STUDY OF THE TAUTOMERISM OF 4- AND 2-CARBALKOXY-3-THIOPHANONES

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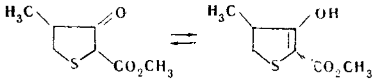
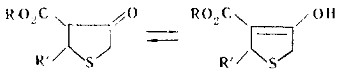
The equilibrium positions of 4-carbomethoxy-3-thiophanone (I), 2-carbomethoxy-4-methyl-3-thiophanone (II), 4,5-dicarbomethoxy-3-thiophanone (III), and 4-carbethoxy-5-phenyl-3-thiophanone (IV) in acetonitrile, dioxane, and alcohols was determined. The Meyer equation is satisfied for ketones I and II paired with acetylacetone and for III and IV paired with methyl cyclopentanone-2-carboxylate in alcohol solutions.

Heterocyclic β-keto esters may differ substantially from their carbocyclic analogs with respect to their tautomeric properties. Thus the equilibrium position is shifted markedly to favor the enol form on passing from esters of cyclopentanone-2-carboxylic acids to esters of 3-thiophanone-4-carboxylic acids [1]. It is observed that the Meyer equation is not satisfied for heterocyclic β-keto esters paired with carbocyclic β-keto esters because of different solvation of the heteroatoms of the ketone and enol forms as a consequence of the difference in the conformations of these forms [2, 3]. The unusual deviations from the Meyer equation are associated with the change in the chemical type of the heterocyclic β-keto esters under the influence of interaction in the ring [4]. The determination of the equilibrium position of heterocyclic β-keto esters in a number of solvents is therefore of considerable interest.

We have studied the tautomerism of 4-carbomethoxy-3-thiophanone (I), 2-carbomethoxy-4-methyl-3-thiophanone (II), 4,5-dicarbomethoxy-3-thiophanone (III), 4-carbethoxy-5-phenyl-3-thiophanone (IV), and 4-carbethoxy-5-phenyl-3-thiophanone (V). The results of a qualitative treatment of the spectral data for I and II were presented in [1]. In this paper, major attention is directed to a quantitative study of the tautomerism of I-V.



II



I, III, IV

I $R = CH_3$, $R' = H$; III $R = CH_3$, $R' = CO_2CH_3$; IV $R = C_2H_5$, $R' = C_6H_5$

Equation (1), which is equivalent to the Meyer equation, was used in comparing the effect of the solvent on the equilibrium of two tautomers with two forms, of which only one absorbs in the spectrum:

$$\frac{\varepsilon_{T_1 S_n}}{\varepsilon_{T_1 S_n} - \varepsilon_{T_1 S_1}} = \text{const} \frac{\varepsilon_{T_2 S_n}}{\varepsilon_{T_2 S_n} - \varepsilon_{T_2 S_1}}, \qquad (1)$$

where ε_{TS} is the molar extinction coefficient of tautomer T in solvent S [5]. Satisfaction of Eq. (1) means satisfaction of the Meyer equation for a given pair of tautomers. The $M_{TS} = \varepsilon_{TS_n} (\varepsilon_{TS_n} - \varepsilon_{TS_1})$ values are more accessible and, through the arbitrary selection of a standard solvent, can be determined with greater accuracy than the equilibrium constants [6].

The molar extinction coefficient of the absorbing form of a tautomer with two forms in equilibrium was found from Eq. (2):

$$\varepsilon_{0T_1} = \frac{\varepsilon_{T_1 S_1} \varepsilon_{T_1 S_2} (K_{T_2 S_2} - K_{T_2 S_1})}{\varepsilon_{T_1 S_1} K_{T_2 S_2} - \varepsilon_{T_1 S_2} K_{T_2 S_1}} \qquad (2)$$

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where ε_{TS} is the molar extinction coefficient of tautomer T in solvent S, and K_{TS} is the equilibrium constant of tautomer T in solvent S.

