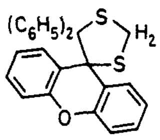
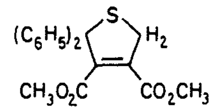
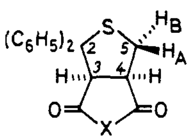


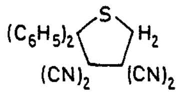
8 84%



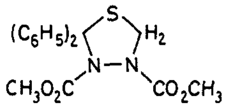
9 70%



10 X = O 97%
11 X = NCH$_3$ 80%
12 X = NC$_6$H$_5$ 79%



13 89%



14 72%

action. The formation of **2** from diazomethane and thiobenzophenone consists of two 1,3-dipolar cycloadditions separated by a 1,3-dipolar cycloreversion (**3** → **5** + N$_2$).

The highly selective 1,3-dipole **5** does not interact with dimethyl fumarate, methyl propiolate, phenylacetylene, carbon disulfide, phenyl isocyanate, or phenyl isothiocyanate; formation of the dimer **4** signals insufficient dipolarophilic activity. Thiocarbonyl compounds appear to be the best dipolarophiles toward **5**; competition experiments are planned.

In contrast to Schönberg's claim,[4] 1:1 and 1:2 products are formed side by side when one reverses the procedure, i.e., on introducing thiobenzophenone slowly into stirred ethereal diazomethane at 20 °C; 22% (**7** + **6**) and 18% dimer **4** were isolated in addition to 50% **2**. It is astonishing that as much as 50% 1,3-dithiolane was formed under conditions of low stationary concentration of thiobenzophenone.

Acenaphthyne

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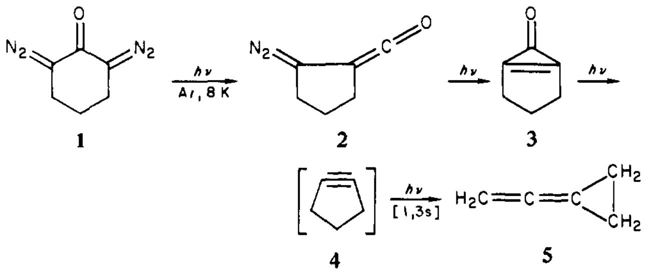
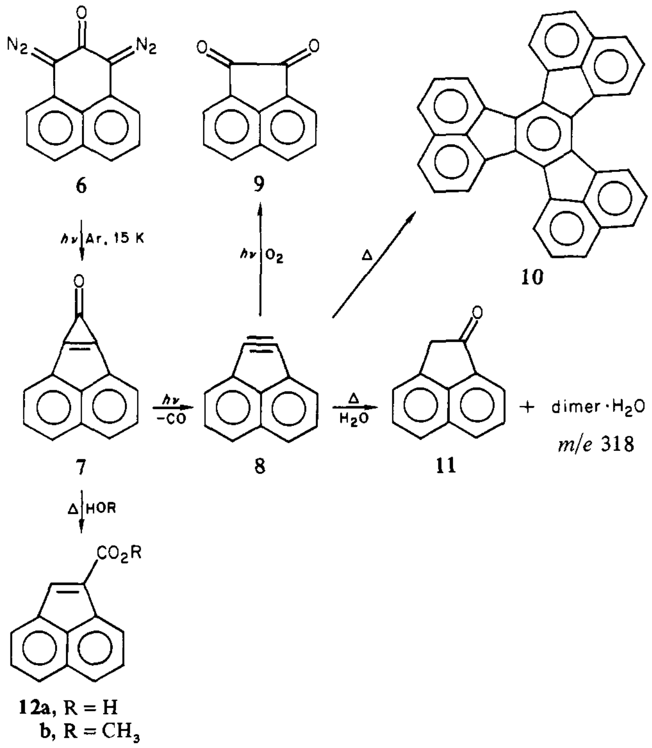
Evidence for the existence of cycloalkynes as strained as cyclopentyne[1] and norbornyne[2] has been available for several years. Attempts to generate strained acetylenes such as cyclobutyne[1,3] and acenaphthyne[4] have been unsuccessful. The observed products in the latter two cases can be rationalized without recourse to the free acetylene. We now wish to report the synthesis, spectroscopic characterization, and chemistry of acenaphthyne, the most strained acetylene available for study.

