by Whitten.[5] (3) We have independently synthesized these high-valent dimers by the oxidation of ruthenium(II) carbonyl porphyrins with *tert*-butyl hydroperoxide. We are currently investigating the structural and chemical properties of the metal-metal bond in **4**. The conversion of ruthenium(II) porphyrins to stable ruthenium(IV)-porphyrin complexes via O_2 is without precedent in iron porphyrin chemistry.[4] This encourages us in our own attempts to prepare ruthenium analogues of the high-valent iron porphyrin intermediates involved in the catalytic cycle of cytochrome P-450.

Acknowledgment. We are grateful to Dr. B. D. Santariero for the X-ray photographic analyses and space group determination of **10**. Financial support for this work was provided by the National Institutes of Health, Grants GM17880 (to J.P.C.) and HL13157 (to J.A.I.) and the National Science Foundation, Grant CHE78-09443 (to J.P.C.). NMR experiments were performed on instruments supported by the NIH Grant RR00701 and NSF Grants 23633 (Stanford Magnetic Resonance Laboratory, 360 MHz), GP28142, and CHE77-08810 (Stanford University).

Diazomethane and Thiobenzophenone: Mechanistic Elucidation of the Schönberg Reaction

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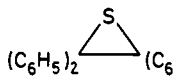
Two reaction modes of diazoalkanes with aromatic thioketones have been described: the formation of thiiranes, e.g., **1** + N_2 from diphenyldiazomethane and thiobenzophenone,[1] and 1,3-dithiolanes, e.g., **2** + N_2 from diazomethane and 2 mol of thiobenzophenone.[2,3] Schönberg et al.[4] have studied reactions of 18 diazoalkanes with 32 thiocarbonyl compounds over the range of 40 years;[5] in no case have 1:1 and 1:2 products of type **1** and **2** been isolated side by side.



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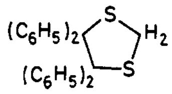

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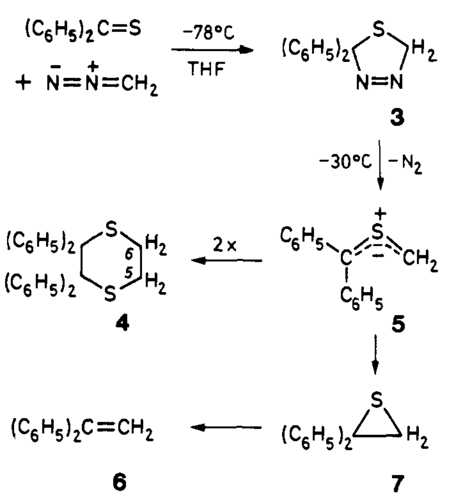
We added an excess of ethereal diazomethane to thiobenzophenone[6] in ether *at 20 °C*, and after a vigorous reaction with N_2 evolution had taken place, we isolated 4,4,5,5-tetraphenyl-1,3-dithiolane (**2**)[7] in 95% yield. Obviously, the second molecule of thiobenzophenone is consumed faster by an intermediate than the first one by diazomethane. On introducing diazomethane in THF into the blue solution of thiobenzophenone *at −78 °C*, a surprisingly rapid decolorization made a titration feasible; now the stoichiometry was 1:1, and no N_2 was eliminated. Evaporation of the solvent at −78 °C left 2,2-diphenyl-1,3,4-thiadiazoline (**3**) in colorless crystals which went "pfft" around −20 °C.



Nitrogen was liberated from the THF solution of **3** *at −30 °C*, and 2,2,3,3-tetraphenyl-1,4-dithiane (**4**)[8,9] was formed in 95% yield; the mother liquor contained 1% 1,1-diphenylethylene (**6**). The ^1H NMR signals of the ring protons of **4** (AA′BB′ at 35 °C, A_4 at 102 °C) reveal hindered inversion; in the ^{13}C NMR spectrum C5 and C6 are equivalent whereas the phenyls are pairwise different. A two-step head-head dimerization of the *thiocarbonyl ylide* **5** with the first bond being formed between the CH_2 groups is conceivable.

