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Decomposition of Sulfonyl Azides and *tert*-Butyl Azidoformate By Transition Metal Carbonyls

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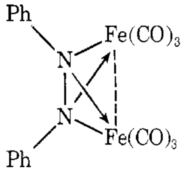
Iron and cobalt complexes $[Fe(RSO_2N)_2CO{\cdot}H_2O]_n$ and $[Co(RSO_2N)_2CO{\cdot}\frac{1}{2}H_2O]_n$ which are deficient of terminal and bridging metal carbonyls have been isolated from the reaction of methane-, benzene-, and *p*-toluenesulfonyl azide with iron pentacarbonyl, diiron nonacarbonyl, and dicobalt octacarbonyl. Hydrolysis of these with dilute hydrochloric acid leads to the corresponding *N,N'*-bis(sulfonyl)urea. Possible structures for the complexes involving coordination of a sulfonyl oxygen to the metal are presented and supporting evidence for such coordination is given. Free singlet sulfonyl nitrenes are not formed in these decompositions. The decomposition of *tert*-butyl azidoformate with iron pentacarbonyl and diiron nonacarbonyl gave impure complexes, still containing terminal and bridging carbonyls, which could be hydrolyzed to give mainly *tert*-butyl carbamate, di-*tert*-butyl iminodicarboxylate, and *N,N*-bis(*tert*-butoxycarbonyl)urea.

Despite the large volume of information available on the thermal and photochemical decomposition of organic azides,[1b,2-4] studies pertaining to the decomposition of organic azides by transition metal carbonyls have only recently appeared. Phenyl azide, which thermolyzes only above 120°, decomposes at room temperature in the presence of diiron nonacarbonyl to give a low yield of the nitrene product, azobenzene. The main product is the complex **1**, which decomposes spontaneously in solution to the urea complex **2**.[5]



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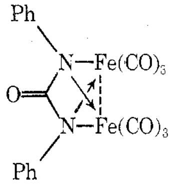

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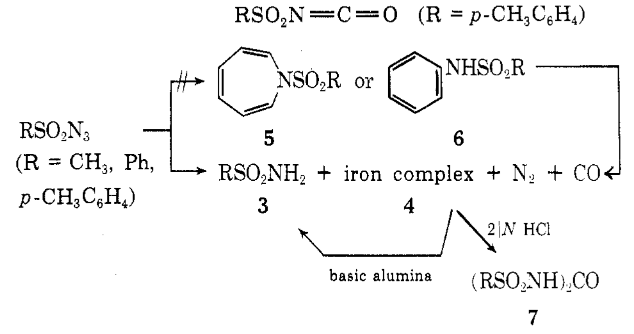
A similar complex was obtained from 2-azidobiphenyl, together with the urea and nitrene-derived products.[6] As part of our interest in generating sulfonyl nitrenes under mild conditions to study their behavior with aromatic compounds under kinetic control conditions,[3,7] we now report the results for the decomposition of sulfonyl azides and *tert*-butyl azidoformate by transition metal carbonyls.

Results and Discussion

The decomposition of excess methane-, benzene-, and *p*-toluenesulfonyl azide and *p*-toluenesulfonyl isocyanate with diiron nonacarbonyl at room temperature (heterogeneous) or iron pentacarbonyl at 60–65° (homogeneous) in benzene gave a low yield of the corresponding sulfonamide (**3**) and a high-melting amorphous iron complex (**4**) devoid of both terminal and bridging iron carbonyls. *N*-Sulfonylazepines (**5**), the expected aromatic addition products if discrete nitrenes were formed, were not detected nor were the corresponding sulfonanilides (**6**). Thus, no free singlet sulfonylnitrenes are generated in these catalyzed decompositions.



The nmr spectra of these complexes could not be obtained owing to their paramagnetic nature (*vide infra*) and their insolubility in solvents that did not effect their decomposition, and the mass spectra could not be determined owing to their insufficient volatility. Elemental analyses (reproducible from run to run) satisfied an empirical formula corresponding to $Fe(RSO_2N)_2CO{\cdot}H_2O$. Hydrolysis of these complexes with dilute hydrochloric acid gave the corresponding *N,N'*-bis(sulfonyl)urea (**7**) in high yield (70–80%), while chromatography on basic alumina gave the corresponding sulfonamide (80%). The crystal structure of the complexes obtained in this study could not be determined because of our inability to obtain them crystalline. They gave blue solutions in dimethyl sulfoxide from which the complex could not be recovered.

The stoichiometry of the reaction was found to be azide: $Fe_2(CO)_9$ = 4. For the decomposition of methanesulfonyl azide with diiron nonacarbonyl, the molar ratio of nitrogen to carbon monoxide evolved was 0.68. The calculated molar ratio, in which seven molecules of carbon monoxide are lost from diiron nonacarbonyl and four molecules of nitrogen are evolved from methanesulfonyl azide, is 0.57. The observed ratio is expected to be higher since a low yield of methanesulfonamide was also formed.

