a volume of 10 ml., and then treated with 0.2 g. of *p*-phenylphenacyl bromide and 10 ml. of ethanol. After refluxing 1.3 hr. and cooling, the mixture was filtered to yield 0.24 g. of crude *p*-phenylphenacyl butyrate, m.p. 60–80°; recrystallization from dilute ethanol gave prisms, m.p. 80–81°; when mixed with a authentic sample (m.p. 78–80°), the melting point was not depressed.

Deacylation of 3,5-Diphenyl-2-isopropyl-4-(3-methylbutanoyl)-phenol to 3,5-Diphenyl-2-isopropylphenol (XXI).—A 0.5-g. sample of ketophenol XV and 5 mg. of camphorsulfonic acid were heated at 205° for 4 hr. The residue, which had an isovaleric acid odor, was dissolved in ether and washed with sodium bicarbonate solution; the ether solution was dried and concentrated to dryness. The residue (0.42 g.) had hydroxyl (3600 cm.$^{-1}$) and carbonyl (1750 cm.$^{-1}$, ester) absorption and is believed to contain principally the phenol XXI and its isovalerate ester (XVIII). A 0.36-g. portion of the residue was saponified by refluxing for 24 hr. with a mixture of 10 g. of sodium hydroxide, 10 ml. of water, and 10 ml. of ethanol. There was obtained 0.30 g. of crude phenol XXI which was crystallized from hexane to yield 0.21 g., m.p. 112–115°. Recrystallization gave colorless prisms of **3,5-diphenyl-2-isopropylphenol (XXI)**, m.p. 114–115°; infrared band (potassium bromide) at 3500 cm.$^{-1}$ (OH) (carbonyl absent).

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.54; H, 6.94.

The aqueous alkaline portions (including the sodium bicarbonate extracts) were combined, acidified with sulfuric acid, diluted with water, and distilled. The first 1200 ml. of distillate contained 0.00119 equivalent of acid (by direct titration with 0.1 *N* sodium hydroxide) and the next fraction (700 ml.) contained 0.0008 equivalent; total, 0.00127 equivalent (94.5%) of isovaleric acid. The neutralized distillate was concentrated and the *p*-phenylphenacyl ester prepared; 0.16 g., m.p. 76–77°, was obtained; the melting point was not depressed when the material was mixed with an authentic sample (m.p. 73–75°).

Deacylation of 2-Butyl-3,5-bis(4-methylphenyl)-4-hexanoylphenol.—A 0.5-g. sample of the ketophenol XVI and 5 mg. of camphorsulfonic acid were heated at 200–210° for 3.5 hr. The residue was saponified by the procedure described previously; reflux time, 24 hr. The product, believed to be mainly 2-butyl-3,5-bis(4-methylphenyl)phenol (XXII), was obtained as an oil which failed to crystallize from hexane on chilling to −15°.

The aqueous alkaline portion was concentrated to near dryness and diluted with water to a volume of 25 ml. The solution was acidified with sulfuric acid and extracted with ether. After drying the solution and removing the ether the residue was distilled to yield 0.08 g. of hexanoic acid, b.p. 185° (690 mm.), $n^{25}D$ 1.4165, neut. equiv., 120 (calcd. 116.2). The *p*-phenylphenacyl ester was prepared, m.p. 63–64°; when mixed with an authentic sample, m.p. 63–64°, the melting point was not depressed.

3,5-Diphenyl-2-ethylphenol (XX) from 3,5-Diphenyl-6-ethyl-2-cyclohexen-1-one (XXIII).—A 1.0-g. sample of 3,5-diphenyl-6-ethyl-2-cyclohexen-1-one (XXIII) (prepared by the procedure of Dieckmann[19]) was mixed with 0.3 g. of 10% palladium-on-charcoal catalyst and the mixture heated gently with a flame for 15 min. (until bubbling ceased). The combined product of two such runs was extracted with boiling chloroform several times and the extracts were filtered. Concentration of the filtrate gave 1.43 g. of orange oil which was crystallized from hexane to yield 0.45 g. of crude XX, m.p. 76–81°; two recrystallizations from hexane raised the melting point to 82–83° (colorless prisms); infrared bands (Nujol) at 3500 and 3600 cm.$^{-1}$ (hydroxyl); carbonyl absorption was absent; λ_{max} 238 mμ (ε 25,300), shoulders at 260 mμ (ε 15,600) and 300 mμ (ε 4400).

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 88.06; H, 6.68.

Reactions of Enamines with Electrophilic Sulfur Compounds

MARTIN E. KUEHNE

Department of Chemistry of the University of Vermont, Burlington, Vermont

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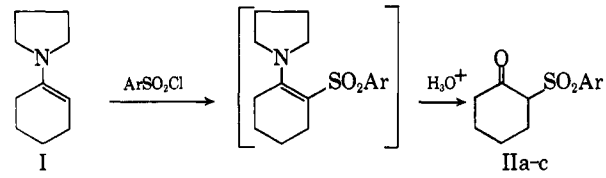
The reaction of 1-pyrrolidinocyclohexene and arylsulfonyl chlorides led, on hydrolysis, to 2-arylsulfonylcyclohexanones. With *o*-, *m*-, or *p*-nitrobenzenesulfenyl chloride, 2-mono- and 2,6-bis(*o*-, *m*-, and *p*-nitrophenylsulfenyl)cyclohexanones were obtained. Intermediate bisnitrophenylsulfenyl enamines were isolated. Only monosubstitution products were obtained from 1-pyrrolidinocyclohexene and *m*- or *p*-nitrophenyl disulfides and from 6-methyl-1-pyrrolidinocyclohexene and *o*-nitrobenzenesulfenyl chloride. From propane-1,3-dithiol-di-*p*-toluenesulfonate and 1-pyrrolidinocyclohexene, the 1,2-cyclohexanedione mono-1,3-propanedithiol ketal was obtained.

