The Role of Sulfur in Beckmann Fragmentation

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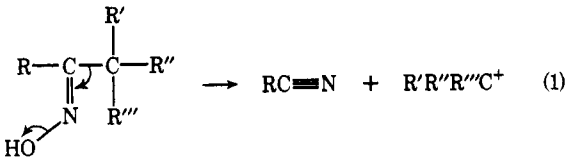
Abstract: Oximes of two cyclic β-keto sulfides, **2** and **9**, have been shown capable of undergoing carbonium ion fragmentation under certain Beckmann conditions. These findings cast doubt on a mechanism earlier proposed in which sulfur effects nucleophilic displacement on nitrogen and support, instead, the normal fragmentation mechanism.

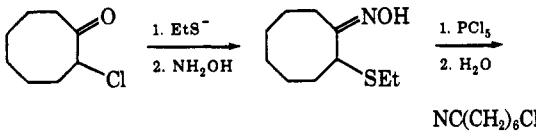
Oximes substituted at an α carbon by groups capable of stabilizing a positive charge frequently undergo fragmentation rather than rearrangement when subjected to Beckmann conditions (eq 1). A variety of



(1)

substituents, notably alkyl, aryl, hydroxy, alkoxy, and amino, can stabilize the intermediate carbonium ion and facilitate fragmentation.[1-3]

This paper is concerned with the mechanism of oxime fragmentation when one of the α substituents is thioalkyl, –SR. In an early paper,[2] which generalized the Beckmann fragmentation reaction, it was suggested, on the basis of a report[4] that oximes containing α-thioaryl substituents fragmented with phosphorus pentachloride, that sulfur stabilized the carbonium ion fragment by electron release in the same way as do nitrogen and oxygen. This reaction acquired practical significance with the subsequent discovery by Autrey[5] and Ohno[6] of efficient methods of introducing a thioalkyl substituent α to a ketone, and the demonstration that fragmentation of the resulting oximes provided a selective cleavage to products with different functional groups at each terminus; examples are shown in eq 2[6a] and 3.[5c]



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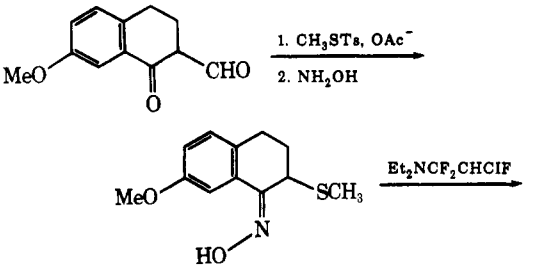
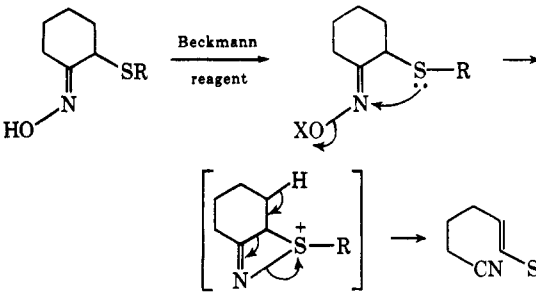


(3)

While it was at first[5a,6b] assumed that the role of sulfur in these cases was to provide resonance stabilization for the presumed carbonium ion intermediate, Autrey and Scullard[5c] later proposed an alternative mechanism. Arguing that there was neither theoretical support nor experimental evidence for resonance electron donation by sulfur, they concluded that sulfur stabilization of an α-carbonium ion was unimportant in influencing the fragmentation. They proposed that rather than fragmentation to a carbonium ion intermediate, the sulfur initiates the reaction by nucleophilic displacement on the oxime nitrogen, leading to a 1,2-thiazetine intermediate which fragments (eq 4).



(4)

It appeared to us that the usual carbonium ion fragmentation mechanism could not be discarded so easily, since there is ample evidence in the literature to support the argument that sulfur is indeed capable of stabilizing an adjacent carbonium ion.

(a) α-Chloro thioethers, while much less reactive than the corresponding α-chloro ethers, still hydrolyze thousands of times more rapidly than saturated alkyl chlorides.[7] Chloromethyl phenyl thioether undergoes first-order hydrolysis even ten times faster than *tert*-butyl chloride, a result which Bordwell, *et al.*,[8] have attributed to the stabilization of the carbonium ion by sulfur.