The decomposition of methanesulfonyl azide with dicobalt octacarbonyl in benzene at room temperature gave a

Table I
^{57}Fe Mössbauer Data of Some Iron(III) Complexes

Compd	Temp, °K	Isomer shift, δ	Quadrupole splitting, ΔE
4, R = CH_3	78	0.459 ± 0.023	0.863 ± 0.008
$HFe(H_2O)EDTA$[a]	78	0.457	0.422
$Fe(terpy)_3Cl_3$[b]	77	0.46	0.54
$[Fe(phen)_2Cl_2]ClO_4$[c]	80	0.39	0.05
$Sr_3[Fe(C_2O_4)_3]_2 \cdot 2H_2O$[d]	78	0.45	0.00

[a] Reference 12. [b] Reference 13. [c] Reference 14. [d] Reference 15.

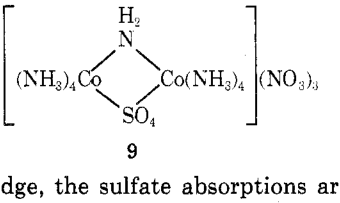
cobalt complex (8), also devoid of terminal and bridging metal carbonyls, as the major product and a low yield of methanesulfonamide. Elemental analysis (also reproducible) satisfied an empirical formula corresponding to $Co(CH_3SO_2N)_2CO \cdot \frac{1}{2}H_2O$ for the complex.

It is suggested that coordination of one of the sulfonyl oxygen atoms to the metal is the stabilizing factor which accounts for the absence of both bridging and terminal metal carbonyls in these complexes. Possible structures considered initially for the iron complexes were iron(II) dimeric and polymeric structures. The observed magnetic moment for the iron complex (4, R = CH_3) was found to be 5.93 BM, however, and this corresponds to an iron(III) high-spin complex. Magnetic moments for iron(III) high-spin complexes vary from 5.7 to 6.0 BM.[8] A metal–metal bond is unlikely in these complexes, since the observed magnetic moment approaches zero for binuclear complexes with metal–metal bonds.[9] It is not surprising that these complexes are high spin if the sulfonyl oxygen is coordinating to the metal because ligands having donor atoms of high electronegativity, especially oxygen and nitrogen, form high-spin complexes.[10,11]

The Mössbauer data for the iron complex (4, R = CH_3) and some related iron(III) complexes are listed in Table I. The observed isomer shift (δ 0.489) is in excellent agreement with that of other iron(III) complexes. Since the quadrupole splitting (ΔE) is high, the iron is clearly in a very unsymmetrical environment.

The infrared spectra of these iron and cobalt complexes exhibited a number of intense absorptions. The strong absorptions at *ca.* 3500–3200 and perhaps that at 1625 cm^{-1} could be due to either "lattice" water or coordinated water. If "lattice" water, it should have been lost on vacuum drying at 100° but was not. The intense absorption at 1625 cm^{-1} is more probably due to a >C=N– moiety and/or less likely to a perturbed organic carbonyl function.

The two sets of absorptions at 1340, 1360, 1255 and 1150, 1115, 1080 cm^{-1} for the cobalt complex are assigned respectively to the asymmetric and symmetric stretching modes of two different sulfonyl groups. If a sulfonyl oxygen is coordinated to cobalt or iron through oxygen, the two oxygen atoms of the sulfonyl groups are no longer equivalent and the degenerate vibrations are expected to be split. For the binuclear complex **9**, in which the sulfate group is a bidendate bridge, the sulfate absorptions are observed as two sets of bands at 1170, 1105, 1060, and 641, 571 cm^{-1}.[16] In comparison, the free sulfate ion exhibits only strong absorption at 1104 and 613 cm^{-1}. Similarly, the iron complexes exhibited two sets of absorptions at 1345, 1310, 1270 and 1165, 1130, and 1070 cm^{-1}.



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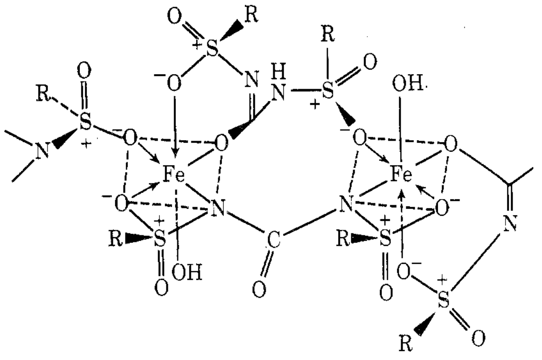
Possible structures for these complexes are suggested in **10 and 11,** which fit all the known properties of these molecules. It is appreciated, of course, that numerous variants on stereochemistry and positional isomerism are possible, and these structures are presented only as a basis for future discussion. The polymeric nature of these complexes is suggested by their amorphous character and their insolubility. Of the two possibilities we would tend to favor 11 in view of the absence of a normal urea $\nu_{C=O}$ in the infrared spectra.



