analytical data it was considered to be 4-thiochrom-one-2-carboxylic acid, lit.[14] mp 234–235°.

Registry No.—**2**, 16808-50-7; **3**, 16723-50-5; **4**, 16723-52-7; **5**, 16723-53-8; **6**, 16723-54-9; **7**, 16723-55-0; **8**, 16723-56-1; **9**, 16723-57-2; **10**, 16723-58-3; **11a**, 16723-59-4; **11b**, 2765-44-8; **12a**, 16723-60-7; **13a**, 16723-61-8; **13b**, 16723-68-5; **15a**, 16723-62-9; **16a**, 16723-63-0; **17a**, 16723-64-1; **18a**, 16723-65-2; **19b**, 16723-69-6; **20a**, 16723-66-3; 8-carbomethoxythiochroman-4-one, 16723-70-9; β-(2-carbomethoxythiophenoxy)propionic acid, 16723-72-1; 4-thiochromone-2-carboxylic acid, 16723-71-0.

Acknowledgment.—The authors gratefully acknowledge financial support of this work by the National Research Council of Canada and the Department of University Affairs for the Province of Ontario.

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[14] J. Schmutz, M. Lauener, R Hirt, and M. Sanz, *Helv. Chim. Acta*, **34**, 767 (1951).

Chemistry of Aliphatic Disulfides. XVII. Studies on the Alkoxide Cleavage of 3,6-Dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione[1,2]

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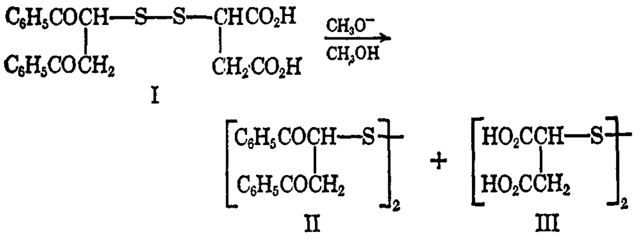
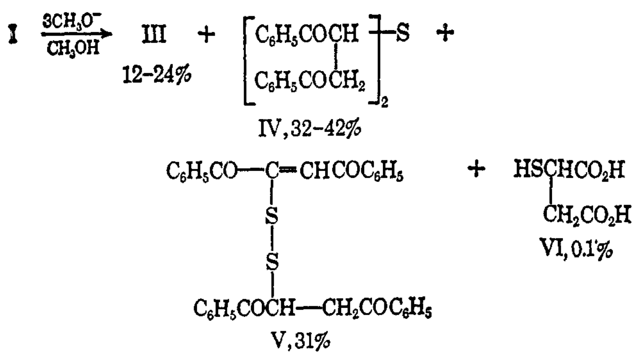
Treatment of 3,6-dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II) with potassium ethoxide in ethanol provides 3,5-dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV) and potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VII) as the major products. A mechanism for cleavage of II involving α elimination of a mercaptide is proposed. Compound II is shown to be formed by disulfide interchange during the alkoxide cleavage of 6,7-dibenzoyl-3-carboxyl-4,5-dithiaheptanoic acid (I).

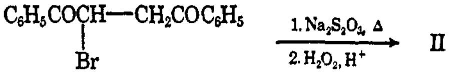
In a previous study,[4] the alkoxide cleavage of 6,7-dibenzoyl-3-carboxy-4,5-dithiaheptanoic acid (I) was examined. The products (III–V) formed by the action of 3 equiv of methoxide ion on I suggested that I was initially converted into 3,6-dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II) and 2,2′-dithiosuccinic acid (III). Although II could not be isolated, its presence was implied by the formation of IV and V, which were presumably produced by the action of methoxide ion on II. Since III was present as the tetrasodium salt, further cleavage of the negatively charged disulfide by methoxide should be minimal and indeed III was isolated in reasonable yield.





Although the mechanism for base-catalyzed disulfide interchange (I → II + III) has not been rigorously established, the process probably involves the direct attack of base on the sulfur–sulfur bond rather than initial abstraction of hydrogen atoms α or β to the disulfide bond. The further decomposition of II, however, seemed likely to involve α and/or β elimination of mercaptide.[5,6] Thus a study of the action of alkoxide on II might be expected to provide data on the relative importance of these two pathways and give some indication of the favored route for base-catalyzed decomposition of symmetrical and unsymmetrical disulfides.

Ethoxide Cleavage of II.—The desired substrate, II, was prepared by oxidation of the corresponding Bunte salt. The oxidation provided a mixture of diastereoisomers which were readily separated by fractional recrystallization to give a 49% yield of an isomer, mp 115–116°, and a 14% yield of an isomer, mp 137°. Both isomers were cleaved by the action of alkoxide under similar conditions and no significant differences in product analysis were observed.



Treatment of II with 1 equiv of potassium ethoxide in ethanol provided 3,5-dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV) in 71.6% yield and potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VII) in

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[1] This investigation was supported by Public Health Service Fellowship 5-F3-GM-31, 871-02, and by Research Grant RG-7966 from the National Institute of General Medical Sciences, U. S. Public Health Service.