Since the initial work of Stork and his collaborators on the alkylation and acylation of enamines,[1] this class of compounds has gained increasing recognition as reactive intermediates in organic synthesis. While previous interest focused mainly on the use of enamines in the formation of carbon to carbon bonds, this report describes some reactions of enamines with electrophilic sulfur derivatives.

A few other studies in this area were indicated recently. Thus the reaction of 1-piperidinopropene with benzenesulfonyl chloride gave 2-benzenesulfonyl-1-piperidinopropene,[2] but alkylsulfonyl chlorides and enamines led to 3-aminotrimethylene sulfones.[2,3] These may arise either from cyclization of initially formed α-sulfonylimmonium intermediates, postulated in analogy to precursors of arylsulfonyl enamines, or from addition of a sulfur analog of ketene to the enamines. A third example is the reaction of sulfur dichloride with the bispyrrolidine enamine of bicyclo[3.3.1]nonane-2,6-dione which gave 2-thiaadamantane-4,8-dione on hydrolysis.[4]

We have found that the pyrrolidine enamine of cyclohexanone I reacts with *p*-acetamidobenzenesulfonyl chloride, *p*-nitrobenzenesulfonyl chloride, and *p*-toluenesulfonyl chloride[5] to give the corresponding arylsulfonyl ketones IIa–c on hydrolysis.



I IIa–c

a, Ar = *p*-acetamidophenyl
b, Ar = *p*-nitrophenyl
c, Ar = *p*-tolyl

(1)(a) G. Stork, R. Terrell, and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954); (b) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *ibid.*, **85**, 207 (1963).

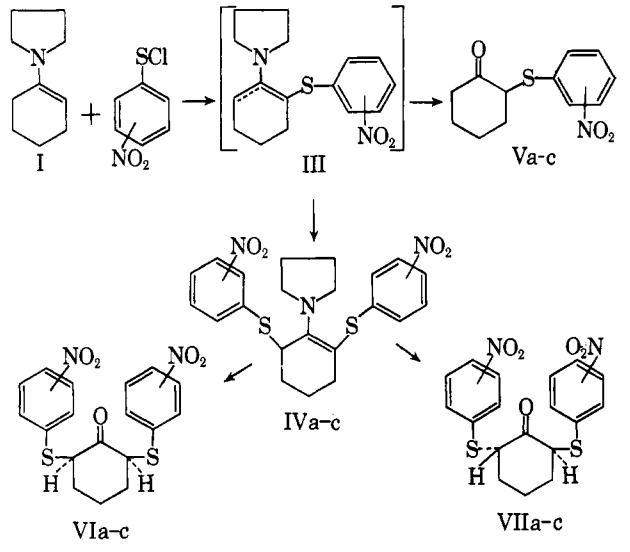
(2) G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962).

(3) G. Stork and I. Borowitz, *J. Am. Chem. Soc.*, **84**, 313 (1962).

(4) H. Stetter, H. Held, and A. Schulte-Oestrich, *Ber.*, **95**, 1687 (1962).

(5) Also indicated by G. Stork, Abstracts, 16th National Organic Symposium, June, 1959, pp. 44–52.

In addition to the sulfone IIa, the reaction mixture from *p*-acetamidobenzenesulfonyl chloride and 1-pyrrolidinocyclohexene gave a small amount of 2-*p*-acetamidobenzenesulfenylcyclohexanone and, similarly, the reaction with *p*-nitrobenzenesulfonyl chloride yielded also the bis-*p*-nitrobenzenesulfenyl enamine IVa and 2-*p*-nitrobenzenesulfenylcyclohexanone Va. These products presumably arose from the corresponding sulfenyl chlorides.[6]

