Reactions of Ketenimines with Peracids, Ozone, and Methylene-Transfer Reagents[1]

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The reaction of *N*-phenyldimethylketenimine (1) with peracids gives acetone, phenyl isocyanide, and α-acyloxyamide 2. Treatment of 1 with ozone also yields the first two of these products. These observations are rationalized in terms of reactive heterocyclic intermediate 3. The reaction of 1 with dimethylsulfonium ylide gives imine 5, whereas dimethyloxosulfonium ylide converts 1 to imine 6. These products are thought to be derived from 2,3-sigmatropic rearrangements of intermediates 8 and 10, formed by nucleophilic attack of the respective ylides on 1. Reaction of amide 12 with dibromotriphenylphosphorane leads to bromoketenimine 13. Ozone converts 13 to pivaloyl bromide and *tert*-butyl isocyanide. Reaction of 13 with MCPBA gives 15, as does its reaction with *m*-chlorobenzoic acid.

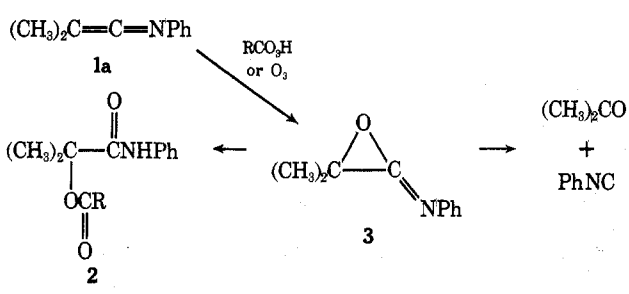
In connection with our interest in the chemistry of heterocyclic analogs of methylenecyclopropanes,[2] we have attempted to utilize the ketenimine function as a synthetic precursor of such species by serving as an acceptor of O, NR, and CR_2 moieties from appropriate donor reagents as indicated in eq 1.

$$R_2C{=}C{=}NR \xrightarrow{X} R_2C\overset{X}{\diagup\diagdown}C{=}NR \qquad (1)$$

$$X = O, NR, CR_2$$

The reaction of *N*-phenyldimethylketenimine (1) with peracids was examined first. Treatment of a cold CH_2Cl_2 solution of 1 with 1 equiv of peracetic acid gave a 65% yield of acetone, a 19% yield of α-acetoxydimethylacetanilide (**2a**), and substantial amounts of phenyl isocyanide (as determined by ir). Oxidation with *m*-chloroperbenzoic acid (MCPBA) gave acetone (33%) and the *m*-chlorobenzoxyamide **2b** (22%) in addition to phenyl isocyanide. Similar results were reported earlier by Kagen and Lillien for the peracid oxidation of *N*-*p*-tolyldiphenylketenimine.[3] The most straightforward rationalization of these facts invokes oxygen transfer to 1 leading to heterocyclic intermediate 3 (Scheme I). This reactive species can react with

Scheme I

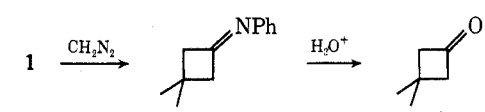


a, R = CH_3
b, R = *m*-ClC_6H_4

carboxylic acid to give amide 2. Alternatively, fragmentation of 3 generates ketone and isocyanide. Species such as 3 have not been isolated and characterized, but they have been implicated as transient intermediates in the thermal transformations of their valence isomers, α-lactams, to ketone and isocyanide products.[4-6]

Ozone transfers oxygen to certain hindered olefins resulting in epoxides,[7] and related oxygen-transfer processes have recently led to the synthesis of an α-lactone[8] and an allene oxide[9] from appropriate cumulene precursors. The isolation of the reactive α-lactone at low temperature suggested extension of this procedure to ketenimine 1. Reaction of 1 equiv of O_3 with 1 in dilute CH_2Cl_2 solution at −78° followed by warming to room temperature produced acetone (90%), phenyl isocyanide (34%), and polymeric material as determined by nmr analysis of the crude reaction mixture. Examination of the reaction mixture at −78° by low-temperature infrared techniques revealed only acetone and isocyanide, indicating that the decomposition of any reactive intermediates was complete at this temperature. These results also seem best rationalized by invoking intermediate 3 with subsequent fragmentation leading to ketone and isocyanide.