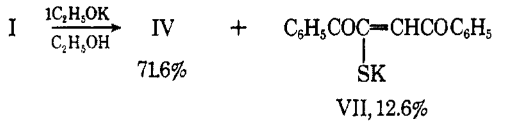
[2] For part XVI of the series, see R. G. Hiskey and A. J. Dennis, *J. Org. Chem.*, **33**, 563 (1968).

[3] Special Fellow, National Institute of General Medical Sciences, 1967–1968.

[4] R. G. Hiskey and J. A. Kepler, *ibid.*, **29**, 3678 (1964).

[5] N. A. Rosenthal and G. Oster, *J. Soc. Cosmet. Chem.*, **5**, 286 (1954); *J. Amer. Chem. Soc.*, **83**, 445 (1961); J. P. Danehy and J. A. Kreuz, *ibid.*, **83**, 1109 (1961); D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 1 (1951); J. M. Swan, *Nature*, **179**, 965 (1957).

[6] The reaction of water-soluble disulfides with aqueous alkali has recently been studied by J. P. Danehy and W. E. Hunter, *J. Org. Chem.*, **32**, 2047 (1967).

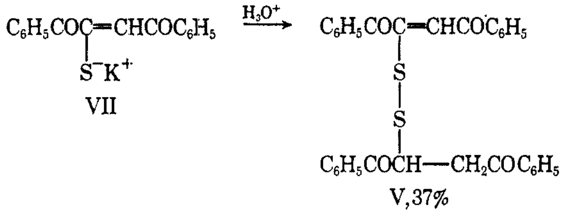


$$\mathrm{I}\xrightarrow[C_2H_5OH]{1C_2H_5OK}\underset{71.6\%}{\mathrm{IV}} + \underset{\text{VII, 12.6\%}}{C_6H_5CO\underset{SK}{C}{=}CHCOC_6H_5}$$

12.6% yield. When the added base concentration was increased to 2 equiv of ethoxide per equivalent of disulfide, 1,4-diphenyl-1,4-butanedione (VIII) was isolated in 30.8% yield. Under these conditions the yield of IV was reduced to 16.1% and the yield of VII increased to 40.3%.

$$\mathrm{I}\xrightarrow[C_2H_5OH]{2C_2H_5OK}\underset{16.1\%}{\mathrm{IV}} + \underset{40.3\%}{\mathrm{VII}} + \underset{\text{VIII, 30.8\%}}{C_6H_5COCH_2CH_2COC_6H_5}$$

Comparison of the cleavage of II, using 1 equiv of ethoxide, with the previous data obtained by cleavage of I[4] indicated that substantial amounts of the sulfide, IV, were produced in each case. However, cleavage of I provided significant amounts of the unsymmetrical disulfide, V, whereas the enethiolate, VII, was obtained in the present investigation. This apparent discrepancy was resolved by examination of the work-up procedures used in the two reactions. In the present investigation VII was obtained after the aqueous extract of the reaction mixture was adjusted to pH 9 using carbon dioxide; in our earlier studies V resulted by neutralization of the aqueous extract with hydrochloric acid. Thus VII is a likely precursor of V. Evidence for this relationship was obtained by neutralization of VII with dilute hydrochloric acid; under these conditions V was produced in 37% yield. Dimerizations of this type involving the enol and keto forms of thioketones have been previously reported for thioketones containing electron-withdrawing groups.[7]



$$\underset{\text{VII}}{C_6H_5CO\underset{S^-K^+}{C}{=}CHCOC_6H_5}\xrightarrow{H_3O^+}\underset{\text{V, 37\%}}{\begin{array}{c}C_6H_5COC{=}CHCOC_6H_5\\ |\\ S\\ |\\ S\\ |\\ C_6H_5COCH{-}CH_2COC_6H_5\end{array}}$$

Methoxide Cleavage of I.—When I was treated with 3 equiv of potassium methoxide in methanol and the aqueous extract of the cleavage mixture adjusted to pH 9 with carbon dioxide, the enethiolate VII was obtained in 33% yield. In addition, VIII, which was not reported in the previous studies, was isolated in 5% yield.

$$\mathrm{I}\xrightarrow[CH_3OH]{3CH_3O^-}\underset{62\%}{\mathrm{III}} + \underset{38\%}{\mathrm{IV}} + \underset{33\%}{\mathrm{VII}} + \underset{5\%}{\mathrm{VIII}} + H_2S$$