(b) The acid-catalyzed hydrogen–deuterium exchange of *p*-deuteriothioanisole, while 30–40 times

(1) R. K. Hill and R. T. Conley, *J. Amer. Chem. Soc.*, **82**, 645 (1960).
(2) R. K. Hill, *J. Org. Chem.*, **27**, 29 (1962).
(3) R. T. Conley and S. Ghosh, *Mech. Mol. Migr.*, **4**, 197 (1971).
(4) J. A. Barltrop and K. J. Morgan, *J. Chem. Soc.*, 4486 (1960).
(5) (a) R. L. Autrey and P. W. Scullard, *J. Amer. Chem. Soc.*, **87**, 3284 (1965); (b) *ibid.*, **90**, 4917 (1968); (c) *ibid.*, **90**, 4924 (1968).
(6) (a) M. Ohno, N. Naruse, S. Torimitsu, and I. Terasawa, *ibid.*, **88**, 3168 (1966); (b) M. Ohno and I. Terasawa, *ibid.*, **88**, 5683 (1966); (c) M. Ohno, N. Naruse, S. Torimitsu, and M. Okamoto, *Bull. Chem. Soc. Jap.*, **39**, 1119 (1966); (d) M. Ohno, *Kagaku No Ryoiki*, **22**, 30 (1968); *Chem. Abstr.*, **69**, 9989 (1968).
(7) H. Böhme, *Ber.*, **74**, 248 (1941); H. Böhme and K. Sell, *ibid.*, **81**, 123 (1948); H. Böhme, H. Fischer, and R. Frank, *Justus Liebigs Ann. Chem.*, **563**, 54 (1949).
(8) F. G. Bordwell, G. D. Cooper, and H. Morita, *J. Amer. Chem. Soc.*, **79**, 376 (1957).

slower than *p*-deuterioanisole, is still 50 times faster than deuteriobenzene.[9]

(c) The rate of first-order solvolysis of *p*-methylthiocumyl chloride in 90% aqueous acetone at 25° is 553 times faster than that of cumyl chloride; Brown, *et al.*,[10] have pointed out that the enhanced rate is the result of resonance stabilization of the carbonium ion by sulfur. On the basis of this experiment, the methylthio group has been assigned[11] a σ_p^+ constant of −0.604, compared to −0.778 for methoxy.

These and other results in the literature show that sulfur, though a weaker electron donor than oxygen, is capable of resonance stabilization of an adjacent carbonium ion, and consequently the carbonium ion fragmentation cannot be eliminated out of hand. Moreover, the thiazetine intermediate shown in eq 4 is not a totally satisfactory alternative, since it does not have the anti relationship of C–C and N–X bonds preferred[12] for fragmentation of oxime derivatives.

Regardless of the necessity for, or merits of, the thiazetine mechanism proposed by Autrey and Scullard, it is easily amenable to experimental test. If the sulfur atom were incorporated in the ring of a cyclic β-keto sulfide, a thiazetine intermediate would be geometrically prohibited, and fragmentation of the oxime could not occur if this were an obligatory intermediate. We have accordingly investigated the behavior of the oximes of two representative cyclic keto sulfides to see whether fragmentation is possible.

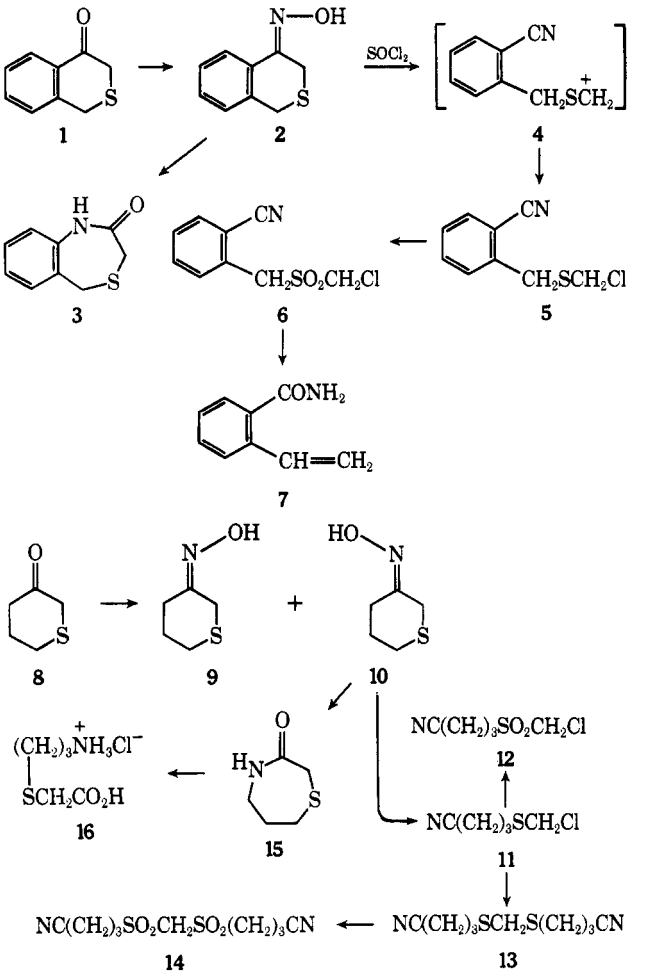
Results

2-Thiaisochroman-4-one (**1**) was prepared by an improved method and converted to its oxime **2**. The oxime is a sharp-melting solid, showing only one spot on tlc and one sharp singlet at δ 3.8 for the C-3 methylene, and thus is a single isomer. By analogy with α-tetralone oxime,[13] this should be the anti isomer; support for this is the finding that the chemical shift of the C-5 hydrogen does not change appreciably on going from the ketone (**1**) to the oxime (**2**).

