

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD RESEARCH INSTITUTE]

Some Nitrogen-Containing Ferrocene Derivatives

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The preparation of several derivatives of ferrocenylamine and a number of *N*-substituted ferrocenecarboxamides is described.

A number of *N*-substituted ferrocenecarboxamides and ferrocenylamine derivatives were prepared for evaluation as high-temperature antioxidants. It had been found¹ that *N*-phenylferrocenecarboxamide inhibited oxidative gelation of a dimethylsilicone fluid, and it was of interest to investigate other ferrocenecarboxamides. Furthermore, many aromatic amines are known to be effective antioxidants, and it seemed possible that if the ferrocene system possessed oxidation-inhibiting properties, ferrocenylamine and its derivatives might show enhanced antioxidant activity.

Two syntheses of ferrocenylamine have been published. One involves lithiation of ferrocene and treatment of ferrocenyllithium with benzyloxyamine.² The other method proceeds through the azide of ferrocenecarboxylic acid, subsequent rearrangement to the isocyanate (isolated from benzyl alcohol as the benzylurethan), and reductive cleavage to the amine.³ Neither method appeared attractive because of poor over-all yields. Consequently, the following possibilities were examined briefly: nitration of ferrocene using (a) fuming nitric acid in glacial acetic acid⁴ at -10° , (b) nitric acid and urea;⁵ nitrosation using (a) ferrocene and sodium nitrite in acetic acid, (b) chloromercuriferrocene⁶ in chloroform with butyl nitrite and hydrochloric acid,⁷ and with gaseous nitrosyl chloride,^{8,9} (c) ferrocenyllithium with nitrosyl chloride^{8,9} in ether. In each case, oxidation to the blue ferricinium salt took place, and only ferrocene was recovered on reduction.

Minor changes in the published procedures for ferrocenylamine afforded some improvement in yield. The reaction between ferrocenyllithium and

benzyloxyamine in our hands gave less than a 1% yield over-all from ferrocene. By substitution of methoxyamine for benzyloxyamine, the over-all yield of ferrocenylamine was increased to 8%, or 28% based on the amount of ferrocene recovered in the lithiation step. Preparation of ferrocenylamine from ferrocenecarboxylic acid by the Curtius rearrangement was also improved by use of milder conditions in the preparation of ferrocenecarboxylic acid chloride and in the hydrogenolysis of ferrocenylamine benzylurethan. The over-all yield of ferrocenylamine by this method was 18% from ferrocenecarboxylic acid, or 7% from ferrocene.

Ferrocenylamine was converted into *N*-ferrocenyl-*p*-toluenesulfonamide in 74% yield by treatment with a slight excess of *p*-toluenesulfonyl chloride in pyridine. 1,3-Diferrocenylurea was obtained in 24% yield by treating ferrocenylamine in pyridine solution with a $1/2$ -molar equivalent of phosgene dissolved in benzene. Reaction of ferrocenylamine in pyridine solution with ferrocenecarboxylic acid chloride in benzene afforded 22% of *N*-ferrocenylferrocenecarboxamide.

It was found that amides of ferrocenecarboxylic acid were best prepared from ferrocenecarboxylic acid chloride by reaction with a molar equivalent of amine in pyridine or an excess of amine in refluxing toluene. Using these methods, amides were prepared from 2-aminothiazole, morpholine, ethanolamine, phenothiazine, and *N*-phenyl-*N*-1-naphthylamine, as well as from ferrocenylamine. In the preparation of 10-(ferrocenylcarbonyl)phenothiazine a second product with the same composition was also obtained. Presence of N—H absorption in the infrared, and carbonyl absorption comparable to that of benzoylferrocene, suggested that carbon-acylation may have occurred to form an isomeric ferrocenylcarbonylphenothiazine. An attempt to prepare *N*-2-thiazolylferrocenecarboxamide directly from ferrocenecarboxylic acid and 2-aminothiazole by the phosphazo reaction¹⁰ resulted in the formation of only 8% of the amide and the recovery of 60% of unreacted acid.

The main product from attempts to condense ferrocenecarboxylic acid and 2-aminothiazole by treatment with dicyclohexylcarbodiimide in chloroform solution was 1-ferrocenylcarbonyl-1,3-dicyclo-

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(5) W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **77**, 68 (1955).