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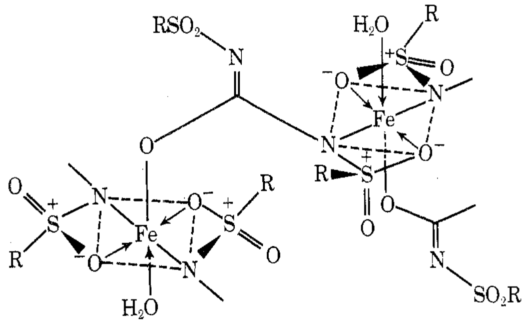


11

No reaction occurred between methanesulfonamide or *N,N'*-bis(methanesulfonyl)urea and diiron nonacarbonyl in benzene at room temperature or between methanesulfonyl azide and diiron nonacarbonyl in aqueous ethanol.

Since aryl azides form iron complexes still retaining terminal and bridging carbonyls,[5,6] we tested the suggestion of sulfonyl oxygen coordination with the metal by studying the decomposition of *o*-azidophenyl methyl sulfone (12) with metal carbonyls. The azide 12 was synthesized from *o*-aminophenyl methyl sulfone.[17]

The heterogeneous decomposition of an excess of 12 with diiron nonacarbonyl gave an impure iron complex exhibiting weak residual metal carbonyls. Attempted purification *via* Soxhlet extraction with benzene resulted in its decomposition to *o*-methanesulfonylaniline and *N,N'*-bis(*o*-methanesulfonylphenyl)urea. The decomposition of an excess of 12 with dicobalt octacarbonyl resulted in the formation of a cobalt complex completely devoid of terminal metal carbonyls, but whose infrared spectrum exhibited strong absorptions at 1605–1598, 1340, 1305, 1265, and 1145, 1125, 1060 cm^{-1}. Elemental analysis corresponded to the empirical formula $Co_2(C_7H_7NO_2S)_2CO \cdot H_2O$. The stoichiometry of the reaction, determined from the relative amount of unconsumed azide, appeared to be azide: $Co_2(CO)_8$ = 2, in contrast to the sulfonyl azide reaction, when the stoichiometric ratio was 4. It is difficult to assign a plausible structure to fit the formula $Co_2(C_7H_7NO_2S)_2CO \cdot H_2O$ without invoking a metal–metal bond. It is clear from the infrared spectrum, however, that a car-

Experimental Section

General. All decompositions of azides with transition metal carbonyl were carried out with oven-dried (120°) glassware in a dry box under an atmosphere of dry nitrogen. Infrared spectra were determined on a Perkin-Elmer 257 grating infrared spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian HA-100 or Perkin Elmer R-20B spectrometer using tetramethylsilane as the internal standard. Mass spectra were recorded on a CEC 21-104 spectrometer. Molecular sieve pellets (Fisher Scientific Co., type 4A, M-237), which were employed for the separation of nitrogen and carbon monoxide, were ground up to 35-48 mesh and activated at 240° for 20 hr in a gas chromatograph (Varian Aerograph A-90-P) using a helium flow rate of 30 ml/min.

o-Azidophenyl methyl sulfone. A mixture of *o*-aminophenyl methyl sulfone (1.8 g, 10.5 mole) (prepared by the method of Cava and Blake[17]) in distilled water (20 ml) and concentrated hydrochloric acid (2.7 ml) was heated on a steam bath until the solution became homogeneous, cooled to 0° and sodium nitrite (0.80 g, 12 mmole) in water (15 ml) added dropwise such that the temperature did not exceed 5°. Sodium azide (0.80 g, 12 mmole) in water (10 ml) was then added dropwise, while the temperature was maintained between 0-5°. The solution was stirred for a further 30 min, poured into ice-water, and the product recrystallized from aqueous ethanol (1:1 v/v) to give *o-azidophenyl methyl sulfone* (1.8 g, 80%) mp 93-94°; ir (KBr) 2140 (N_3), 1305 (SO_2), and 1130 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 8.07 (m, 1H), 7.90-7.17 (m, 3H), 3.26 (s, 3H); mass spec. (70 eV) 197 ($M^{+\cdot}$, 10).

Anal. Calcd for $C_7H_7N_3O_2S$: C, 42.68; H, 3.56. Found: C, 42.76; H, 3.67.

Decompositions of methanesulfonyl azide.

(a) With di-iron nonacarbonyl- Di-iron nonacarbonyl (0.576 g, 1.59 mmole) was added in one portion to a stirred solution of methanesulfonyl azide (1.004 g, 8.31 mmole) in dry benzene (20 ml) at room temperature. The resulting light yellow heterogeneous reaction mixture was stirred at room temperature for a further 8 hr, after which time gas evolution has ceased and it had turned dark brown in color. It was filtered under nitrogen and washed with dry benzene (30 ml) to give a tan amorphous *iron complex* (0.81 g), mp > 300°. Careful sublimation of the material under vacuum (0.02 torr) at an oil bath temperature of 115-120° gave methanesulfonamide (0.088 g, 15%) whose spectrum was identical to that of authentic material. The

unsublimed material was washed and analyzed; ir (KBr) 3520-3260, 2930, 1625, 1430, 1400, 1345, 1310, 1270, 1250, 1165, 1130, 1075-10, 970, 845, and 785-770 cm^{-1}.

