20-mm. pressure. The monohydride content in the product, calculated on the basis of the amount of isobutylene evolved during the reaction, was about 95%.

Isooctane (Phillips Petroleum Co., pure grade), used as solvent, was purified by distillation on Na metal under dry nitrogen.

**Reaction of Alkyl Vinyl Ethers with Diisobutylaluminum Hydride.**—Isobutyl vinyl ether (2.37 g., 0.0237 mole, b.p. 83.5°, $n^{20}\text{D}$ 1.3966) was added under nitrogen, at 25°, to 3.90 g. (0.0275 mole) of diisobutylaluminum hydride. The addition caused a rapid gas evolution which ceased after a few minutes. In order to complete the reaction, the mixture was heated at 120° for 1.5 hr. After cooling the liquid product was diluted with 15 ml. of anhydrous diethyl ether and, cautiously adding drop by drop, 1.9 ml. of water.

The gases evolved during the hydrolysis, collected and analyzed by gas chromatography, contained 0.045 mole of isobutane and 0.009 mole of ethane. Small quantities of isobutylene and *n*-butane were also present.

By extracting the hydrolysis products with ether, 1.58 g. (0.0214 mole) of isobutyl alcohol was recovered.

The gases evolved during the reaction between diisobutylaluminum hydride and isobutyl vinyl ether were collected and analyzed by infrared spectroscopy and gas chromatography. The analyses revealed that the gases consisted almost exclusively of ethylene (0.007 mole, yield 29%).

In other experiments carried out in the presence of $\text{Al}(i\text{-C}_4\text{H}_9)_3$ [moles of $\text{Al}(i\text{-C}_4\text{H}_9)_3$/moles of vinyl ether = 1.0 or 5.1], no gas evolution has been noticed below 50 or below 70°, respectively.

Using 2-ethylhexyl vinyl ether (0.0125 mole), 0.0085 mole of ethylene was recovered (68% yield).

**Reaction of 1-Methyl-2-ethoxyethylene with Diisobutylaluminum Hydride.**—A solution of 2.20 g. (0.0256 mole) of 1-methyl-2-ethoxyethylene (b.p. 69–75°, $n^{20}\text{D}$ 1.3980) in 10 ml. of isooctane was heated under nitrogen at 50° and 5.9 g. (0.042 mole) of diisobutylaluminum hydride was then added with stirring over a period of 1 hr. During the addition, the temperature was gradually raised to 100°. Unreacted alkenyl ether, which distilled, was again introduced into the reaction flask after cooling to 50°, and the reaction was completed, maintaining the mixture at 50° for 1 hr. and then refluxing for 0.5 hr.

The evolved gas contained 0.011 mole of propylene (44% yield).

By hydrolysis of the residual liquid, 0.005 mole of propane was obtained.

**Reaction of 1-Propyl-2-ethoxyethylene with Diisobutylaluminum Hydride.**—Diisobutylaluminum hydride (4.26 g., 0.0300 mole) was added with stirring, over 1 hr., to a boiling solution of 2.3 g. (0.020 mole) of 1-propyl-2-ethoxyethylene (b.p. 121.5–122.5°, $n^{20}\text{D}$ 1.4138) in 10 ml. of isooctane. Two liquid fractions were collected, weighing 0.45 and 0.88 g., respectively. Gas chromatographic analysis showed that the first fraction was predominantly 1-pentene, and the second fraction was 80% isooctane and 20% 1-pentene (35% yield of 1-pentene).

**Reaction of 1-Ethoxycyclohexene with Diisobutylaluminum Hydride.**—Diisobutylaluminum hydride (16.5 g., 0.116 mole) was added with stirring, over 1.5 hr., to a boiling solution of 7.21 g. (0.0572 mole) of 1-ethoxycyclohexene [b.p. 61° (18 mm.), $n^{25}\text{D}$ 1.4552] in 30 ml. of isooctane. The addition rate and heating were so regulated as to achieve a slow distillation of the reaction product. Heating was continued until *ca.* 31 ml. of distillate was obtained. Redistillation through a spiral-packed column gave the following fractions: (A) 1.68 g., b.p. 88–94°, $n^{25}\text{D}$ 1.4158; (B) 2.96 g., b.p. 94–99°, $n^{25}\text{D}$ 1.3985; and (C) 2.20 g., b.p. 99–99.5°, $n^{25}\text{D}$ 1.3901. Gas chromatographic and infrared analysis indicated that such fractions consisted almost exclusively of cyclohexene and isooctane, the total amount of the former being 1.5 g. (0.018 mole) (32% yield).