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hexylurea, the adduct between the acid and the carbodiimide. Ferrocenecarboxylic anhydride (20%) and a small amount of ferrocenecarboxylic acid were also obtained, but none of the amide. The anhydride was identified by comparison with a sample of authentic ferrocenecarboxylic anhydride, prepared in 56% yield by treating ferrocenecarboxylic acid chloride with water in pyridine solution.¹¹ Attempted condensation of ferrocenecarboxylic acid and 2-aminothiazole with dicyclohexylcarbodiimide in acetonitrile solution afforded 1-ferrocenylcarbonyl-1,3-dicyclohexylurea in 86% yield.

EXPERIMENTAL¹²

Ferrocenecarboxylic acid. Although ferrocenecarboxylic acid is available by several synthetic routes,¹³ it was most easily obtained by lithiation of ferrocene in a tetrahydrofuran-ether mixture and carbonation of the lithium salt.¹⁴ The yield was 37%, or 47% based on recovered ferrocene. A 32% yield of the insoluble 1,1'-ferrocenedicarboxylic acid was also obtained.

Ferrocenecarboxylic acid chloride. To a stirred solution of 0.23 g. (0.0011 mole) of phosphorus pentachloride in 2.5 ml. of dry benzene, 0.23 g. (0.0010 mole) of ferrocenecarboxylic acid was added, and stirring at room temperature was continued for 2 hr. with exclusion of atmospheric moisture. The mixture was then decanted and concentrated at 25–30° to remove benzene and phosphorus oxychloride. The acid chloride, obtained as a residual dark oil, was dissolved in benzene or other suitable solvent, and the solution was decanted and used directly for acylation.

Ferrocenylamine from ferrocenecarboxylic acid azide. The procedure of Arimoto and Haven³ was used with minor modifications. Ferrocenecarboxylic acid chloride, prepared as described above, was converted to the acid azide. The yield of azide based on ferrocenecarboxylic acid used was 38%. Ferrocenylamine benzylurethan was obtained in 65% yield upon rearrangement of the azide in benzyl alcohol; it was purified by chromatography on alumina in benzene followed by recrystallization from a mixture of ether and petroleum ether. Reductive cleavage of the urethan (m.p. 113–114°) was accomplished at low pressures. A 5% palla-

dium-on-carbon catalyst (0.20 g.) was added to a solution of 2.70 g. (0.00806 mole) of ferrocenylamine benzylurethan in 80 ml. of absolute ethanol. The mixture was shaken under hydrogen at 50 p.s.i. for 2 hr. at 25° and then at 45° for 2 hr. The solution was filtered, the filtrate was taken to dryness under reduced pressure, and the solid residue was dissolved in 25 ml. of ether. The ether solution was extracted with three 5-ml. portions of 1*N* hydrochloric acid. The aqueous extracts were filtered and then made basic with potassium hydroxide. The precipitate which formed was separated by filtration and dried *in vacuo*, giving 1.28 g. (84%) of crude ferrocenylamine, m.p. 127–137°. Recrystallization from ligroin afforded 1.15 g., m.p. 145–153°. Infrared absorption maxima at 2.95 μ , 6.20 μ , and 6.68 μ corresponded to those reported.³

Ferrocenylamine from ferrocenyllithium. A solution of 13.0 g. (0.070 mole) of ferrocene in 200 ml. of anhydrous tetrahydrofuran was cooled to –30° under a nitrogen atmosphere, and a solution of 0.21 mole of butyllithium in 160 ml. of ether was added dropwise during 25 min. The mixture was stirred for 2 hr. at 0° and 4 hr. at 25°. A solution of 10.3 g. (0.22 mole) of methoxyamine in 75 ml. of anhydrous ether was added dropwise during 30 min. while the reaction mixture was stirred at –20°. The mixture was allowed to warm gradually to room temperature and stirred for 4 hr. Then 10% hydrochloric acid was added slowly with stirring until a pH of 2 was attained in the aqueous layer. The ether layer was separated, dried over magnesium sulfate, and evaporated to give 9.5 g. of ferrocene (73% recovery) after recrystallization from benzene. The aqueous layer was made strongly basic with potassium hydroxide solution, and the precipitate which formed was extracted into ether. The ether extracts were in turn extracted with 2*N* hydrochloric acid, and the acidic solution was made basic as before and again extracted with ether. The final ether extracts were dried over magnesium sulfate and evaporated to a brown solid residue. Recrystallization of this material from an ether-petroleum ether mixture afforded 1.06 g. of ferrocenylamine (8%, or 28% based on the amount of ferrocene recovered), m.p. 140–145°. The infrared spectrum was identical to that reported above. Sublimation at 70° (2 mm.) separated a few mg. of nonvolatile material having essentially the same infrared spectrum; this may have been diaminoferrocene, but was not characterized. The sublimed ferrocenylamine had m.p. 147–152° (lit.^{3,2} m.p. 151–155°, 153–155°).