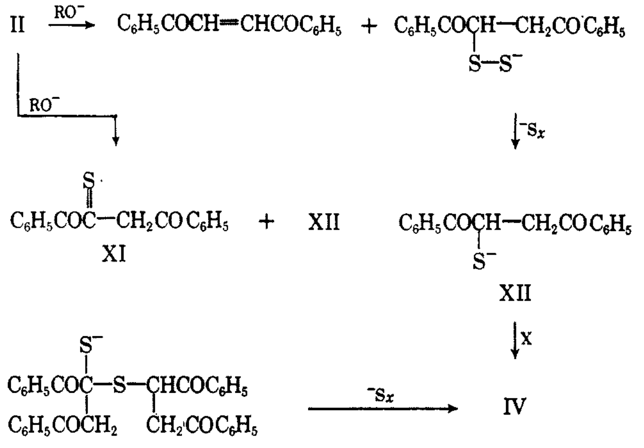
In order to obtain additional evidence on the possible formation of II, during the first stage of the alkoxide decompostion of I, cleavages of I using varying amounts of methoxide were followed by thin layer chromatography. The following information was obtained from the chromatograms: (1) I did not undergo either disulfide interchange or cleavage with 2 or less equiv of methoxide; (2) disulfide interchange of I to provide the symmetrical disulfide II occurred rapidly at methoxide levels greater than 2 equiv and the subsequent cleavage of II occurred at a slightly slower rate; and (3) disulfide interchange could be initiated by treatment of I with 2 equiv of methoxide and catalytic amounts of either the sodium salt of VI or 2-mercapto-1,4-diphenyl-1,4-butanedione (IX).

Additional evidence for disulfide interchange occurring during the alkoxide treatment of I was obtained by quenching the reaction with dilute hydrochloric acid after 5 min; II was isolated in 15.6% yield along with a 12.5% yield of the sulfide IV and 30.7% recovery of starting disulfide I.

$$\mathrm{I}\xrightarrow[2.\ HCl]{1.\ 3NaOCH_3,\ CH_3OH}\underset{15.6\%}{\mathrm{II}} + \underset{12.5\%}{\mathrm{V}}$$

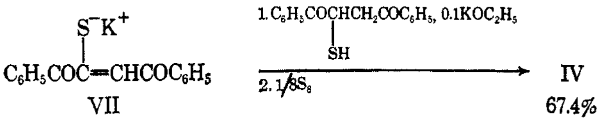
Alkoxide Cleavage of II.—Although the sulfide IV would be the expected product by either α or β elimination of a mercaptide from II, the intermediates in the two pathways could be distinguished (Scheme I). β elimination would proceed *via* 1,4-diphenyl-2-butene-1,4-dione (X), whereas α elimination would generate the thio ketone XI and the mercaptide XII.

SCHEME I



Attempts to isolate X or to detect the substance by thin layer chromatograms of the reaction mixture failed. Attempts to detect 1,4-dibenzoyl-2,6-diphenyl-6-hydroxyfulvene, which is usually a product when *trans*-1,4-diphenyl-2-butene-1,4-dione is treated with potassium ethoxide,[8] were also unsuccessful. In contrast, the enolate form (VII) of the thio ketone XI which would be one of the intermediates by α elimination was obtained in significant yields in cleavages of II.

Additional evidence favoring a mechanistic pathway involving α elimination was obtained by a study of the reaction of 2-mercapto-1,4-diphenyl-1,4-butanedione (IX) with VII. In the presence of catalytic amounts of potassium ethoxide and sulfur the sulfide IV was obtained in 67.4% yield. The formation of IV from VII and IX is consistant with the proposed formation of a hemidithioacetal intermediate in the conversion of II → IV.



$$\underset{\text{VII}}{C_6H_5CO\overset{S^-K^+}{C}{=}CHCOC_6H_5}\xrightarrow[2.\ 1/8S_8]{1.\ C_6H_5CO\underset{SH}{C}HCH_2COC_6H_5,\ 0.1KOC_2H_5}\underset{67.4\%}{\mathrm{IV}}$$

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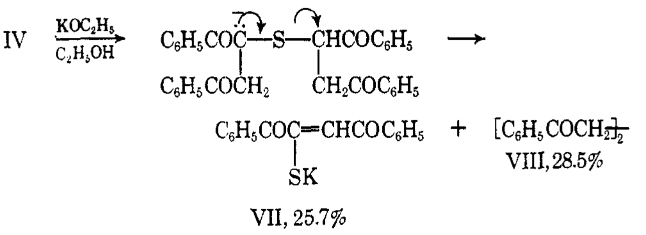
[7] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Amer. Chem. Soc.*, **83**, 2589 (1961).

[8] R. C. Fuson, C. L. Fleming, and P. F. Warfield, *J. Org. Chem.*, **10**, 121 (1945).

The data obtained from the cleavage of II with 2 equiv of ethoxide can also be rationalized by an α elimination mechanism. When an appreciable base concentration is maintained, the sulfide IV also undergoes cleavage. For example, when IV was treated with 1 equiv of potassium ethoxide in ethanol, VII and VIII are obtained in yields of 25.7 and 28.5% along with a 20.9% recovery of IV.



The fact that I undergoes initial disulfide interchange to produce II which then yields the thio ketone XI and mercaptide XII suggests that in this system the direct attack of alkoxide on the sulfur–sulfur bond is the favored process. Decomposition of the symmetrical disulfide II then occurs by α rather than β elimination.