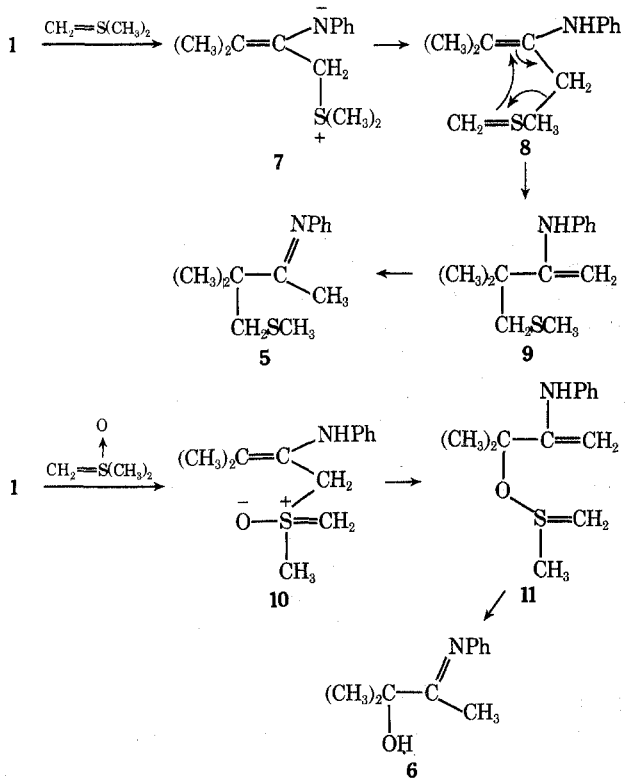
Attempts to promote the reaction indicated by eq 1 with X = NR and CR_2[10,11] were less productive. Thus, the thermal addition of ethyl diazoacetate to 1 was unsuccessful. A Simmons–Smith addition to 1 also failed, even using conditions which were successful in the preparation of aziridines from imino esters.[12] Likewise, phenyl azide gave no isolable adducts with ketenimine 1; only polymeric products were obtained. The addition of diazomethane to 1 gave a small quantity (5% yield) of 2,2-dimethylcyclobutanone (4), after hydrolysis of the crude reaction mixture. This reaction proceeded very slowly and attempts to isolate other products from the crude reaction mixture were unsuccessful. It is likely that the cyclobutanone is derived from its anil. The latter is undoubtedly formed by stepwise addition of CH_2 units from diazomethane, similar to the reaction of diazomethane with ketenes.[13]



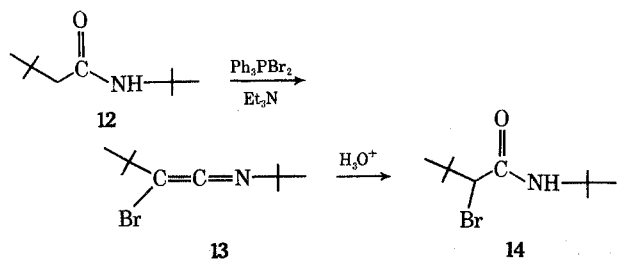
The reactions of 1 with sulfur ylides proceeded more cleanly, but gave unanticipated products. Thus, the slow addition of 1 to dimethylsulfonium methylide at −20° gave a 40% yield of 3,3-dimethyl-4-(methylthio)-2-butanone anil (5). The structure of anil 5 was assigned on the basis of its characteristic spectroscopic data and its hydrolysis to aniline and the corresponding ketone. On the other hand, treatment of 1 with dimethyloxosulfonium methylide in DMSO at room temperature led to anil 6, which was also hydrolyzed to the corresponding ketone.