***N*-Ferrocenyl-*p*-toluenesulfonamide.** A solution of 0.080 g. (0.00040 mole) of ferrocenylamine in 0.8 ml. of pyridine was treated with 0.095 g. (0.00050 mole) of *p*-toluenesulfonyl chloride and the mixture was heated for 1 hr. on the steam bath. On addition of water (5 ml.) to the cooled solution, a dark oil separated which solidified after a few minutes standing. This dark solid was separated by filtration and crystallized from a mixture of benzene and ligroin to give 0.105 g. (74%) of *N*-ferrocenyl-*p*-toluenesulfonamide, m.p. 168–174°. After two recrystallizations from a benzene-ligroin mixture, 0.085 g. of material was obtained, m.p. 177–179°. The infrared spectrum showed a strong $\text{—SO}_2\text{—}$ absorption at 8.58–8.65 μ and N—H absorption at 3.05 μ .

Anal. Calcd. for $\text{C}_{17}\text{H}_{17}\text{FeNO}_2\text{S}$: C, 57.48; H, 4.82; Fe, 15.72. Found: C, 57.76; H, 4.89; Fe, 15.65.

1,3-Diferrocenylurea. A solution of 0.240 g. (0.0012 mole) of ferrocenylamine in 1.5 ml. of pyridine was cooled to 5°, and a benzene solution (0.95 ml.) containing 0.059 g. (0.00060 mole) of phosgene was added dropwise with stirring. After addition was complete, the mixture was allowed to stand for 60 hr. at room temperature. Water (5 ml.) was added and the mixture was extracted with three 5-ml. portions of chloroform. The combined chloroform extracts were dried over magnesium sulfate, filtered, and concentrated to a solid residue. Crystallization of this material from a benzene-chloroform mixture afforded 0.061 g. (24%) of crude 1,3-diferrocenylurea, which was recrystallized from methanol. 1,3-Diferrocenylurea did not melt below 250°. The

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(12) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Under these conditions, ferrocene exhibits a liquid crystal region from about 140° to 173°, where true melting is observed by sudden decrease in viscosity and loss of birefringence. This phenomenon seems not to have been reported, probably because the rapid sublimation of ferrocene near the melting point makes its observation by this method difficult. Infrared spectra were determined on KBr disks with a Perkin-Elmer spectrophotometer, model 21, and on a Beckman spectrophotometer, model IR4. All the compounds prepared in this study were monosubstituted ferrocene derivatives; most showed infrared bands at 3.22–3.27 μ due to aromatic C—H bands, at 9.00–9.08 μ and 9.97–10.03 μ characteristic of monosubstitution, and weak maxima or shoulders at 7.07–7.10 μ . The few exceptions are mentioned along with the bands listed as characteristic for each compound.

(13) (a) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 484 (1957); K. L. Rinehart, Jr., K. L. Motz, and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957); (b) P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson, and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

(14) D. W. Mayo, P. D. Shaw, and M. Rausch, *Chem. and Ind.*, 1388 (1957).

infrared spectrum showed prominent amide absorption maxima at 6.04 μ and 6.35 μ and N—H absorption at 3.05 μ .

Anal. Calcd. for $C_{21}H_{20}Fe_2N_2O$: C, 58.91; H, 4.71. Found: C, 58.57; H, 5.03.

N-Ferrocenylferrocenecarboxamide. Ferrocenecarboxylic acid chloride obtained from 0.092 g. (0.00040 mole) of the free acid was dissolved in 0.5 ml. of benzene and added slowly to a solution of 0.080 g. (0.00040 mole) of ferrocenylamine in 0.5 ml. of pyridine. A brown precipitate formed immediately. The mixture was allowed to stand overnight and then heated on a steam bath for 45 min. The precipitate was separated by filtration and dissolved in chloroform. A small amount of chloroform-insoluble material was removed by filtration. Upon extraction of the chloroform solution with 2% sodium bicarbonate solution and acidification of the extracts, 0.023 g. (25%) of unreacted ferrocenecarboxylic acid was recovered. The extracted chloroform solution was dried and concentrated to a solid residue which was recrystallized from benzene, then from methanol, giving 0.035 g. (22%) of *N-ferrocenylferrocenecarboxamide*. This compound did not melt below 300°. The infrared spectrum showed amide absorption bands at 6.10 μ and 6.40 μ , and an N—H band at 3.03 μ . *N-Ferrocenylferrocenecarboxamide* ignited on combustion for microanalysis; the low values obtained for carbon may be explained by this fact.