The Meyer equation is satisfied for tautomers T_1 and T_2. Tautomer T_2 was taken as the standard. In some cases, Eq. (3) was used along with Eq. (2) for finding the molar extinction coefficient of the absorbing form of a tautomer with two forms in equilibrium:

$$\varepsilon_{0T_1}=\frac{\varepsilon_{T_2S_2}\varepsilon_{T_2S_1}(\varepsilon_{T_1S_1}-\varepsilon_{T_1S_2})+n\varepsilon_{T_1S_1}\varepsilon_{T_1S_2}(\varepsilon_{T_2S_2}-\varepsilon_{T_2S_2})}{n(\varepsilon_{T_1S_1}\varepsilon_{T_2S_2}-\varepsilon_{T_2S_1}\varepsilon_{T_1S_2})}, \qquad (3)$$

where ε_{TS} is the molar extinction coefficient of tautomer T in solvent S, and $n=\varepsilon_{0T_2}/\varepsilon_{0T_1}$.

The Meyer equation is satisfied for tautomers T_1 and T_2. Tautomer T_2 was taken as the standard. It is assumed that the molar extinction coefficient of the absorbing form is independent of the nature of the solvent [6, 7]. The conditions and possibilities for the use of Eqs. (2) and (3) were examined in detail in [8].

Bands of only the enol form (chelate C=O at 1670 cm^{-1}, C=C at 1630 cm^{-1}) are present in the IR spectrum of crystalline I at 1600-1800 cm^{-1}. The UV spectra of I in acetonitrile, alcohols, dioxane, and hexane (Table 1) were recorded and are in good agreement with those obtained in [1]. On passing from neutral to alkaline solutions, the absorption maximum is shifted from 247 to 281 nm. A shift of this sort is characteristic for β-keto esters [9].

It is known that the molar extinction coefficients of enols do not depend significantly on the nature of the solvent [7, 9] and that the rate of establishing equilibrium is usually the lowest in nonpolar solvents. The substantial differences between the molar extinction coefficients of the keto–enol forms in a given solvent and in the most nonpolar solvent, under the condition that the spectra of the solution recorded at different time intervals after its preparation are the same, were considered by us to be proof of the high rate of establishing equilibrium. When the molar extinction coefficients of the keto–enol forms in the spectra of solutions recorded at definite time intervals differed substantially, the spectra were recorded until there were no longer any changes in them; this was evidence for the establishment of equilibrium. The spectra of solutions of I 30 min and several days after preparation of the solutions were identical. The molar extinction coefficients of I in acetonitrile, alcohols, and dioxane differed substantially from the molar extinction coefficient in hexane. On the basis of the above, we concluded that the rate of establishing equilibrium in solutions of I is high at low concentrations ($\sim 5 \cdot 10^{-3}$ M). The molar extinction coefficients of I in acetonitrile, alcohols, and dioxane, which are presented in Table 1, are considered to be close to the equilibrium values. It was necessary to select the standard state in order to calculate the M_{TS} values of I. In [6], the molar extinction coefficient of acetoacetic ester in the standard state was taken as 100, while the molar coefficients of other keto–enols in the standard state were calculated in pairs with acetoacetic ester from the equation presented in the paper. In subsequent papers, the extinction of keto–enols in the standard state was calculated in pairs with acetoacetic ester or in pairs with another keto–enol, the standard state of which corresponded to the standard state of acetoacetic ester. This enables us to consider the ratios of the M_{TS} values of any two studied keto–enols without any additional conversions. The standard state of I was selected from the standard state of acetylacetone (VI) [6]. The following extinction values of I in the standard state were obtained for various solvent pairs: 496 for acetonitrile–methanol, 478 for acetonitrile-ethanol, 482 for acetonitrile–isobutyl alcohol, and 458 for methanol–isobutyl alcohol. The M_{TS} values for I in solutions (Table 1) were calculated on the basis of the average value (480).