**Reaction of 1-Methoxy-1-hexyne with Diisobutylaluminum Hydride.**—Diisobutylaluminum hydride (7.19 g., 0.0506 mole) was added over 1 hr. to a stirred solution of 3.80 g. (0.0339 mole) of 1-methoxy-1-hexyne [b.p. 75° (77 mm.), $n^{20}\text{D}$ 1.4240] in 10 ml. of anhydrous isooctane. A slow distillation was achieved during the addition of the hydride by careful heating. Redistillation through a spiral-packed column gave a fraction, b.p. 71–75°, $n^{25}\text{D}$ 1.3942, which was 80% 1-hexyne, as shown by gas chromatographic and infrared analysis (32% yield).

**Attempted Synthesis of the Adduct (A) between Diisobutylaluminum Hydride and Isobutyl Vinyl Ether.**—Isobutyl vinyl ether, 4.48 g. (0.0448 mole), $n^{20}\text{D}$ 1.3966, was added at 0° with stirring to an equimolar amount of diisobutylaluminum hydride dissolved in 10 ml. of isooctane. The solution was then slowly heated and kept at 20° for 1 hr. No gas evolution was observed.

Cautious addition at 10–15° of an excess of pure methanol and subsequent distillation yielded a mixture which, as shown by gas chromatographic analysis, consisted of methanol, isooctane, traces of isobutyl alcohol, and isobutyl vinyl ether. The peak given by the last compound disappeared completely from the chromatogram after refluxing the mixture with dilute sulfuric acid.

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## Studies of Quinoid Structures. VII.[1] Reaction of Benzonitrile Oxide with *o*-Quinones

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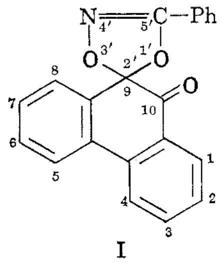
The 1,3-dipolar addition of nitrile oxides with *p*-quinones was first observed by Quilico, *et al.*,[2] to lead to condensed isoxazoles. The formation of 1,3,4-dioxazoles by the addition of nitrile oxides to suitably activated carbonyl groups has been reported by Huisgen and Mack.[3] In this Note we describe the reaction of benzonitrile oxide with *o*-quinones to give dioxazoles I and II and the reaction with *o*-quinonimines to give oxadiazoles. The yellow product from phenanthraquinone was shown to be the 1:1 adduct, namely 9(10)-phenanthrone-10(9)-spiro(4′,5′-dehydro-5′-phenyl)-1′,3′,4′-dioxazole (I). The infrared($\nu_{\text{C=O}}$ at 1689 cm.$^{-1}$ [4] and $\nu_{\text{N-O}}$ at 1345 cm.$^{-1}$) and n.m.r. data ($\tau$ = 1.8–2.7 p.p.m.), characteristic for aromatic protons only, are consistent with this structure. The adduct gave a 2,4-dinitrophenylhydrazone but no product with *o*-phenylenediamine (*i.e.*, absence of *o*-quinoid structure). Oxidation of I with chromic anhydride gives phenanthraquinone.



I

The reactivity of one carbonyl group only in phenanthraquinone has been observed in several other cases: *e.g.*, (i) with nitromethane it gives 9-keto-10-nitromethyl-9,10-dihydro-10-phenanthrol,[5] (ii) with diazo-

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[1] Part VI: W. I. Awad, A. K. Fateen, and M. A. Zayed, *J. Org. Chem.*, **26**, 2112 (1961).

[2] A. Quilico, *et al.*, *Gazz. chim. ital.*, **80**, 140 (1950).