Experimental Section[9]

Preparation of 3,4-Dibenzoyl-1,1,1-triphenyl-2-thiabutane.—To a solution of 21.4 g (0.09 mol) of *trans*-1,4-diphenyl-2-butene-1,4-dione in 400 ml of hot 2-propanol was added a solution of 25.0 g (0.09 mol) of triphenylmethylmercaptan in 250 ml of hot 2-propanol. Piperidine (1 ml) was added and the mixture stirred at 60° for 1 hr. After stirring an additional 12 hr at room temperature the colorless solid was removed by filtration and washed with 100 ml of 2-propanol to give 42.7 g (91.5%) of 3,4-dibenzoyl-1,1,1-triphenyl-2-thiabutane, mp 142–144°. Recrystallization from benzene–hexane raised the melting point to 145–146° (lit.[4] mp 146–147°).

Preparation of 6,7-Dibenzoyl-3-carboxy-4,5-dithiaheptanoic Acid (I).—A solution containing 2.12 g (0.0132 mol) of bromine in 60 ml of dry ethyl acetate was added to a stirred suspension of 6.0 g (0.0186 mol) of lead thiocyanate in 60 ml of dry ethyl acetate at ice bath temperature. After discharge of the bromine color 5.44 g (0.0594 mol) of anhydrous zinc chloride was added followed by dropwise addition over a 2-hr period of a solution containing 6.16 g (0.0012 mol) of 3,4-dibenzoyl-1,1,1-triphenyl-2-thiabutane in 200 ml of dry ethyl acetate. The mixture was stirred for an additional 0.5 hr at ice-bath temperature followed by addition of a solution containing 1.80 g (0.012 mol) of mercaptosuccinic acid in 80 ml of dry acetic acid. After 2 hr the ice bath was removed; the mixture was stirred at 24° for 5 hr; and then it was filtered giving a colorless filtrate. The ethyl acetate was removed *in vacuo* and the resulting acetic acid solution poured into 800 ml of cold water precipitating a colorless solid which was collected by filtration, washed with water, and dried *in vacuo* for 12 hr. After washing with 300 ml of warm *n*-hexane, the solid was dissolved in the minimum amount of acetone and applied to a 4.5 × 15 cm column of silica gel (100 g, 0.05–0.20 mm). The effluent was monitored by thin layer chromatograms [solvent system, chloroform (90)–methanol (5)–acetic acid (5)]. The unreacted S-trityl compound was eluted with chloroform followed by elution of the desired compound with ethyl acetate. Recrystallization from ethyl acetate–hexane gave 2.87 g (57%) of 6,7-dibenzoyl-3-carboxy-4,5-dithiaheptanoic acid (I), mp 185–188° (lit.[4] mp 187–188°).

Bromo-1,4-diphenyl-1,4-butanedione was prepared according to the procedure of Schultz,[10] mp 132–133° (lit.[11] mp 139°).

Preparation of 3,6-Dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II).—To a solution of 12.7 g (0.04 mol) of 2-bromo-1,4-diphenyl-1,4-butanedione in 120 ml of hot absolute ethanol was added a solution of 9.9 g (0.04 mol) of sodium thiosulfate pentahydrate in 120 ml of water. The mixture was heated at reflux temperature for 1.5 hr. The solvent was removed *in vacuo* and the solid residue treated with 150 ml of water. The mixture was filtered leaving a small amount of solid. A solution of 7.2 ml of 30% hydrogen peroxide in 8 ml of 6 *N* sulfuric acid was added to the filtrate and the solution sitrred at 27° for 24 hr to give 9.0 g of crude product, mp 95–104°. The sample was recrystallized from 850 ml of methanol with the colorless solid forming at room temperature collected by filtration to give 1.54 g (14.3%) of II, mp 135–137°. Recrystallization from methanol raised the melting point to 137°.

Anal. Calcd for $C_{32}H_{26}O_4S_2$: C, 71.35; H, 4.87; S, 11.90; mol wt, 538. Found: C, 71.61; H, 4.98; S, 11.69; mol wt, 536, 538 (osmometry, benzene).

The infrared spectrum (KBr) showed a doublet at 1675 cm^{-1}. The nmr spectrum ($DCCl_3$) showed three multiplets centered at τ 2.5 (10.3 H), 5.2 (1.0 H), and 6.3 (1.8 H). The ultraviolet spectrum showed λ_{max}^{EtOH} 248 mμ (ε 50,000).

The filtrate from the separation of the higher melting isomer was reduced to a volume of 600 ml and cooled to give 5.26 g (49%) of II, mp 114–118°. Recrystallization from methanol changed the melting point to 115–116°.

Anal. Calcd for $C_{32}H_{26}O_4S_2$: C, 71.35; H, 4.87; S, 11.90; mol wt, 538. Found: C, 71.09; H, 4.80; S, 12.06; mol wt, 538 (mass spectrometry).

The infrared spectrum (KBr) showed a doublet at 1670 cm^{-1} and was quite similar but not identical with the spectrum of the higher melting isomer. The nmr spectrum ($DCCl_3$) showed three multiplets centered at τ 2.3 (10.5 H), 5.0 (1.0 H), and 6.3 (2.0 H). The ultraviolet spectrum showed λ_{max}^{EtOH} 246 mμ (ε 48,600).

3,5-Dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV) was prepared according to the procedure of Hiskey and Kepler,[4] mp 196–197° (lit.[4] mp 194–196°).