Work by Trost[5] on bis(diazo) ketones as precursors for cyclopropenones and acetylenes suggested the possibility of a general synthesis of strained alkynes suitable for argon matrix studies. Our first experiments began with 2,6-diazocyclohexanone (**1**).



Irradiation (>274 nm) of **1** matrix isolated in argon at 8 K gave first a diazoketene (**2**, 2118, 2120 cm^{-1}) and then a cyclopropenone (**3**, 1870 cm^{-1}). Continued irradiation (>254 nm) of **3** caused decarbonylation and gave ultimately the allene **4** identified by infrared comparison with an authentic sample. The reactions in the matrix are very clean, and the only products apparent in the infrared spectrum are the allene **4** and carbon monoxide. The allene **4** is sensibly derived from cyclopentyne **5** by a [1,3s]-sigmatropic shift. The conversion of **5** to **4** is faster than the conversion of **3** to **5** and observation of **5** is difficult. Application of the same techniques to problems in which a [1,3s]-sigmatropic shift is not possible thus seemed appropriate.

Therefore we focused our interest on 1,3-bis(diazo)-1,2-dihydrophenalen-2-one (**6**), which was synthesized from 1,2-dihydrophenalene-1,2,3-trione 2-hydrate in two steps. Reaction with *p*-toluenesulfonylhydrazine in methanol (3 days at room temperature) affords 3-diazo-1-tosylhydrazone 1,2-dihydrophenalen-2-one, which is cleaved by 1 N aqueous NaOH (10 h, room temperature) to give **6** as light-sensitive, dark-yellow needles (mp 160 °C dec).[6] Irradiation (>364 nm) of **6** matrix isolated in argon at 15 K rapidly gave the cyclopropenone **7** easily identified



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[2] Gassman, P.; Atkins, T. *J. Am. Chem. Soc.* **1970**, *92*, 5810. *Tetrahedron Lett.* **1975**, 3035. Gassman, P.; Valcho, J. *J. Am. Chem. Soc.* **1975**, *97*, 4768. Gassman, P.; Gennick, I. *Ibid.* **1980**, *102*, 6863.

[3] Wittig, G.; Wilson, E. *Chem. Ber.* **1965**, *98*, 451.

[4] Rasheed, K. *Tetrahedron* **1966**, *22*, 2957. Wittig, G.; Krebs, A. *Chem. Ber.* **1961**, *94*, 3260. Nakayama, J.; Segiri, T.; Ohya, R.; Hoshino, M. *J. Chem. Soc., Chem. Commun.* **1980**, 791. Cadogan, J.; Rowley, A.; Wilson, N. *Liebigs Ann. Chem.* **1978**, 74.

[5] Trost, B. M.; Williams, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7421.

[6] The structure of **6** as a 1,3-bis(diazo) 2-ketone rather than a 1,2-bis(diazo) 3-ketone has been established by X-ray analysis of the monohydrazone precursor; G. Maas, M. Regitz, O. Ganster, and G. Eistert, submitted for publication in *Chem. Ber.*