The ratios of the M_{TS} values of I and VI and 1- and 2-carbethoxy-1-cyclopentanone (VII) were found. They are also presented in Table 1. The satisfaction of Eq. (1) is characterized by the maximum deviation of the equation constant from the average value. As seen from Table 1, the deviation of the equation constant for I and VI from the average value does not exceed the limits of the error in the determination of the ratios. Thus the Meyer equation is satisfied for the I-VI pair within the limits of experimental error. The molar extinction coefficient of enol I was calculated for this pair from Eq. (2). It was found to be 8200 ± 200. The primary number is the arithmetic mean of the values for nine pairs of states. The error was determined as the mean-square error under the assumption that the deviations from the Meyer equation obey the law of random errors. The value found is in agreement with the absorption of I in hexane and the IR spectrum of I in CCl_4 [1].

TABLE 1. UV Absorption and M_{TS} Values for I in Solution and Ratios of the M_{TS} Values of I, VI, and VII

Solvent	λ,mm	ε_{TS}	M_{T_1S}	M_{T_6S}/M_{T_1S}	M_{T_7S}/M_{T_1S}
Acetonitrile	247	1950±30	1,326±0,006	1,210±0,025	0,936±0,011
Methanol	247	3000±45	1,190±0,003	1,205±0,010	0,920±0,003
Ethanol	248	3800±60	1,144±0,002	1,212±0,009	0,940±0,002
Isobutyl alcohol	248	4800±70	1,111±0,001	1,209±0,011	0,936±0,002
Dioxane	247	3500±50	1,159±0,003	1,188±0,012	0,919±0,003
Hexane	248	7600±110			

TABLE 2. UV Absorption and M_{TS} Values for II in Solutions and M_{TS} Ratios of II, VI, and VII in Solutions

Solvent	λ,mm	ε_{TS}	M_{T_2S}	M_{T_2S}/M_{T_6S}	M_{T_2S}/M_{T_7S}
Acetonitrile	310	254±4	1,264±0,006	0,788±0,016	1,018±0,013
Methanol	313	352±5	1,177±0,003	0,821±0,006	1,076±0,004
Ethanol	315	424±6	1,143±0,003	0,825±0,006	1,062±0,004
Isobutyl alcohol	315	566±8	1,103±0,002	0,821±0,009	1,060±0,003
Dioxane	315	446±7	1,135±0,002	0,824±0,008	1,066±0,003
Hexane	315	1032±15			

Compound II was obtained as a liquid. The IR spectrum of liquid II at 1600-1800 cm^{-1} contains intense bands of the keto form at 1722 cm^{-1} (ester C=O) and 1745 cm^{-1} (ketone C=O), and bands of medium intensity of the enol form at 1655 cm^{-1} (chelate C=O) and 1600 cm^{-1} (C=C). The UV spectra of II in acetonitrile, alcohols, dioxane, and hexane (Table 2) were recorded. There are three maxima at 233, 262, and 310-315 nm in all of the spectra. The intensities of the latter two maxima increase in the order acetonitrile < methanol < ethanol < isobutyl alcohol < dioxane < hexane. The UV spectra of dimer II, which is a model keto form, were recorded. As seen from the spectrum, the absorptionof the dimer decreases as the wavelength increases, and there is an inflection at 242 nm. In conformity with the spectrum of the dimer, the maxima observed in the spectra of II should be ascribed to the enol form. The absorption of the keto form at 315 nm is low. The UV spectra of II differ sharply from the spectra of I, but great similarity to the spectra of 4-carbomethoxy-1,3-dithia-5-cyclohexanone, the enol form of which has a chelate ring conjugated with the double bond [10], is observed. The spectra of solutions of II are identical 30 min and several days after preparation. The molar extinction coefficients of II in acetonitrile, alcohols, and dioxane differ substantially from the molar extinction coefficient in hexane. All of this makes it possible to conclude that the rate of establishing equilibrium in solutions of II is high at low concentrations and to consider the molar extinction coefficients of II in acetonitrile, alcohols, and dioxane, which are presented in Table 2, to be equilibrium values. The absorption of II at ~315 nm was used for a quantitative study of the tautomerism of this compound. The standard state of II was selected from the standard state of acetylacetone [6]. The following absorption values of II in the standard state for solvent pairs were obtained: 59 for methanol–ethanol, 53 for methanol–isobutyl alcohol, and 48 for ethanol–isobutyl alcohol (average value 53). The M_{TS} values for II in solutions were calculated on the basis of the average value and are presented in Table 2 together with the M_{TS} values of II and VI and II and VII.

