Registry No.—Diacetone alcohol, 123-42-2.

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Notes

Valence Isomers. Substituent Effects on the Equilibrium between 2*H*-Pyrans and Cis Dienones[1,2]

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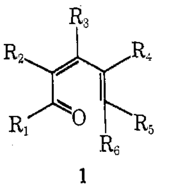
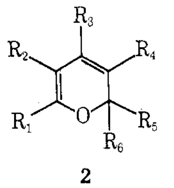
Received October 24, 1973

We have recently reported[3] that the system **1a** $\rightleftharpoons$ **2a** exists almost completely as the cis dienone **1a**, and that **2a** has a fleeting, but spectroscopically demonstrable, existence in the synthesis of the system. We have also reported unequivocally that the bicyclic system **3** exists 95% as the 2*H*-pyran at ambient temperatures,[4,5] whereas systems related to **4** exclusively favor the cis dienone owing to the fact that the corresponding valence isomers of **4** would have two relatively unstable exocyclic double bonds.[6,7] Other substituent factors that shift the position of the equilibrium between the valence isomers to the 2*H*-pyran are two alkyl substituents on C-2 of the 2*H*-pyran[8-11] and substituents which extend the conjugation, *e.g.*, phenyl groups.[12]

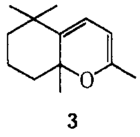


1

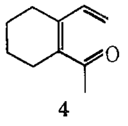


2

a, $R_1 = R_3 = R_5 = Me$; $R_2 = R_4 = R_6 = H$
b, $R_1 = R_5 = Et$; $R_3 = Me$; $R_2 = R_4 = R_6 = H$
c, $R_1 = R_5 =$ *t*-Bu; $R_3 = Me$; $R_2 = R_4 = R_6 = H$
d, $R_1 = R_2 = R_4 = R_5 = Me$; $R_3 = Et$; $R_6 = H$



3



4

The only case, here reported, which has been clearly observed to have a significant fraction of the 2*H*-pyran present in equilibrium with the cis dienone is the sterically hindered system **1d** $\rightleftharpoons$ **2d**. The equilibrium **1d** $\rightleftharpoons$ **2d** is clearly discernible by the lone proton substituent, which discloses that the system exists as 70–75% **2d** (quartet, $J = 6.0$ Hz, 0.7 H at δ 4.35) and 25–30% **1d** [quartet of quartets at higher resolutions, $J(\mathrm{H, CH_3}) = 7.00$ and $J(\mathrm{H,allyl\ CH_3}) \cong 1.0$ Hz, 0.3 H at δ 5.25]. The methyl group R_5 at δ 1.2 also confirms the *ca.* 70% equilibrium concentration of **1d** by its coupling[13] with the lone proton ($J = 6.0$ Hz) and low integration curve (*ca.* 2 H).

The methyl portion of the ethyl group centered at δ 0.95 also lends support to the equilibrium mixture in that it appears as two nearly superimposed triplets in the ratio of about 3:1 (total 3 H). All of the other protons are in a very complex pattern between δ 1.5 and 2.4. No 4*H*-pyran was present in the spectral sample since it would be clearly discernible by its high methyl peak at δ 0.65 and the broad single hydrogen peak at δ 2.5.

The ketone **1d** exhibits an unusually high, weak carbonyl band at 5.83 μ, presumably because of lack of orbital overlap with the conjugated double bond system because of the extreme steric interactions within the molecule.

In compounds **1a–c** and **2a–c**, it is more difficult to elucidate the position of the equilibrium. In compounds **1a** $\rightleftharpoons$ **2a**, the transient presence of the 2*H*-pyran is clear,[3] the cis character has been established,[14] and the trace ($\leq$5%) presence of the 2*H*-pyran in the purified product is retained in the nmr spectrum. However, close examination of the nmr spectra of **1b** $\rightleftharpoons$ **2b** and **1c** $\rightleftharpoons$ **2c** suggests that in these cases the increase in the substituent bulk of R_1 and R_5 shifts the equilibrium so that as much as 20–25% of the 2*H*-pyran is present at ambient temperatures. In both the ethyl and *tert*-butyl cases (**b**, **c**) the protons R_2, R_4, and R_6 in the ketone form integrate for less than one proton each, and the small peaks in the δ 4–6 range, characteristic of those protons in the 2*H*-pyran form,[3] are slightly stronger than in the methyl case (**a**), accounting for about 0.8 protons over-all in each case.