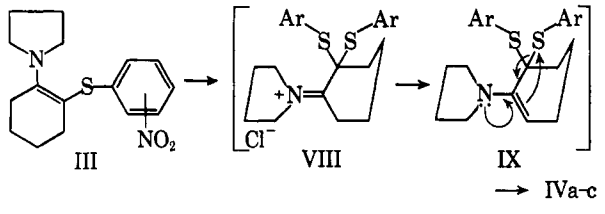


a, *p*-nitrophenyl
b, *o*-nitrophenyl
c, *m*-nitrophenyl

Indeed, reaction of *o*-nitrobenzenesulfenyl chloride and 1-pyrrolidinocyclohexene yielded, after hydrolysis, a mixture of the bis-*o*-nitrobenzenesulfenyl enamine IVb, the α-sulfenyl ketone Vb, and the epimeric α,α'-disulfenyl ketones VIb and VIIb. A separable mixture of the disulfenyl ketones VIb and VIIb also was obtained on acid hydrolysis of the purified disulfenyl enamine IVb. Analogous results were found in the reaction of *m*-nitrobenzenesulfenyl chloride with 1-pyrrolidinocyclohexene where the disulfenyl ketones VIc and VIIc and the monosulfenyl ketone Vc were isolated. The epimeric 2,6-diarylsulfenylcyclohexanones VIa,b,c and VIIb,c could be divided into two groups on the basis of their infrared carbonyl absorptions at 1720–1725 and 1700–1710 cm.$^{-1}$, respectively. The monosubstituted arylsulfenylcyclohexanones Va–c showed carbonyl absorption at 1705–1710 cm.$^{-1}$. (Empirical comparison of differences in absorption near 815 and 730 cm.$^{-1}$, however, could suggest a reversed grouping of the *m*-nitrophenyl pair, VIc and VIIc.) Stereochemical assignments of the epimeric groups were based on nuclear magnetic resonance spectra of the 2,6-di-*m*-nitrobenzenesulfenylcyclohexanone pair, VIc and VIIc, which alone was sufficiently soluble in suitable solvents. The compound showing axial protons α to the carbonyl group at higher field (5.9 τ *vs.* 5.5 τ) and some separation of methylene protons into axial and equatorial groups (about 8.1 and 7.6 τ *vs.* about 7.8 τ) was assigned the *cis* configuration VIc, which would be expected to be more rigid than the *trans* epimer VIIc where protons are averaged in a rapid interchange of two equivalent conformers.

Each of the nitrobenzenesulfenyl chlorides on reaction with 1-pyrrolidinocyclohexene formed predominantly the 2,6-disubstitution product, thus displaying a reaction course which is contrary to the cumulative experience of enamine chemistry, where one has always found a preference for the formation of monosubstitution products. The preferential formation of 2,6-disubstitution products with one equivalent or less of the electrophile indicates a higher nucleophilic reactivity of an α-carbon in an initially produced monosubstituted enamine intermediate III as compared with the starting enamine I. While this relationship is not readily rationalized for a 6-substituted 1-pyrrolidinocyclohexene, the direct precursor of the products IVa,b,c, it could be expected for the thioether substituted enamine, where negative charge density at the α-carbon might be increased due to stabilization of a more polarized enamine by the adjacent sulfur substituent. A 2,2-disubstituted immonium chloride intermediate VIII, formed from III, would undergo loss of a proton in the basic reaction medium to give the 2,2-disubstituted enamine IX, which could rearrange to the 2,6-disubstituted products IVa–c.

Some analogy to this new rearrangement can be seen in the transformation of 2-bromo-2-methylcholestan-3-one to the 4-bromo ketone.[7] In the present case the driving force of the rearrangement should arise from the formation of the conjugated nitrophenylsulfenyl enamine system as well as from a relief of steric compression in the α,α-disubstituted enamine where overlap of the unshared nitrogen electrons and the double bond requires a structure with steric repulsion between a sulfur substituent and one methylene group of the pyrrolidine ring.

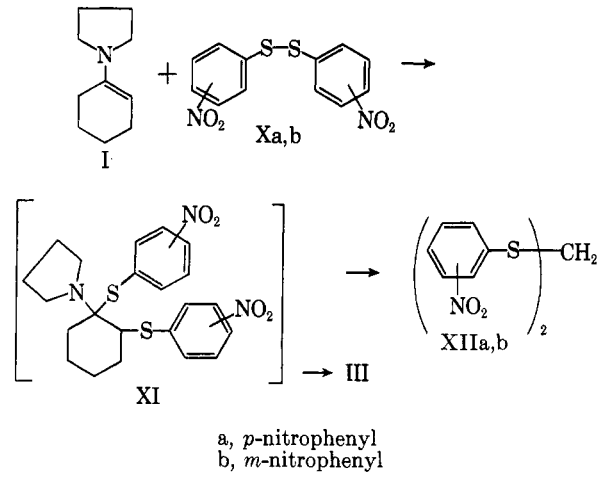


In contrast to the reactions with nitrobenzenesulfenyl chlorides, the addition of *p*- and *m*-nitrobenzenedisulfides Xa,b to 1-pyrrolidinocyclohexene and hydrolysis led mostly to monosubstituted ketones. This reaction course may be due to the formation of the dithioether intermediates XIa,b and a reflection of the higher nucleophilicity of aryl sulfide ions as compared with chloride ion. The reversibly formed adducts XIa,b can eliminate aryl sulfide ion, which is then removed from the reaction mixture by slow reaction with the solvent methylene dichloride, thus forming the thioacetals XIIa,b. (See p. 2126, Col. 1.)

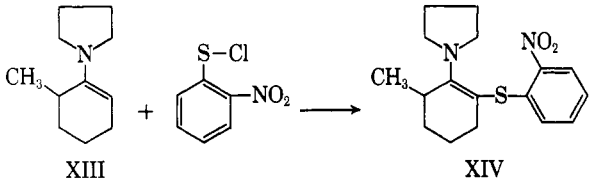
A monosubstituted enamine XIV was the only isolated reaction product from the addition of *o*-nitrobenzenesulfenyl chloride to 6-methyl-1-pyrrolidinocyclohexene XIII. Here lack of further reaction can be explained by a higher energy of an immonium salt-like transition state arising from the substituted enamine XIV as compared with the unsubstituted enamine XIII. The presence of an alkyl substituent

(6) While sulfenyl chlorides appear to be contaminants in the commercial sulfonyl chlorides, they also may have been generated in the reaction mixtures since the sulfenyl products were found, albeit in somewhat smaller yield, even when *p*-nitrobenzenesulfonyl chloride of analytical purity was used.