1,4-Diphenyl-1,4-butanedione (VIII) was prepared according to the procedure of Conant and Lutz,[11] mp 144–145° (lit.[12] mp 144–145°).

Preparation of 2-Mercapto-1,4-diphenyl-1,4-butanedione (IX).—To a solution containing 16.4 g (0.032 mol) of 3,4-dibenzoyl-1,1,1-triphenyl-2-thiabutane in 250 ml of chloroform and 500 ml of methanol was added a solution containing 0.544 g (0.032 mol) of silver nitrate and 2.53 g (0.032 mol) of pyridine in 15 ml of methanol. The solution was stirred at 27° in the dark for 4.5 hr. The reaction mixture was poured into 1.5 l. of methanol precipitating a solid which was washed with 100 ml of methanol and 500 ml of hexane to give 11.2 g of pale yellow solid, mp 107–109°.

A stirred suspension of 11.2 g of the silver mercaptide in 400 ml of methanol was treated with hydrogen sulfide for 15 min. Chloroform (400 ml) was added and the mixture warmed to 40°. Silver sulfide was removed by filtration and the filtrate evaporated *in vacuo* to give 7.3 g (85%) of colorless solid, mp 122–124°. Recrystallization from methanol raised the melting point to 124–125°.

Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22; S, 11.86; mol wt, 270. Found: C, 70.90; H, 5.27; S, 11.65; mol wt, 270 (mass spectrometry).

The solid gave a positive mercaptan test with sodium nitroprusside. The infrared spectrum (KBr) showed a weak peak at 2560 cm^{-1} and a strong doublet at 1675 cm^{-1}. The nmr spectrum ($DCCl_3$) showed a multiplet centered at τ 2.30 (9.8 H), an octet centered at 5.15 (1.0 H), an octet centered at 6.23 (1.9 H), and a doublet centered at 8.02 (1.0 H). The ultraviolet spectrum showed λ_{max}^{EtOH} 246 mμ (ε 43,600).

Preparation of 3-Benzoyl-1,6-diphenyl-4-thia-1,6-hexanedione.—To a solution of 270 mg (1 mmol) of 2-mercapto-1,4-diphenyl-1,4-butanedione and 84 mg (1 mmol) of potassium ethoxide in 15 ml of absolute ethanol was added a solution containing 199 mg (1 mmol) of 2-bromoacetophenone in 10 ml of absolute ethanol. The reaction mixture was stirred at 70° for 1 hr. The mixture was cooled, the resulting white solid was removed by filtration and washed with water to give 337 mg (87%) of 3-benzoyl-1,7-diphenyl-4-thia-1,6-hexanedione, mp 128–133°. Recrystallization from ethanol raised the melting point to 140°.

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[9] Melting points were taken on a Fisher-Johns block and are uncorrected. Spectra were determined on Perkin-Elmer Models 237B and 257 (infrared), Perkin-Elmer Model 202 (ultraviolet), Varian Associates A-60 (nmr), and Hitachi Perkin-Elmer RMU-6E (mass spectrometry). Osmometric molecular weights were determined using a Mechrolab Model 301A vapor pressure osmometer. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

[10] P. C. Schultz, *Ber.*, **35**, 168 (1902).

[11] J. B Conant and R. E. Lutz, *J. Amer. Chem. Soc.*, **45**, 1303 (1923).

[12] B. Holmberg, *Ark. Kemi Mineral. Geol.*, **6**, 1 (1916).

Anal. Calcd for $C_{24}H_{20}O_3S$: C, 74.20; H, 5.19; S, 8.26; mol wt, 388. Found: C, 74.23, 74.49; H, 5.23, 5.18; S, 8.36, 8.45; mol wt, 388 (mass spectrometry).

The infrared spectrum (KBr) showed strong peaks at 1665 and 1680 cm^{-1}. The nmr spectrum ($DCCl_3$) showed a multiplet centered at τ 6.05 (2.0 H) along with an ABX system which consisted of two doublets centered at τ 5.00 (1.0 H, J_{AX} = 4 cps, J_{BX} = 9 cps) and an apparent octet centered at τ 6.29 (1.7 H, J_{AB} = 19 cps, J_{AX} = 4 cps, J_{BX} = 9 cps).

Cleavage of 6,7-Dibenzoyl-3-carboxy-4,5-dithiaheptanoic Acid (I) with 3 Equiv of Potassium Methoxide.—To a solution of 836 mg (2 mmol) of 6,7-dibenzoyl-3-carboxy-4,5-dithiaheptanoic acid (I) in 65 ml of dry methanol was added with stirring a solution containing 0.42 g (6 mmol) of potassium methoxide in 10 ml of methanol. The solution took on a yellow color which changed to red within 30 min. The solution was stirred at 27° for 20 hr. The solid was removed by filtration and washed with methanol to give a colorless solid and red filtrate.

The solid was washed with 25 ml of water to give 89 mg (17.6%) of 3,5-dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV), mp 181–185°. Recrystallization from ethanol–chloroform raised the melting point to 193–195° (lit.[4] mp 194–196°). The sample was found to be identical with authentic IV by mixture melting point determination and infrared spectra comparison.