Anal. Calcd for $C_3H_6FeN_2O_5S_2 \cdot H_2O$: C, 12.51; H, 2.78; N, 9.72; S, 22.21; Fe, 19.37. Found: C, 12.47; H, 2.94; N, 9.79; S, 21.92; Fe, 19.23.

The original benzene filtrate was chromatographed on silica gel (100 g). Elution with ether (150 ml) gave a colorless oil (0.22 g, 1.9 mmole) whose ir spectrum was identical with that of methanesulfonyl azide. No other compounds were eluted.

The unsublimed material (0.75 g) was added to 2*N* HCl (12 ml) and stirred for ca. 15 min at room temperature, whereupon *N*,*N'*-bis(methanesulfonyl)urea (0.41 g, 72%), mp 199-200° (lit[20] 200-204°) separated and was washed with water; ir (KBr) 3250 and 3220 (NH), 1715 (CO), 1315 (SO_2), and 1125 cm^{-1} (SO_2); nmr (DMSO-d_6): δ 9.45 (NH, 2H, D_2O exchange), 3.30 (s, 6H).

Repetition of this experiment and column chromatography on basic alumina (120 g) of the iron complex from methanesulfonyl azide (5.8 mmole) and di-iron nonacarbonyl (3.35 mmole) gave methanesulfonamide (0.48 g, 80%) on elution with ether-methanol (1:1 v/v, 150 ml).

(b) With iron pentacarbonyl. Iron pentacarbonyl (0.400 g, 2.04 mmole) was added to a stirred solution of methanesulfonyl azide (0.803 g, 6.63 mmole) in dry benzene (25 ml). The resulting homogeneous yellow solution was heated at *ca.* 60-65° with vigorous stirring for 6 hr, after which time the reaction mixture was dark brown. It was cooled to room temperature, filtered under nitrogen, and the solids washed with benzene (30 ml) to give the crude tan amorphous iron complex (0.55 g), mp > 300°. Careful sublimation of this material gave methanesulfonamide (0.03 g, 7%). The unsublimed material had an ir spectrum identical to that of the iron complex prepared as under (a).

Anal. Calcd for $C_3H_6FeN_2O_5S_2 \cdot H_2O$: C, 12.51; H, 2.78. Found: C, 12.71; H, 2.73.

The original benzene filtrate was chromatographed on silica gel (100 g). Elution with ether (175 ml) gave a colorless oil (0.30 g, 2.5 mmole) whose ir spectrum was identical to that of starting methanesulfonyl azide. No other compounds were eluted.

The unsublimed material (0.51 g) was added to stirred 2 *N* HCl (14 ml). After stirring for ca. 15 min, *N*,*N'*-bis(methanesulfonyl)urea (0.30 g, 99%) was obtained.

(c) With dicobalt octacarbonyl. Dicobalt octacarbonyl (1.04 g, 3.03 mmole) was added to a stirred solution of methanesulfonyl azide (2.955 g, 24.4 mmole) in dry benzene (50 ml). The resulting wine-colored homogeneous reaction mixture was stirred at room temperature for 7 hr, filtered under nitrogen, and the solid washed with benzene (25 ml) to give a light blue solid (1.64 g, 96%), mp > 300°. Sublimation of part of this material (0.14 g) as in (a) gave methanesulfonamide (*ca.* 4-5 mg). The material which did not sublime was analyzed; ir (KBr) 3540-3180, 2920, 1625, 1560-1535, 1405, 1340, 1310, 1255, 1195, 1150, 1115, 1080, 960, 935, 845, and 765 cm^{-1}.

Anal. Calcd for $C_3H_6CoN_2O_5S_2 \cdot 1/2H_2O$: C, 12.87; H, 2.50. Found: C, 12.70; H, 2.65.

The benzene filtrate was evaporated under vacuum to give a colorless oil (1.34 g, 11.1 mmole) whose ir spectrum was identical to that of starting methanesulfonyl azide.

The unsublimed material (1.50 g) was added to 2*N* HCl (14 ml). After stirring for *ca.* 35 min, *N*,*N'*-bis(methanesulfonyl)urea (0.89 g, 77%) was obtained.

Decompositions of benzenesulfonyl azide

(a) With di-iron nonacarbonyl. By a procedure similar to that described above, di-iron nonacarbonyl (0.713 g, 1.96 mmole) and benzenesulfonyl azide (2.11 g, 11.6 mmole) gave a tan amorphous iron complex (1.41 g, 88%), mp > 300°; ir (KBr) 3500-3300, 3060, 1590, 1570, 1480, 1450, 1405, 1350-1260, 1165, 1130, 1070, 1025, 1000, 920, 840-830, 755, 725, and 680 cm^{-1}.

Anal. Calcd for $C_{13}H_{10}FeN_2O_5S_2 \cdot H_2O$: C, 37.82; H, 2.92; N, 6.79. Found: C, 38.01; H, 3.09; N, 6.70.