Products 5 and 6 from the sulfur ylide reactions appear to be generated by related processes as outlined in Scheme II. Thus, nucleophilic attack of dimethylsulfonium ylide leads to 7 which tautomerizes (probably intramolecularly) to ylide 8. A 2,3-sigmatropic rearrangement[14] of 8 gives 9, the precursor of its tautomer, isolated product 5. A related process using adduct 10 from 1 and dimethyloxosulfonium ylide, but involving the S→O linkage in the 2,3-sigmatropic transformation, leads to 11. Tautomerization and loss of the sulfur moiety from this species gives α-hydroxy anil 6.

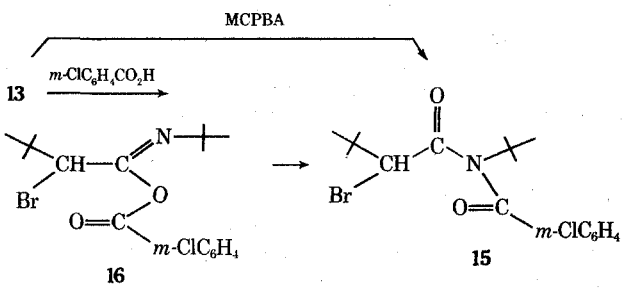
Scheme II



Several attempts were made to prepare ketenimines with sterically large substituent groups, since such substituents should be useful in stabilizing the potentially reactive small-ring heterocycles sought in this study. However, attempts to prepare the imidoyl chlorides[15] derived from *N-tert*-octyl- or *N*-adamantylisobutyramides gave only *tert*-octyl and 1-adamantyl chlorides.[16,17] A ketenimine was obtained from the reaction of amide **12** with Ph_3PBr_2 and triethylamine,[18] but bromoketenimine **13** was the product instead of the expected material. Compound **13** was characterized spectrally and by its hydrolysis to bromo amide **14**.



The reaction of **13** with O_3 gave *tert*-butyl isocyanide and pivaloyl bromide as major products. The acid bromide was characterized by a 5.55-μ carbonyl band in the ir and conversion to methyl pivalate upon addition of methyl alcohol to the reaction mixture. This reaction of **13** with O_3 is consistent with the related transformation of **1** induced by this reagent. On the other hand, MCPBA converted **13** to amide **15** in good yield. A small amount of bis-*m*-chlorobenzoyl peroxide was also obtained. Compound **15** is also formed by reaction of **13** with *m*-chlorobenzoic acid, undoubtedly by Chapman rearrangement of termediate **16**.[19] The exact nature of the MCPBA reaction is not clear at this time.



Experimental Section

General. Nmr spectra were recorded on a Varian HR-220 spectrometer using CCl_4 as solvent. Infrared spectra were obtained with a Perkin-Elmer Infracord Model 137 spectrophotometer on neat samples. Mass spectra were recorded on AEI MS-9 and Varian CH-7 spectrometers. Gas chromatography (glpc) was performed on Aerograph 1200 and A700 instruments. Yields determined by glpc were obtained by comparison of peak areas against an internal standard and are corrected for compound response. Melting points are corrected. Anhydrous $MgSO_4$ was routinely used as a drying agent. Microanalyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

***N*-Phenyldimethylketenimine (1).** The ketenimime was prepared following the literature procedure:[15] bp 53–55° (0.6 mm); ir 5.00 (broad), 6.31, and 6.76 μ; nmr δ 1.72 (s, 6) and 7.13 (m, 5).