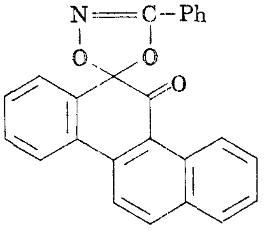
[3] R. Huisgen and W. Mack, *Tetrahedron Letters*, 583 (1961); see also *Angew. Chem.*, **75**, 614 (1963).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1960, p.132.

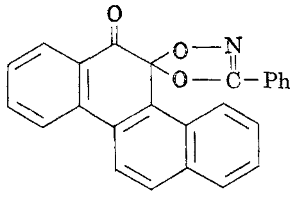
[5] A. I. Yakubovich, *J. prakt. Chem.*, **142**, 37 (1932).

methane an epoxide is obtained,[6] and (iii) photochemical addition of furocoumarins with the same quinone gives the corresponding oxetan.[7] The unreactivity of both carbonyl groups could arise from steric hinderance.

Chrysenequinone yields also a similar product, namely, 1,2-benz-9(10)-phenanthrone-10(9)-spiro(4',5'-dehydro-5'-phenyl)-1',3',4'-dioxazole (II). It gives a dinitrophenylhydrazone (DNP) and its infrared spectrum shows $\nu_{\text{N-O}}$ at 1345 cm.$^{-1}$ and $\nu_{\text{C=O}}$ at 1666 cm.$^{-1}$. Formula II is preferred to IIa on steric grounds.[8]

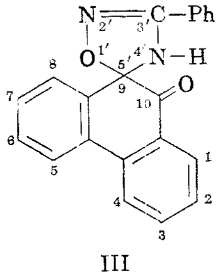


II

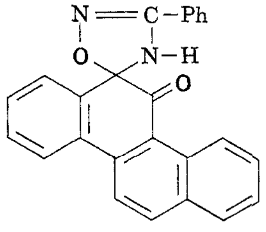


IIa

Phenanthraquinonimine and chrysenequinonimine give with benzonitrile N-oxide a product to which structures 9(10)-phenanthrone-10(9)-spiro(2',3'-dehydro-3'phenyl)-1',2',4'-oxadiazole (III) and 1,2-benz-9(10)-spiro-(2',3'-dehydro-3'-phenyl)-1',2',4'-oxadiazole (IV) are assigned, respectively. We believe that the >C=NH bond rather than >C=O is involved in the reaction, since these compounds are stable to both acids and alkalies, the DNP derivatives of these compounds are different from those of the corresponding quinone derivatives, and the >C=O stretching frequency at 1689 and 1666 cm.$^{-1}$ is still present in the infrared spectra of III and IV, respectively. Furthermore, the infrared spectra of III and IV revealed NH stretching frequency at 3425 and 3333 cm.$^{-1}$ and N-O stretching frequency at 1356 and 1351 cm.$^{-1}$, respectively (for the structure of chrysenequinonimine, *cf.* Awad, and Raouf[8]).



III



IV

Oxidation of these compounds with chromic anhydride gives the corresponding quinones.

The ultraviolet spectrum of I, $\lambda_{\max}$ 238 m$\mu$ ($\epsilon_{\max}$ 36,500), 275 m$\mu$ ($\epsilon_{\max}$ 10,600), and III, $\lambda_{\max}$ 250 m$\mu$ ($\epsilon_{\max}$ 35,000), 274 m$\mu$ ($\epsilon_{\max}$ 11,400), indicate that both compounds are of similar structure. The similarity between II and IV can also be deduced from the ultraviolet spectral data [for II, $\lambda_{\max}$ 230 m$\mu$ ($\epsilon_{\max}$ 27,000), 263 (25,200), 285 (21,600); for IV, $\lambda_{\max}$ 235 m$\mu$ ($\epsilon_{\max}$ 29,200), 259 (30,200), 282 (27,200)].

## Experimental Section

Melting points are uncorrected. Analyses were carried out by Alfred Bernhardt, Max Planck Institute, Mülheim, Ruhr, Germany. Infrared spectra were measured on a Perkin-Elmer Infracord Model 137 spectrophotometer in KBr wafers. Ultraviolet spectra were measured on a Perkin-Elmer, Spectracord Model 4000A spectrophotometer in ethyl alcohol solutions. The n.m.r. spectrum[9] was measured in $CDCl_3$ solution using a Varian A-60 spectrometer.