As seen from Table 2, the deviation of the constant of Eq. (1) for II and VI from the average value in dioxane and alcohols does not exceed the limits of the error in determining the ratios. Thus the Meyer equation is satisfied for the I-VI pair in these solvents within the limits of the experimental error. The molar extinction coefficient of the enol at 315 nm was calculated for this pair from Eq. (2). It was found to be 1050 ± 20. The primary number is the arithmetic mean of the values for five pairs of states. The error was determined as the mean-square error under the assumption that the deviations from the Meyer equation obey the law of random errors. The value found is equal to the absorption of II in hexane.

In a qualitative study of the tautomerism of II by IR spectroscopy, we concluded that its equilibrium position does not differ substantially from the equilibrium position of VII [1]. The results of a quantitative study indicate that the equilibrium position is shifted markedly to favor the enol on passing from VII to II. This is in agreement with the shifts in the equilibrium that we observed on passing from 4-carbomethoxy-1,3-dithia-5-cyclohexanones to 2-carbomethoxy-1-cyclohexanone [10]. The incorrect conclusion of the

TABLE 3. UV Absorption and M_{TS} Values for III in Solutions and Ratios of the M_{TS} Values of III and VI and III and VII in Solutions

Solvent	λ,mm	ε_{TS}	M_{T_3S}	M_{T_6S}/M_{T_3S}	M_{T_7S}/M_{T_3S}
Acetonitrile	243	2250±34	1,630±0,015	0,985±0,024	0,761±0,015
Methanol	243	2800±40	1,451±0,010	0,988±0,012	0,755±0,006
Ethanol	245	3000±45	1,408±0,008	0,984±0,011	0,764±0,005
Isobutyl alcohol	245	3200±50	1,373±0,008	0,978±0,015	0,757±0,005
Dioxane	244	2650±40	1,489±0,011	0,925±0,014	0,715±0,006

TABLE 4. UV Absorption and M_{TS} Values for IV in Solutions and Ratios of the M_{TS} Values of IV and VI and IV and VII in Solutions

Solvent	λ,mm	ε_{T_4S}	M_{T_4S}	M_{T_4S}/M_{T_6S}	M_{T_4S}/M_{T_7S}
Acetonitrile	246	4280±60	1,359±0,007	0,847±0,017	1,095±0,014
Methanol	246	5190±80	1,278±0,006	0,891±0,009	1,167±0,008
Ethanol	247	5540±80	1,256±0,004	0,906±0,008	1,167±0,005
Isobutyl alcohol	248	6400±100	1,214±0,004	0,904±0,011	1,167±0,005
Dioxane	247	5190±80	1,278±0,008	0,928±0,011	1,200±0,007
Hexane	248	7700±100			

qualitative study is associated either with the fact that the molar extinction coefficients of the chelate ring at 1600-1800 cm^{-1} are anomalously low or with the low rate of establishing equilibrium in concentrated solutions of II. In [1], it was noted that the equilibrium is shifted to favor the enol when hydrogen chloride is bubbled into CCl_4 solutions of II.

The IR spectrum of liquid III at 1600-1800 cm^{-1} contains intense bands of the keto form at 1725 cm^{-1} (ester C=O) and 1740 cm^{-1} (ketone C=O), of the enol form at 1650 cm^{-1} (chelate C=O) and 1610 cm^{-1} (C=O), and an absorption band of a non keto–enol ester group at 1735 cm^{-1}. There is one absorption maximum which is affiliated with the enol form, in the UV spectra of solutions of III (Table 3). The spectra of solutions of III are identical 30 min and several days after preparation. The molar extinction coefficients of III in acetonitrile and alcohols differ substantially from the molar extinction coefficient in dioxane. This indicates a high rate of establishing equilibrium in acetonitrile and alcohol solutions of III. The absorption of III in these solutions can be considered to be the equilibrium value. The intensities were used for a quantitative study of the equilibrium of III in solutions. The standard state of III was selected from the standard state of 2-carbomethoxy-1-cyclopentanone (VII) [6]. The following absorption values of III in the standard state were obtained for solvent pairs: 909 for acetonitrile–methanol, 857 for acetonitrile–ethanol 886 for acetonitrile–isobutyl alcohol, and 828 for methanol–isobutyl alcohol. (The average value was 870.) The M_{TS} values for III in solutions were calculated on the basis of the average value and are presented in Table 3 together with the ratios of the M_{TS} values of III and VI and III and VII.