(7) C. Djerassi, N. Finch, and R. Mauli, *J. Am. Chem. Soc.*, **81**, 4997 (1959).



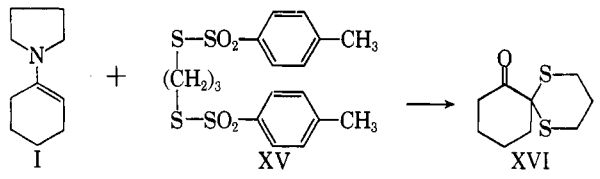
at C-6 should hinder electrophilic attack at C-2 of 1-pyrrolidinocyclohexene[8] in a quasi chair or boat conformation due to steric strain arising from either (a) 1,3-diaxial repulsion of the approaching electrophile by the substituent[9] or (b) coplanarity of the substituent and an α-methylene group of the heterocycle in the transition state. Because of the simultaneous high steric requirements of the methyl and sulfur substituents, electrophilic attack on enamine XIV would lead to a transition state with a twisted ring conformation where overlap stabilization between nitrogen, double bond, and the thioaryl system is reduced.



The predominant formation of disubstitution products from the reactions of pyrrolidinocyclohexene with arylsulfenyl halides and monosubstitution products with aryl disulfides as well as the monosubstitution reaction of 6-methyl-1-pyrrolidinocyclohexene with *o*-nitrobenzenesulfenyl chloride also could be explained in another way on the basis of previous observations in enamine chemistry.

It has been found[1] that an excess of very reactive electrophiles can lead to disubstitution products whereas less reactive, more discriminant electrophiles will give rise to monosubstitution products. In the present experiments this would require destructive removal of a part of the enamine, but not of the sulfenyl chloride, before the apparently instantaneous electrophilic attack is possible. Since product yields were far from quantitative, such a reaction course must be considered, but it should be recalled that disubstitution products were isolated predominantly even when the sulfenyl chloride was introduced as a minor impurity in the reaction of *p*-nitrobenzenesulfonyl chloride.

Finally, it was of interest to see if a 2,2-dithiosubstituted cyclohexanone could be obtained from 1-pyrrolidinocyclohexene and thus to find some support for the postulated 2,2-disubstituted immonium intermediate VIII. This was achieved by a reaction of 1-pyrrolidinocyclohexene I with the di-*p*-toluenesulfonate of propane 1,3-dithiol XV. This reaction, which clearly favored disubstitution on the same carbon, led, after hydrolysis, to the α-thioketal ketone XVI. Structural assignment was confirmed by an n.m.r. spectrum which showed two nonequivalent axial and equatorial protons of the α-methylene ketone (6.9 and 6.7 τ). This last reaction has been of value in some natural product work of this laboratory where the introduction of a thioketal blocking group was desired.[10]



Experimental

2-(4-Acetamidobenzenesulfonyl)cyclohexanone (IIa).—A solution of 38.6 g. (0.165 mole) of *p*-acetamidobenzenesulfonyl chloride and 16.2 g. (0.165 mole) of triethylamine in 1 l. of methylene chloride was cooled in ice and 25.0 g. (0.165 mole) of 1-pyrrolidinocyclohexene added under nitrogen. After 18 hr. at room temperature the solvent was removed under vacuum, an excess of dilute hydrochloric acid and enough methanol to maintain a homogeneous solution were added, and the solution stirred 90 min. at room temperature. Addition of water, extraction with methylene chloride, concentration, and crystallization from ethyl acetate gave 15.9 g. of sulfone (33% yield), m.p. 184–185°, after recrystallization.

Anal. Calcd. for $C_{14}H_{17}NO_4S$: C, 56.90; H, 5.80; N, 4.74; CH_3CO, 14.6. Found: C, 56.84; H, 5.83; N, 4.75; CH_3CO, 14.6 (by 4-hr. reflux in sulfuric acid).

Chromatography of the concentrated ethyl acetate filtrate on alumina (Woelm, neutral, activity II) gave 0.80 g. of material, m.p. 98–135°, eluted with 1:1 benzene–methylene chloride in the initial fractions and 1.8 g. (3.7% additional yield) of the sulfone. Recrystallization of the less polar material from benzene and cyclohexane produced 0.20 g., m.p. 122–124°, of 2-*p*-acetamidobenzenesulfenylcyclohexanone.

Anal. Calcd. for $C_{14}H_{17}NO_2S$: C, 63.84; H, 6.51; N, 5.32. Found: C, 64.01; H, 6.54; N, 5.24.

2-(4-Methylbenzenesulfonyl)cyclohexanone (IIc).—At 30°, a solution of 25.2 g. (0.13 mole) of *p*-toluenesulfonyl chloride in 300 ml. of methylene chloride was added to 20.0 g. (0.13 mole) of 1-pyrrolidinocyclohexene and 13.4 g. (0.13 mole) of triethylamine, in 100 ml. of methylene chloride. After 18 hr. 2.5 g. of triethylamine hydrochloride was filtered off, the reaction mixture concentrated under vacuum, dissolved in 500 ml. of benzene, and an additional 11.7 g. of triethylamine hydrochloride removed. After concentration under vacuum the residue was heated for 15 min. on a steam bath with an excess of dilute hydrochloric acid. Extraction of the cooled solution with methylene chloride, concentration, solution in hot cyclohexane, concentration, and trituration with hot ligroin gave 9.9 g. of crystals, m.p. 63–70°, and 13.1 g. of oil. Repeated recrystallization from ligroin produced 5.4 g., m.p. 76–78° (lit.[11] m.p. 76–80°), and 4.0 g., m.p. 65–75°. Distillation of the oil from a jacketed flask at bath temp. 130–200° (0.001 mm.) gave 8.3 g. of gummy crystals. All fractions (total crude, 17.7 g., 54% yield) had almost identical infrared spectra and each gave a 2,4-dinitrophenylhydrazone, m.p. 204–205°, recrystallized from methylene chloride and ethanol.

