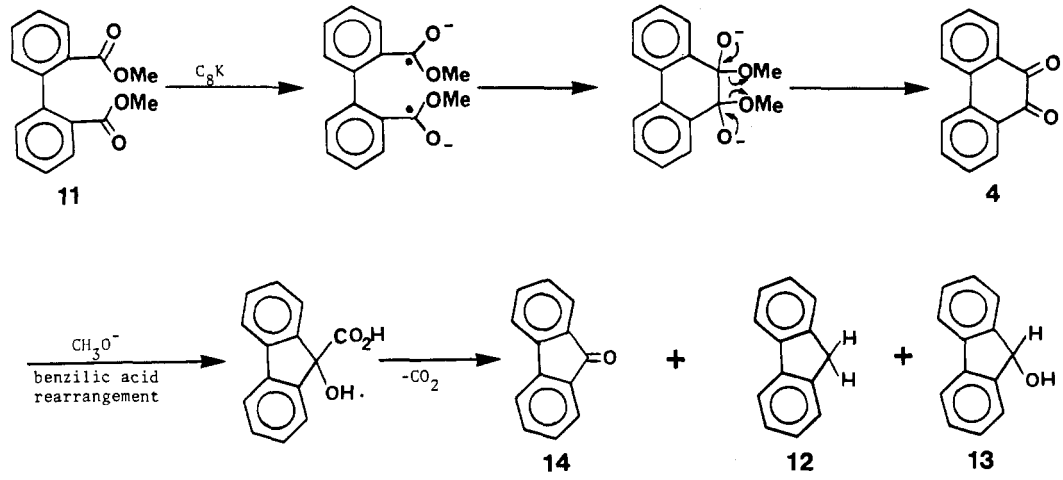


Figure 3. Reaction of C_8K with dimethyl diphenate (11).

phenone and benzil with C_8K we postulated the following: (a) Treatment of aromatic acid esters with C_8K should provide an enhancement of the reductive coupling step of the condensation, and (b) if an α-diketone is indeed an intermediate in the acyloin condensation reactions of aromatic acid esters, then excess of C_8K should afford a further reaction, namely, the ring-closure reaction to yield phenanthrenequinone.

These considerations led lus to investigate the reaction of C_8K with aromatic acid esters. A series of esters were treated with C_8K under several reactions conditions, and the results are shown in Table I. We found that methyl benzoate (**6a**) and ethyl benzoate (**6b**) were converted to phenanthrenequinone (**4**) in a one-pot reaction. In the same manner, methyl and ethyl esters of *p*-toluic acid (**7a** and **7b**) and methyl ester of cumic acid (methyl *p*-isopropylbenzoate) (**8**) afforded phenanthrenequinone derivatives **9** and **10**, respectively (Figure 2, Table I). Samples that were analyzed by TLC in the course of the reaction of **6** showed the formation of benzil, which gradually disappeared with the formation of **4**.

When dimethyl diphenate (**11**) was treated with C_8K, three major products were obtained (See Figure 3 and Table I): phenanthrenequinone (**4**), fluorene (**12**) and fluorenol (**13**). Traces of fluorenone (**14**) were also found. The formation of **12** and **13** is attributed to a further reaction of **4** with potassium methoxide (i.e., a benzilic acid rearrangement) followed by decarboxylation to fluorenol, which undergoes transformation to **12** and **14**. Support for this conclusion was obtained through the observation

Table I. Reaction of C_8K with Aromatic Acid Esters

ester	product	yield (THF), %	yield (DME), %
6a	4	30	30
6b	4	30	30
7a	9	26	40
7b	9	41	38
8	10	30	30
11	4	30	13
	12	16	27
	13	30	19
	14	5	4

that treatment of fluorenone with C_8K yielded only **12** and **13**.

The bimolecular reactions of **6–8** involve two steps: (I) formation of benzil from the ester, following the classical acyloin condensation pattern; (II) the conversion of benzil to phenanthrenequinone[3] (Figure 2). The combination of these two synthetic steps in one reaction and the facile conversion of very simple and inexpensive starting compounds into complex products make the reaction of aromatic acid esters with C_8K an attractive and valuable synthetic tool. Although the overall yields of the reaction are not high, the efficiency of the coupling step is much better than in the classical acyloin condensation. Furthermore, the succeeding ring closure provides a new entry to the preparation of phenanthrenequinone derivatives from readily available single ring compounds.

Our results are also interesting from the mechanistic point of view. In all the various reactions of C_8K that lead to phenanthrenequinone formation, the mechanistic pathway involves the conversion of $\mathbf{3}^{2-}$ to **4**. In the case of the aromatic esters, it seems that dianion $\mathbf{3}^{2-}$ is formed by reduction of benzil (**3**) with excess C_8K, the benzil having been formed by cleavage of two methoxy groups from the biradical coupling product (Figure 2).

These results shed light on the controversial mechanism of the acyloin reaction,[5,6] proving that benzil *is* an intermediate in this condensation. The fact that a dianion of an α-diketone is essential to the further ring-closure process on the one hand and the formation of the diketone **4** from the diphenic acid ester on the other may serve as evidence for the existence of benzil as a key intermediate in the acyloin condensation sequence.