Treatment of the oxime with phosphorus pentachloride, polyphosphoric acid, or toluenesulfonyl chloride in pyridine, or rearrangement of the oxime tosylate in aqueous ethanol, effected normal Beckmann rearrangement to a lactam, identified as the known[14a] 3,5-dihydro-4,1-benzothiazepin-2(1*H*)-one (**3**). This lactam is the product of normal Beckmann rearrangement of the anti oxime **2**, in which the aryl ring, trans to the hydroxyl, migrates. Only with PCl_5 was there evidence of any fragmentation (nitrile absorption in the ir of crude product), but no pure nitrile could be isolated.

Thionyl chloride, however, led to exclusive fragmentation, affording a crystalline nitrile in over 80% yield. Infrared and nmr spectra allowed the assignment of the chloromethyl thioether structure **5**. Chromic oxide oxidation gave the α-chloro sulfone **6**, whose structure was confirmed unambiguously by Ramberg–Backlund rearrangement to *o*-vinylbenzamide (**7**) (Scheme I).

Scheme I



The only plausible mechanism[14b] for formation of **5** is fragmentation of the oxime to the resonance-stabilized cation **4**, followed by capture by chloride ion.

The ability of cyclic oximes of this class to fragment was verified in a second example. 3-Thiacyclohexanone (**8**) was prepared as described by Leonard and Figueras.[15] Nmr analysis of the oxime, mp 77–77.5°, showed it to be an approximately 50:50 mixture of syn and anti isomers, **9** and **10**; two sharp singlets at δ 3.2 and 3.4 correspond to the C-2 methylene in the mixture of geometrical isomers. Repeated fractional crystallization from hexane gave a pure isomer, mp 96°, which showed only the singlet at δ 3.4; from the mother liquors a mixture enriched in the other isomer was obtained. The configurations of the oxime isomers were assigned by use of the nmr shift reagent tris(dipivalomethanato)europium, Eu(DPM)$_3$. Adding increasing

(9) S. Oae, A. Ohno, and W. Tagaki, *Bull. Chem. Soc. Jap.*, **35**, 681 (1962).

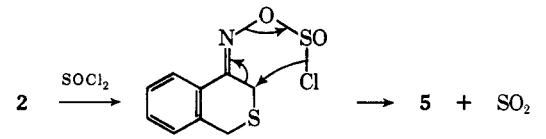
(10) H. C. Brown, Y. Okamoto, and T. Inukai, *J. Amer. Chem. Soc.*, **80**, 4964 (1958).

(11) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

(12) C. A. Grob, *Bull. Soc. Chim. Fr.*, 1360 (1960).

(13) E. C. Horning, V. L. Stromberg, and H. A. Lloyd, *J. Amer. Chem. Soc.*, **74**, 5153 (1952).

(14) (a) M. Uskoković, G. Grethe, J. Iacobelli, and W. Wenner, *J. Org. Chem.*, **30**, 3111 (1965). We thank Dr. Uskoković for his kindness in sending us a sample of lactam **3**. (b) A referee has suggested an alternative cyclic mechanism for thionyl chloride fragmentation.



We consider this mechanism unlikely since it ascribes no role to sulfur and should lead to fragmentation of any oxime regardless of the α substituent.

(15) N. J. Leonard and J. Figueras, Jr., *J. Amer. Chem. Soc.*, **74**, 917 (1952).

amounts of $Eu(DPM)_3$ to a mixture of the oximes in CS_2 caused the two α-methylene singlets to shift downfield. Extrapolation to an equimolar ratio of $Eu(DPM)_3$ to oxime gave a calculated shift of 15.5 ppm for the 3.2 singlet, 8.5 ppm for the 3.4 singlet, and 31 ppm for the hydroxyl proton. Since the α carbon syn to the oxime hydroxyl should experience a greater shift than that anti,[16] the pure isomer of mp 96° is assigned the anti configuration **10**.[17]

The pure anti oxime was used in all the Beckmann experiments. However, although no change in the nmr spectrum occurred when the oxime was allowed to stand several days in benzene, carbon tetrachloride, chloroform, pyridine, or alkaline D_2O, addition of a drop of chloroform saturated with gaseous HCl caused immediate isomerization. Within 2 min the singlet at δ 3.4 was replaced by singlets of equal intensity at 3.4 and 3.2. Consequently, any Beckmann conditions which involve or liberate acid will certainly equilibrate the oxime isomers before rearrangement.