In the ethyl case **b**, further support to the significant presence of the 2*H*-pyran is given by the fact that there is at shoulder on the spike at δ 2.08, due to the methyl groups R_3, and there is a significant multiplet pattern in the δ 1.4–2.08 region which would be due to the methylene group of R_5 in the 2*H*-pyran form.

The *tert*-butyl case **c** shows two principal peaks at δ 1.10 and 1.15, but they account for only 75% of the *tert*-butyl protons. A smaller pair of peaks at δ 1.08 accounts for the remaining *tert*-butyl protons.

Assessment of chemical and spectral data to establish the presence of valence isomers and the position of their dynamic equilibrium requires considerable care. No one method, save perhaps for nmr spectroscopy, is reliable for this assessment. For example, several systems have been clearly demonstrated spectroscopically to exist exclusively in the cis-dienone form;[6,7,15] yet the Diels–Alder adduct isolated was exclusively that of the 2*H*-pyran. The clear indication is that the 2*H*-pyran is the more active Diels–Alder diene and the techniques cannot be used as proof of the 2*H*-pyran as the major isomer present at ambient temperatures, as was done in one other report.[16]

Infrared spectroscopy is ambiguous, since both the conjugated carbonyl and the 2*H*-pyran are expected to have a band at or below 5.96 μ.[17] The cis dienones **1a–c** do indeed have strong bands near or just below 5.96 μ, but they are not the usual most intense bands in the spectra, presumably because of the rapid dynamic equilibrium process with the valence isomer. The 2*H*-pyran **3** has a strong distinct band at 6.06 μ with weak shoulders at higher wave numbers, whereas the predominantly 2*H*-pyran compound **1d** $\rightleftharpoons$ **2d** has a strong hand at 5.96 μ in addition to the weaker but distinct band at 5.84 μ.

Ultraviolet spectroscopy is also quite ambiguous, since most of the cases presented in the literature have calculated valves for both isomers which are quite close in value based on the empirical Woodward's rules which were developed from steroidal models. We have, through numerous literature examples, shown that the vinyl ether of the 2*H*-pyran should have a contribution of 10–15 nm to the $\lambda_{\max}$,[14] and not zero as presented in the rules.

In view of these spectral and chemical difficulties, it is recommended that some reports on 2*H*-pyrans and cis dienones be reevaluated.[11,16] Compounds **1a** and **2a** have been recently reported,[11] but with the conclusion based on ultraviolet spectroscopy that the final product is the trans dienone, as opposed to our reports that it is the cis product.[3,14] The difference in the experimental technique most probably accounts for the real differences in the spectral values reported. One case[11] was done under neutral and acid conditions, whereas the other experiments[3,14] were always kept neutral to basic.

Conclusions

Evidence presented in this paper indicates that for simple cis dienone 2*H*-pyran systems (**1** $\rightleftharpoons$ **2**) increasing the steric bulk of the alkyl substituents shifts the equilibrium from the cis dienone toward the 2*H*-pyran.

Great caution is advised in the interpretation of chemical and spectral data for cis dienones and 2*H*-pyrans. Several techniques should be employed along with nmr spectroscopy, which probably is the most reliable tool.

A report[11] that the dienone product is the trans isomer was probably due to the fact that it was an acid-catalyzed rearrangement.

Experimental Section

5-Methyl-*cis*-4-*trans*-6-nonadien-3-one (1b) and 2,6-diethyl-4-methyl-2*H*-pyran (2b) were prepared and purified as previously described.[18] Distillation to remove the minor, lower boiling 4*H*-pyran by-product afforded the mixture **1b** $\rightleftharpoons$ **2b:** bp 123° (50 mm); $n^{20}{}_{\mathrm{D}}$ 1.4975; ir (neat) 5.84 (shoulder), 5.95, 6.13, and 6.32 μ; nmr (CCl_4) δ 1.0 (two nearly superimposed t, $J = 7.0$ Hz, 6 H), 1.78 (m, 2 H), 1.95 (d, $J = 1$ Hz, 3 H), 2.40 (m, 2 H), 5.88 (s, <1 H), 6.15 and 7.60 (AB part of an ABX pattern, $J_{AB} = 16$, $J_{AX} = 1$, and $J_{BX} = 6$ Hz, <2 H) plus smaller 2*H*-pyran (**3**) peaks at δ 4.4, 4.8, and 5.2 accounting for about 0.7 H.