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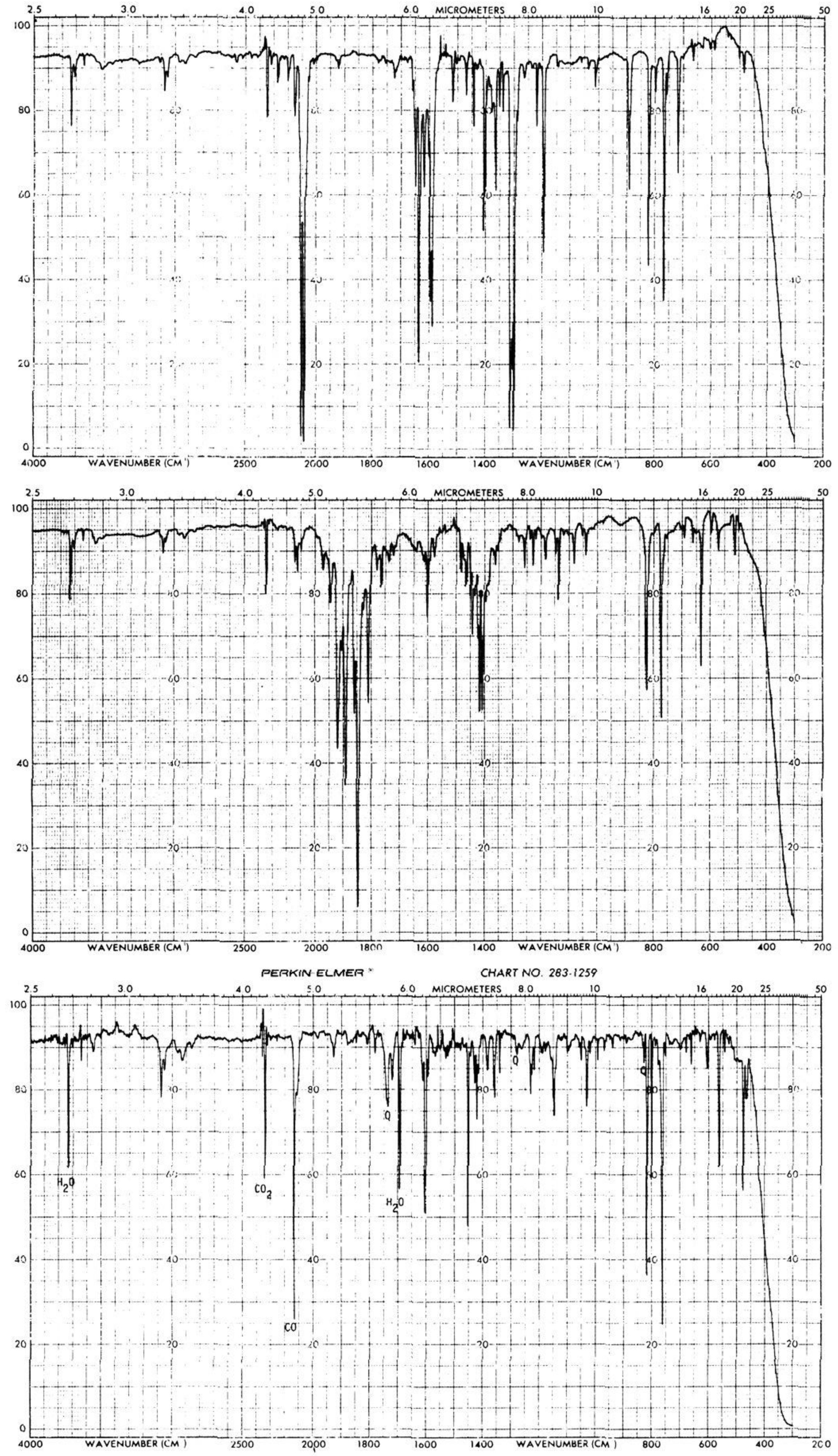

Figure 1. (a) Infrared Spectrum of 1,3-bis(diazo)phenalen-2-one (**6**) at 24 K. Sample was sublimed at 96 °C and codeposited with 72 mm of argon over 150 min. (b) Infrared spectrum of cyclopropenone **7** at 15 K formed on irradiation (77 min, $\lambda > 364$ nm) of bis(diazo)phenalenone (**6**) matrix isoalted in argon. (c) Infrared spectrum of acenaphthyne (**8**) at 15 K formed on irradiation (2354 min, $\lambda > 302$ nm) of cyclopropenone **7** matrix isolated in argon at 15 K. Ordinate expanded to simulate a 2-fold increase in concentration. Q = acenaphthoquinone.