Anal. Calcd. for $C_{21}H_{18}Fe_2NO$: C, 61.03; H, 4.65; N, 3.39. Found: C, 60.35, 60.16; H, 4.89, 4.88; N, 3.64.

N-2-Thiazolylferrocenecarboxamide. Ferrocenecarboxylic acid chloride prepared from 0.092 g. (0.00040 mole) of the acid was dissolved in 0.5 ml. of benzene and added to a solution of 0.040 g. (0.00040 mole) of 2-aminothiazole in 0.5 ml. of pyridine. After the mixture was allowed to stand at room temperature for 40 hr., 5 ml. of 2*N* hydrochloric acid and 5 ml. of benzene were added. The benzene layer was separated, the aqueous layer was extracted twice with 5-ml. portions of benzene, and the benzene solutions were combined. Extraction of the benzene solution with 2% sodium carbonate solution permitted the recovery of 0.010 g. of ferrocenecarboxylic acid. The extracted benzene solution was dried over magnesium sulfate, filtered and concentrated to a solid residue. The solid was recrystallized from ligroin, and 0.046 g. (37%) of *N-2-thiazolylferrocenecarboxamide*, m.p. 183–188°, was obtained. After further recrystallization from aqueous methanol, the product melted at 190.5–192.0°. The infrared spectrum showed amide bands at 6.05 μ and 6.53 μ ; N—H absorption was observed at 2.92 μ . The characteristic C—H band¹² near 3.25 μ was obscured by broad absorption in this region.

Anal. Calcd. for $C_{14}H_{15}FeN_2OS$: C, 53.86; H, 3.88; Fe, 17.9. Found: C, 54.10; H, 4.08; Fe, 17.5.

4-(Ferrocenylcarbonyl)morpholine was obtained by the above procedure using ferrocenecarboxylic acid chloride prepared from 0.69 g. (0.0030 mole) of acid and 0.30 g. (0.0035 mole) of morpholine in 2.0 ml. of pyridine. Extraction with benzene and recrystallization from ligroin gave 0.35 g. (39%) of amide, m.p. 127.5–130°. The infrared spectrum showed strong amide absorption at 6.20 μ . The band at 10.0 μ characteristic of monosubstituted ferrocene¹² was partially obscured in this compound by a maximum at 9.93 μ .

Anal. Calcd. for $C_{16}H_{17}FeNO_2$: C, 60.22; H, 5.73. Found: C, 60.36; H, 5.79.

N-[2-(Ferrocenylcarboxy)ethyl]ferrocenecarboxamide was obtained by the same procedure (for *N-2-thiazolylferrocenecarboxamide*) using ferrocenecarboxylic acid chloride prepared from 0.92 g. (0.0040 mole) of acid and 0.098 g. (0.0016 mole) of ethanolamine in 2.5 ml. of pyridine. The product precipitated on acidification of the reaction mixture. Extraction of the mixture with benzene recovered 14% of ferrocenecarboxylic acid. The solid product was extracted with chloroform and 0.18 g. (10%) of amide, m.p. 202–204°, was obtained after recrystallization from methanol. The infrared spectrum showed amide bands at 6.13 μ and 6.53 μ and ester carbonyl absorption at 5.86 μ .

Anal. Calcd. for $C_{21}H_{22}Fe_2NO_2$: C, 59.42; H, 4.78. Found: C, 59.13; H, 5.00.

N-Phenyl-N-1-naphthylferrocenecarboxamide. Ferrocenecarboxylic acid chloride, prepared from 0.92 g. (0.0040 mole) of the acid, was dissolved in 15 ml. of toluene and treated with 1.75 g. (0.0080 mole) of *N*-phenyl-1-naphthylamine. The mixture was heated under reflux for 4 hr., then concentrated to remove the solvent. The residue was triturated with ether to remove unreacted amine. After several recrystallizations of the ether-insoluble material from benzene, 0.35 g. (20%) of *N-phenyl-N-1-naphthylferrocenecarboxamide* was obtained, m.p. 237–240°. The infrared spectrum showed amide carbonyl absorption at 6.13 μ .