As seen from Table 3, the deviation of the constant of Eq. (1) for III-VII from the average value in acetonitrile and alcohols does not exceed the limits of the error in determining the ratios. Thus the Meyer equation is satisfied for the III-VIII pair in these solvents. The molar extinction coefficient of enol III at 245 nm was calculated from Eq. (3) for this pair. It was found to be 3570 ± 25. The primary number is the arithmetic mean of the values for 10 pairs of states. The error was determined as the mean-square error under the assumption that the deviations from the Meyer equation obey the law of random errors. On the basis of [11], the molar extinction coefficient of enol VII was assumed to be 11,000 in the calculation.

Only bands of the enol form at 1680 cm^{-1} (C=O) and 1620 cm^{-1} (C=C) are present in the IR spectrum of crystalline IV at 1600-1800 cm^{-1}. The UV spectra of IV in solutions contain an intense maximum at ~250 nm, which is affiliated with the enol, and a branch of intense phenyl absorption, the maximum of which lies below 220 nm. This branch disappears beyond 250 nm. Its intensity at 220 nm is 7200-7800 in a number of solvents. However, since the phenyl group is included in both tautomeric forms and a high enol content might have been expected in solutions of IV, we used the absorption at 250 nm for the quantitative study of the tautomerism of IV. The data on the UV absorption of IV are presented in Table 4. The spectra of solutions of IV are identical 1 h and several days after preparation, and the absorption in acetonitrile, alcohols, and dioxane differs from the absorption in hexane. This indicates a high rate of establishing equilibrium in solutions of IV, and we consider the molar extinction coefficients of IV, which are presented in Table 4, to be equilibrium values. The standard state of IV was selected as the standard state of VII. The following absorption values of IV in the standard state for solvent pairs were obtained: 1161 for methanol–ethanol, 1130 for methanol–isobutyl alcohol, and 1112 for ethanol–isobutyl alcohol. (The average value was 1130.) The M_{TS} values for IV in solutions were calculated on the basis of the average value.

As seen from Table 4, the constants of Eq. (1) for IV-VII in methanol, ethanol, and isobutyl alcohol are identical. Thus the Meyer equation is ideally satisfied for the IV-VII pair in these solutions. The molar extinction coefficient of enol IV at 247 nm was calculated from Eq. (3) for this pair. It was found to be 7700. This number contains one certain and one doubtful figure. Almost all of the molar extinction coefficients presented in Tables 1-4 have two certain figures. Numbers with one certain figure are therefore obtained in calculations from formulas (2) and (3). When there are deviations from the Meyer equation, there is an additional error, which we calculated from the law of random errors. The molar extinction coefficient of enol IV that we found is equal to the absorption of IV in hexane. To a certain degree, this confirms the accuracy of the calculations.

The IR spectrum of crystalline sulfoxide V at 1600-1800 cm^{-1} contains two bands at 1660 and 1680 cm^{-1}, which can be ascribed to the absorption of the chelate ring of the enol form. One's attention is drawn to the frequencies. They are too high for the chelate ring. However, we observed a similar increase in frequencies during the formation of the hydrochlorides of N-butyl-4-carbomethoxy-3-piperidones [12]. In addition, no appreciable change in the absorption frequencies of the chelate ring is observed on passing from I to its methiodide [13]. There is an absorption maximum in the UV spectra of V in solutions. Only a descending branch of intense phenyl absorption and, apparently, of a sulfoxide group (ε 9600-10,300 at 230 nm) is observed in them. The spectra in acetonitrile, methanol, ethanol, and alcohols differ only slightly. An intense absorption maximum of the anion (ε 9600 at 285 nm) appears in the spectrum of an alcohol solution in the presence of alkali. The position of the anion maximum indicates that the absorption maximum of the enol should be ~245 nm. It does not appear either because of the low percentage of enol in equilibrium or because of the small molar extinction coefficient of enol V. The UV spectra of V do not make it possible to draw even a qualitative conclusion regarding the enol content in its solutions.