Anal. Calcd. for $C_{19}H_{20}N_4O_6S$: C, 52.78; H, 4.66; N, 12.96. Found: C, 53.05; H, 4.65; N, 13.05.

In an alternative procedure the total reaction product after hydrolysis was chromatographed on alumina (Woelm, neutral, activity II) and 7.2 g. (21% yield) of the crystalline sulfone eluted with 5:1 petroleum ether–benzene, together with 5.0 g. of the oily material and 0.75 g. of pyrrolidine *p*-toluenesulfonamide,

(8) Such hindrance is found in the alkylation of analogous enamines; *cf.* ref. 1.

(9) W. R. W. Williamson, *Tetrahedron*, **3**, 314 (1958).

(10) R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives, and R. B. Kelly, *J. Chem. Soc.*, 1131 (1957).

(11) J. Weinstock, R. G. Pearson, and F. G. Bordwell, *J. Am. Chem. Soc.*, **78**, 3468 (1956).

more rapidly eluted than the sulfone, m.p. 120–121° (lit.[12] m.p. 121°).

2-(4-Nitrobenzenesulfonyl)cyclohexanone (IIb), 2-(4-Nitrobenzenesulfenyl)cyclohexanone (Va), and 2,6-Di(4-nitrobenzenesulfenyl)-1-pyrrolidinocyclohexene (IVa).—A solution of 22.2 g. (0.10 mole) of *p*-nitrobenzenesulfonyl chloride (Eastman, recrystallized three times from cyclohexane, m.p. 77–79°. *Anal.* Calcd. for $C_6H_4ClNO_4S$: C, 32.52; H, 1.82. Found: C, 32.50, H, 1.95.) in 150 ml. of chloroform was added, with cooling, to 10.1 g. (0.10 mole) of triethylamine and 15.1 g. (0.10 mole) of 1-pyrrolidinocyclohexene in 150 ml. of chloroform, under nitrogen. After 18 hr. at room temperature the solvent was removed under vacuum, the residue taken up in 250 ml. of benzene, and 12.0 g. of triethylamine hydrochloride filtered off. Concentration under vacuum, addition of 200 ml. of methanol, filtration, and recrystallization from methanol gave 1.2 g. of IVa, m.p. 178–179°.

Anal. Calcd. for $C_{22}H_{23}N_3O_4S_2$: C, 57.77; H, 5.07; N, 9.19; S, 14.02. Found: C, 57.84; H, 5.18; N, 8.67; S, 13.92.

To the methanolic solution 23 ml. of 10% hydrochloric acid was added and, after 30 min. at room temperature, the solution was poured into water and extracted with methylene chloride. Concentration under vacuum and chromatography on 220 g. of Florisil gave 0.2 g., m.p. 91–93°, of crude Va, eluted with 1:2 petroleum ether–benzene; 2.5 g., m.p. 80–112°, of a mixture of IIb and Va in four fractions eluted with 1:2 petroleum ether–benzene; and 3.7 g., m.p. 113–120°, of crude IIb, eluted in ten fractions with benzene. Recrystallization of the crude Va from methanol, then from cyclohexane gave a sample with m.p. 97–98°, infrared, ν_{max} 1710 cm.$^{-1}$ (C=O) in potassium bromide.

Anal. Calcd. for $C_{12}H_{13}NO_3S$: C, 57.38; H, 5.22; N, 5.58; S, 12.77. Found: C, 57.70; H, 5.27; N, 5.57; S, 12.88.

Recrystallization of crude IIb from methanol gave 2.4 g. of sulfone, m.p. 120–121°; 0.8 g., m.p. 113–115°; and 0.5 g., m.p. 105–110° (mixtures of IIb and Va).

Anal. Calcd. for $C_{12}H_{13}NO_5S$: C, 50.88; H, 4.63; N, 4.95. Found: C, 50.89; H, 4.60; N, 5.14.

In another experiment with unrecrystallized *p*-nitrobenzenesulfonyl chloride 3.0 g. of IVa was obtained. Chromatography of the acid hydrolysis mixture on 170 g. of alumina (Woelm, neutral, activity II) gave 1.0 g. of Va and 1.5 g. of IIb and 2.9 g. of a mixture, m.p. 76–83°, all eluted with 1:9 petroleum ether–benzene.

2,6-Di(4-nitrobenzenesulfenyl)cyclohexanone (VIa).—A suspension of 0.30 g. (0.64 mmole) of 2,6-di(4-nitrobenzenesulfenyl)-1-pyrrolidinocyclohexene in 25 ml. of methanol and 15 ml. of 3% hydrochloric acid was digested until all orange material had been converted to a white precipitate. Filtration and recrystallization from ethyl acetate and heptane gave 0.22 g. (83% yield), m.p. 128–132°; recrystallized from ethyl acetate to m.p. 134–135°, infrared, ν_{max} 1725 cm.$^{-1}$ (C=O) in potassium bromide.