The filtrate from separation of IV was evaporated *in vacuo* leaving a red solid which was treated with 50 ml of water. Filtration left 133 mg of a mixture of IV and 1,4-diphenyl-1,4-butanedione (VIII). The mixtue was triturated in 10 ml of hot ethanol. Filtration gave an additional 101 mg (20%) of IV (total yield of IV, 190 mg 37.6%). The filtrate was cooled to give 22 mg (4.6%) of VIII, mp 140–143°. Recrystallization from ethanol raised the melting point to 144–145° (lit.[11] mp 144–145°). The sample was found to be identical with authentic VIII by mixture melting point determination and infrared spectra comparison.

The aqueous filtrates were combined and treated with carbon dioxide until pH 9 was reached. The solution was evaporated *in vacuo* leaving a red solid which was treated with a solution containing 2 ml of absolute ethanol in 50 ml of ether. The mixture was filtered to give a yellow solid and red filtrate.

The solid was dissolved in 10 ml of water and acidified with 6 *N* hydrochloric acid. The solution was evaporated *in vacuo* leaving a white solid which was extracted with 300 ml of ether. The ether was removed *in vacuo* to give 188 mg (62%) of 2,2'-dithiodisuccinic acid (III), mp 160–165°. Recrystallization from ethyl acetate–hexane raised the melting point to 164–166° (lit.[12] mp 167–168°). The sample was found to be identical with authentic III by infrared spectra comparison.

The filtrate from the separation of the salt of III was evaporated *in vacuo* to give 202 mg (33%) of potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VII), mp 116–121° (lit.[2] mp 118–121°). The sample was found to be identical with authentic sample by infrared spectra comparison.

Thin Layer Chromatographic Studies of Disulfide Interchange of 6,7-Dibenzoyl-3-carboxy-4,5-dithiaheptanoic Acid (I).—The methanolic sodium methoxide solution used in the disulfide interchange studies was standardized by titration with standard 0.100 *M* hydrochloric acid and found to be 0.046 *M*. Thin layer chromatography was conducted on 3 × 7 cm Eastman K301R2 silica gel sheets. The solvent system was benzene–hexane (7:3) with iodine vapor used for development.

A. **Treatment of I with Sodium Methoxide.**—I (9.6 mg, 0.023 mmol) was treated with 1 ml (0.046 mmol) of 0.046 *M* sodium methoxide solution. Periodic checks by thin layer chromatography during a 1.5-hr period gave no indication of disulfide interchange or cleavage. Increments (0.1 ml, 0.0046 mmole) of 0.046 *M* sodium methoxide were added with thin layer chromatography checks made after 2, 10, and 15 min. The addition of the first increment giving a ratio of I:$NaOCH_3$ 1:2.2 brought about no observable change. The addition of a second increment of 0.1 ml of sodium methoxide giving I:$NaOCH_3$ 1:2.4 showed after 10 min a spot of same R_f value as 3,6-dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II). The addition of a third increment of 0.1 ml of sodium ethoxide giving I:$NaOCH_3$ 1:2.6 showed after 2 min a weak spot of same R_f value as II along with a strong spot of same R_f value as 3,5-dibenzoyl-1,7-diphenyl-4-thia-1,7-hexanedione (IV).

B. **Treatment of I with 2 Equiv of Sodium Methoxide and the Sodium Salt of 2-Mercapto-1,4-diphenyl-1,4-butanedione.**—I (19.2 mg 0.046 mmol) was treated with 2 ml of (0.092 mmol) of 0.046 *M* sodium methoxide. A solution of 1.32 mg (0.0046 mmol) of 2-mercapto-1,4-diphenyl-1,4-butanedione (IX) and 0.1 ml (0.0046 mmol) of 0.046 *M* sodium methoxide solution was added giving a ratio of I:$NaOCH_3$:mercaptide 1:2:0.1. After 2 min the thin layer chromatogram showed a spot of the same R_f value as II. Periodic checks gave no trace of cleavage products.

C. **Treatment of I with 2 Equiv of Sodium Methoxide and the Sodium Salt of Mercaptosuccinic acid.**—I (19.2 mg, 0.046 mmol) was treated with 2 ml (0.092 mmol) of 0.046 *M* sodium methoxide solution. A solution of 0.73 mg (0.0046 mmol) of mercaptosuccinic acid and 0.3 ml (0.0138 mmol) of 0.046 *M* sodium methoxide solution was added. Thin layer chromatograms revealed no changes within 15 min. A second increment of 0.73 mg (0.0046 mmol) of mercaptosuccinic acid and 0.3 ml (0.0138 mmol) of sodium methoxide was added giving a ratio of I:$NaOCH_3$:mercaptide 1:2:0.2. After 10 min a spot having the same R_f value as II was observed on the thin layer chromatogram. Periodic checks gave no trace of cleavage products.