**Action of Benzonitrile N-Oxide on Phenanthraquinone.**—An ethereal solution of benzonitrile oxide (from 10 g. of PhCCl-NOH) was refluxed with phenanthraquinone (1 g.) in anhydrous ether (100 ml.) for 2 hr. on a water bath. The reaction mixture was kept overnight at room temperature. After evaporation the product separated and was collected, washed with ether, and recrystallized from benzene to give yellow crystals, m.p. 178–180° (1.2 g., yield 90%). *Anal.* Calcd. for $C_{21}H_{13}NO_3$: C, 77.05; H, 4.00; N, 4.28. Found: C, 77.01; H, 4.04; N, 4.36.

The 2,4-dinitrophenylhydrazone derivative was crystallized from benzene, m.p. 304°. *Anal.* Calcd. for $C_{27}H_{16}N_5O_6$: N, 17.20. Found: N, 16.69.

**Action of Benzonitrile N-Oxide on Phenanthraquinonimine.**—Phenanthrenequinonimine (1 g.) was treated with the ethereal solution of benzonitrile oxide (from 10 g. of PhCCl-NOH) as mentioned above. The precipitated solid after removal of most of the ether was recrystallized from benzene, yielding yellow crystals, m.p. 156° (yield 1.1 g., 80%). *Anal.* Calcd. for $C_{21}H_{14}N_2O_2$: N, 8.60. Found: N, 8.53.

The 2,4-dinitrophenylhydrazone derivative was obtained from benzene as red crystals, m.p. 190–192°.

**Action of Benzonitrile N-Oxide on Chrysenequinone.**—The ethereal solution of benzonitrile N-oxide (from 10 g. of PhCCl-NOH) was refluxed with chrysenequinone (1 g.) in anhydrous ether, and the reaction was completed as mentioned before. The precipitated solid was filtered off, washed with ether, and crystallized from benzene giving orange-red crystals, m.p. 215° (yield 1.2 g., 90%). *Anal.* Calcd. for $C_{25}H_{15}NO_3$: C, 79.56; H, 4.01; N, 3.71. Found: C, 79.73; H, 4.00; N, 3.93.

The DNP derivative was crystallized from benzene, m.p. 192–194°. *Anal.* Calcd. for $C_{31}H_{19}N_5O_6$: C, 65.96; H, 3.56. Found: C, 66.60; H, 3.58.

**Action of Benzonitrile N-Oxide on Chrysenequinonimine.**—The ethereal solution of benzonitrile oxide (from 10 g. of PhCCl-NOH) was refluxed with chrysenequinonimine (1 g.) in anhydrous benzene for 2 hr. The reaction was completed as usual and the precipitated solid was filtered off, washed with ether, and crystallized from toluene, yielding yellow crystals, m.p. 201–205° (yield 0.8 g.). *Anal.* Calcd. for $C_{25}H_{16}N_2O_2$: C, 79.77; H, 4.28; N, 7.44. Found: C, 79.04; H, 4.24; N, 7.99.

The DNP derivative was crystallized from benzene, m.p. 294°. *Anal.* Calcd. for $C_{31}H_{19}N_6O_5$: C, 67.02; H, 3.42. Found: C, 67.29; H, 3.55.

**Action of Concentrated $H_2SO_4$ on I and II.**—A mixture of concentrated $H_2SO_4$ (3 ml.) and 2 g. of I or II was heated on a water bath for few minutes. The compound dissolved in the acid and solution turned dark green. The contents of the reaction vessel was poured portionwise with stirring into ice-cold water; yellow crystals separated, were filtered off, washed with water, and recrystallized from benzene to give unchanged material (melting point and mixture melting point).

**Action of Chromic Acid on I and II.**—Chromic anhydride (0.2 g.), dissolved in the least amount of glacial acetic acid, was heated with 0.2 g. of I or II on a water bath for 10 min. The contents of the reaction vessel was poured portionwise into ice-cold water with shaking. The oxidation product was crystallized from ethyl alcohol and proved to be phenanthraquinone or chrysenequinone (melting point and mixture melting point), respectively.