Rate measurements for **3** → **5** at −45 °C indicate first order with half-lives of 34 min in $CDCl_3$, 55 min in THF, 58 min in ethyl acetate, and 65 min in methanol. The data do not exclude a fast subsequent reaction **5** + **3** → **4** + N_2 which is regarded less likely.[10]

When the THF solution of **3**, kept at −78 °C, was added portionwise to stirred ether at 20 °C, the yield of dimer **4** dropped to 41%, and 38% (**6** + **7**) was observed; $t_{1/2} \sim 16$ h at 20 °C was estimated for the sulfur extrusion, **7** → **6**, on the basis of ^1H NMR spectra.[11] Due to the lower concentration of **5** and the higher temperature coefficient of the cyclization **5** → **7** (compared with dimerization), this electrocyclic ring closure of **5** to the thiirane **7** becomes competitive. Kellog et al.[12] established the conrotatory course of thiocarbonyl ylide cyclization.

Loss of N_2 from **3** in the presence of dipolarophiles allowed an interception of the thiocarbonyl ylide **5**. After generating **3** in THF at −78 °C, 1 equiv dipolarophile was added and the solution warmed to −30 °C. When the N_2 evolution had ceased, the cycloadducts **2** and **8**–**14** were isolated in the yields stated.[9,13] Thiobenzophenone as dipolarophile provided the dithiolane **2** in 96% yield, thus clarifying the mechanism of the Schönberg re-

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(1) Staudinger, H.; Siegwart, J. *Helv. Chim. Acta* **1920**, *3*, 833–852.

(2) Bergmann, E.; Magat, M.; Wagenberg, D. *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 2576–2584.

(3) Schönberg, A.; Černik, D.; Urban, W. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2577–2581.

(4) Schönberg, A.; König, B.; Singer, E. *Chem. Ber.* **1967**, *100*, 767–777. The authors review ~100 products from diazoalkanes and thiocarbonyl compounds in tables and state "Leider waren alle Versuche, dem Chemismus der Reaktionen durch Isolierung von Zwischenprodukten oder auf andere Weise näher zu kommen, bisher erfolglos".

(5) Last paper: Schönberg, A.; Knöfel, W.; Frese, E.; Praefcke, K. *Chem. Ber.* **1970**, *103*, 938–948.

(6) N_2 atmosphere for all experiments to protect thiobenzophenone from autoxidation.

(7) Mp 207–209 °C dec (blue melt); 166–167 °C,[2] 199–200 °C;[3] ^1H NMR ($CDCl_3$) δ 3.73 (s, CH_2).

(8) **4**: mp 166–169 °C dec; the colorless crystals turn violet on exposure to sun light. ^1H NMR (C_6H_5Br) δ 2.66–3.43 (AA′BB′, 4 H, 4-H_2 and 5-H_2) at 35 °C, 2.90 (s, A_4) at 102 °C, coalescence at 74 °C. ^{13}C NMR ($CDCl_3$) δ 64.5 (C1 and C2), 31.4 (C4 and C5), 144.7 and 146.3 (quaternary, aromatic C).

(9) Satisfactory CH and S analyses were obtained for all new compounds except **3**.

(10) The disappearance of the ^1H NMR singlet for CH_2 of **3** at δ 3.73 was measured against δ 6.47 of trichloroethylene as internal standard, 48 values over 3 half-lives. In addition, volumetric analysis of the N_2 evolution from the magnetically stirred solution was carried out.

(11) **7** was not obtained pure. Its decrease in the mixture with **6** was diagnosed from the CH_2 singlet integrals at δ 2.98 for **7** and 5.38 for **6**.

(12) Buter, J.; Wassenaar, S.; Kellogg, R. M. *J. Org. Chem.* **1972**, *37*, 4045–4060.

(13) Selected ^1H NMR signals ($CDCl_3$, δ): **8**, mp 165–167 °C, 4.08 (s, CH_2); **9**, mp 140–142 °C, 3.47, 3.71 (2s, $2OCH_3$), 4.01 (s, CH_2); **10**, mp 126–128 °C, 2.64 (dd, $J_{5A,5B} = 12.5$ Hz, $J_{4,5B} = 7.5$ Hz, 5-H_B), 3.23 (d, $J_{5A,5B} = 12.5$ Hz, 5-H_A), 3.78 (t, $J_{3,4} = J_{4,5B} = 7.5$ Hz, 4-H), 4.33 (d, $J_{3,4} = 7.5$ Hz, 3-H); **11**, mp 174–176 °C, 2.70 (dd, $J_{5A,5B} = 12.8$ Hz, $J_{4,5B} = 7.6$ Hz, 5-H_B), 3.29 (dd, $J_{5A,5B} = 12.8$ Hz, $J_{4,5A} = 1.0$ Hz, 5-H_A), 3.62 (dt, $J_{3,4} = J_{4,5B} = 7.6$ Hz, $J_{4,5A} = 1.0$ Hz, 4-H), 4.12 (d, $J_{3,4} = 7.6$ Hz, 3-H), 2.84 (s, NCH_3); **12**, m 208–209 °C, **13**, mp 177–178.5 °C, 4.43 (s, CH_2); **14**, mp 98–100 °C, 3.28, 3.46 (2s, $2OCH_3$), 4.63 and 5.13 (AB, $J = 9.8$ Hz, CH_2).

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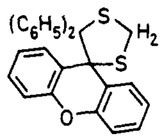
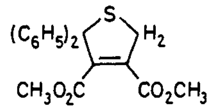
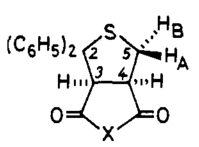


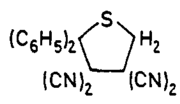
8 84%



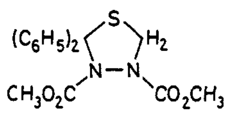
9 70%



10 X = O 97%
11 X = NCH_3 80%
12 X = NC_6H_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 ($\mathbf{3} \rightarrow \mathbf{5} + N_2$).

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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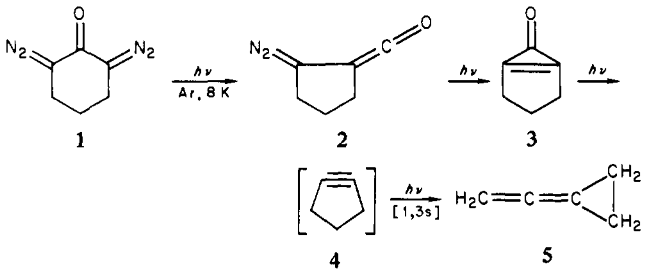
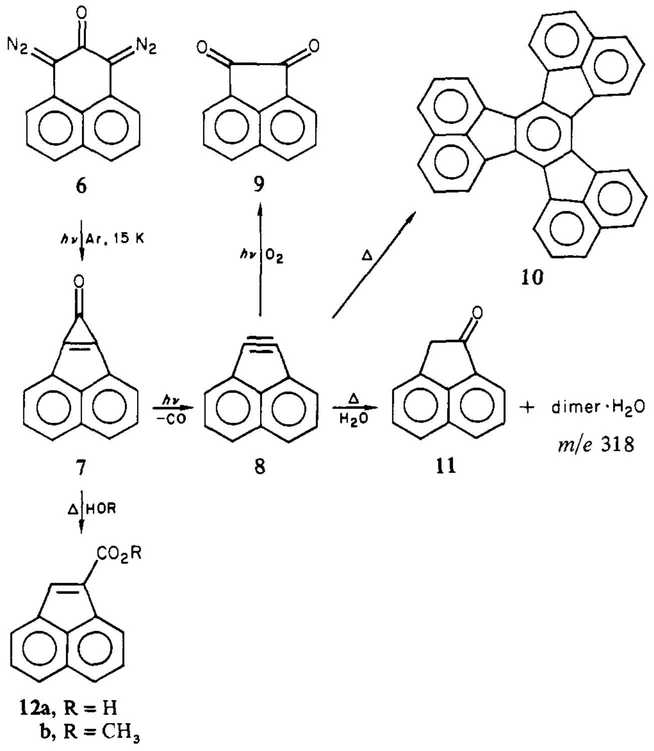
Evidence for the existence of cycloalkynes as strained as cyclopentyne[1] and norbornyne[2] has been available for several years. Attempts to generate strained acetylenes such as cyclobutyne[1,3] and acenaphthyne[4] have been unsuccessful. The observed products in the latter two cases can be rationalized 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



12a, R = H
b, R = CH_3

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[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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