Treatment of the oxime with either concentrated sulfuric or polyphosphoric acid simply regenerated the parent ketone **8**. This was unexpected since an isomeric oxime, 4-thiacyclohexanone oxime, has been reported to rearrange normally under these conditions.[19]

A vigorous reaction leading to fragmentation occurred when a benzene solution of the oxime was treated with thionyl chloride. A liquid nitrile was isolated in good yield, whose infrared and nmr spectra were consistent with structure **11**, the chloromethyl thioether analogous to **5**. The presence of the chloromethyl group was shown by a two-proton singlet at δ 4.6. Oxidation with chromic oxide gave the crystalline α-chloro sulfone **12**, while brief exposure to water led to the mercaptal **13**; formaldehyde was identified in the aqueous solution by a positive test with chromotropic acid. The facile hydrolysis is characteristic of α-chloromethyl sulfides.[7]

When phosphorus pentachloride was used as the reagent, and the reaction mixture submitted to the usual aqueous work-up, mercaptal **13** was the only product, isolated in high yield. Though a satisfactory elemental analysis could not be obtained, the structure was consistent with the ir and nmr spectra, particularly a singlet at δ 3.7, and oxidation with peracetic acid gave the crystalline, analytically pure disulfone **14**. Since formaldehyde could again be detected in the aqueous solution resulting from work-up of the PCl_5 reaction mixture, it appears that the fragmentation product **11** was initially formed in this reaction as well and hydrolyzed during work-up.

Even the mildest Beckmann conditions generally possible, *p*-toluenesulfonyl chloride in pyridine, led to mercaptal **13** as the major product. There was also isolated in 11% yield a crystalline lactam, identified as the known[20] thiazepinone **15** by hydrolysis to the amino acid hydrochloride **16**.

We interpret these results as largely consistent with the stereochemical requirements for fragmentation. Grob, in his elegant studies on stereochemistry of fragmentation reactions of α-amino oximes,[12] concluded that the coplanar trans elimination possible in anti oximes was much preferred for fragmentation but isolated both rearrangement and fragmentation products from syn oximes. The anti oxime **10** used in this study has the requisite trans-coplanar conformation and consequently undergoes the carbonium ion fragmentation with most reagents used. The HCl liberated in tosyl chloride–pyridine apparently isomerizes the oxime to a mixture of syn and anti isomers, with **10** undergoing fragmentation and **9** rearranging to lactam **15**. Oxime **2**, with the oxime hydroxyl syn to sulfur, is much more reluctant to fragment and does so only with the fairly vigorous reagent thionyl chloride.

In any case, these two examples clearly demonstrate that oximes of cyclic β-keto sulfides can fragment, and indeed, given the necessary geometry, fragmentation is the major pathway under Beckmann conditions. Since the thiazetine intermediate proposed by Autrey and Scullard cannot be formed in these cases, it appears to represent an unlikely pathway for the cleavage of any thioether oximes. None of the evidence reported here or in any of the earlier studies of β-keto sulfide oximes vitiates the original carbonium ion fragmentation mechanism.

Experimental Section

Melting points were determined in a Thomas-Hoover oil immersion apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian HA-100 spectrometer by Mr. C. Pape; chemical shifts are recorded in ppm (δ), with tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 237B spectrophotometer. Ultraviolet spectra were recorded on a Cary Model 15 spectrophotometer. Elemental analyses were performed at Galbraith Microanalytical Laboratories and at the University of Georgia.

2-Thiaisochroman-4-one (1). The yield of this ketone was improved by a modification of the published procedure.[21] A mixture of 20 g of benzylmercaptoacetic acid, 60 g of phosphorus pentoxide, and 30 g of Celite in 400 ml of benzene was refluxed overnight, cooled, and washed successively with water, aqueous sodium bicarbonate, and saturated brine. Concentration of the benzene solution left a light red oil which crystallized on standing; recrystallization from pentane (Norite) gave 14.4 g (80%) of colorless crystals; mp 60° (lit.[21] mp 60–61°); nmr ($CDCl_3$) δ 3.5 (2 H, s), 3.9 (2 H, s), 7.1–7.4 (3 H, m), 8.0 (1 H, m).