2,2,5,8,8-Pentamethyl-*cis*-4-*trans*-6-nonadien-3-one (1c) and 2,6-(1,1-dimethylethyl)-4-methyl-2*H*-pyran (2c) were similarly prepared from the pyrylium salt.[19] Distillation at 126–128° (32 mm) produces the system **1c** $\rightleftharpoons$ **2c:** $n^{20}{}_{\mathrm{D}}$ 1.4770; ir (neat) 5.99 (m), 6.14 (w), 6.35 μ (s); nmr (CCl_4) δ 1.0 (two s, 4 H), 1.10 and 1.15 (two s, 14 H), 2.0 (broad s, 3 H), 6.10 (d, $J = 16$ Hz, <1 H), 6.2 (s, <1 H under portion of d centered at 6.1), 7.58 (d, $J = 16$ Hz, <1 H). Smaller characteristic peaks assigned to the 2*H*-pyran **3** are discernible in the normal spectrum at δ 4.4, 4.8 and 5.2 totally accounting for <1 H.

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 81.16; H, 11.97. A 2,4-dinitrophenylhydrazone was obtained, mp 165–167°.

Anal. Calcd for $C_{20}H_{28}N_4O_4$: C, 61.84; H, 7.27. Found: C, 61.81; H, 7.48.

4-Ethyl-3,5-dimethyl-*cis*-3-*trans*-5-heptadien-2-one (1d) and 4-ethyl-2,3,5,6-tetramethyl-2*H*-pyran (2d) were also prepared from the pyrylium salt[20] using 3-ethyl-2-pentene.[21] Separation of **3d** $\rightleftharpoons$ **4d** from the 4*H*-pyran major product was achieved on a Nester-Faust adiabatic spinning band column with a 50:1 reflux ratio with a second similar distillation of the higher boiling material. The desired product boils at 90° (18 mm) or 128° (32 mm), $n^{20}{}_{\mathrm{D}}$ 1.4794, and the 4*H*-pyran at 88° (18 mm). The product decomposes within a few weeks even when stored under nitrogen in the freezer. Refer to text for salient spectral data.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.79; H, 10.81.

A compound, mp 144–146°, presumably the semicarbazone, was isolated.

Registry No.—1b, 38391-02-5; **1c,** 38391-05-8; **1c** 2,4-dinitrophenylhydrazone, 51310-42-0; **1d,** 51310-43-1; **1d** semicarbazone, 51310-44-2; **2b,** 51310-45-3; **2c,** 51310-46-4; **2d,** 51310-47-5; **3,** 5552-30-7.

Supplementary Material Available. Nmr spectra for isomers 1a–d and 2a–d will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-1942.

References and Notes

(1) Support from the Old Dominion University Research Foundation and from the Society of the Sigma Xi is gratefully acknowledged. A preliminary report of this work was presented: T. A. Gosink, Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970, p 132. This report terminates the author's efforts in this field.

(2) See paragraph at end of paper regarding supplementary material.

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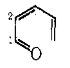

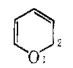

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Reactions of Sulfur Dichloride with Active Methylene Compounds. A New Synthesis of 1,3-Dithietanes

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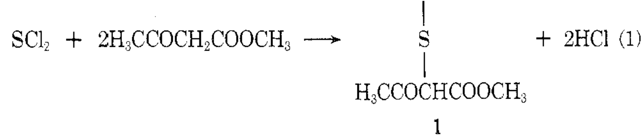
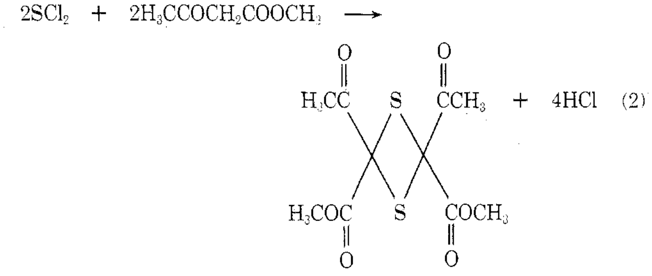
Sulfur dichloride (SCl_2) reacts with active methylene compounds under mild conditions to give sulfurated products in good yields. The course of product formation was dependent upon the reactivity of the active methylene moiety and the stoichiometry of the reaction. For example, sulfides 1 were produced with sulfur dichloride and a β-keto ester in a 1:2 ratio (eq 1).



$$\mathrm{SCl_2 + 2H_3CCOCH_2COOCH_3 \longrightarrow \begin{array}{c}H_3CCOCHCOOCH_3\\|\\S\\|\\H_3CCOCHCOOCH_3\end{array} + 2HCl}\quad(1)$$

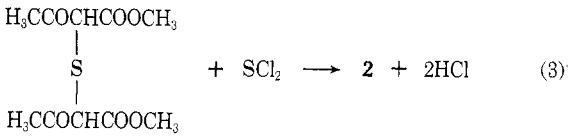
1

However, 1,3-dithietanes (2) were obtained when the stoichiometry of this reaction was changed according to eq 2.