Hydrolysis of this material (1.30 g) as before with 2*N* HCl gave *N*,*N'*-bis(benzenesulfonyl)urea monohydrate (0.84 g, 78%). The latter was dehydrated in a dry pistol at 100°/0.02 mm to *N*,*N'*-bis(benzenesulfonyl)urea, mp 155-157° (lit.[20] 155-156°).

(b) With iron pentacarbonyl. By a procedure similar to that described above, iron pentacarbonyl (0.395 g, 2.01 mmole) and benzenesulfonyl azide (1.21 g, 6.51 mmole) gave a tan amorphous iron complex (0.81 g, 98%), mp > 300°, whose ir spectrum was identical to that of the iron complex obtained in (a).

Hydrolysis of part of this material as before gave *N*,*N'*-bis(benzenesulfonyl)urea monohydrate (80%).

Decomposition of p-Toluenesulfonyl Azide With Excess Iron Pentacarbonyl.- By a procedure similar to that described above, iron pentacarbonyl (0.525 g, 2.68 mmole) and *p*-toluenesulfonyl azide (0.976 g, 4.96 mmole) gave a tan amorphous iron complex. Careful sublimation of this material gave *p*-toluenesulfonamide (0.040 g, 5%). Hydrolysis of the unsublimed material as before with 2*N* HCl gave *N*,*N'*-bis(*p*-toluenesulfonyl)urea monohydrate. Recrystallization from aqueous ethanol (1:1 v/v) and dehydration in a drying pistol at 100°/0.02 mm gave *N*,*N'*-bis(*p*-toluenesulfonyl)urea, mp 155-156° (lit[20] 155-159.5°).

Decomposition of p-Toluenesulfonyl Isocyanate with Di-iron Nonacarbonyl.- Di-iron nonacarbonyl (0.23 g, 0.062 mmole) was added in one portion to a stirred solution of *p*-toluenesulfonyl isocyanate (1.35 g, 6.87 mmole) in dry benzene (20 ml). This was stirred at room temperature for 12 hr, filtered under nitrogen, and washed with benzene to give a tan colored solid (*ca.* 0.29 g), mp > 300°. The filtrate was concentrated under vacuum to give a colorless oil. Upon the addition of water to this material, a white solid precipitated (0.76 g, 4.4 mmole) which had an ir spectrum identical to that of authentic *p*-toluenesulfonamide.

Hydrolysis of the iron complex with 2*N* HCl as before gave *N*,*N'*-bis(*p*-toluenesulfonyl)urea monohydrate (0.079 g).

Decomposition of O-Azidophenyl Methyl Sulfone

(a) With di-iron nonacarbonyl. Di-iron nonacarbonyl (0.71 g, 1.9 mmole) was added in one portion to a stirred solution of *o*-azidophenyl methyl sulfone (0.94 g, 4.8 mmole) in dry benzene (50 ml). As the reaction mixture was stirred at room temperature it became wine-colored (*ca.* 2 hr), and then dark brown (26 hr). The reaction mixture was filtered and washed with benzene (50 ml) to give a light brown impure complex (0.21 g), decomp. 155°. This material was placed in a Soxhlet extractor and extracted continuously for 54 hr with benzene (30 ml). A white crystalline solid separated and was identified as *N,N'-bis(o-methanesulfonylphenyl)urea* (0.06 g), mp 256-259°; ir (KBr) 3280 (NH), 1675 (CO), 1310 (SO_2), and 1160 cm^{-1} (SO_2); nmr (DMSO-d_6) δ 9.68 (NH, 2H, D_2O exchange), 8.40 (d, H_3 and H_6, $J_{3,4} = J_{5,6} = 8.5$ Hz), 8.21 (t, H_5, $J_{4,5} = 6.5$ Hz), 7.88 (t, H_4), 3.82 (s, 3H).

Anal. Calcd for $C_{15}H_{16}N_2O_5S_2$: C, 48.90; H, 4.38. Found: C, 49.06; H, 4.51.

The benzene extract from the Soxhlet extraction was chromatographed on silica gel (100 g). Benzene-ether (1:1 v/v, 150 ml) and ether (75 ml) eluted *o*-methanesulfonylaniline (0.03 g). No other compounds were eluted.

The original benzene filtrate was chromatographed on silica gel (150 g). Benzene-ether (1:1 v/v, 150 ml) gave *o*-azidophenyl methyl sulfone (0.17 g, 0.86 mmole). Benzene-ether (1:4 v/v, 100 ml) and ether (150 ml) eluted *o*-methanesulfonylaniline (0.18 g, 27%). No other compounds were detected.

(b) With dicobalt octacarbonyl. By a procedure similar to that described above, dicobalt octacarbonyl (0.497 g, 1.16 mmole) and *o*-azidophenyl methyl

sulfone (1.67 g, 8.48 mmole) gave a grey cobalt complex (0.43 g), decomp. 160-165°.