The results of a quantitative study of the tautomerism of I-IV demonstrate that replacement of the CH_2 group by a sulfur atom and introduction of substituents into the five-membered ring of β-keto esters lead to a considerable change in the equilibrium position. Thus ethanol solutions of I, II, III, IV, and VII contain 46, 40, 84, 72, and 4% enol, respectively. The bond lengths and angles, as well as the barriers to rotation about the bonds in the $>S$ group differ from the analogous characteristics of the CH_2 group. All of these differences may serve as the reason for the observed shift in the equilibrium position on passing from VII to I. However, we have observed that the equilibrium positions of VII and 5-methyl-4-carbethoxytetrahydro-3-furanone are extremely close [14]. The bond lengths and angles of the $>O$ group are close to the bond lengths and angles of the $>CH_2$ group, while the barriers to rotation about the bonds of the $>O$ group differ only slightly from the barriers to rotation about the bonds of the $>S$ group. The most probable reason for the high percentage of enol in I as compared with VII is therefore a decrease in the angular strain in the enol form of I. The introduction of phenyl and carbethoxy substituents into I results in a shift of the equilibrium position to favor the enol. This indicates the existence of steric interactions of the 4,5-substituents in the thiophane ring. In solutions, I and II contain about the same amount of the enol form, although there is conjugation between the double bond and the chelate ring in the enol of II. It is known that conjugation with a chelate ring leads to an increase in the percentage of enol in equilibrium [15]. It is apparent that some other effects that compensate for the action of conjugation are operating in II.

When the CH_2 group is replaced by a heteroatom and substituents are introduced into the ring of β-keto esters, the interaction of the β-dicarbonyl grouping and the chelate ring with solvents may change, and, as a consequence of this, the chemical type of the β-keto ester may be disrupted. Different solvation of the heteroatoms in the ketone and enol forms of heterocyclic β-keto esters is also possible because of the difference in the conformations of the forms. In either case, one will observe deviations from the Meyer equation for a pair of heterocyclic and carbocyclic β-keto esters. When the solvation of the heteroatoms of the forms is different, one observes even more of an increased additional shift in the equilibrium position to favor one of the forms, even in a series of monotypic solvents. For two tautomers of different chemical types, the Meyer equation can be satisfied in a series of solvents with the same solvation mechanism (usually this involves solvents of the same chemical type), but it will not be satisfied in a series of solvents of different types. As seen from the data presented above, the Meyer equation is satisfied, within the limits of the experimental error, for I and II paired with acetylacetone, which, in this case, is equivalent to a carbocyclic β-keto ester. Thus, in the case of I and II, there are no differences in the solvation of the sulfur atoms in the ketone and enol forms, and the chemical type of the keto–enol does not change. The Meyer equation is well satisfied in alcohols for III and IV paired with VII. This indicates that the solvation of the sulfur atoms in the tautomeric forms of III and IV is the same. The nonfulfillment of the Meyer equation for these pairs in acetonitrile and dioxane may indicate a certain change in the chemical type of III and IV.

In conclusion, it should be noted that the results of our study demonstrate the restricted character of the conclusions drawn in [11], in which the molar extinction coefficients of the enols of acetoacetic ester and carbocyclic β-keto esters with five to nine atoms in the ring were found from the UV spectra and the results of bromometric titration. They ranged from 11,000 to 13,000, and it would seem that one might have concluded that ε_{TS} of the chelate ring is stable to steric effects. However, the data on heterocyclic β-keto esters presented here and in [14] indicate the opposite.