The oxime 2 was prepared as previously described.[22] Recrystallization from benzene–ligroin gave colorless needles: mp 134–135° (lit.[22] mp 134–135°); ir ($CHCl_3$) 3560, 3290, 3000, 2930, 1610, 1280, 950 cm^{-1}; nmr (d_6-acetone) δ 3.7 (2 H, s), 3.8 (2 H, s), 7.0–7.2 (3 H, m), 7.9 (1 H, m).

Reaction of 2-Thiaisochroman-4-one Oxime with Beckmann Reagents. (a) *p*-Toluenesulfonyl Chloride in Pyridine. A solution of 1.0 g of oxime **2** and 1.2 g of *p*-toluenesulfonyl chloride in 25 ml of pyridine was refluxed 24 hr, poured onto ice, and distributed between dilute hydrochloric acid and chloroform. The chloroform extracts were dried and concentrated to about 10 ml, then diluted with pentane until the solution became turbid. The solid which

(16) Z. W. Wolkowski, *Tetrahedron Lett.*, 825 (1971).

(17) This assignment is opposite to that which would have been made on the basis of solvent shifts. The α-methylene singlets were shifted upfield by changing the solvent from carbon tetrachloride to benzene, 6 Hz for the 96° isomer, 12 Hz for the other isomer. On the basis of the results of Karabatsos, *et al.*,[18] the 96° isomer would have been assigned the syn configuration.

(18) G. J. Karabatsos, R. A. Taller, and F. M. Vane, *J. Amer. Chem. Soc.*, **85**, 2326 (1963).

(19) (a) C. Barkenbus, J. F. Diehl, and G. R. Vogel, *J. Org. Chem.*, **20**, 871 (1955); (b) M. A. Dmitriev, P. T. Arteev, G. A. Sokol'skiĭ, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2053 (1960); *Chem. Abstr.*, **55**, 12392 (1961).

(20) M. F. Shostakovskiĭ, M. S. Rabinovich, M. M. Levitov, T. P. Verkhovtseva, E. V. Preobrazhenskaya, G. N. Kulikova, and O. A. Kalinovskiĭ, *Zh. Obshch. Khim.*, **31**, 1453 (1961); *Chem. Abstr.*, **55**, 22177 (1961).

(21) (a) A. K. Kiang and F. G. Mann, *J. Chem. Soc.*, 1909 (1951); (b) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).

(22) R. Lesser and A. Mehrlander, *Ber.*, **56**, 1642 (1923).

crystallized on standing was recrystallized from chloroform–pentane (Norite), yielding 0.81 g (81%) of colorless needles of lactam **3**; mp 218–219° (lit.[14a] mp 218–223°); uv (EtOH) λ_{max} 238 nm (ε 9000); ir 3200, 3060, 2950, 1675, 1490, 1280, 1170, 760 cm^{-1}; nmr ($CDCl_3$) δ 3.2 (2 H, s), 4.0 (2 H, s), 7.3–7.4 (4 H, m). The melting point was not depressed by admixture with an authentic sample[14a] of 3,5-dihydro-4,1-benzothiazepin-2(1*H*)-one supplied by Dr. M. Uskoković.

Concentration of the mother liquors from crystallization of the lactam left a residue which showed no nitrile absorption in the infrared.

(b) Rearrangement of the Tosylate in Aqueous Ethanol. A cold solution of 1.0 g of oxime **2** in 20 ml of acetone and 10 ml of 5% KOH was treated with 1.2 g of *p*-toluenesulfonyl chloride and refluxed 1 hr. On cooling, 1.45 g (78%) of light yellow crystals of the oxime tosylate, mp 147°, separated and was collected.

A solution of 1.0 g of the tosylate and 6 g of potassium acetate in 35 ml of water and 15 ml of ethanol was refluxed 30 hr. The solution was concentrated to remove the ethanol, diluted with water, and extracted with chloroform. Concentration of the extracts left a solid tan residue, which was recrystallized from chloroform–pentane to afford 0.35 g (65%) of colorless needles of lactam **3**, mp 218–219°, identical with the product from part a.

(c) Phosphorus Pentachloride. A solution of 1.0 g of oxime **2** in 25 ml of dry benzene was treated with 1.4 g of phosphorus pentachloride in small portions, stirred overnight at room temperature, then poured onto 100 g of ice, and extracted with chloroform. The extracts were washed with aqueous bicarbonate, dried, and concentrated, and the residue was crystallized from chloroform–pentane, yielding 0.52 g (52%) of lactam **3**, light yellow needles, mp 217–218°. The ir and nmr spectra were identical with those of the product from part a. Concentration of the mother liquors left a residue which exhibited both lactam (1675) and nitrile (2235) bands in the ir, though a pure nitrile could not be isolated.