Anal. Calcd. for $C_{15}H_{14}Co_2N_2O_5S_2 \cdot H_2O$: C, 35.85; H, 3.21; N, 5.59. Found: C, 36.19; H, 3.40; N, 5.41.

The benzene filtrate was chromatographed on silica gel (100 g). Benzene-ether (1:1 v/v, 250 ml) eluted starting *o*-azidophenyl methyl sulfone (1.19 g, 6.04 mmole). Benzene-ether (1:4 v/v, 100 ml) and ether (75 ml) eluted *o*-methanesulfonylaniline (0.12 g, 8.5%). No other compounds were detected.

Decomposition of tert-Butyl Azidoformate

(a) Di-iron nonacarbonyl and excess azidoformate. Di-iron nonacarbonyl (0.486 g, 1.35 mmole) was added in one portion to a stirred solution of freshly distilled *tert*-butyl azidoformate (bp 96-97°/42 mm; 1.19 g, 8.34 mmole) in dry benzene (25 ml). The resulting heterogeneous reaction mixture was stirred at room temperature for a further 10 hr, filtered under nitrogen, and washed with dry benzene (20 ml) to give a rust-colored solid (0.65 g), decomp. 270°; ir (KBr) 2205 (N=C=O), 2055 and 1980 cm^{-1} (terminal CO). Sublimation of this material at 120°/0.02 mm caused its decomposition; ir (KBr) 2205 (N=C=O) cm^{-1}.

Evaporation of the filtrate under vacuum gave a light yellow oil whose ir spectrum was identical to that of starting *tert*-butyl azidoformate.

(b) With excess di-iron nonacarbonyl. Di-iron nonacarbonyl (1.572 g, 4.31 mmole) was added in one portion to a solution of freshly distilled *tert*-butyl azidoformate (1.557 g, 10.83 mmole) in dry benzene (20 ml). The resulting heterogeneous reaction mixture was stirred at room temperature overnight, filtered under nitrogen, and washed with dry benzene to give a rust-colored solid. The filtrate was evaporated under vacuum but no organic material remained. The solid was chromatographed on basic alumina (175 g). Benzene-ether (4:1 v/v, 150 ml) eluted di-*tert*-butyl iminodicarboxylate (0.133 g, 11%), mp 118-119° (from hexane) (lit[21] 119-121°); ir (KBr) 3260 (NH), 1795, 1775, and 1760 cm^{-1} (urethane CO); nmr ($CDCl_3$), δ 6.80 (s, NH, 1H, D_2O exchange), 1.47 (s, 18H).

Anal. Calcd for $C_{10}H_{19}NO_4$: C, 35.35; H, 8.76. Found: C, 35.41; H, 8.98.

Benzene-ether (1:1 v/v, 150 ml) eluted *tert*-butylcarbamate (0.108 g, 8.5%), mp 104-106° (hexane) (lit[22] 108-109.5°); ir (KBr) 3440, 3320, 3250, 3200 and 1675 cm^{-1} (urethane CO); nmr ($CDCl_3$) δ 4.65 (s, NH_2, 2H, D_2O exchange), 1.42 (s, 9H). Ether (250 ml) and ether-methanol (10:1 v/v, 150 ml) eluted *N,N'-bis(tert-butoxycarbonyl)urea* (0.56 g, 40%), mp 122-124° (hexane); ir (KBr) 3220 (NH), 1790 (urethane CO), and 1725 cm^{-1} (urea CO); nmr ($CDCl_3$) δ 8.82 (NH, 2H, D_2O exchange), 1.47 (s, 18H); mass spec. (70 eV): no parent ion at *m/e* 260.

Anal. Calcd for $C_{11}H_{20}N_2O_5$: C, 50.77; H, 7.69. Found: C, 51.06; H, 7.81.

No other compounds were eluted.

(c) With excess iron pentacarbonyl. A solution of freshly distilled *tert*-butyl azidoformate (2.55 g, 17.8 mmole) and iron pentacarbonyl (3.74 g, 19.0 mmole) in dry benzene (70 ml) was boiled under reflux for 12 hr with vigorous stirring. The reaction mixture was cooled to room temperature, filtered under nitrogen, and washed with benzene (50 ml) to give a rust-colored solid (ca. 2.46 g); ir (KBr) 2205 (N=C=O) cm^{-1}. This was added to 2*N* HCl (20 ml) with vigorous stirring at room temperature. The resulting homogeneous yellow solution was stirred for a further 10 min, and then extracted with ether (2 x 250 ml). The combined ether extracts were dried ($MgSO_4$), and evaporated under vacuum to give a light yellow oil which was chromatographed on basic alumina (150 g). Benzene-ether (3:1, v/v, 175 ml) gave a white solid (0.48 g, 25%), mp 115-116°, whose ir spectrum was identical to that of di-*tert*-butyl iminodicarboxylate. Benzene-ether (1:1 v/v, 150 ml) eluted a white solid (0.106 g, 5.1%), mp 104-105°, whose ir spectrum was identical to that of *tert*-butylcarbamate. Ether (150 ml) eluted a white solid (0.07 g, 3%) whose ir spectrum was identical to that of *N*,*N'*-bis(*tert*-butoxycarbonyl)urea. Ether-methanol (10:1 v/v, 100 ml) eluted an oily solid (0.075 g, 5%) which crystallized with difficulty from benzene-hexane (1:2 v/v) to give white plates of a compound tentatively identified as *N-tert-butoxycarbonyl urea*, mp 185-187°; ir (KBr) 3385, 3360, 3230, 1715 (urethane CO), 1690 cm^{-1} (urea CO).