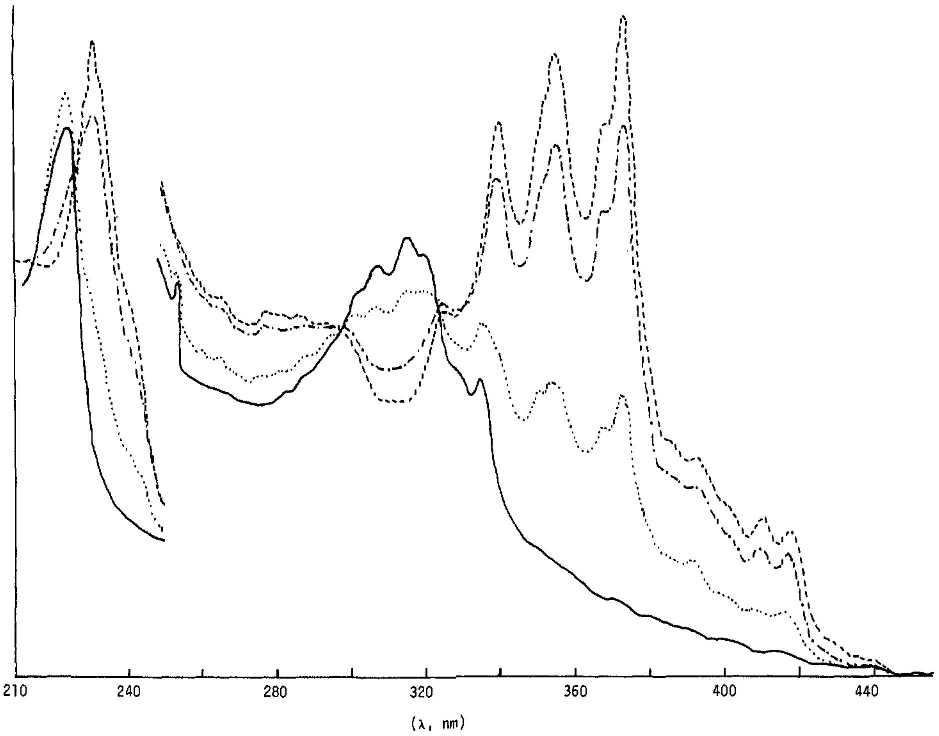

Figure 2. Ultraviolet spectrum of cyclopropenone **7** (solid trace) at 15 K formed on irradiation (85 min., λ > 416 nm) of bis(diazo)phenalenone (**6**) (dashed trace) matrix isolated in argon. Intermediate traces were obtained after 4 and 19 min of irradiation.

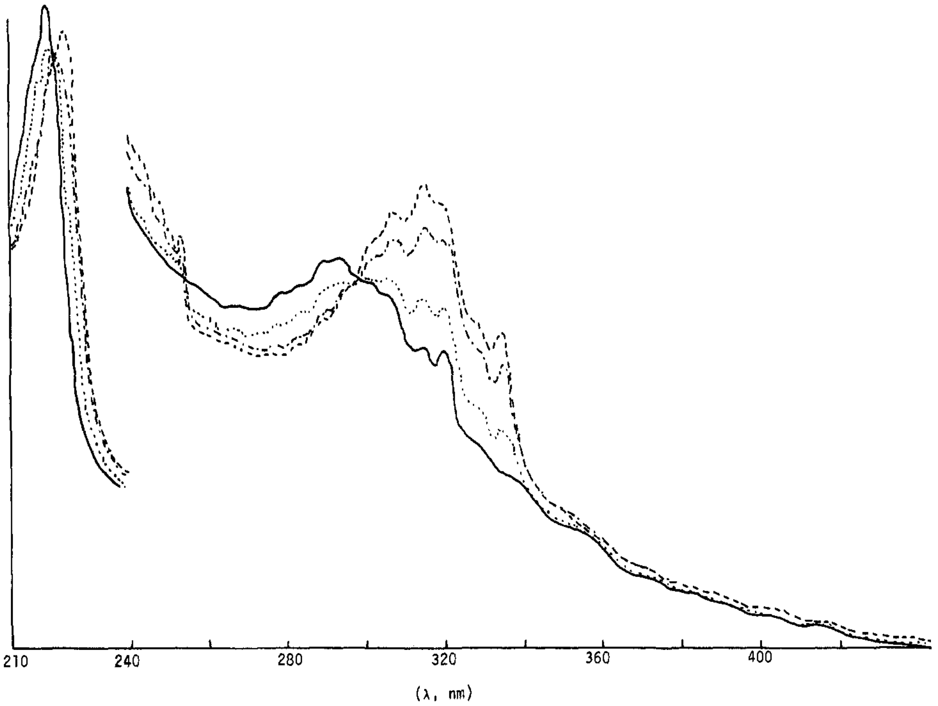

Figure 3. Ultraviolet spectrum of acenaphthyne (**8**) (solid trace) at 15 K formed on irradiation (66 min, λ > 302 nm) of cyclopropenone **7** (dashed trace) matrix isolated in argon. Intermediate traces were obtained after 1.6 and 10.5 min of irradiation.