Reaction of *N*-Phenyldimethylketenimine with Peracetic Acid. To an ice-cold, mechanically stirred slurry of 1.1 g of Na_2CO_3 and 0.5 g of **1** in 20 ml of CH_2Cl_2 was added dropwise a solution of 0.73 g of peracetic acid[2] in 5 ml of CH_2Cl_2. The mixture was stirred at 0° until a negative starch–iodide test was obtained. The inorganic salts were removed by filtration and the filtrate was washed with $NaHCO_3$ solution and water and dried. After concentration, pentane was added and the solution was cooled to yield 0.14 g (19%) of light yellow, crystalline α-acetoxydimethylacetanilide (**2a**), which was purified by sublimation: mp 105.0–105.5°; ir (CCl_4) 2.96, 5.72, 5.90, 6.25, 6.55, 6.92, and 8.20 μ; nmr ($CDCl_3$) δ 1.73 (s, 6), 2.10 (s, 3), 7.0–7.6 (m, 5), and 7.86 (m, 1); mass spectrum *m/e* (rel intensity) 221 (15), 129 (16), 101 (18), 93 (80), 69 (38), 59 (49), and 43 (100).

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.84. Found: C, 65.12; H, 7.11.

The volatile products were determined by glpc as 65% acetone and phenyl isocyanide. (Repeated attempts to obtain reproducible analyses of phenyl isocyanide by glpc were unsuccessful; however, ir revealed substantial quantities of the isocyanide.)

Reaction of *N*-Phenyldimethylketenimine with MCPBA. To an ice-cold, mechanically stirred mixture of 0.93 g of **1** in 30 ml of CH_2Cl_2 was added dropwise a solution of 1.27 g of MCPBA in 30 ml of CH_2Cl_2. The mixture was stirred at 0° until a negative starch–iodide test was obtained. The reaction mixture was washed with $NaHCO_3$ solution and water and dried. After concentration, 150 ml of pentane was added and the solution was cooled to yield 0.44 g (22%) of crystalline α-*m*-chlorobenzoxydimethylacetanilide (**2b**), which was recrystallized from ether–pentane to give white prisms: mp 107.5–108.5°; ir (CCl_4) 3.0, 5.76, 5.86, 6.24, 6.56, and 8.00 μ; nmr ($CDCl_3$) δ 1.81 (s, 6), 7.0–8.1 (m, 10); mass spectrum *m/e* (rel intensity) 317 (3), 227 (7), 225 (27), 141 (33), 139 (100), 111 (21), 59 (12), 43 (13), and 41 (20).

Anal. Calcd for $C_{17}H_{16}NO_3Cl$: C, 64.26; H, 5.08. Found: C, 64.16; H, 5.17.

The volatile products were determined by glpc as 33% acetone and phenyl isocyanide. (Ir revealed substantial quantities of phenyl isocyanide.)

Reaction of *N*-Phenyldimethylketenimine with Ozone. To a solution of 55 mg of **1** in 5 ml of CH_2Cl_2 at −78° was added 1 equiv of O_3 from a Welsbach ozone generator. Examination of the reaction mixture by ir at −78° in the 4–6.5-μ region revealed only absorptions at 4.75 (phenyl isocyanide) and 5.83 μ (acetone). Analysis of the reaction mixture by nmr using added cyclohexane as internal standard indicated 90% acetone and 34% phenyl isocyanide.

Reaction of 1 with Diazomethane. A solution of diazomethane (0.2 mol) in 100 ml of ether was prepared from *N*-methylnitrosourea and dried over KOH for 1 hr at 0°. This solution was decanted into a 250-ml erlenmeyer flask and a solution of 3 g (0.2 mol) of **1** in 10 ml of ether was added. The solution was held at 0° for 120 hr in the dark. The resulting mixture was washed with water and the ether was dried. Solvent removal gave 3.7 g of a viscous yellow liquid which showed a very complex nmr spectrum. Attempts to induce crystallization failed. The liquid was hydrolyzed by stirring with 1 *N* HCl for 8 hr. The aqueous layer was extracted with ether, and the extract was dried and concentrated to give 1.6 g of yellow liquid from which 2,2-dimethylcyclobutanone (**4**) was isolated by glpc.[13] In one experiment the yield

of 4 was found to be 5% by nmr analysis of the hydrolyzed mixture.