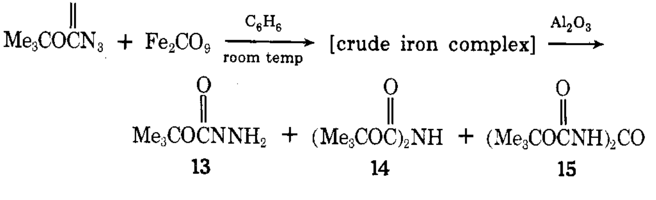
Anal. Calcd for $C_6H_{12}N_2O_3$: C, 45.00; H, 7.55; N, 17.48. Found: C, 45.06; H, 7.66; N, 17.25.

The original benzene filtrate was evaporated under vacuum to give a light yellow oil which was chromatographed on basic alumina (100 g). Benzene-ether (4:1 v/v, 150 ml) eluted di-*tert*-butyl iminodicarboxylate (0.107 g, 5.5%). Elution with ether (100 ml) gave *tert*-butylcarbamate (0.055 g, 2.6%), and further elution with ether gave *N*,*N'*-bis(*tert*-butoxycarbonyl)urea (0.054 g, 2.4%). Ether-methanol (10:1 v/v, 125 ml) eluted an oily solid (0.040 g) which crystallized with difficulty from hexane. Sublimation of this material at 65°/0.05 mm gave 5,5-dimethyloxazolidone, mp 77-79° (lit[23] 80°); ir (KBr) 3250 (NH), 1720 cm^{-1} (C=O); mass spec. (70 eV) *m/e* 115 ($M^{+\cdot}$, 10). No other compounds were eluted.

Gas Analysis of the Decomposition of Methanesulfonyl Azide with Di-iron Nonacarbonyl. - The apparatus consisted of a mercury bubble trap, a three-way glass stopcock, rubber tubing (2 in), a glass tube, a rubber septum and a round-bottomed flask (50 ml). A solution of methanesulfonyl azide to be decomposed in degassed benzene (20 ml) was frozen in a dry ice-acetone bath and then the appropriate amount of di-iron nonacarbonyl was added. The system was evacuated to 0.02 mm, and the frozen reaction mixture was then allowed to warm to room temperature. It was then stirred at room temperature and the evolved gases were analyzed by g.l.c. using a 5 ft x 1/4 in 4A molecular sieve (35-48 mesh) column at an oven temperature of 72° and a helium flow rate of 30 ml/min. The ratio of N_2/CO was found to be 0.68.

bonyl group, if present in this complex, must be seriously perturbed by the metal. The structure of this complex remains to be determined as well.

Since the >S=O ↔ >$^+$S–O$^-$ bond is more polar than a carbonyl function, it was expected that the latter might not function as efficiently as the former in displacing metal-bonded carbonyl groups. This, indeed, appears to be the case. The decomposition of *tert*-butyl azidoformate by di-iron nonacarbonyl gave an iron complex which did exhibit terminal metal carbonyl absorptions at 2055 and 1980 cm^{-1}. This material was thermally unstable when heated to 120° under high vacuum. Chromatography of the complex on basic alumina gave *tert*-butyl carbamate (**13**), di-*tert*-butyl iminodicarboxylate (**14**), and *N*,*N'*-bis(*tert*-butoxycarbony l)urea (**15**) in 11, 9, and 40% yields, respectively.



$$Me_3CO\overset{O}{\overset{\|}{C}}N_3 + Fe_2CO_9 \xrightarrow[\text{room temp}]{C_6H_6} [\text{crude iron complex}] \xrightarrow{Al_2O_3} \underset{\textbf{13}}{Me_3CO\overset{O}{\overset{\|}{C}}NNH_2} + \underset{\textbf{14}}{(Me_3CO\overset{O}{\overset{\|}{C}})_2NH} + \underset{\textbf{15}}{(Me_3CO\overset{O}{\overset{\|}{C}}NH)_2CO}$$

The decomposition of *tert*-butyl azidoformate with iron pentacarbonyl at *ca.* 65° in benzene gave an impure iron-containing material devoid of both bridging and terminal metal carbonyls. Dilute acid hydrolysis followed by chromatography on basic alumina gave **13, 14, 15,** and *N-tert*-butoxycarbonylurea in 5, 25, 3, and 5% yields, respectively. If the filtrate was chromatographed on basic alumina without prior acid hydrolysis, the following products were obtained: **13** (2.6%), **14** (5.5%), **15** (2.4%), and 5,5-dimethyloxazolidone (2%).