Anal. Calcd. for $C_{18}H_{16}N_2O_5S_2$: C, 53.48; H, 3.99; N, 6.93; S, 15.86. Found: C, 53.56; H, 3.93; N, 6.90; S, 16.06.

2-(2-Nitrobenzenesulfenyl)cyclohexanone (Vb), *cis*- and *trans*-2,6-Di(2-nitrobenzenesulfenyl)cyclohexanone (VIb and VIIb), and 2,6-Di(2-nitrobenzenesulfenyl)-1-pyrrolidinocyclohexene (IVb).—To a stirred, cooled solution of 15.1 g. (0.10 mole) of 1-pyrrolidinocyclohexene and 10.1 g. (0.10 mole) of triethylamine in 100 ml. of methylene chloride, was added dropwise 19.0 g. (0.10 mole) of *o*-nitrobenzenesulfenyl chloride in 100 ml. of methylene chloride. After 20 hr. at room temperature the solution was shaken for 10 min. with an excess of dilute hydrochloric acid, washed with water, concentrated under vacuum, and triturated with methanol, thus giving 17.6 g. of a mixture of red and yellow crystalline materials. Several fractional recrystallizations gave 3.2 g. (8% yield) of yellow VIb, m.p. 180–181°, infrared, ν_{max} 1720 cm.$^{-1}$ (C=O) in potassium bromide, from dimethylformamide or dioxane; 0.7 g. (2% yield) of yellow VIIb, m.p. 153–154°, infrared, ν_{max} 1710 cm.$^{-1}$ (C=O) in potassium bromide, from methylene chloride and ethanol; 5.3 g. (12% yield) of IVb, red, m.p. 173–174°, from benzene; 1.0 g. (4% yield) of Vb, m.p. 113–114°, infrared, ν_{max} 1710 cm.$^{-1}$ (C=O) in potassium bromide, from cyclohexane.

Anal. Calcd. for $C_{12}H_{13}NO_3S$ (Vb): C, 57.38; H, 5.22; N, 5.58. Found: C, 57.44; H, 5.27; N, 5.66.

Anal. Calcd. for $C_{18}H_{16}N_2O_5S_2$ (VIb): C, 53.48; H, 3.99; N, 6.93; S, 15.86. Found: C, 53.17; H, 4.07; N, 7.04; S, 15.82.

Anal. Calcd. for $C_{18}H_{16}N_2O_5S_2$ (VIIb): C, 53.48; H, 3.99; N, 6.93. Found: C, 53.68; H, 4.11; N, 6.91.

Anal. Calcd. for $C_{22}H_{23}N_3O_4S_2$ (IVb): C, 57.77; H, 5.07; N, 9.19; S, 14.02. Found: C, 58.53; H, 5.17; N, 8.44; S, 13.86.

In a second experiment trituration of the crude reaction product with methanol gave 17.4 g. of red solid, 1.0 g. of brown solid on partial concentration, and 4.6 g. of residue on complete concentration of the methanol washings. Digestion of the major crop in 100 ml. of methanol and an excess of dilute hydrochloric acid until no red solid remained, cooling in ice, and filtration gave 11.1 g. of material. Treatment with hot benzene produced 3.9 g. (10% yield) of insoluble VIb. Concentration and crystallization from tetrahydrofuran gave 4.9 g. (12% yield) of VIIb. Concentration of the tetrahydrofuran and crystallization from cyclohexane led to 3.1 g. (12% yield) of Vb.

Hydrolysis of 2,6-Di(2-nitrobenzenesulfenyl)-1-pyrrolidinocyclohexene (IVb).—A suspension of 0.30 g. (0.65 mmole) in 30 ml. of methanol and 5 ml. of 3% hydrochloric acid was digested for 15 min. when all of the red solid had been converted to the yellow product. Filtration and recrystallization from dimethylformamide furnished 0.22 g. (83% yield) of a mixture of VIb and VIIb, m.p. 155–170°. Recrystallization from 80 ml. of benzene gave 0.1 g. of VIb, m.p. 181°.

Equilibration of *cis*- and *trans*-2,6-Di(2-nitrobenzenesulfenyl)-cyclohexanone (VIb and VIIb).—Heating of 0.10 g. of either VIb, m.p. 181°, or VIIb, m.p. 153°, in 5 ml. of dimethylformamide and 2 drops of 10% hydrochloric acid for 10 min. on a steam bath, cooling, addition of 1 ml. of water, and filtration gave 0.090 g. of a mixture of isomers, m.p. 165–167°, with identical infrared spectra and mixture melting points.