by the characteristic complex pattern centered about the intense band at 1850 cm^{-1} in the infrared spectrum (Figure 1). The conversion of **6** to **7** was also followed by ultraviolet spectroscopy[7] in a separate experiment. Irradiation (>416 nm) of **6** caused the disappearance of **6** with concomitant appearance of new maxima at 335, 320, 315, and 307 nm (Figure 2). The observation of isobestic points at 206, 298, and 324 nm show that no ground-state intermediate is involved in the conversion of **6** to **7**. Irradiation (>302 nm) of **7** gave rise to carbon monoxide (2138 cm^{-1}) and acenaphthyne (**8**). The intense bands at 817 and 760 cm^{-1} in the infrared spectrum of **8** show that the acenaphthene skeleton is intact (cf. the same bands in **6** and **7**; acenaphthylene has strong bands at 830 and 770 cm^{-1}). The carbon–carbon triple bond stretch cannot be assigned, but the band at 1930 cm^{-1} is a possibility. When the irradiation (>302 nm) of the cyclopropenone **7** was monitored by ultraviolet spectroscopy, the new bands at 219 and 295 nm appeared as the absorption of **7** decreased. Isosbestic points at 298 and 255 nm were observed for this process (Figure 3).

The chemistry of acenaphthyne **8** provides ample evidence for

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(7) A sapphire sample plate was used for UV experiments and a cesium iodide plate for infrared experiments. The vacuum shroud was equipped with two potassium bromide windows and one quartz window.

the structural assignment. The product reacts with oxygen in the matrix to give acenaphthoquinone (**9**)[8] identified by IR comparison with an authentic sample. Warming to room temperature gives decacylene (**10**) which can be detected in the crude product and which has been isolated by HPLC and identified by comparison with authentic decacyclene (mass spectrum, UV spectrum, and HPLC retention). Trace amounts of water trap acenaphthyne giving acenaphthenone (**11**) which was isolated by HLPC and identified by comparison (mass spectrum, UV spectrum, and HPLC retention) with the authentic material and another compound (*m/e* 318) which corresponds to the hydrated dimer. The dimer of benzyne can be trapped in similar fashion with methanol.[9] Larger amounts of water increase the yield of acenaphthenone and the hydrated dimer but also lead to premature reaction with cyclopropenone **7** giving the acid (**12a**, identified by its mass spectrum). Similar experiments with methanol (0.7% in argon) give the ester **12b** (mass spectrum) and a trace (M^+, 6% of the ester, base peak) of a product with *m/e* 182 corresponding to acenaphthyne plus methanol.

Acknowledgment. This research was supported by Grant CHE 79-00964 from the National Science Foundation and Grant GM-24427 from the National Institutes of Health.

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[9] Chapman, O. L. *Pure Appl. Chem.* **1974**, *40*, 511.

Additions and Corrections

Radical Anion and Radical Trianion of 1,4-Bis(dimethylphosphino)benzene [*J. Am. Chem. Soc.* **1978**, *100*, 6504]. W. Kaim and H. Bock,* Institute of Inorganic Chemistry, University of Frankfurt, Frankfurt, West Germany.

The ESR spectra reported have been reassigned according to recent investigations:

i. The first species is not the radical anion of the title compound, but of its oxide $R_2P(O)-C_6H_4-P(O)R_2$, as has been proven by comparison:[1] phosphane oxides, even if present in only minimal amounts, are more easily reduced than the corresponding phosphanes.[2] The ESR spectrum of the unoxidized 1,4-bis(dimethylphosphino)benzene radical anion actually had been recorded and exhibits an unusual line width effect.[3] Therefore, the correct interpretation could only be achieved by comparison with the ESR spectra of closely related radical anions.[3]

ii. The "radical trianion" of 1,4-bis(dimethylphosphino)benzene is in fact the radical anion of 4,4′-bis(dimethylphosphino)biphenyl, which is formed via P-aryl cleavage.[4] The assignment has been confirmed by comparison with the ESR spectrum of the authentic species.[3] The misinterpretation has been facilitated by the missing ESR coupling constant $a_{H(3,3')}$ which must be smaller than 0.003 mT, and especially by the fact that different ESR data for this radical anion had been reported previously.[5] That latter species,[5] however, may be recognized as the corresponding phosphane oxide radical anion $R_2P(O)-C_6H_4-C_6H_4-P(O)R_2^{-\cdot}$.[3] A literature search[6] suggests further confusion between radical anions of phosphanes and their oxides.[3]

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[1] W. Kaim, *Z. Naturforsch., B*, **36**, 150 (1981).