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Registry No.—Diiron nonacarbonyl, 15321-51-4; iron pentacarbonyl, 13463-40-6; dicobalt octacarbonyl, 10210-68-1; methanesulfonyl azide, 1516-70-7; methanesulfonyl azide iron complex, 51779-40-9; methanesulfonyl azide cobalt complex, 51898-91-0; benzenesulfonyl azide, 938-10-3; benzenesulfonyl azide iron complex, 51779-42-1; *p*-toluenesulfonyl azide, 941-55-9; *p*-toluenesulfonyl isocyanate, 4083-64-1; *o*-aminophenyl methyl sulfone, 2987-49-7; *o*-azidophenyl methyl sulfone, 51779-31-8; *N,N'*-bis(*o*-methanesulfonylphenyl)urea, 51806-01-0; *tert*-butyl azidoformate, 1070-19-5; di-*tert*-butyl iminodicarboxylate, 51779-32-9; *tert*-butyl carbamate, 4248-19-5; *N,N'*-bis(*tert*-butoxycarbonyl)urea, 51779-33-0; *N-tert*-butoxycarbonylurea, 31598-86-4.

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Synthesis of Dihalomethyl and α-Haloalkyl Sulfones by the Halogenative Decarboxylation of α-Aryl- and α-Alkylsulfonylalkanecarboxylic Acids

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The synthesis by brominative decarboxylation of meta- and para-substituted bromomethyl and α-bromobenzyl benzyl sulfones is described. Included are nine $\mathrm{ArCH_2SO_2CH_2Br}$, four $\mathrm{PhCHBrSO_2CH_2Ar}$, and five $\mathrm{ArCHBrSO_2CH_2Ph}$ types. The nine bromomethyl benzyl sulfones were prepared from the dibromomethyl benzyl sulfones by reduction. Halogenative decarboxylations of α-cyclopropylsulfonyl-α-phenylacetic acid and phenylsulfonylacetic acid in refluxing carbon tetrachloride using *N*-halosuccinimides are described. Phenylthioacetic acid with *N*-chlorosuccinimide in $\mathrm{CCl_4}$ gave mainly phenylthio-α-chloroacetic acid at 25° and mainly phenyl chloromethyl sulfide at 77°. Mechanisms for these reactions are discussed.

The halogenative decarboxylation of α-carboxyalkyl sulfones has been used as a preparative method for haloalkyl and dihalomethyl sulfones since before the turn of the century.[1] Sulfone carboxylic acids of the type $\mathrm{ArSO_2CH_2CO_2H}$ give aryl dihalomethyl sulfones, $\mathrm{ArSO_2CHX_2}$ (X = Cl, Br, or I), whereas $\mathrm{ArSO_2CHRCO_2H}$ types give $\mathrm{ArSO_2CHXR}$.[1] Since the corresponding sulfides, $\mathrm{ArSCH_2CO_2H}$, $\mathrm{ArSCHRCO_2H}$, $\mathrm{RSCH_2CO_2H}$, and $\mathrm{RSCHR'CO_2H}$, are readily available from reactions of ArSNa or RSNa with $\mathrm{ClCH_2CO_2H}$ or $\mathrm{ClCHRCO_2H}$ or from reactions of RX with $\mathrm{HSCH_2CO_2Na}$ or $\mathrm{HSCHRCO_2Na}$, these provide convenient starting materials. The corresponding sulfone carboxylic acids are obtained in high yield by oxidation. The latter react readily with halogens in aqueous acetic acid solution to give good yields, *e.g.*, of dihalomethyl aryl or alkyl sulfones.[1,2] It is often convenient to carry out the preparation of the sulfide, oxidation, bromination, and decarboxylation all in a single reaction vessel, as in the preparation of bis-α-bromobenzyl sulfone.[3] In the present study this method has been extended to the preparation of a number of other α-halo sulfones, *e.g.*

$$\mathrm{ArCH_2X} \xrightarrow[\text{3. NaBr}]{\substack{\text{1. HSCH}_2\text{CO}_2\text{Na} \\ \text{2. excess 30\% H}_2\text{O}_2}} \mathrm{ArCH_2SO_2CHBr_2}$$

Use of excess hydrogen peroxide in step 2 ensures complete oxidation of the sulfide and serves to generate bromine in the halogenation step.

This method can also serve as a route to bromomethyl alkyl or aryl sulfones, since the dibromomethyl sulfones are readily reduced to bromomethyl sulfones by sulfite ion[2] (see Experimental Section).

$$\mathrm{ArCH_2SO_2CHBr_2} + \mathrm{SO_3}^{2-} + 2\mathrm{H_2O} \xrightarrow{\mathrm{H_2O-EtOH}} \mathrm{ArCH_2SO_2CH_2Br} + \mathrm{SO_4}^{2-} + \mathrm{Br}^- + \mathrm{H_3O}^+$$

A number of types of α-bromobenzyl benzyl sulfones have now been prepared by this general route.