2-(3-Nitrobenzenesulfenyl)cyclohexanone (Vc) and *cis*- and *trans*-2,6-Di(3-nitrobenzenesulfenyl)cyclohexanone (VIc and VIIc).—To a stirred, ice-cooled solution of 7.5 g. (0.05 mole) of 1-pyrrolidinocyclohexene in 50 ml. of methylene chloride and 5.0 g. (0.05 mole) of triethylamine was added slowly 9.5 g. (0.05 mole) of *m*-nitrobenzenesulfenyl chloride[13] in 50 ml. of methylene chloride. After stirring for 24 hr. at room temperature, the reaction mixture was concentrated to dryness under vacuum, the residue taken up in 60 ml. of benzene, and 7.0 g. of triethylamine hydrochloride separated by filtration. Concentration under vacuum, solution in methylene chloride, thorough extraction with 1% hydrochloric acid, and concentration under vacuum left a gum which was separated into 3.0 g. of an insoluble mixture of 2,6-disubstituted cyclohexanone epimers (VIc and VIIc), and material soluble in hot cyclohexanone and 100 ml. of cold methanol. Chromatography of the methanol and cyclohexane concentrates on 90 g. of Florisil gave 3.3 g. (26% yield) of gummy 2-substituted ketone (Vc) eluted with 1.2 l. of 1:1 petroleum ether–benzene. Recrystallization of this material from cyclohexane gave 2.4 g. m.p. 56–57°, infrared, ν_{max} 1705 cm.$^{-1}$ (C=O) in potassium bromide.

Anal. Calcd. for: $C_{12}H_{13}NO_3S$: C, 57.38; H, 5.22; N, 5.58. Found: C, 57.63; H, 5.14; N, 5.73.

From the mother liquors 0.75 g. of the corresponding dinitrophenylhydrazone derivative was obtained, m.p. 178–180°, after recrystallization from ethanol.

Anal. Calcd. for: $C_{18}H_{17}N_5O_6S$: C, 50.15; H, 3.99; N, 16.23. Found: C, 50.32; H, 4.02; N, 15.95.

With 600 ml. of benzene 0.35 g. of epimeric 2,6-disubstitution products (VIc and VIIc) was eluted (total 3.35 g., 33% yield). Fractional crystallization of portions of the epimeric mixture from carbon tetrachloride followed by ethyl acetate gave the more soluble *trans* epimer (VIIc), m.p. 143–144°, infrared, ν_{max} 1700 cm.$^{-1}$ (C=O) in potassium bromide.

Anal. Calcd. for: $C_{18}H_{16}N_2O_5S_2$: C, 53.48; H, 3.99; N, 6.93. Found: C, 53.61; H, 4.11; N, 6.93.

The less soluble *cis* epimer (VIc), m.p. 145–146°, infrared, ν_{max} 1720 cm.$^{-1}$ (C=O) in potassium bromide was isolated in smaller amount with the approximate ratio of epimers 2:1.

Anal. Calcd. for $C_{18}H_{16}N_2O_5S_2$: C, 53.48; H, 3.99; N, 6.93. Found: C, 53.72; H, 4.25; N, 6.95.

6-Methyl-2-(2-nitrobenzenesulfenyl)-1-pyrrolidinocyclohexene (XIV).—A solution of one equivalent of *o*-nitrobenzenesulfenyl chloride in methylene chloride was added to 8.2 g. (0.05 mole) of 6-methyl-1-pyrrolidinocyclohexene and triethylamine, with the reaction conducted and worked up as described before. Trituration of the benzene concentrate with 50 ml. of methanol gave 6.1

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g. of red crystalline product, m.p. 90–91°, which could be recrystallized from ligroin without change in melting point.

Anal. Calcd. for $C_{17}H_{22}N_2O_2S$: C, 64.11; H, 6.96; N, 8.80. Found: C, 64.36; H, 7.06; N, 8.64.

Chromatography of mother liquors material in benzene on florisil gave 0.20 g. of methylene-di-*o*-nitrobenzenesulfide (XIIc), m.p. 175–177° (lit.[14] m.p. 170°).

Anal. Calcd. for $C_{13}H_{10}N_2O_4S_2$: C, 48.45; H, 3.13; N, 8.69; S, 19.90. Found: C, 48.52; H, 3.07; N, 8.63; S, 19.87.

Reaction of 1-Pyrrolidinocyclohexene (I) with *m*- and *p*-Nitrobenzene Disulfides (Xa,b).—To a solution of 7.5 g. (0.05 mole) of enamine and 5.0 g. (0.05 mole) of triethylamine in 50 ml. of methylene chloride was added 7.7 g. (0.025 mole) of (a) *p*-nitrobenzene disulfide or (b) *m*-nitrobenzene disulfide with 180 ml. of methylene chloride, slowly with stirring and cooling in ice. After standing at room temperature for 20 hr., the solvent was removed under vacuum and the residue triturated with cyclohexane to give the following compounds.

(a) 1.4 g. of methylene-di-*p*-nitrobenzene sulfide (XIIa), m.p. 181–182° (lit.[15] m.p. 179°), recrystallized from benzene.

Anal. Calcd. for $C_{13}H_{10}N_2O_4S_2$: C, 48.45; H, 3.13; N, 8.69; S, 19.90. Found: C, 48.75; H, 3.11; N, 8.70; S, 19.82.

(b) 7.7 g. of solid which could be separated by methanol into soluble amine hydrosulfide and 4.3 g. of insoluble methylene-di-*m*-nitrobenzene sulfide (XIIb), m.p. 140–141°, recrystallized from ethanol.

Anal. Calcd. for $C_{13}H_{10}N_2O_4S_2$: C, 48.45; H, 3.13; N, 8.69; S, 19.90. Found: C, 48.62; H, 3.11; N, 9.43; S, 19.79.