(d) Polyphosphoric Acid. Oxime **2** (2.0 g) was stirred into polyphosphoric acid and heated at 140° for 20 min. The mixture was cooled and hydrolyzed with 200 ml of water and then extracted with chloroform. After being washed with water, the extracts were dried and concentrated, and the solid residue was recrystallized from chloroform–pentane to afford colorless needles of lactam **3**, 1.3 g (65%), mp 218°, with ir and nmr spectra identical with those of the product from part a.

(e) Thionyl Chloride. A solution of 2.0 g of oxime **2** in 25 ml of benzene was treated with 6.0 ml of thionyl chloride and stirred overnight at room temperature. The benzene and excess thionyl chloride were removed at reduced pressure and the residue was chromatographed through an alumina column. Elution with benzene yielded 1.76 g (81%) of the nitrile **5** as a colorless oil which crystallized on standing to long deliquescent needles; determination of melting point and elemental analysis was not possible because of the strong deliquescence: ir (neat) 3050, 3010, 2960, 2235, 1600, 1480, 1450, 1230, 765, 740, 685 cm^{-1}; nmr ($CDCl_3$) δ 3.9 (2 H, s), 4.5 (2 H, s) 7.1–7.3 (4 H, m).

Oxidation of Thioether 5. A solution of 2.0 g of thioether **5** in 25 ml of glacial acetic acid was added dropwise to a cooled (ice bath) solution of chromic oxide (3.0 g) in 25 ml of acetic acid. The reaction mixture was heated at 95° for 30 min, then poured into 250 ml of ice water, neutralized with 10% aqueous sodium hydroxide, and extracted with chloroform. Concentration of the extracts left a solid residue which was recrystallized from chloroform–pentane to afford 1.96 g (85%) of sulfone **6**: mp 133°; ir ($CHCl_3$) 3020, 2950, 2235, 1345, 1150 cm^{-1}; nmr ($CDCl_3$) δ 4.8 (2 H, s), 5.0 (2 H, s), 7.4–7.6 (4 H, m).

Anal. Calcd for $C_9H_8ClNO_2S$: C, 47.06; H, 3.51; N, 6.09. Found: 46.87; H, 3.49; N, 5.80.

Rearrangement of Chloro Sulfone 6. A solution of 1.0 g of chloro sulfone **6** in 20 ml of 2 *N* sodium hydroxide was refluxed 2 hr, cooled, and extracted with ether. Concentration of the dried extracts left a colorless residue which was recrystallized from chloroform to yield 0.51 g (78%) of *o*-vinylbenzamide: mp 152–153° (lit.[23] mp 154°); ir (KBr) 3340, 3170, 1655, 1620, 1400, 1125, 1000, 920, 775 cm^{-1}; nmr (acetone-d_6) δ 5.2 (1 H, q, J = 11 and 2 Hz), 5.7 (1 H, q, J = 17 and 2 Hz), 6.9–7.5 (5 H, m).

3-Thiacyclohexanone (8). This ketone was prepared as described by Leonard and Figureas:[15] bp 82–83° (4 mm) (lit. bp 80° (4 mm)); ir (neat) 2920, 1710, 1430, 1325, 1240, 960, 765 cm^{-1}; nmr (CCl_4) δ 2.4 (4 H, m), 2.8 (2 H, m), 3.1 (2 H, s).

Oxime. To a mixture of 25 g of ketone **8** and 19.3 g of hydroxylamine hydrochloride in 40 ml of water was added, with stirring, a solution of 14.5 g of anhydrous sodium carbonate in 35 ml of water. Steam was passed into the flask to melt the solid which had formed during the addition, and the mixture was stirred at room temperature for 1 hr. The solid oxime was collected and recrystallized from aqueous ethanol, giving colorless prisms: 24.2 g (84%); mp 76–77° (lit.[15] mp 77–77.5); ir (CCl_4) 3600, 3260, 2950, 2860, 1660, 1450, 950 cm^{-1}; nmr (CCl_4) δ 2.0–2.8 (6 H, m), 3.2 and 3.4 (2 H, two singlets), 9.2 (1 H, s).

Seven recrystallizations of the oxime mixture from boiling hexane (125 ml of hexane/g of oxime) gave the pure anti oxime **10**, short needles, mp 96° (19%); the melting point was not raised by further recrystallization. A small amount of ether was added in the last two recrystallizations to aid in the initial dissolution of the oxime. The number of recrystallizations required for complete purification could be decreased to five by seeding the solutions with the pure anti isomer: nmr (CCl_4) δ 2.1–2.3 (4 H, m), 2.7 (2 H, m), 3.4 (2 H, s), 9.2 (1 H, s).

