Communications to the Editor

Catalytic Automerization of Phenanthrene[1]

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Automerization is a chemical process involving an automorphism of the carbon–carbon framework of the molecule.[2] Since the date when the term was coined 20 years ago,[2a] many more such chemical transformations were discovered, both by organic and inorganic chemists, complemented by examples identified later as automerization reaction but not realized as such prior to 1967.[1b]

Aromatic compounds such as benzene,[3a] pyrene,[3b] naphthalene,[3c] and benz[*a*]anthracene[3d] automerize but at very high temperature, $t > 1000$ °C. Such conditions are well beyond the common temperature ranges of most chemical syntheses.

In the present paper, our interest is focused upon the catalytic automerization of phenanthrene, which unlike previous examples occurs under normal chemical conditions.

By submitting [1-^{13}C]- or [3-^{13}C]phenanthrene to an excess (three molar equivalents) of a catalyst consisting of an $AlCl_3$–NaCl mixture (1:1 molar ratio) at temperatures/times ranging from 160 °C/180 min to 220 °C/10 min under argon atmosphere without solvent, followed by decomposition with dilute hydrochloric acid and extraction with *n*-hexane, a 25–75% recovery of labeled phenanthrene was achieved. A transfer of ^{13}C was clearly evidenced by ^{13}C NMR spectroscopy,[4a] as shown in Figure 1.[4b]

In the presence of $AlCl_3$·NaCl, [1-^{13}C]phenanthrene was in part coverted into [3-^{13}C]phenanthrene: spectra (b) and (c) in Figure 1. However, [3-^{13}C]phenanthrene under similar conditions transferred the label into two positions, i.e., mainly C-1 and less C-4: spectra (d) and (e) in Figure 1. At this stage of our investigations, transfers of the label to the quaternary positions cannot be reliably assessed, nor can a small amount of [2-^{13}C]-phenanthrene in the automerized [3-^{13}C]phenanthrene.

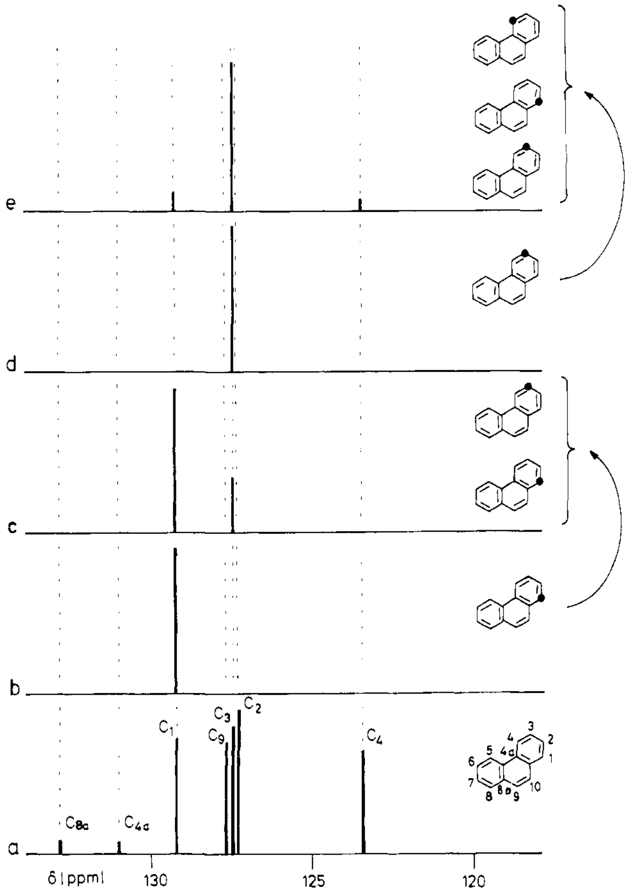

Figure 1. ^{13}C NMR spectra of phenanthrenes in acetone-d_6 with internal TMS. Chemical shifts (δ, ppm) are as follows: C-1, 129.31; C-2, 127.43; C-3, 127.48; C-4, 123.48; C-9, 127.62; C-8a, 132.92; C-4a, 131.07. The spectral width is 250 Hz; pulse width 18 μs; pulse delay 2.5 s: (a) natural abundance spectrum of unlabeled phenanthrene, (b) [1-^{13}C]-phenanthrene, (c) [1-^{13}C]phenanthrene after exposure to the catalyst, (d) [3-^{13}C]phenanthrene, (e) [3-^{13}C]phenanthrene after exposure to the catalyst.