**Reaction of *o*-Phenylenediamine with I and II.**—*o*-Phenylenediamine (0.1 g.) in ethyl alcohol was heated with 0.2 g. of I or II for 15 min. The reaction mixture was cooled and diluted

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(6) F. Arndt, J. Amende, and W. Ender, *Monatsh.*, **59**, 202 (1932).

(7) Private communication from S. Farid, Max Planck Institute, Abt. Strahlenchemie, Mülheim, Ruhr, Germany.

(8) W. I. Awad and A. R. A. Raouf, *J. Am. Chem. Soc.*, **77**, 1013 (1955).

(9) The authors wish to thank Mr. S. Farid, Max Planck Institute, Abt. Strahlenchemie, Mülheim, Ruhr, Germany, for kindly measuring this spectrum.

with water to complete precipitation. The yellow precipitate was filtered off and recrystallized from benzene. It proved to be the starting material (melting point and mixture melting point).

## Phosphonic Acids and Esters. XIII. Nylen and Arbuzov Reactions with Propargyl Bromide[1]

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*Received August 9, 1965*

The treatment of propargyl bromide (**1**) with sodium diethylphosphonate in tetrahydrofuran has been reported to give a mixture of diethyl 1-propynylphosphonate (**2a**) and diethyl propargylphosphonate (**3a**)[3]; infrared studies showed **2a** to be the dominant isomer in the mixture.

$$\underset{\mathbf{2}}{CH_3C{\equiv}CP(O)(OR)_2} \qquad \underset{\mathbf{3}}{HC{\equiv}CCH_2P(O)(OR)_2}$$

$$\begin{array}{l}\mathbf{a},\ R = C_2H_5\\ \mathbf{b},\ R = CH_3\end{array}$$

This Nylen reaction was repeated using sodium dimethylphosphonate in order to prepare the phosphonates **2b** and **3b** for proton magnetic resonance (p.m.r.) studies. In our hands, the only isomer isolated was dimethyl 1-propynylphosphonate (**2b**), identified by its p.m.r. spectrum ($CH_3$–C, doublet, $\tau$ = 7.96 p.p.m., $^4J_{PH}$ = 4.6 c.p.s.; $CH_3$–O, doublet, $\tau$ = 6.35 p.p.m., $J_{PH}$ = 11 c.p.s.). The infrared characteristics of **2b** were consistent with those reported for **2a**.[3] In addition to the appropriate phosphorus–oxygen stretching frequencies, a strong band was observed at 2217 cm.$^{-1}$ (RC≡CR stretch). A weak band characteristic of terminal acetylenes (–C≡C– stretch), possibly owing to the presence of **3b**, was observed at 2092 cm.$^{-1}$, although p.m.r. analysis indicated the product to contain significantly less than 1% of **3b**. Identical results were obtained with sodium diethylphosphonate in a repetition of the reported[3] reaction. Only **2a** was isolated with less than 1% contamination by **3a** although a weak band was observed at 2071 cm.$^{-1}$, possibly indicative of the presence of **3a**. In neither reaction product was the ≡C–H stretching absorption (*ca.* 3300 cm.$^{-1}$) expected for **3a** or **3b** observed, although Guthrie and co-workers[3] reported a weak band at 3290 cm.$^{-1}$ for their product.[4]

As an alternative route to the propargylphosphonates, Arbuzov reactions between **1** and triethyl and trimethyl phosphites were carried out. Triethyl phosphite and **1** reacted exothermically at 90° and, again, **2a** was the only product isolated (15%).[6] Jensen and co-workers had previously reported a 5% yield of a material identified as **2a** from the same reaction.[7] However, the corresponding reaction of **1** with trimethyl phosphite under identical conditions led to completely unexpected results. A mixture of phosphonates was formed from which **3b** could be isolated in 5% yield. The structure of this product was established unambiguously by its p.m.r. spectrum ($H$–C≡, doublet of triplets, $\tau$ = 7.82 p.p.m., $^4J_{PH}$ = 6.7 c.p.s., $^4J_{HH}$ = 2.8 c.p.s.; –$CH_2$–, doublet of doublets, $\tau$ = 7.30 p.p.m., $^2J_{PH}$ = 21.9 c.p.s.; $CH_3$–O, doublet, $\tau$ = 6.27 p.p.m., $J_{PH}$ = 11 c.p.s.). The infrared spectrum of **3b** showed a strong ≡C–H stretch at 3322 cm.$^{-1}$ and a weak terminal acetylenic (–C≡C–) stretch at 2123 cm.$^{-1}$. This material was contaminated with less than 5% of a mixture of **2b** and dimethyl allenylphosphonate as determined by p.m.r. spectroscopy. The infrared spectrum is consistent with this assignment showing weak bands at 2212 and 1976 cm.$^{-1}$ attributable to a disubstituted acetylene and an allene, respectively. The reasons for the pronounced differences in the products obtained from the two Arbuzov reactions are not apparent.