[2] Cf. K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **90**, 1118 (1968).

[3] W. Kaim and H. Bock, *Chem. Ber.*, **114**, 1576 (1981).

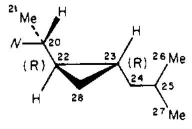
[4] Cf. K. Issleib and H. O. Fröhlich, *Z. Naturforsch., B*, **14**, 349 (1959).

[5] A. H. Cowley and M. H. Hnoosh, *J. Am. Chem. Soc.*, **88**, 2595 (1966).

[6] P. Schipper, E. H. J. M. Jansen, and H. M. Buck, *Top. Phosphorus Chem.*, **9**, 407 (1977).

Isolation and Structure Elucidation of 22(*S*),23(*S*)-Methylenecholesterol. Evidence for Direct Bioalkylation of 22-Dehydrocholesterol [*J. Am. Chem. Soc.* **1980**, *102*, 7113-4]. Pierre-Alain Blanc and Carl Djerassi,* Department of Chemistry, Stanford University, Stanford, California 94305.

Our continuing studies on steroidal cyclopropanes confirm that in this paper we correctly showed the absolute configuration of naturally occurring 22,23-methylenecholesterol (i) to be opposite to that (22(*R*),23(*R*),24(*R*)) of gorgosterol (ii, X = CH_3; N = cholesterol nucleus). Therefore, we referred to the natural material as the 22(*S*),23(*S*)-isomer. In fact this is a misapplication of the Cahn–Ingold–Prelog rules (*Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385–415): even though of opposite absolute configuration, the natural 22,23-methylenecholesterol (i) should also be referred to as 22(*R*),23(*R*). This is so because the 22(*R*) indication in the related sterols gorgosterol (ii, X = CH_3) and demethylgorgosterol (ii, X = H) is based on a higher priority of C-23 over C-20, which is for demethylgorgosterol due to methyl substitution on C-24; 23(*R*) then results from the priority of C-22 over C-24. However, lack of the C-28 methyl group in 22,23-methylenecholesterol (i) leads to an inversion of the sequences around C-22 and C-23. Regarding the 22-carbon atom, C-20 now assumes priority over C-23, while the sequence around C-23 is H < C-24 < C-28 < C-22.



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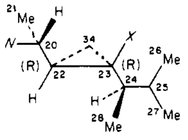

ii

Complete Thermodynamic Analysis of the Hydration of Thirteen Pyridines and Pyridinium Ions. The Special Case of 2,6-Di-*tert*-butylpyridine [*J. Am. Chem. Soc.* **1979**, *101*, 7141]. Edward M. Arnett* and B. Chawla, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260.

Page 7144: The values for di-*tert*-butylpyridine (2,6-DTBP) in Table IV should be corrected as follows:

	reads	should read
$\Delta G^{g \to H_2O}$ (B)	3.87	0.40
$\delta \Delta G^{g \to H_2O}$ (B)	4.29	0.82
$\delta \Delta G^{g \to H_2O}$ (BH^+)	15.00	11.50
$\delta(T\Delta S_s^\circ)$ (B)	−5.99	−2.52
$\delta(T\Delta S_s^\circ)$ BH^+	−8.33	−4.8

Chiral Perturbation of Olefins by Deuterium Substitution. The Optical Activity and Circular Dichroism Behavior of (1*S*)-[2-^{2}H]Norbornene and Deuterated Apobornenes [*J. Am. Chem. Soc.* **1980**, *102*, 7228]. Leo A. Paquette,* Christopher W. Doecke, Francis R. Kearney, Alex F. Drake, and Stephen F. Mason, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (L.A.P., C.W.D., and F.R.K.), and King's College, London WC2R 2LS, England (A.F.D. and S.F.M.).

Although the title and introduction to this paper carry the correct absolute configurational descriptors for the deuterated olefins, six examples of inadvertent transposition of the *R/S* notation can be found later in the text: