formed by decomposition of an excited adduct in the O(^{3}P) reaction pathway, rather than by the formation and subsequent photolysis of an isolable ketene. While spin conservation dictates that the initial adduct be a triplet, intersystem crossing to the singlet ketocarbene may precede product formation.

The reaction of atomic oxygen with a 50:50 mixture of 2-pentyne and methanol produced no detectable amounts of methyl 2-ethylbutyrate or methyl 2-methylpropionate and only traces of C_3 and C_5 hydrocarbons. This result indicates that the ketene-forming rearrangement of the O(^{3}P)–alkyne adduct is intramolecular, in that it proceeds without the migrating group becoming detached from the adduct. This pattern is in contrast to that of O(^{3}P) plus olefin reactions, in which migrating alkyl radicals become detached from the molecule during rearrangement.[4] The Wolff rearrangement of α-diazo ketones is also intramolecular.[10]

Experimental Section

Reaction Technique. Procedures for the reaction of atomic oxygen, generated in situ by the mercury photosensitized decomposition of nitrous oxide, have been described previously.[11] The alkynes were obtained commercially and distilled before use. Relative rate constants of the alkynes vs. cyclopentene were determined by the method of Cvetanovic and converted to the usual standard, 2-methylpropene, using the figure $k_{\text{cyclopentene}}/k_{\text{2-methylpropene}} = 1.19$.[4]

Product Analysis. The VPC substrates most often used were noncondensable gases, 5A molecular sieves; hydrocarbon products, DC710; and carbonyl and ester products, dinonyl phthalate. Authentic samples of 3-buten-2-one, 1-penten-3-one, *trans*-3-penten-2-one, cyclopropyl methyl ketone, methyl 2-methylpropionate, and the hydrocarbon products were obtained commercially for comparison of spectra and VPC retention times. Cyclopropyl ethyl ketone and 4-hexen-3-one were prepared by reaction of diethylcadmium with the appropriate acid chloride.[12] Spectra of the other carbonyl and ester products were routinely predictable or available from the literature.[13]

trans-2-Methylcyclopropanecarboxaldehyde was prepared by reaction of 2-butenal with diiodomethane and zinc–silver couple.[14] The published NMR spectrum of this compound contains uncorrected errata. We found the spectrum (in CCl_4) to be δ 0.9–1.4 (m, 6 H), 1.9 (m, 1 H), and 9.08 (d, 1 H).

Acknowledgment. We gratefully acknowledge the support of this research by The Robert A. Welch Foundation.

Registry No.—Atomic oxygen, 17778-80-2; *trans*-2-methylcyclopropanecarboxaldehyde, 50991-21-4.

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(8) The reaction rates of the acetylenes at 25 ± 2 °C (relative to 2-methylpropene as 1.00) were 2-butyne, 0.55; 1-pentyne, 0.74; 2-pentyne, 0.71; and 3,3-dimethyl-1-butyne, 0.99. Atomic oxygen would react with these alkynes at least 100 times faster than with methanol ($k_{\text{ethanol}}/k_{\text{2-methylpropene}} = 0.0072$).[9]
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Oxidation of *p*-Toluenesulfonylhydrazide to 1,2-Di(*p*-toluenesulfonyl)hydrazine

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p-Toluenesulfonylhydrazide (**1**) and catalytic amounts of cobalt salts in solution react with aqueous hydrogen peroxide to give 1,2-di(*p*-toluenesulfonyl)hydrazine (**4**) (or its tautomer **5**) as the major product. The same reactants in the presence of stoichiometric amounts of cobalt salts produce the more complete oxidation products of cobalt sulfonate and cobalt sulfinate salts. A reaction (Scheme I) patterned after the Haber–Weiss decomposition scheme is expected to produce the free radicals which subsequently oxidize the sulfonhydrazide.[2-4]