In each experiment, along with phenanthrene, higher molecular weight compounds were isolated: e.g., phenanthrene recovery ranged from 25% at 185 °C/1 h or 160 °C/3 h to 75% at 200 °C/10 min. These side reactions, which probably involve intermolecular Scholl-type dehydrogenating condensations,[6] precluded the observation of equilibrium conditions.

Three putative mechanisms can be imagined for this automerization. One, previously described,[2a] has a key intermediate a spiroindene derivative A, resulted by protonation at a quaternary carbon B, which proceeds in a minor way relative to protonation at positions 9 and 10 yet, unlike the latter process, can lead to scrambling. The same intermediate B might ring-open to a vinylic biphenyl-type cation C.

A different biphenyl derivative, D, might result by addition of $AlCl_3$ to the C-9–C-10 bond, a process which unlike the protonation from Scheme I involves the most reactive segment in phenanthrene.

The proton-catalyzed automerization of biphenyl derivatives, a known process[7] since 1963, would bring about the scrambling

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[1] (a) Taken in part from the Ph.D Thesis of A.S. and the B.Sc. Thesis of A.N. Presented in part at the Third International Symposium on the Synthesis and Applications of Isotopically Labeled Compounds, July 17–21, 1988, Innsbruck, Austria, Abstract p 195, and at the Third National Congress of Chemistry, Bucharest, September 21–24, 1988, Abstract 52, p 160. (b) Gheorghiu, M. D.; Schiketanz, A.; Balaban, A. T. Manuscript in preparation.

[2] (a) Balaban, A. T.; Farcasiu, D. *J. Am. Chem. Soc.* **1967**, *89*, 1958. (b) Balaban, A. T.; Farcasiu, D.; Koptyug, V. A.; Isaev, I. S.; Garfinkel, M. I.; Rezvukhin, A. I. *Tetrahedron Lett.* **1968**, 4757. (c) Staab, H. A.; Haenel, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 548. *Chem. Ber.* **1970**, *103*, 1095.

[3] (a) Scott, L. T.; Roelofs, N. H.; Tsang, T.-H. *J. Am. Chem. Soc.* **1987**, *109*, 5456. (b) Scott, L. T.; Kirms, M. A.; Berg, A.; Hansen, P. E. *Tetrahedron Lett.* **1982**, *23*, 1859. (c) Scott, L. T.; Agopian, G. K. *J. Am. Chem. Soc.* **1977**, *99*, 4506. (d) Scott, L. T.; Tsang, T.-H.; Levy, L. A. *Tetrahedron Lett.* **1984**, *25*, 1661. For a general discussion, see: Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52.

[4] (a) The ^{13}C NMR spectra were run first on the crude reaction mixture, then on samples submitted to chromatography on neutral alumina (eluted with hexane), and in some instances on samples resulting from preparative gas-liquid chromatography (silicone SE30 10% on chromosorb W 30–80 mesh, 200–270 °C, with a gradient of 50/min, ϕ = 10 mm; rechecked analytically on a 20-m capillary column). The UV spectra of an automerized sample resulted from preparative GLC and of commercial phenanthrene are also identical. (b) All ^{13}C NMR spectra quoted in literature[5] for phenanthrene were obtained in chloroform-*d* which leads to accidentally isochronous signals for C-2 and C-3. This is an unfortunate case, since the automerization involving these positions cannot be observed by using this solvent for spectra. We found that on running the ^{13}C NMR spectra in acetone-d_6, the C-2 and C-3 peaks are clearly distinguishable, although they appear closely togehter ($\Delta\nu$ = 0.83 Hz).

[5] Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980; p 116.

[6] Balaban, A. T.; Nenitzescu, C. D. In *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1964; Vol. 2, p 979.