The aqueous layer was neutralized with Na_2CO_3 and saturated with NaCl. Extraction with ether and normal work-up gave 1.5 g of aniline.

Reaction of 1 with Trimethylsulfonium Methylide. To a predried flask cooled to −40° containing 7.75 g of trimethylsulfonium iodide and 150 ml of THF under N_2 was slowly added 25.3 ml of 1.5 *N* *n*-butyllithium in hexane. After stirring for 15 min, a solution of 5.0 g of 1 in 15 ml of THF was added dropwise and the temperature was allowed to warm to −20° over 1 hr. The cooling bath was removed and the solution was warmed to room temperature and carefully poured into 300 ml of water. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were dried and concentrated. Distillation gave 1.83 g (42%) of a yellow liquid identified as 3,3-dimethyl-4-(methylthio)-2-butanone anil (**5**): bp 90–92° (0.005 mm); ir 6.04 μ; nmr δ 1.29 (s, 6), 1.75 (s, 3), 2.14 (s, 3), 2.79 (s, 2), and 6.3–7.4 (m, 5); mass spectrum *m/e* (rel intensity) 221 (0.2), 206 (15), 174 (100), 118 (69), and 77 (55).

Anal. Calcd for $C_{13}H_{19}NS$: C, 70.54; H, 8.65; N, 6.33. Found: C, 70.53; H, 8.70; N, 6.55.

Hydrolysis of 5. An 80-mg sample of 5 in 15 ml of ether was stirred with 1 *N* HCl for 3 hr. The layers were separated and the aqueous layer was extracted with 15 ml of ether. The ether extracts were dried and the solvent was removed to give 36 mg (68%) of 3,3-dimethyl-4-(methylthio)-2-butanone purified by glpc: ir 5.85 μ; nmr δ 1.17 (s, 6), 2.07 (s, 3), 2.09 (s, 3), and 2.59 (s, 2).

Anal. Calcd for $C_7H_{14}OS$: C, 57.49; H, 9.65; S, 21.92. Found: C, 57.63; H, 9.89; S, 22.3.

The aqueous solution was neutralized with Na_2CO_3 and treated in the usual fashion to yield 26 mg (86%) of aniline.

Reaction of 1 with Dimethyloxosulfonium Methylide. A 2.0-g sample of 1 in 5 ml of anhydrous DMSO was added slowly to a stirred solution of 15 mmol of dimethyloxosulfonium methylide[20] in 50 ml of DMSO. After stirring for 15 min at 30° the reaction was diluted with H_2O and extracted with pentane. The combined extracts were washed with H_2O and dried. Removal of the solvent gave 1.23 g (50%) of yellow liquid identified as 3-hydroxy-3-methyl-2-butanone anil (**6**): ir 3.0, 6.02, 6.27 μ; nmr δ 1.32 (s, 6), 1.77 (s, 3), 4.68 (s, 1), 6.56 (d, 2, *J* = 6 Hz), 6.93 (t, 1, *J* = 6 Hz), and 7.12 (d, 2, *J* = 6 Hz); mass spectrum *m/e* (rel intensity) 177 (8) 162 (7), 118 (100), 77 (52); exact mass, 177.1144 (calcd for $C_{11}H_{15}NO$, 117.1154).

Hydrolysis of 6. A 200-mg sample of 6 was stirred with 30 ml of 10% HCl for 30 min. The solution was saturated with NaCl and extracted with ether. After drying, removal of the solvent gave 62 mg (64%) of 3-hydroxy-3-methyl-2-butanone identified by ir comparison.[21]

The aqueous layer was neutralized with Na_2CO_3 and extracted with ether. After drying, the solvent was removed to give 82 mg (79%) of aniline.