Cleavage of 6,7-Dibenzoyl-3-carboxy-4,5-dithiaheptanoic Acid (I) with Sodium Methoxide in Methanol. Isolation of 3,6-Dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II).—A solution of 836 mg (2 mmol) of 6,7-dibenzoyl-3-carboxy-4,5-dithiaheptanoic acid (I) in 65 ml of dry methanol was treated with a solution containing 32.4 mg (6 mmol) of sodium methoxide in 10 ml of methanol. The reaction mixture was stirred at 27° for 5 min and acidified with 6 *N* hydrochloric acid. The solvent was removed *in vacuo* and the resulting solid dried *in vacuo* for 24 hr. The solid was dissolved in a minimum amount of chloroform and applied to a 1 × 36 cm column of silica gel (15 g, 0.05–0.20 mm). The effluent was monitored by thin layer chromatography [solvent system, chloroform (90)–methanol (5)–acetic acid (5)]. Using chloroform as the eluent, the first fraction gave 64 mg (12.5%) of 3,5-dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV), mp 188–190° (lit.[4] mp 194–196°).

The second fraction provided 83 mg (15.6%) of 3,6-dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II), mp 111–114°. Recrystallization from methanol raised this to 114–116°. The sample was found to be identical with the lower melting isomer, mp 115–116°, of an authentic sample by mixture melting point determination and infrared spectra comparison.

Elution with ethyl acetate provided 359 mg (30.7%) of starting disulfide I, mp 182–186°. No attempt was made to isolate other cleavage products.

Cleavage of 3,6-Dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II) with 1 Equiv of Potassium Ethoxide.—To a solution of 0.168 g (0.002 mol) of potassium ethoxide in 45 ml of absolute ethanol was added 1.08 g (0.002 mol) of 3,6-dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II, mp 115–116°). The disulfide reacted immediately giving a clear red solution. After 10 min solid formation was observed. The mixture was stirred at 27° for 24 hr. The solid was filtered and washed with water to give 0.53 g (52%) of 3,5-dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV), mp 183–186°. Recrystallization from ethanol–chloroform raised the melting point to 195–197° (lit.[4] mp 194–196°). The sample was found to be identical with authentic sample by mixture melting point determination and infrared spectra comparison.

The filtrate from separation of IV was evaporated *in vacuo* leaving a red residue which was triturated in 50 ml of water. Filtration gave an additional 0.20 g (19.6%) of IV, mp 178–184°. The total yield of IV was 0.73 g (71.6%). The aqueous filtrate was treated with carbon dioxide until pH 9 was reached. The solution was evaporated *in vacuo* leaving red solid which was treated with 10 ml of ethanol. The mixture was filtered removing potassium carbonate and the filtrate evaporated *in vacuo* to give 0.18 g (12.6%) of potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VIII), mp 119–122° (lit.[13] mp 118–121°). The sample was found to be identical with an authentic sample by infrared spectra comparison.

Acidification of Potassium 1,4-Diphenyl-2-butene-1,4-dione-2-mercaptide (VIII).—To a solution of 1.90 g (0.0062 mol) of potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VII) in 50 ml of water was added 6 *N* hydrochloric acid until pH 1 was reached. The resulting turbid mixture was extracted with two 50-ml portions of ethyl ether. The ether extracts were dried and evaporated *in vacuo* leaving a yellow solid which was recrystallized from ethanol–chloroform to give 0.60 g (36.8%) of 3,6-dibenzoyl-1,8-diphenyl-4,5-dithia-2-octene-1,8-dione (V), mp 162–167° (lit.[4] mp 174–180°). The sample was found to be identical with authentic V by infrared spectra comparison.

Cleavage of 3,6-Dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II) with 2 Equiv of Potassium Ethoxide.—To a solution of 0.168 g (0.002 mol) of potassium ethoxide in 20 ml of absolute ethanol was added 0.538 g (0.002 mol) of 3,6-dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II, mp 137°). The disulfide reacted immediately giving a clear red solution. The mixture was stirred at 27° for 24 hr. The solid was filtered and washed with water to give 0.082 g (16.1%) of 3,5-dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV), mp 182–185°. Recrystallization from ethanol–chloroform raised the melting point to 193–195° (lit.[4] mp 194–196°).

The filtrate from separation of IV was evaporated *in vacuo* leaving a red residue which was triturated in 50 ml of water. Filtration gave 0.153 g (30.8%) of 1,4-diphenyl-1,4-butanedione (VIII), mp 137–141°. Recrystallization from ethanol raised this to 143–145° (lit.[11] mp 144–145°). The sample was found to be identical with an authentic sample by mixture melting point determination and infrared spectra comparison.

The aqueous filtrate from separation of VIII was treated with carbon dioxide until pH 9 was reached. The solution was evaporated *in vacuo* leaving a red solid which was treated with 20 ml of absolute ethanol. The mixture was filtered removing potassium carbonate and the filtrate evaporated *in vacuo* to give 0.247 g (40.3%) of potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VII), mp 117–120° (lit.[13] mp 118–121°).