Long-range $P^{31}$–$H^1$ couplings, $^4J_{PH}$, were observed for both the propynyl (**2a** and **2b**, 4.6 c.p.s.) and propargyl (**3b**, 6.7 c.p.s.) phosphonates; analogous, but smaller, four-bond $H^1$–$H^1$ couplings (2–3 c.p.s.) are normally observed in acetylenic systems.[8] In **3b**, a normal $H^1$–$H^1$ coupling (2.8 c.p.s.), comparable in magnitude with that observed in **1** (2.6 c.p.s.), is seen. It should be noted that the magnitude of the long-range coupling constant ($^4J_{PH}$) is greater when the phosphorus atom is bonded to the tetrahedral carbon atom than when it is bonded to the sp hybridized atom. A similar trend has been observed in other H—C—C≡C—P and H—C=C—C—P systems.[9,10] The magnitude of the geminal $P^{31}$–$H^1$ coupling constant (21.9 c.p.s., presumably negative) observed in **3b** is the same as that found for a large number of allyl- and benzylphosphonates[9]; the presence of the second $\pi$ system in **3b** apparently does not cause a further decrease in the magnitude of the geminal coupling constant, contrary to the results observed for geminal $H^1$–$H^1$ coupling constants.[11] This behavior is consistent with that observed for geminal $P^{31}$–$H^1$ coupling constants in a number of other organophosphorus systems.[9]

Long-range (four-, five-, six-, and eight-bond) $P^{31}$–$H^1$ couplings have been observed previously in P—(C≡C)$_n$—R (R = H or $CH_3$; $n$ = 1–3) systems.[12] Those couplings most closely comparable with the ones observed in the present study were seen in $(C_6H_5)_2P(O)C{\equiv}CCH_3$ and the corresponding sulfide for which $^4J_{PH}$ = 3.8 and 4 c.p.s., respectively.[12]

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[1] Part XII: C. E. Griffin, R. B. Davison, and M. Gordon, *Tetrahedron*, in press.

[2] National Science Foundation Cooperative Graduate Fellow, 1961–1964.

[3] C. M. Welch, E. J. Gonzales, and J. D. Guthrie, *J. Org. Chem.*, **26**, 3270 (1961).

[4] These workers also cited the formation of a deep wine red color upon treatment of their product with an alkaline solution of sodium 3,5-dinitrobenzoate[5] as being diagnostic for the presence of **3**. No corresponding color reaction was observed with the products obtained in this study or with the model active hydrogen compound, ethyl propiolate.

[5] B. C. Saunders and B. P. Stark, *Tetrahedron*, **4**, 197 (1958).

[6] The p.m.r. spectra of all distillation fractions from this reaction and the two Nylen reactions were examined carefully, and in no case was any evidence indicative of the formation of **3a** or **3b** obtained. Spectra were determined at amplitudes such that a minimum of 1% of **3a** or **3b** could have been detected in the fractions.

[7] H. I. Jacobson, M. J. Griffin, S. Preis, and E. V. Jensen, *J. Am. Chem. Soc.*, **79**, 2608 (1957).

[8] S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

[9] M. Gordon, Ph.D. Thesis, University of Pittsburgh, 1965.

[10] Possible explanations for this behavior will be discussed in a more complete study of long-range phosphorus–proton coupling constants.

[11] M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

[12] C. Charrier, M-P. Simonnin, W. Chodkiewicz, and P. Cadiot, *Compt. rend.*, **258**, 1536 (1964).