2

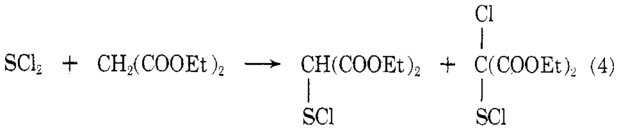
1,3-Dithietanes (2) were also synthesized by the reaction of sulfur dichloride with sulfides 1 (eq 3).



$$\begin{array}{c}\mathrm{H_3CCOCHCOOCH_3}\\|\\\mathrm{S}\\|\\\mathrm{H_3CCOCHCOOCH_3}\end{array} + \mathrm{SCl_2} \longrightarrow \mathbf{2} + \mathrm{2HCl}\quad(3)$$

1

Diethyl malonate, in sharp contrast to the results on the reaction of β-diketones and β-keto esters with SCl_2, reacted with sulfur dichloride according to eq 4.

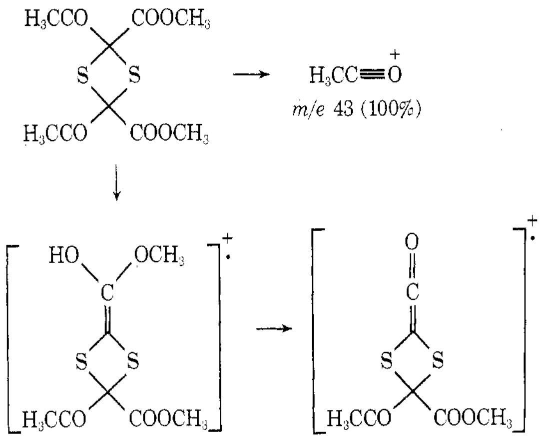


$$\mathrm{SCl_2 + CH_2(COOEt)_2 \longrightarrow \begin{array}{c}CH(COOEt)_2\\|\\SCl\end{array} + \begin{array}{c}Cl\\|\\C(COOEt)_2\\|\\SCl\end{array}}\quad(4)$$

The representative examples of the reactions of sulfur dichloride with active methylene compounds and the characterization data of the resultant products are summarized in Table I.[1]

A noteworthy feature of the reactions of sulfur dichloride reported here is the ready synthesis of 1,3-dithietanes (2) from β-diketones and β-keto esters. The structure of these 1,3-dithietanes is based on their nmr (absence of active methylene or methine hydrogens) and C, H, S analytical data. In addition to this, the mass spectral fragmentation pattern of 2 was similar to that expected for disubstituted β-keto esters (Scheme I),[2] and their desulfurization with Raney nickel regenerated the corresponding β-keto ester starting material.

Scheme I



The sulfides 1 are capable of existence in meso or *dl*-pair configuration. The 1,3-dithietanes of type 2, on the other hand, may involve cis–trans isomerism. Assignments in this regard have not been established and are beyond the scope of our current interests in this area.

Although the reactions of sulfenyl halides with various organic compounds are well known,[3] it is surprising that only few reactions of sulfur dichloride with organic compounds have so far been explored. These examples include the addition of SCl_2 to olefins,[3,4] dienes,[3,5] and carbon suboxide,[6] and the brief report on the reaction of SCl_2 with ethyl acetoacetate[7] and β-diethylaminoacrolein.[8] The present sequence of reactions thus opens a new area in organosulfur chemistry with many mechanistic and synthetic possibilities.

Experimental Section[9]

Reaction of Sulfur Dichloride with Active Methylene Compounds in a 1:2 Ratio. Bis(α-carbomethoxyacetonyl) Sulfide (1). A solution of 29.03 g (250 mmol) of methyl acetoacetate in 100 ml of ethyl acetate was cooled to 10° and then 14.4 g (125 mmol) of sulfur dichloride was added to it in 10 min with efficient stirring. The stirring was continued for an additional 1 hr at 25° and the