Anal. Calcd. for $C_{27}H_{21}FeNO$: C, 75.18; H, 4.91. Found: C, 75.42; H, 4.88.

10-(Ferrocenylcarbonyl)phenothiazine. A toluene solution (15 ml.) of ferrocenecarboxylic acid chloride prepared from 0.99 g. (0.0043 mole) of acid was treated with 1.71 g. (0.0086 mole) of phenothiazine as described for *N-phenyl-N-1-naphthylferrocenecarboxamide*. The residue, after removal of toluene, was dissolved in benzene and separated into 3 components by chromatography on 20 g. of alumina. Elution with benzene afforded 0.80 g. of unreacted phenothiazine, followed in a second fraction by 0.55 g. of 10-(ferrocenylcarbonyl)phenothiazine (30%), m.p. 163–165° after recrystallization from methanol. The infrared spectrum showed amide carbonyl absorption at 6.12 μ .

Anal. Calcd. for $C_{23}H_{17}FeNOS$: C, 67.17; H, 4.16; S, 7.81. Found: C, 67.33; H, 4.27; S, 7.65.

Elution of the chromatogram with 10% ether in benzene afforded an isomeric product, which was recrystallized from ether, m.p. 203–204°. That acylation of an aromatic ring in phenothiazine may have occurred to give a ferrocenyl ketone was suggested by the infrared spectrum. Presence of a band at 3.01 μ identical with the N—H band in phenothiazine indicated absence of reaction on the nitrogen. Absorption at 6.27 μ and 6.38 μ due to aromatic unsaturation in phenothiazine was also present, as well as the characteristic ferrocene bands¹² at 3.25 μ , 7.08 μ , 9.05 μ , and 10.00 μ . A strong band at 6.17 μ compared favorably with the ketone carbonyl absorption of benzoylferrocene at 6.13 μ .¹⁵

Anal. Calcd. for $C_{23}H_{17}FeNOS$: C, 67.17; H, 4.16; S, 7.81. Found: C, 66.91; H, 4.39; S, 7.34; 7.42.

Ferrocenecarboxylic anhydride. Ferrocenecarboxylic acid chloride, obtained from 0.23 g. (0.0010 mole) of the free acid, was dissolved in 7.5 ml. of dry benzene. The solution was cooled to 5–10°, and 1.0 ml. of pyridine was added dropwise, followed by the addition of 0.10 ml. of water to the cold solution.¹¹ The solution was agitated for 30 min., allowed to stand overnight, and filtered. The filtrate was washed with *N* hydrochloric acid to remove pyridine until the aqueous wash solutions were strongly acidic (pH 2). The benzene solution was washed with four 6-ml. portions of 1% aqueous sodium carbonate to remove ferrocenecarboxylic acid. After acidification of the basic solutions and extraction with ether, 0.055 g. of ferrocenecarboxylic acid (24%) was recovered from the ether extracts. The extracted benzene solution was washed with water and dried over magnesium sulfate. Filtration and evaporation of the solution afforded a dark reddish oil which crystallized on standing. After recrystallization from ligroin, 0.123 g. (56%) of ferrocenecarboxylic anhydride was obtained, m.p. 140–142°, m.p. 143–145° after further recrystallization. The infrared spectrum showed strong carbonyl absorption bands at 5.67 and 5.84 μ . The monosubstituted ferrocene band¹² near 10.0 μ was obscured by a maximum at 9.90 μ . A strong and distinct band at 8.06 μ was assigned tentatively to the C—O—C grouping, although the band was displaced from the expected range.

Anal. Calcd. for $C_{22}H_{18}Fe_2O_3$: C, 59.77; H, 4.10. Found: C, 60.06; H, 4.34.

(15) N. Weliky and E. S. Gould, *J. Am. Chem. Soc.*, **79**, 2742 (1957).