EXPERIMENTAL

The data on the preparation and physical constants of I and II are presented in [1].

4-Carbomethoxy-3-thiophanone (I). This compound was obtained by the method in [16] and had bp 118-120° (11 mm), n_D^{25} 1.5250, d_4^{25} 1.2753, and mp 38°.

Carbomethoxymethyl 2-Carbomethoxy-1-propyl Sulfide. Methyl methacrylate [75 g (0.75 mole)] was added dropwise in the course of 1 h at 40° to a mixture of 87 g (0.83 mole) of methyl thioglycolate and 1 ml of piperidine, and the reaction mass was allowed to stand for 10 h. It was then washed, dried with magnesium sulfate, and distilled to give 133 g (80%) of a product with bp 134° (10 mm) and n_D^{20} 1.4690.

2-Carbomethoxy-4-methyl-3-thiophanone (II). Carbomethoxymethyl 2-carbomethoxy-1-propyl sulfide [16.7 g (0.082 mole)] was added with stirring at 70° to a suspension of 4.7 g (0.087 mole) of sodium methoxide in absolute toluene. The next day, the reaction mixture was poured into a mixture of ice water and hydrochloric acid, and the toluene layer was separated and treated with 200 ml of 10% sodium hydroxide. The alkaline solution was acidified with acetic acid and extracted with ether. The ether extract was dried with magnesium sulfate, the ether was removed in vacuo, and the residue was distilled to give 6 g (47%) of a product with bp 122° (10 mm), n_D^{20} 1.4989, and d_4^{20} 1.2750. Found: C 48.4; H 5.7; S 18.8%; $C_7H_{10}O_3S$; Calculated: C 48.3; H 5.8; S 18.4%.

Dimer of 2-Carbomethoxy-4-methyl-3-thiophanone. A 1 M solution of ferric chloride was added dropwise to a solution of 6 g of thiophanone II in methanol until the ferric ion was no longer decolorized. A dark oil began to separate at the end of the addition. It was recrystallized from ethanol to give 2 g (21%) of a substance with mp 127-129°.

Carbomethoxymethyl 1,2-Di(carbomethoxy)ethyl Sulfide. Piperidine (20 drops) was added with stirring and cooling to a mixture of 13.5 g (0.43 mole) of methyl thioglycolate and 18 g (0.13 mole) of dimethyl fumarate. The mixture became completely liquid during the addition. After 1 h, 40 ml of absolute benzene was added and the mixture was refluxed for 12 h on a water bath. The mixture was then washed with water, sodium hydroxide solution, and water. The benzene was removed in vacuo, and the residue was distilled to give 41 g (66%) of a product with bp 152-154° (0.2 mm).

4,5-Dicarbomethoxy-3-thiophanone (III). Carbomethoxymethyl 1,2-(carbomethoxy)ethyl sulfide [15 g (0.06 mole)] was added dropwise with cooling and stirring to a suspension of 2.8 g (0.052 mole) of sodium methoxide in absolute benzene. The reaction mixture was refluxed for 2 h and poured into ice water and hydrochloric acid. The benzene layer was separated, the benzene was removed in vacuo, and the residue was distilled to give 5 g (38%) of a product with bp 109-110° (0.2 mm), n_D^{20} 1.5040, and d_4^{20} 1.3198. Found: C 43.7; H 4.6; S 15.1%. $C_8H_{10}O_5S$. Calculated: C 44.0; H 4.6; S 14.6%.

5-Phenyl-4-carbethoxy-3-thiophanone (IV). This compound was obtained by the method in [17] and had mp 76-77°.

5-Phenyl-4-carbethoxy-3-thiophanone 1-Oxide (V). A total of 1.5 ml of 24% hydrogen peroxide was added to a solution of 0.4 g of IV in 15 ml of acetone. After 3 days, the acetone was removed in vacuo, and the residue was recrystallized from 50% ethanol to give 0.3 g (65%) of a product with mp 139° (mp 139-140° [17]).

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