Reaction of *N*-Adamantylisobutyramide with Phosphorus Pentachloride. To an ice-cold, mechanically stirred slurry of 17.8 g of *N*-adamantylisobutyramide in 100 ml of benzene was added 16.8 of PCl_5 in small portions. The mixture was warmed to room temperature and heated to reflux for 3 hr. The solvent was removed at reduced pressure to yield 11.2 g (82%) of light yellow crystals of 1-chloroadamantane, which were purified by sublimation, mp 163–165° (lit.[22] mp 165°).

The reaction of *N*-*tert*-octylisobutyramide in a similar fashion gave 22% of 2-chloro-2,4,4-trimethylpentane identified by ir comparison.[23]

***N*-*tert*-Butylbromo-*tert*-butylketenimine (13).** To an ice-cold solution of triphenylphosphine in 300 ml of CH_2Cl_2 was slowly added 46.8 g of Br_2. The solution was allowed to warm to room temperature and 50 g of *N*-*tert*-butyl-3,3-dimethylbutyramide in 175 ml of CH_2Cl_2 was added dropwise. After the solution was stirred at 30° for 1 hr, 200 ml of triethylamine was added and the solution was heated to reflux for 12 hr. The solvent was removed at reduced pressure and the resulting solid was digested several times with pentane. The pentane extracts were dried and concentrated, and the residue was distilled to yield 17.7 g (40%) of *N*-*tert*-butylbromo-*tert*-butylketenimine (**13**) as a yellow liquid: bp 40–41° (9.5 mm); ir 4.98 μ; nmr δ 1.16 (s, 9) and 1.27 (s, 9); mass spectrum *m/e* (rel intensity) 233 (5), 231 (5), 177 (5), 175 (5), 162 (15), 160 (15), 57 (100), and 41 (70); exact mass, 233.0594 (calcd for $C_{10}H_{18}BrN$, 233.0602).

Hydrolysis of 13. A solution of 100 mg of 13 in 20 ml of ether was shaken with 15 ml of 1 *N* HCl. The ether layer was dried and the solvent was removed to yield 92 mg (85%) of *N*-*tert*-butyl-2-bromo-3,3-dimethylbutyramide (**14**).[24]

Reaction of 13 with Ozone. To a solution of 193 mg of 13 in 7 ml of $CFCl_3$ at −78° was added 1 equiv of O_3. The solution was warmed to room temperature and the crude reaction mixture was examined by nmr and ir, which indicated that approximately equal quantities of pivaloyl bromide (ir 5.55 μ;[25] nmr δ 1.28) and *tert*-butyl isocyanide (ir 4.71 μ;[26] nmr δ 1.56[27]) were formed in addition to several other unidentified products. After stirring with 0.5 g of CH_3OH for 5 min, the solution was poured into water and extracted with ether. The extracts were dried and concentrated to yield 105 mg of yellow liquid. Purification by glpc gave 33 mg (34%) of methyl pivalate.[28]

Reaction of 13 with MCPBA. To an ice-cold, mechanically stirred mixture of 1.0 g of 13 in 30 ml of CH_2Cl_2 was added dropwise a solution of 0.77 g of MCPBA in 25 ml of CH_2Cl_2. The mixture was stirred at 0° until a negative starch–iodide test was obtained. The reaction mixture was washed with $NaHCO_3$ solution and water and then dried. After concentration, 100 ml of pentane was added and the solution was cooled to yield 65 mg (9%) of bis-*m*-chlorobenzoyl peroxide identified by comparison with the published ir.[29] Additional cooling gave 1.22 g (72%) of crystalline *N*-*tert*-butyl(*N*-*m*-chlorobenzoyl)-2-bromo-3,3-dimethylbutyramide (**15**), which was recrystallized from pentane to give white prisms: mp 110.5–111.5°; ir (CCl_4) 5.87 and 5.98 μ; nmr ($CDCl_3$) δ 1.07 (s, 9), 1.48 (s, 9), 3.63 (s, 1) 7.45 (t, 1, *J* = 6 Hz), 7.59 (d, 1, *J* = 6 Hz), 7.89 (d, 1, *J* = 6 Hz), and 8.0 (s, 1).