Slow recrystallization of the concentrated mother liquors from crystallization of the anti oxime gave long fibrous crystals, mp 67–68°, mixed with the short needles of the anti oxime. Nmr analysis of the lower melting crystals showed they were enriched (about 70% pure) in the syn isomer (**9**), major methylene singlet at δ 3.2. No solvent system was found which would further purify the 70% syn-oxime crystals.

Reaction of 3-Thiacyclohexanone Oxime with Beckmann Reagents.

(a) Sulfuric Acid. Oxime **10** (1.0 g) was added slowly with cooling to 25 ml of concentrated sulfuric acid and kept overnight at room temperature. Ice–water (200 ml) was added and the mixture extracted with chloroform. Concentration of the dried extracts left 0.60 g of ketone **8**, identified by its ir spectrum.

(b) Polyphosphoric acid. Oxime **10** (2.0 g) was stirred into 25 ml of polyphosphoric acid; the mixture was heated at 115° for 25 min, poured onto ice, and extracted with chloroform. Concentration of the extracts left 1.7 g of ketone **8**, identified by ir.

(c) Phosphorus Pentachloride. To a solution of 1.0 g of oxime **10** in 25 ml of ether was slowly added 1.9 g of phosphorus pentachloride in small portions, causing the ether to gently reflux. The reaction mixture was stirred overnight protected from atmospheric moisture, poured onto ice, and extracted with chloroform. The extracts were washed with water, saturated sodium bicarbonate solution, and brine, then dried, and concentrated. The yellow oily residue was chromatographed over silica gel; elution with benzene–ethyl acetate gave 0.69 g (85%) of the colorless liquid mercaptal **13**, which was further purified by bulb distillation (Kügelrohr) at 155° (bath) (1 mm): ir (neat) 2940, 2250, 1450, 1425, 1260 cm^{-1}; nmr ($CDCl_3$) δ 2.0 (4 H, m), 2.5 (4 H, t, J = 7.5 Hz), 2.8 (4 H, t, J = 7.0 Hz), 3.7 (2 H, s). Satisfactory elemental analysis was not obtained.

Anal. Calcd for $C_9H_{14}N_2S_2$: C, 50.42; H, 6.59; N, 13.07. Found: C, 49.83; H, 6.76; N, 11.62.

Oxidation of Mercaptal 13. A solution of 300 mg of mercaptal **13** in 1.0 ml of glacial acetic acid was treated with 850 mg of 30% hydrogen peroxide, stirred overnight at room temperature, and concentrated at reduced pressure. Dilution of the residue with water precipitated the sulfone **14**, which was recrystallized from aqueous ethanol. A second recrystallization from chloroform yielded 320 mg (82%) of colorless plates: mp 221°; ir (KBr) 2980, 2930, 2255, 1425, 1325, 1135, 860, 775 cm^{-1}; nmr (d_6-acetone) δ 2.2 (4 H, m), 2.8 (4 H, t, J = 8 Hz), 3.6 (4 H, t, J = 7.5 Hz), 5.2 (2 H, s).

Anal. Calcd for $C_9H_{14}N_2O_4S_2$: C, 38.85; H, 5.07; N, 10.07. Found: C, 38.88; H, 5.00; N, 9.98.

(d) Thionyl Chloride. A solution of 1.0 g of oxime **10** in 20 ml of benzene was stirred overnight with 3.0 ml of thionyl chloride. The solvent and excess reagent were removed at reduced pressure, and the residue was chromatographed over alumina. Elution with benzene afforded 0.82 g (72%) of liquid chloromethyl thioether **11**: ir (neat) 3000, 2920, 2255, 1430, 1240, 750 cm^{-1}; nmr ($CDCl_3$) δ 2.0 (2 H, m), 2.5 (2 H, t, J = 7 Hz), 2.9 (2 H, t, J = 7 Hz), 4.6 (2 H, s).

The thioether was characterized by oxidation to the sulfone **12**. To a cooled solution of 2.0 g of chromic oxide in 20 ml of glacial acetic acid was slowly added a solution of 0.82 g of sulfide **11** in 15 ml of acetic acid. The mixture was heated at 95° for 30 min, diluted with 200 ml of ice–water, neutralized with 10% sodium hydroxide, and extracted with chloroform. Concentration of the extracts left a viscous oil which solidified on standing; recrystalliza-

(23) S. Negishi and Y. Tamura, *J. Polym. Sci., Part A-1*, **5**, 2911 (1967).

tion from chloroform–pentane gave 0.79 g (78%) of large colorless plates; mp 58°; ir (neat) 3000, 2940, 2260, 1420, 1320, 1150, 880, 750 cm^{-1}; nmr ($CDCl_3$) δ 2.3 (2 H, m), 2.6 (2 H, t, J = 7 Hz), 3.3 (2 H, t, J = 7 Hz), 4.5 (2 H, s).