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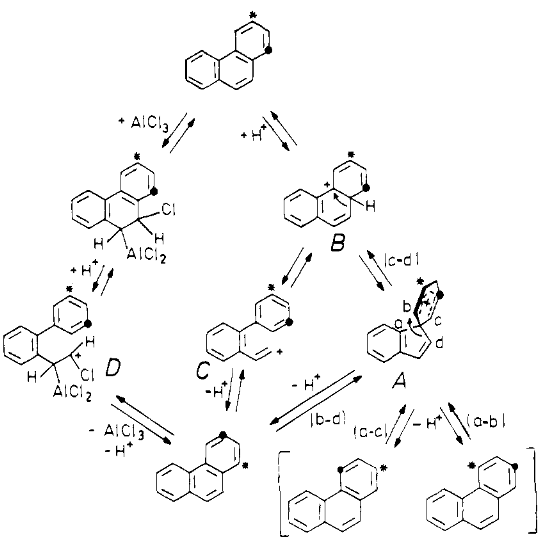
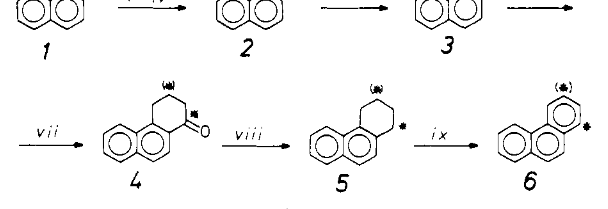
Scheme I[a]



[a] Possible reaction mechanisms: In the mechanism involving intermediate A, letters a–d denote carbon atoms which become bonded as indicated on the arrows. The two bracketed products do not appear in the automerization of [1-^{13}C]phenanthrene.

of the ^{13}C label in other positions of the ring containing the label, explaining the minor amount of C-4 transfer from C-3.

The syntheses of [1-^{13}C]- and [3-^{13}C]phenanthrene were based on 1-(chloromethyl)naphthalene (**1**), using nine synthetical steps. Synthons having one carbon ($^{13}CO_2$) and two carbons (malonate) were attached to 1-(chloromethyl)naphthalene in an order depending on the desired position of the label. The labeling started by carbonation with $^{13}CO_2$ (generated from $Ba^{13}CO_2$ of 55–80% content) of the corresponding Grignard derivative **1** or **2**. The ultimate precursor of the appropriately labeled phenanthrene was 4-(1-naphthyl)butanoic acid (**3**). Cyclization in the presence of polyphosphoric acid (PPA) yielded 1,2,3,4-tetrahydrophenanthren-1-one (**4**). Clemmensen reduction of **4**, followed by dehydrogenation of the 1,2,3,4-tetrahydrophenanthrene (**5**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), afforded the labeled phenanthrene (**6**).



(i) $NaCH(CO_2Et)_2$, (ii) H_2O/H^+, (iii) $LiAlH_4$/THF, (iv) PBr_3, (v) Mg, (vi) $^{13}CO_2/H^+$, (vii) PPA, (viii) Zn(Hg)/HCl, (ix) DDQ.

For **3** (1-^{13}C), read the (i)–(vi) sequence, while for **3** (3-^{13}C), the order is (v), (vi), (iii), (iv), (i), (vii)–(ix).

In conclusion, we presented evidence for the first example of catalyzed automerization of a condensed polycyclic benzenoid hydrocarbon which takes place under normal chemical conditions. We are engaged in a thorough study of the catalytic phenanthrene automerization and in reinvestigating the same reaction of [1-^{13}C]naphthalene.

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Registry No. 1, 86-52-2; **2**, 27650-86-8; [β-^{11}C]-**2**, 118018-25-0; [1-^{13}C]-**3**, 66229-92-3; [3-^{13}C]-**3**, 118018-26-1; [1-^{13}C]-**4**, 69062-73-3; [3-^{13}C]-**4**, 118018-27-2; [1-^{13}C]-**5**, 118018-28-3; [3-^{13}C]-**5**, 118018-29-4; [1-^{13}C]-**6**, 118018-30-7; [3-^{13}C]-**6**, 118018-31-8; $AlCl_3$, 7446-70-0; $NaCH(CO_2Et)_2$, 996-82-7; $NaAlCl_4$, 7784-16-9; barium [^{13}C]carbonate, 51956-33-3; [4-^{13}C]phenanthrene, 118018-32-9.