Experimental Section

General Methods. All C_8K preparations and reactions were carried out in flame-dried glassware under argon atmosphere. Tetrahydrofuran was dried over potassium metal and distilled prior to use; dimethoxyethane was dried by distillation over lithium aluminum hydride. NMR spectra were recorded on Bruker WH-300 pulsed FT spectrometer operating at 300.133 MHz. Chemical shifts are expressed in ppm downfield from Me_4Si. Mass spectra were determined on Varian MAT 311 (70 eV). A Perkin-Elmer 157 G spectrophotometer was used for IR spectra. Melting points (°C) are uncorrected.

Preparation of Starting Esters 6–8 and 11. All the esters were prepared from the appropriate acids and alcohols according to the literature procedure.[7]

Preparation of C_8K.[8] Graphite powder (2.4 g, BDH, synthetic) was placed in a 100-mL argon-flushed and flame-dried three-necked round-bottomed flask at 150 °C, magnetically stirred and kept under argon atmosphere. After 15 min, 1 g (25 mmol) of clean potassium metal was added in slices. The stirring at 150 °C was continued until the bronze-colored C_8K was formed. The reagent was cooled to room temperature and kept under argon.

3,6-Diisopropylphenanthrenequinone (10). Freshly prepared C_8K (25 mmol), placed in the apparatus described above, was covered with 50 mL of dry solvent (dimethoxyethane or tetrahydrofuran) and kept at 25 °C under argon atmosphere. Magnetic stirring was started, and a solution of 710 mg (4 mmol) of methyl *p*-isopropylbenzoate (**8**) in 50 mL of solvent was dropped into the reaction mixture over 20 min. The reaction was monitored by TLC (SiO_2; methylene chloride/petroleum ether, 1:2). After **8** had disappeared, the mixture was stirred for 1 h and then cooled to 0 °C, and 10 mL of water was added to the solution.[9] The reaction mixture was filtered through a fritted glass funnel, and the filter cake was washed with two 25-mL portions of ether. The combined filtrate was washed twice with water (20 mL), the organic phase was dried over magnesium sulfate and filtered, and the solvent was removed by evaporation. The crude product (400 mg) was then purified on a chromatographic preparative plate (SiO_2; methylene chloride/petroleum ether 1:2). Crystallization from methanol gave 175 mg of **10** (30% yield): mp 155–157 °C; ^1H NMR ($CDCl_3$) 8.1 (d, 1 H, J = 8 Hz), 7.82 (s, 1 H), 7.27 (d, 1 H, J = 8 Hz), 3.11 (sept, 1 H, J = 7 Hz), 1.34 (d, 6 H, J = 7 Hz); IR 1672, 1600, 1455, 1376, 1282, 1060, 830 cm^{-1}; MS, m/e 292.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.21; H, 6.89. Found: C, 82.41; H, 6.99.

Reaction of C_8K with Aromatic Esters: General Procedure. The procedure described above was applied to all aromatic acid esters and to diphenic acid ester. In a typical experiment the reaction time was 90–120 min. The melting points and spectra of the products were identical with the literature data. Melting point values of these products[10] are as follows: **4**, 206–208 °C; **9**, 113–116 °C; **12**, 114–116 °C, **13**, 152–153 °C; **14**, 81–83 °C.

Reaction of C_8K with Fluorenone. Freshly prepared C_8K (25 mmol) was covered by 50 mL of dry dimethoxyethane and kept at room temperature under argon atmosphere. Fluorenone (360 mg, 2 mmol) in 20 mL of dimethoxyethane was added, and the reaction mixture was magnetically stirred for 1 h. The reaction was worked up as described above. After chromatographic separation (SiO_2 preparative plate; methylene chloride/petroleum ether, 1:4) fluorene (150 mg; 0.94 mmol; 47%), mp 114–117 °C (lit. mp 117 °C) and flurenol (185 mg; 1.03 mmol; 25%), mp 151–153 °C (lit. mp 154 °C) were obtained. The products' spectra were identical with those of authentic samples.

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Registry No. **4**, 84-11-7; **6a**, 93-58-3; **6b**, 93-89-0; **7a**, 99-75-2; **7b**, 94-08-6; **8**, 20185-55-1; **9**, 60566-01-0; **10**, 108744-18-9; **11**, 5807-64-7; **12**, 86-73-7; **13**, 1689-64-1; **14**, 486-25-9; C_8K, 12081-88-8.

(6) An alternative mechanism has been suggested by: *Bloomfield*, J. J.; Owsley, D. C.; Einsworth, C.; Robertson, R. E. *J. Org. Chem.* **1975**, *40*, 893.

(7) Vogel, A. I. *Practical Organic Chemistry*, 3rd ed.; Longmans: New York, 1964; p 781.

(8) This procedure is modified, see: Lalancette, J. M.; Rollin, G.; Dumas, P. *Can. J. Chem.* **1972**, *50*, 3058.

(9) Addition of water to the reaction mixture at this stage does not involve any violent reaction.

(10) Literature mp: **4**, 208–210 °C; **9**, 212–213 °C; **12**, 117 °C; **13**, 153 °C; **14**, 83 °C. From: Heilbron, I. *Dictionary of Organic Compounds*, 5th ed.; Chapman and Hall: New York, 1982.

Synthesis of 5′-Carboxy-*N*′-nitrosonornicotine and 5′-([^{14}C]Carboxy)-*N*′-nitrosonornicotine[1]

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N′-Nitrosonornicotine (**1**) and the related nitrosamines that are formed from the tobacco alkaloids are considered to be among the most important compounds responsible

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