Anal. Calcd for $C_{17}H_{23}BrClNO_2$: C, 52.53; H, 5.96; N, 3.60. Found: C, 52.79; H, 5.96; N, 3.51.

Reaction of 13 with *m*-Chlorobenzoic Acid. A mixture of 200 mg of 13 and 148 mg of *m*-chlorobenzoic acid in 30 ml of CH_2Cl_2 was stirred at room temperature for 6 hr. The solution was washed with $NaHCO_3$ and water and dried. The solvent was removed to yield 252 mg (75%) of crystalline 15 which was recrystallized from pentane. The spectral characteristics of 15 were identical regardless of the method of preparation.

Registry No. 1, 14016-34-3; **2a**, 49633-47-8; **2b**, 49633-48-9; **4**, 1192-33-2; **5**, 49633-49-0; **6**, 49633-50-3; **13**, 49633-51-4; **15**, 49633-52-5; 3,3-dimethyl-4-(methylthio)-2-butanone, 49633-53-6; *N*-*tert*-butyl-3,3-dimethylbutyramide, 49633-54-7.

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Reactions of 1,4-Quinone *N,N'*-Dibenzenesulfonylimines, 1,4-Quinones, and 1,4-Quinone *N,N'*-Dibenzoylimines with Secondary Diazo Compounds. Structures of Alleged Arocyclopropenes

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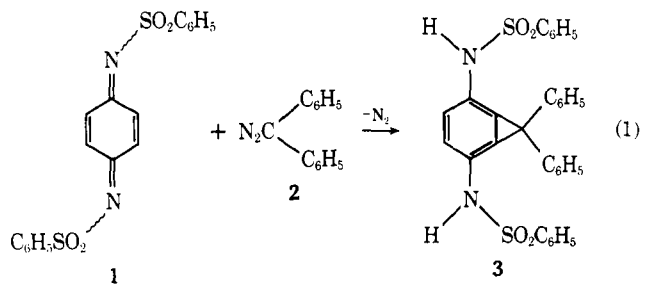
1,4-Benzoquinone *N,N'*-dibenzenesulfonylimine (1) reacts with diphenyldiazomethane (2) with loss of nitrogen to give cyclopropane **8**. Similarly reactions of 2 and of 9-diazofluorene (5) with 1,4-naphthoquinone dibenzenesulfonylimine (4) yield cyclopropanes **9** and **10**. Benzocyclopropene **3** and naphthocyclopropenes **6** and **7** are not obtained. Sulfonylimine 1 and 5 produce mono- and biscyclopropanes, **14** and **15**. Reaction of 8 with cyclopentadiene yields **11**; 8 undergoes acid-catalyzed ring opening of its cyclopropyl group and tautomerization in aqueous acetic acid and in methanol to form **12** and **13**. Rapid syn-anti isomerization about its benzenesulfonylimine nitrogens occurs when 1 is warmed; at 25° the benzenesulfonylimine groups in 4 are syn to the hydrogens at C-2 and C-3 of the 1,4-naphthoquinone moiety. In refluxing benzene, 1,4-benzoquinone (17) reacts with 5 with loss of nitrogen to give cyclopropane **16** and biscyclopropane **23**. Similarly 1,4-naphthoquinone (18) and 5 at 78° yield cyclopropane **22**. Quinones 17 and 18 also react with 1-diazoacenaphthenone (21) to form cyclopropanes **24** and **25**. Cyclopropanes 16 and 22, in the presence of hydrogen chloride, incorporate methanol (2 equiv) and undergo ring opening to yield **30** and **31**, respectively. Thermolysis of 22 results in its isomerization to quinone **32** and decomposition to **18**, bifluorenylidene (**33**), and 9,9'-bifluorenyl (**34**). The reactions of 2 and 5 with 1,4-benzoquinone *N,N'*-dibenzoylimine (**35**), and with the naphtho analog **37**, are successful only in the synthesis of cyclopropane **36** from **35** with 2. Attempts to isomerize **8**, **9**, **10**, **16**, and **22** to arocyclopropenes have been unsuccessful.