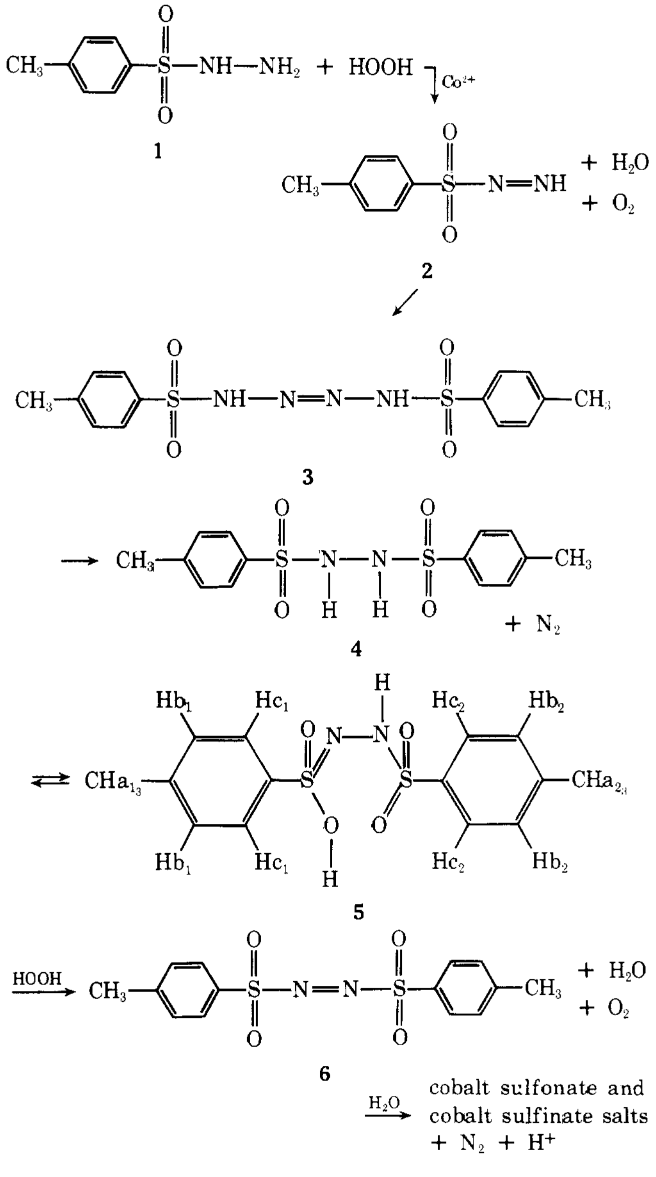
Scheme I

$$\mathrm{HOOH} + \mathrm{Co}^{2+} \longrightarrow \mathrm{HO}\cdot + \bar{\mathrm{O}}\mathrm{H} + \mathrm{Co}^{3+}$$

$$\mathrm{HOOH} + \mathrm{Co}^{3+} \longrightarrow \mathrm{HOO}\cdot + \mathrm{H}^+ + \mathrm{Co}^{2+}$$

The isolation of **4** or **5** as the major product strongly suggests that *p*-toluenesulfonylhydrazide (**1**) undergoes reactions (Scheme II) similar to those of primary alkyl and aryl hydra-

Scheme II



zines. It is expected that *p*-toluenesulfonylhydrazide (**1**) decomposes by oxidation to the corresponding sulfondiazene[1] **2** which dimerizes to form the corresponding sulfontetrazene[1] **3**. The formation of the sulfondiazene is consistent with the findings of McBride and Kruse, who showed that 1,1-dialkylhydrazines are oxidized by halogens to form the corresponding diazenes.[5] McBride and Bens showed that tetrazenes are formed by the dimerization of the dialkyldiazene and its conjugate acid in aqueous media.[6] There is reason to expect the sulfontetrazene to disproportionate in the same manner as the corresponding alkyl and aryl tetrazenes, which explains the formation of **4** or **5** along with the liberation of nitrogen. Horner and Fernekess found that semicarbazide reacts similarly in aqueous media to give the corresponding 2-tetrazene which subsequently produces the disubstituted hydrazine along with nitrogen.[7] Overberger and Marks found analogous oxidation products of disubstituted primary hydrazines from $KMnO_4$ oxidation in acetone.[8] Similar reactions were reported by Schlenk and Bergemann.[9]

The disproportionation of the sulfontetrazene **3** is expected to form sulfonamidyl biradical species in producing **4** or **5**. The formation of biradical species from the corresponding tetraphenyltetrazene in concentrated sulfuric acid was suggested by Hammond et al.[10] Tolles et al. produced cation radicals upon reacting tetramethyl-2-tetrazene with tetranitromethane, and Cowley and Waters obtained dimethylamino radicals by pyrolysis of the same species.[11,12] Michejda and Campbell suggested that tetramethyl-2-tetrazene coordinates with zinc chloride in anhydrous tetrahydrofuran to give the same biradical species.[13] The presence of cobalt ions in the reaction media suggests similar participation in the formation of biradical species, and the formation of a charge transfer complex is not ruled out.