1-Ferrocenylcarbonyl-1,3-dicyclohexylurea. A solution of 0.046 g. (0.00020 mole) of ferrocenecarboxylic acid in 5 ml. of acetonitrile was treated with 0.020 g. (0.00042 mole) of 2-aminothiazole, followed by 0.043 g. (0.00042 mole) of dicyclohexylcarbodiimide. An orange-brown crystalline solid began to crystallize from the solution after standing 1 hr. at room temperature. After 20 hr., 1 drop of glacial acetic acid was added (to destroy any unreacted carbodiimide) and the mixture was filtered. Unreacted 2-aminothiazole (0.20 g.) was recovered from acidic extracts of the filtrate. The filtrate was concentrated to an orange-brown solid which was combined with the precipitate collected on the filter. The combined product was recrystallized from aqueous methanol and from ligroin to give 0.075 g. (86%) of 1-ferrocenylcarbonyl-1,3-dicyclohexylurea, m.p. 171–172°.

Anal. Calcd. for $C_{24}H_{32}FeN_2O_2$: C, 66.05; H, 7.39; N, 6.42. Found: C, 66.32; H, 7.59; N, 6.50.

The infrared spectrum showed N—H absorption at 3.05 μ and carbonyl absorption at 6.20 μ , but a strong band at 5.89 μ could not be assigned with certainty.¹⁶

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(16) The identity of the compound was verified by comparison with the spectrum of an authentic sample¹⁷ of 1-benzoyl-1,3-dicyclohexylurea, which also showed a strong band at 5.88 μ and N—H absorption at 3.02 μ , although the carbonyl peak was at 6.07 μ . Both compounds showed aromatic CH absorption at 3.25 μ , CH_2 bands at 3.42 μ and 3.50 μ , and unassigned maxima at 6.48–6.53 μ , 6.88 μ , 8.11 μ , and 11.21 μ . 1-Ferrocenylcarbonyl-1,3-dicyclohexylurea showed an additional peak at 2.93 μ which was not assigned.

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[CONTRIBUTION NO. 113 FROM THE INSTITUTO DE QUÍMICA DE LA UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO]

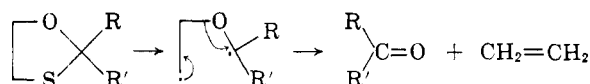
Desulfuration Experiments with 1,3-Oxathiolan-5-ones

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By condensation of mercaptodiphenylacetic acid with several aldehydes and ketones, 1,3-oxathiolan-5-ones were prepared, and by desulfuration with Raney nickel the original carbonyl compound was regenerated. When an electron attracting group is present in alpha position to the oxathiolanone ring, diphenylacetic ester is formed. Diphenylketene or the corresponding biradical is regarded as the probable intermediate in the desulfuration mechanism.

It has been shown¹ that on desulfuration of oxathiolanes formed by condensation of β -mercaptoethanol with steroidal ketones the original carbonyl compound is regenerated and the β -mercaptoethanol moiety is converted to ethylene or ethylene derivatives by the following mechanism:



On the other hand no ethyl ether was obtained.

Later Djerassi *et al.*^{2,3} studied this reaction in more detail by carrying out the condensation of β -mercaptoethanol derivatives with several additional ketones. Following desulfuration they isolated the moieties corresponding to the original carbonyl compound and to the β -mercaptoethanol derivative. In polar solvents these authors found an introduction of oxygen in the β -mercaptoethanol moiety^{2,3} whereas in benzene as the solvent the corresponding ethylenes or ethanes are obtained due to fission and rearrangement of the intermediate 1,4-biradical.¹ On the other hand, Jaeger and

Smith⁴ have described a saturation of the 1,4-biradical yielding the ethyl ether when there is an electron attracting group in the alpha position to the oxathiolane ring.

The above mentioned results stimulated us to study the influence of a carbonyl group in the oxathiolane ring on the course of the desulfuration reaction.

Diphenyl substituted oxathiolanones can be prepared conveniently by condensation of mercaptodiphenylacetic acid (I) with carbonyl compounds.⁵ Several 1,3-oxathiolan-5-ones have been prepared in this manner by Bistrzycki and Brenken.⁶ Using *p*-toluenesulfonic acid as the condensing agent, we have prepared the previously reported 2,4,4 triphenyloxathiolan-5-one (IIa).⁶ 9-Anthraldehyde⁷ yielded 2(9-anthryl), 4,4-diphenyl-1,3-oxathiolan-5-one (IIb). This yellow substance has the interesting property that when exposed to sunlight the crystals become bluish green and change back to yellow immediately when returned to dim light. This phenomenon can be repeated several times but the intensity of the color change gradually decreases until the substance remains

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(4) R. A. Jaeger and H. Smith, *J. Chem. Soc.*, 160 (1955).

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