Treatment of 3,5-Dibenzoyl-1,7-diphenyl-3-thia-1,7-heptanedione (IV) with 1 Equiv of Potassium Ethoxide.—To a solution of 0.168 g (0.002 mol) of potassium ethoxide in 20 ml of absolute ethanol was added 1.04 g (0.002 mol) of 3,5-dibenzoyl-1,7-diphenyl-3-thia-1,7-heptanedione (IV). The sulfide reacted immediately giving a red solution containing a small amount of solid. The mixture was stirred at 26° for 24 hr. The solid was filtered and washed with water to give 0.37 g of a mixture of IV and 1,4-diphenyl-1,4-butanedione (VIII). The mixture was triturated in 20 ml of warm ethanol. Filtration gave 0.22 g (20.9%) of recovery IV, mp 186–190° (lit.[4] mp 194–196°). The filtrate was cooled to give 0.11 g (11.5%) of VIII, mp 142–144° (lit.[11] mp 144–145°).

The original filtrate was evaporated *in vacuo* leaving a red gum which was partitioned between 60 ml of water and 60 ml of ether. The ether layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo* to give an additional 0.16 g (17%) of VIII, mp 138–143°. Total yield of VIII was 0.27 g (28.5%). Recrystallization from ethanol raised the melting point to 143–145° (lit.[11] mp 144–145°).

The aqueous layer was treated with carbon dioxide until pH 9 was reached. The solution was evaporated *in vacuo* to give 0.32 g (25.7%) of potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VII), mp 116–119° (lit.[2] mp 118–121°).

Addition of 2-Mercapto-1,4-diphenyl-1,4-butanedione (IX) to Potassium 1,4-Diphenyl-2-butene-1,4-dione-2-mercaptide (VII).—Potassium ethoxide (8.4 mg 0.1 mol) in 0.1 ml of ethanol was added to 270 mg (1 mmol) of IX in 5 ml of ethanol. The mixture was cooled and filtered to give 346 mg of a mixture of 3,5-was added to a solution of 306 mg (1 mmol) of VII in 5 ml of ethanol. After 30 min 32.1 mg (0.125 mmol) of sulfur was added and the mixture stirred at 28°. After 24 hr the mixture dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV) and sulfur. The mixture was triturated in 20 ml of acetone. Filtration gave 18 mg of sulfur, mp 115–117°. The filtrate was evaporated *in vacuo* to give 341 mg (67.4%) of IV, mp 176–179°. Recrystallization from ethanol–chloroform raised the melting point to 193–195° (lit.[4] mp 194–196°).

Registry No.—II, 4006-76-2; IX, 16704-51-1; 3-benzoyl-1,6-diphenyl-4-thia-1,6-hexanedione, 16704-52-2.

Di-*t*-Butylthioketene

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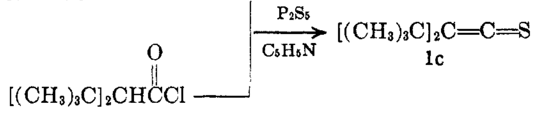
Di-*t*-butylthioketene (**1c**) may be prepared by heating either di-*t*-butylacetyl chloride or di-*t*-butylketene with phosphorus pentasulfide in pyridine. Thioketene **1c**, in contrast to other nonhalogenated thioketenes reported previously, shows no tendency to dimerize or polymerize on storage at room temperature. It may be converted into O esters (**3**) of di-*t*-butylthioacetic acid by reaction with methyl or ethyl alcohol, into di-*t*-butylthioacetanilide (**4**) by reaction with aniline, and into the S-oxide by oxidation with hydrogen peroxide or monoperphthalic acid. Spectral evidence indicates that there is a substantial barrier to rotation about the C_1–C_2 bond axis of the esters (**3**) and the anilide (**4**).

Although there have been several attempts to prepare thioketenes since the discovery of ketene and its homologs, these have usually given only polymers or dimers.[1–4] Apparently, only two attempts to prepare the monomers have been successful. Howard prepared thioketene (**1a**) by pyrolysis of *t*-butyl ethynyl sulfide and found it to be unstable at temperatures above −80°.[5] More recently, Raasch prepared bis(trifluoromethyl)thioketene (**1b**) by pyrolysis of its dimer, 2,4-bis[2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene]-1,3-dithietan, and found that the monomer is stable for many months when kept in glass bottles at room temperature.[6] Raasch attributed the stability of this thioketene to the strongly electron-withdrawing trifluoromethyl groups.

Newman, *et al.*, described the preparation of di-*t*-butylketene and commented upon its extreme unreactivity, which is apparently due to steric hindrance.[7]

In the hope that a similarly substituted thioketene would also be more stable than its less sterically hindered homologs, we undertook the preparation of di-*t*-butylthioketene (**1c**). We prepared the compound successfully by the reactions summarized in Scheme I.

SCHEME I



$$\left.\begin{array}{l}[(CH_3)_3]_2C{=}C{=}O\\ [(CH_3)_3C]_2CH\overset{\overset{\displaystyle O}{\|}}{C}Cl\end{array}\right\}\xrightarrow[C_5H_5N]{P_2S_5}\underset{\mathbf{1c}}{[(CH_3)_3C]_2C{=}C{=}S}$$

When a solution of di-*t*-butylketene in pyridine was refluxed with phosphorus pentasulfide for 15 hr, it was

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