The oxidation of *p*-toluenesulfonylhydrazide (**1**) continues beyond intermediate **4** or **5** under more energetic conditions. Oxidation to the corresponding azo compound **6** and subsequent hydrolysis can explain the apparent formation of a mixture of sulfonate and sulfinate salts in equimolar amounts.

Structure **4** or **5** (mol wt 340) closely explains the value obtained for the equivalent weight (341) based on the titration of one active proton per molecule. Either structure **4** or **5** explains the strong acidity.

The NMR spectrum of **4** or **5** in acetone-d_6 shows only benzylic methyl and aromatic protons similar to the spectra of *p*-toluenesulfonamide and acetone-*p*-toluenesulfonhydrazone. No N–H absorption is found at 6.4 ppm and is probably lost in the background. However, an infrared spectrum of this sample clearly shows N–H absorption at 1360 cm^{-1}. Normal sulfonamide S=O stretching absorption is observed at 1170 and 1360 cm^{-1}. Together, the data support **4**. However, broad infrared absorption at 2600–3100 cm^{-1} suggests possible hydrogen bonding or proton exchange with one of the sulfonyl groups such as in the tautomeric form **5**. The NMR spectrum of the aromatic protons shows splitting of the downfield doublet. A possible assignment consistent with **5** is given in which b_1 and b_2 protons of **5** are nearly coincident while c_1 and c_2 protons are slightly nonequivalent owing to the different sulfur atom bonding. This suggests that **5** is the predominant species.

The strong 2.4-ppm benzylic methyl peak is just slightly downfield relative to *p*-toluenesulfonamide (approximately 2.44 vs. 2.42 ppm). The addition of D_2O to **4** or **5** in acetone-d_6 produces two benzylic peaks, one overlapping *p*-toluenesulfonamide. Therefore, the addition of D_2O appears to be hydrolyzing **5** to a new species.

The cobalt sulfonate–cobalt sulfinate product mixture is nearly insoluble in acetone-d_6. The NMR spectrum is not too informative; however, the infrared spectrum of the solid does show that the sample is a mixture of the sulfonate and sulfinate salts, and water of crystallization is contained. The 1000–1300-cm^{-1} region is very typical of alkylbenzenesulfonates. The absorption at 900–1000 cm^{-1} is very typical of sulfinate salts. Water peaks are at 1640 and 3000–3600 cm^{-1}, and the Karl Fischer test indicates that 1 mol of water of crystallization is contained per mole of cobalt salt. The elemental analysis closely fits the calculated analysis for an equimolar product mixture of cobalt sulfonate and cobalt sulfinate salts.

Experimental Section

p-Toluenesulfonylhydrazide (**1**) was obtained from Eastman Organic and twice recrystallized (mp 110 °C) from 95% ethanol. Nuodex cobalt octoate (in solution) was obtained from Tenneco Chemical Corp., analyzed for Co (12.0%), and used directly. Baker Analyzed Reagent 30% hydrogen peroxide (aqueous) was analyzed for active hydrogen peroxide (33.57%) using an iodometric method[14] and used directly. All other solutions were of reagent quality. Elemental analyses were made by Truesdail Labs, Los Angeles, Calif., and the NMR and IR spectra were obtained by Chevron Research Corp., Richmond, Calif.

Oxidation of *p*-Toluenesulfonylhydrazide to 1,2-Di(*p*-toluenesulfonyl)hydrazine. A solution of 22.5 g (0.12 mol) of *p*-toluenesulfonylhydrazide and 1.2 g (0.0024 mol) of cobalt octoate (solution) in 250 ml of absolute methanol was adjusted to 30 °C with stirring. Hydrogen peroxide (30%) (12.2 g, 0.12 mol) was added slowly with continuous stirring. The mixture exothermed to 40 °C with bubbling, and a rose-colored solution was formed which remained clear. A gas slowly evolved until after 4 h when a white precipitate formed. Mixing was continued for 16 h. The solution was chilled to −10° and the precipitate collected by suction filtration through fine sintered glass. This yielded 9.5 g (93% based upon the limited availability of hydrogen peroxide). The precipitate was twice recrystallized in 100 ml of a mixture of 1 part concentrated HCl to 15 parts 95% ethanol and finally washed in 30 ml of cold 95% ethanol and dried at 110 °C. This yielded 5.0 g (53%) of fine, white needles: mp 182–183 °C; equiv wt 341.3 ± 3.2 (determined by titration with aqueous 0.01 N NaOH in acetone to the phenolphthalein end point); H_2O 0.01% (by Karl Fischer); IR (neat) 1170, 1360, 2600–3100 (broad), 3260 cm^{-1}; NMR (acetone-d_6) δ 2.44 (s, 3), 7.35 (d, 2, J = 8 Hz), 7.72 (d, 2, J = 8 Hz).