Anal. Calcd for $C_5H_8ClNO_2S$: C, 33.06; H, 4.44; N, 7.71. Found: C, 32.88; H, 4.24; N, 7.54.

(e) *p*-Toluenesulfonyl Chloride. A solution of 1.0 g of oxime **10** and 1.8 g of *p*-toluenesulfonyl chloride in 25 ml of pyridine was stirred at room temperature for 24 hr. The reaction mixture was poured onto ice, acidified with dilute hydrochloric acid, and extracted with chloroform. After the mixture was washed with water and dried, concentration of the chloroform extracts left a residue which showed both nitrile and lactam absorption in the ir. Two recrystallizations from chloroform–pentane yielded 0.11 g (11%) of lactam **15**, colorless needles: mp 141° (lit.[20] mp 141–142.5°); ir (KBr) 3220, 2910, 1655, 1490, 1430, 1290, 1155, 950, 760 cm^{-1}; nmr ($CDCl_3$) δ 1.9–2.1 (2 H, m), 2.8 (2 H, m), 3.2 (2 H, s), 3.1–3.3 (2 H, m).

Anal. Calcd for C_5H_9NOS: C, 45.77; H, 6.91; N, 10.68. Found: C, 45.73; H, 6.89; N, 10.61.

Concentration of the filtrates from recrystallization of the lactam left an oily nitrile, whose ir and nmr spectra were identical with those of the mercaptal **13** obtained in part c.

The same product mixture of lactam and mercaptal resulted when the oxime tosylate was formed separately in acetone and aqueous sodium hydroxide at room temperature and then heated in ethanolic aqueous sodium hydroxide.

Hydrolysis of Lactam 15. A solution of 100 mg of lactam **15** in 2 ml of concentrated hydrochloric acid was heated at 100° for 2 hr. The reaction mixture, after cooling and diluting with water, deposited needles of the amino acid hydrochloride **16**, mp 138° (lit.[21] mp 137–138.5°).

Iron Carbonyl Complexes of Heptafulvene[1]

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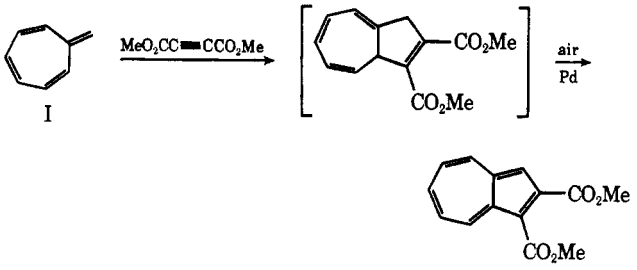
Abstract: The preparation of three iron carbonyl complexes of heptafulvene is described. (Cycloheptatrienyliumylmethyl)-π-cyclopentadienyldicarbonyliron hexafluoroantimonate (IIa) has been prepared from 7-(hydroxymethyl)cycloheptatriene (IV) by preparation of the benzenesulfonate ester, displacement by cyclopentadienyldicarbonyliron anion, and hydride removal. 1,6,7,8-*Tetrahapto*heptafulveneiron tricarbonyl (VII) has been prepared by reaction of IV with diiron nonacarbonyl, followed by distillation at 115°. Further reaction with diiron nonacarbonyl gave heptafulvenediiron hexacarbonyl (XIII). VII appears to be more stable than its 1,2,3,4-h^4 isomer, IXa.

Heptafulvene (I) is one of a group of unsaturated hydrocarbons known as fulvenes, many of which are not isolable because of their high reactivity toward oxygen or tendency to polymerize.[2] In many cases, however, fulvenes can be stabilized as ligands in transition metal complexes.[3]

Heptafulvene was first prepared by Doering and Wiley,[4] who found it to be unisolable even at −80°. It polymerized quickly on contact with acids; the only other reactions reported were hydrogenation to methylcycloheptane and cycloaddition with dimethyl acetylenedicarboxylate. A variety of derivatives of I having



electron-withdrawing groups on the exocyclic carbon have also been prepared.[5] These are generally unstable substances which decompose on warming or on exposure to air. Nonetheless, fairly extensive studies of their chemistry have been made.[5,6]

It appeared to be of value to prepare a stable transition metal derivative of I, from which I itself might be liberated to allow more thorough study of its properties.[7] Moreover, the polyene system of I appeared to offer a variety of sites for metal coordination, so that the organotransition metal complexes themselves were expected to possess interesting properties.

Since acid-catalyzed polymerization of I is thought to involve protonation of the exocyclic double bond,[4] we first sought to prepare a complex in which that re-

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(4) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960); D. W. Wiley, Ph.D. Thesis, Yale University, Sept 1954.

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