Concentration of cyclohexane filtrates, solution in methylene chloride, washing with dilute hydrochloric acid, concentration, and crystallization from cyclohexane gave (a) 2.1 g. (33% yield), m.p. 97–98°, of Va and (b) 5.0 g. (79% yield), m.p. 56–57°, of Vc. In another experiment 7.7 g. (0.025 m.) of *p*-nitrophenyl disulfide and 180 ml. of methylene chloride were added slowly to 3.8 g. (0.025 mole) of enamine and 5.0 g. (0.050 mole) of triethylamine in 50 ml. of methylene chloride with cooling in ice. After 20 hr. at room temperature the concentrated reaction mixture yielded 2.9 g. of methylene-di-*p*-nitrobenzene sulfide (XIIa), 1.7 g. of water-soluble amine hydrosulfide material and 1.3 g. of 2,6-di(4-nitrobenzenesulfenyl)-2-pyrrolidinocyclohexene (IVa), crystallized from 100 ml. of methanol and 20 ml. of ether. Concentration of the mother liquors, and hydrolysis of the residue with excess 1% hydrochloric acid at room temperature for 2 hr. gave 4.0 g. of 2-(4-nitrobenzenesulfenyl)cyclohexanone (Va), 63% yield, after recrystallization from hexane.

1,5-Dithiaspiro[5.5]undecan-1-one (XVI).—A solution of 9.0 g. (0.021 mole) of propane-1,3-dithiol-di-*p*-toluenesulfonate, 4.0 g. (0.068 mole) of triethylamine, and 3.2 g. (0.021 mole) of enamine in 50 ml. of dry dioxane was stirred under nitrogen for 3 hr. and then refluxed 20 hr. After concentration under vacuum, solution in ether, washing with dilute hydrochloric acid, and reconcentration, the crude product was passed over Florisil in 1:1 benzene–petroleum ether. Distillation at 120–180° (0.001 mm.) gave 1.85 g. of oily product which could be purified further by preparative thin layer chromatography on Merck Alumina G with 3:1 cyclohexane–benzene as solvent and redistillation at 140° (0.001 mm.) to give 1.20 g. (28% yield) of product, m.p. 53–54°, from petroleum ether; infrared, ν_{max} 1690 cm.$^{-1}$ (C=O) in potassium bromide.

Anal. Calcd. for $C_9H_{14}S_2O$: C, 53.43; H, 6.98. Found: C, 53.45; H, 7.01.

A dinitrophenylhydrazone, m.p. 154–155°, crystallized from ethanol.

Anal. Calcd. for $C_{15}H_{18}N_4O_4S_2$: C, 47.10; H, 4.74; N, 14.65. Found: C, 47.36; H, 4.96; N, 14.41.

A semicarbazone crystallized from ethanol, m.p. 235–236°.

Anal. Calcd. for $C_{10}H_{18}N_3OS_2$: C, 46.10 H, 6.97; N, 16.13. Found: C, 45.88; H, 6.55; N, 16.26.

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Michael Additions of Nitroform. II. The Nitrite Elimination Reaction[1]

MORTIMER J. KAMLET AND LLOYD A. KAPLAN

Organic Chemistry Division, U. S. Naval Ordnance Laboratory, Silver Spring, Maryland

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In absolute methanol, potassium trinitromethide adds to methyl acrylate, acrylonitrile, and acrylamide to yield the potassium salts of methyl 4,4-dinitro-2-butenoate, 4,4-dinitro-2-butenenitrile, and 4,4-dinitro-2-butenamide. With acrylamide as the augend, a second product, potassium 4,4-dinitro-2-hydroxybutyramide, was formed. Proofs of structure of these new dinitromethyl derivatives are described.

In the first paper in this series,[2] it was reported that the reaction of nitroform with methyl acrylate (I, Y = $COOCH_3$) or methyl vinyl ketone (I, Y = $COCH_3$) yielded, in addition to the Michael adducts II methyl 4,4-dinitro-2-hydroxypimelate (III, Y = $COOCH_3$) and 5,5-dinitro-2-hydroxy-2,8-nonanedione (III, Y = $COCH_3$). In the case of the augend methyl acrylate, a second nitrite elimination product, the potassium salt of methyl 4,4-dinitro-2-butenoate (IV, Y = $COOCH_3$) was isolated in 34% yield from an aqueous methanol system at pH 4.5.

$$HC(NO_2)_3 + CH_2{=}CH{-}Y \xrightarrow[AcOH-AcO^- \text{ or } AcO^-]{MeOH - H_2O}$$

I

$$C(NO_2)_3CH_2CH_2{-}Y + Y{-}(CH_2)_2C(NO_2)_2CH_2\underset{\displaystyle OH}{\underset{|}{CH}}{-}Y + K^+{}^-C(NO_2)_2CH{=}CH{-}Y$$

II III IV

We now wish to report that derivatives analogous to IV can be obtained from the heterogeneous reaction of the potassium salt of nitroform with the appropriate acrylic augend in methanol. Thus stirring a slurry of potassium trinitromethide in absolute methanol with methyl acrylate or acrylonitrile until a constant ultraviolet spectrum was obtained for the insoluble potassium salts, afforded a 48 and 50% yield, respectively, of the potassium salts of methyl 4,4-dinitro-2-butenoate (IV, Y = $COOCH_3$) and 4,4-dinitro-2-butenenitrile (IV, Y = CN). With acrylamide, in addition to the expected potassium salt of 4,4-dinitro-2-butenamide, there also was obtained a yellow potassium salt (V).

(1) Presented in part at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, Abstracts of Papers, p. 560.

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