Anal. Calcd for $C_{14}H_{18}N_2S_2O_5$ (same as $C_{14}H_{16}N_2S_2O_4 \cdot H_2O$): C, 46.92; H, 5.05; N, 7.82; S, 17.89; O, 22.32. Found: C, 46.96; H, 5.20; N, 7.88; S, 18.82; O, 21.14; Co, <50 ppm. Water of crystallization was present in the sample prepared for elemental analysis.

Oxidation of *p*-Toluenesulfonylhydrazide to a Product Mixture of Cobalt Sulfonate and Cobalt Sulfinate Salts. A solution of 22.5 g (0.12 mol) of *p*-toluenesulfonylhydrazide (**1**) and 14.7 g (003 mol) of cobalt octoate (solution) in 250 ml of butyl acetate was adjusted to 40 °C with stirring. Hydrogen peroxide (30%) (12.2 g, 0.12 mol) was added slowly with stirring. The reaction exothermed to 64 °C with vigorous bubbling, and a pink, colloidal suspension was immediately formed. Mixing was continued for 1 h. The solids were collected by centrifugation, washed three times in 30-ml portions of cold butyl acetate, and dried at 110 °C. This yielded 5.5 g (66% based on available cobalt) of a pink powder: mp 220 °C; IR (neat) 810, 930, 950, 1010, 1040, 1180, 1640, 3000–3600 cm^{-1} (broad).

Anal. Calcd for $CoC_{14}H_{16}S_2O_6$ (same as $Co(C_7H_7SO_3)_2 \cdot Co(C_7H_7SO_2)_2 \cdot 2H_2O$): Co, 14.61; C, 41.70; H, 4.00; S, 15.89; O, 23.80. Found: Co (by ignition test), 14.20; C, 42.08; H, 3.94; N, 0.44; S, 15.93; O, 23.41.

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Registry No.—**1**, 1576-35-8; **3**, 60803-17-0; **4**, 14062-05-6; **5**, 60803-18-1; cobalt *p*-toluenesulfonate, 20664-98-6; cobalt *p*-toluenesulfinate, 34045-51-7; cobalt octoate, 1588-79-0.

References and Notes

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A 10-π-Electron Heterocycle: 2,3,4-Tricarbomethoxy-6,7,8,9-dibenzo-1,5-diazonine

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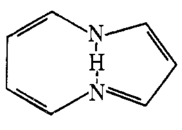
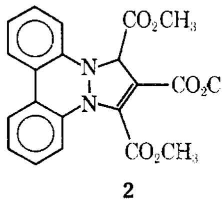
Several years ago we reported[1] the synthesis of some novel heterocycles as potential precursors to derivatives of the 10-π-electron 1,5-diazonine system, **1**, in which the intraannular hydrogen repulsions inhibiting coplanarity in some other potentially aromatic 10-π-electron systems might be relieved by transannular hydrogen bridging as shown.[2]

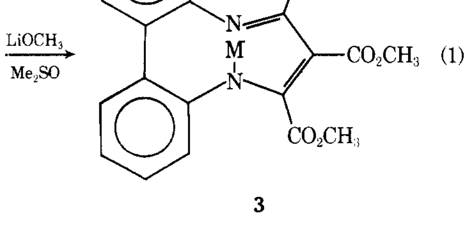


1

Although we did prepare a number of novel heterocycles, including 1,2,3-tricarbomethoxy-1*H*-benzo[*c*]pyrazolo[1,2-*a*]cinnoline (**2**), we were not able to effect the conversion of any of them to 1,5-diazonine derivatives, as in eq 1, by any conditions then tried. Others have reported both theoretical[4] and experimental[5] studies of some of the heterocycles we discussed, but 1,5-diazonine and its derivatives have not yet appeared in the literature. We now wish to report the successful conversion of **2** to 2,3,4-tricarbomethoxy-6,7,8,9-dibenzo-1,5-diazonine (**3**, M = H) and some of its derivatives.