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(7) Wynberg, H.; Wolf, A. P. *J. Am. Chem. Soc.* **1963**, *85*, 3308.

The Resonance Raman Spectrum of a Ferrylporphyrin Cation Radical and Its Photodegradation in the Presence of Methanol

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The intense interest in ferryl porphyrin π-cations continues in view of their proposed intermediacy in a number of important heme enzyme-mediated oxidative processes.[1] Characterization of model compounds by resonance Raman (RR) spectroscopy assumes importance inasmuch as the technique offers promise for detection and structural characterization of the key intermediates in the enzyme systems.[2] We therefore wish to report results of our efforts to obtain the RR spectrum of the most thoroughly studied example of such models; namely, ferryltetramesitylporphine π-cation radical, (OFe)TMP$^{\bullet+}$. In addition, we show that the previously reported RR spectrum of this species,[3] which is in conflict with our own results, actually corresponds to that of a photoproduct.

Solutions of (OFe)TMP$^{\bullet+}$ were prepared at low temperatures (−78 °C) in purified CH_2Cl_2 with *m*-chloroperoxybenzoic acid (mCPBA) and yielded a visible spectrum which was identical with that reported.[4] The RR spectrum of this solution exhibited a well-defined band at 802 cm^{-1} which shifted to 767 cm^{-1} when ^{18}O-labeled (mCPBA)[5] was employed (Figure 1, A and C). In order to demonstrate that the 802-cm^{-1} feature does not correspond to the acylperoxo-coordinated precursor [TMPFe^{3+}(mCPBA$^-$)], a sample was prepared with isotopically scrambled oxidant.[6] As seen in Figure 1B, only the 802- and 767-cm^{-1} features are observed. If the spectra corresponded to such a precursor, trace B is expected to exhibit three bands at 802, 767, and ~784 cm^{-1}, the last being that associated with the ^{16}O-^{18}O-Fe and ^{18}O-^{16}O-Fe linkages. Thus, the unique 802-cm^{-1} feature is most reasonably assigned to ν(Fe–O) of the ferryl fragment of (OFe)TMP$^{\bullet+}$.

It is important to note that the higher frequency RR spectrum observed for this species (Figure 2A) is also consistent with the π-cation radical formulation. Specifically, there is a dramatic decrease in the intensity of all macrocycle modes, ν_4 downshifts

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(1) (a) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032–1033. (b) Schappacher, M.; Weiss, R.; Montiel-Montoya, R.; Trautwein, A.; Tabard, A. *J. Am. Chem. Soc.* **1985**, *107*, 3736–3738. (c) Chin, D.; Balch, A. L.; LaMar, G. N. *J. Am. Chem. Soc.* **1980**, *102*, 1446–1448. (d) Shin, K.; Goff, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 3140–3142.

(2) (a) Ogura, T.; Kitagawa, T. *J. Am. Chem. Soc.* **1987**, *109*, 2177–2179. (b) Oertling, W. A.; Babcock, G. T. *J. Am. Chem. Soc.* **1985**, *107*, 6406–6407. (c) Oertling, W. A.; Babcock, T. T. *Biochemistry* **1988**, *27*, 3331–3338. (d) Paeng, K.-J.; Kincaid, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 7913–7915.

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(5) (a) This shift is in good agreement with that expected based on the harmonic oscillator model. (b) ^{18}O-mCPBA and the scrambled oxygen analogue were prepared as described in ref 5c,d. (c) Johnson, R. A. *Tetrahedron Lett.* **1976**, *5*, 331–332. (d) Braun, G. In *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, Wiley: New York, p 431.

(6) The term "scrambled oxidant" is used to indicate that the oxidant consists of a mixture of isotopes having $-^{16}O-^{16}O-C-$, $-O^{16}-^{18}O-C-$, $-O^{18}O-^{16}O-C-$, and $-^{18}O-^{18}O-C-$ linkages.

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