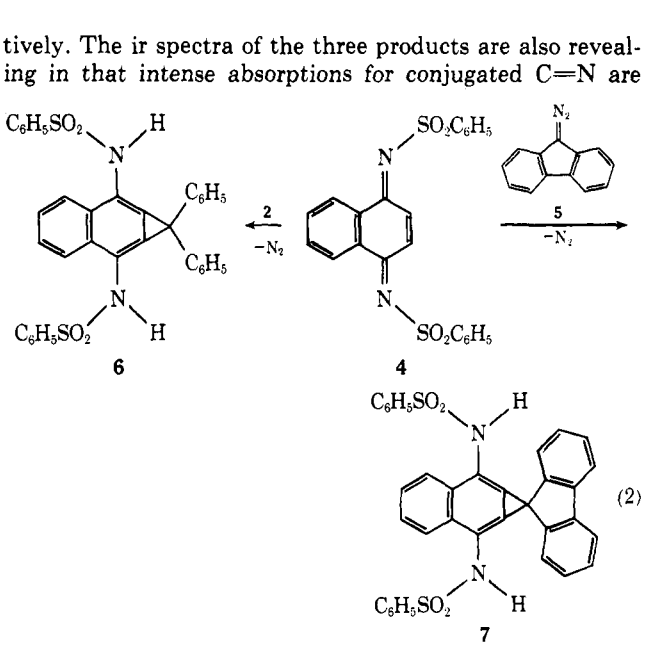
Benzocyclopropenes have recently been synthesized and characterized.[2] It had been earlier reported[3] that 1,4-benzoquinone *N,N'*-dibenzenesulfonylimine (1) and diphenyldiazomethane (2) yield benzocyclopropene **3**[4a] (eq 1) and



(1)

that 1,4-naphthoquinone *N,N'*-dibenzenesulfonylimine (4) reacts with 2 and with 9-diazofluorene (5) to give naphthocyclopropenes **6**[4b] and **7**[4c] (eq 2). We now wish to report a reinvestigation of the products in the prior study[3] of quinone *N,N'*-dibenzenesulfonylimines and diazo compounds. The present summary also includes an investigation of the products of reactions of diazo compounds with 1,4-quinones and 1,4-quinone *N,N'*-dibenzoylimines.

Reactions of 1 and of 4 with 2 and of 4 with 5 do indeed give compounds whose properties match those reported;[3,5] however, they do not show infrared absorption (KBr) for NH stretching. The nmr of the product from 1 and 2 is highly revealing (see Experimental Section) in that singlets for two cyclopropyl hydrogens at δ 4.3 ($CDCl_3$) and for two olefinic hydrogens at δ 6.2 are displayed. Similarly the compounds from 4 with 2 and with 5 show nmr singlets (see Experimental Section) for 2-cyclopropyl hydrogens at δ 4.6 ($CDCl_3$) and 4.55 (DMSO-d_6, 120°), respectively. The ir spectra of the three products are also revealing in that intense absorptions for conjugated C=N are



(2)

exhibited at 6.33–6.40 μ. Reactions of 1 with 2 and of 4 with 2 and with 5 thus yield cyclopropanes **8**, **9**, and **10**, respectively, the products of dipolar reaction of the diazo compounds with the quinone sulfonylimines and loss of nitrogen.

The structure of 8 is further confirmed by its reaction with cyclopentadiene to yield **11**[6] (48%). The chemistry of 8 and its resistance to isomerization to 3 are of some note in that 8 is converted by aqueous hydrochloric acid in refluxing acetic acid and by hydrogen chloride in methanol at