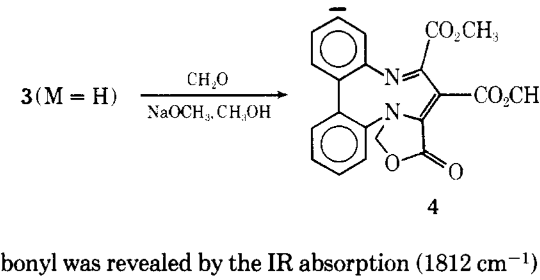
2



3

When a yellow solution of **2** in dimethyl sulfoxide (Me_2SO) is added to a suspension of 2 equiv of lithium methoxide in Me_2SO, the initially formed intense blue-green color slowly fades to an orange yellow. The bright yellow salt (73%, mp 227–230 °C) obtained on workup could not be purified satisfactorily by recrystallization, but analyzed moderately well for the lithium salt of **3** (**3**, M = Li)[6] containing 0.7 equiv of lithium hydroxide. The use of only 1 equiv of lithium methoxide in the reaction gave less than 50% of the product. Sodium methoxide (2 equiv) worked as well, but potassium methoxide was less effective. Acidification of an aqueous solution of the salt with acetic acid gave the more tractable pale yellow **3**, M = H (80%, mp 110–140 °C). Again, only moderately satisfactory combustion analyses could be obtained on chromatographically purified material; but the 1:1 crystalline solvate with Me_2SO (mp 145–147 °C) gave excellent analytical results. The substance also formed well-defined crystalline solvates with carbon tetrachloride and with acetone.

The structure of **3**, M = H, was established by its spectroscopic properties and some chemical transformations. Thus, the methyl ester functions revealed themselves in the IR (1740, 1710 cm^{-1}) and NMR [δ 3.61 (6 H, s), 3.53 (3 H, s)], as did the proton on nitrogen (3380 cm^{-1}, δ 6.76, washed out with D_2O). Rapid proton exchange at 30 °C between the nitrogens in **3**, M = H, resulting in NMR equivalence of the flanking ester methyls, was suggested by the separation of the lower field, six-hydrogen singlet (δ 3.61) into a broad doublet at −10 °C, whose higher field signal merged with the higher field singlet (δ 3.53) at −30 °C to give two peaks of reversed intensity at δ 3.63 (3 H, s) and 3.55 (6 H, broad singlet). The prototropic change was more clearly revealed in the ^{13}C NMR, which transformed from three peaks for the ester methyl carbons (δ 51.7, 52.7, 53.1) at 25 °C to only two peaks (51.5, 52.6) at 50 °C with an accompanying, though less easily interpretable, simplification of the olefinic–aromatic carbons (δ ~120–170). The higher temperature required for equivalence of the methyl signals in the ^{13}C NMR than in the ^1H NMR presumably reflects the larger chemical shift difference. The substance could be converted with methyl iodide and potassium carbonate to the nicely crystalline, yellow *N*-methyl (NMR δ 2.80) derivative **3**, M = CH_3 (68%, mp 203–205 °C), in which all three ester methyls were now differentiated in the NMR (δ 3.61, 3.66, 3.81). Reaction of **3**, M = H, with formaldehyde and sodium methoxide in methanol gave orange-yellow, crystalline lactone **4** (36%, mp 184–186 °C). The lactone carbonyl was revealed by the IR absorption (1812 cm^{-1}), while the NMR of the two different methylene protons betrayed the conformational rigidity of the system (δ 4.68, 1 H, d, *J* = 6 Hz, 5.28, 1 H, d, *J* = 6 Hz[7]). Other spectroscopic data were consistent with structure **4**. Hydrolysis of **3**, M = H, with hot aqueous potassium hydroxide afforded an 85% yield of *o,o′*-diaminobiphenyl, thereby confirming that the N–N bond of **2** had been cleaved, and that more deep-seated transformations of the aromatic nuclei had not taken place. Samples of **3**, M = H, stored for several years in the solid state, showed no evidence of reconversion to any **2**.



4

The heavy substitution by fused benzene rings and carbo-