as well as condensation to a more complex α-pyranone. NMR data indicate that the enediones **3** are obtained as isomeric mixtures, and details of this aspect of these products will be described in a full publication.

The most consistently successful reaction conditions for the preparation of the α-ketoketene dithioacetals employed reaction of the methyl ketone (0.5 mol) with NaH (1.0 mol) in Me$_2$SO or benzene/dimethylacetamide, followed by the slow addition of carbon disulfide (0.5 mol) and then methyl iodide (1.0 mol), occasional cooling being used during this last addition. After 14 h at room temperature, the product was isolated from the reaction mixture by quenching with ice water and subsequent filtration or chloroform extraction.

In the preparation of the enediones **3** where $R \neq R^1$, a choice exists as to which ketone should be utilized as the α-ketoketene dithioacetal component. In addition to the question of availability of the ketone, we found that the α-ketoketene dithioacetal **1** in which R had some electron-withdrawing characteristic was usually the more reactive substrate and resulted in better yields of **3**.

This new synthesis of unsaturated 1,5-diketones now makes readily available a variety of pyrylium salts[22] and pyridine derivatives. Extensions of this reaction are currently under investigation in our laboratory, and full details of these and related transformations will be described in the complete publication.

(22) Potts, K. T.; Cipullo, M.; Ralli, P.; Theodoridis, G. *J. Am. Chem. Soc.*, following paper in this issue.

## Ketene Dithioacetals as Synthetic Intermediates. A Versatile Synthesis of Pyridines, Polypyridinyls, and Pyrylium Salts[1]

Kevin T. Potts,* Michael J. Cipullo, Philip Ralli, and George Theodoridis[†]

*Department of Chemistry, Rensselaer Polytechnic Institute*
*Troy, New York 12181*
*Received February 20, 1981*

Noteworthy among the numerous syntheses of substituted pyridines described[2] in the literature is the use of organolithium compounds for the preparation of arylpyridines,[3] 2,2′-bipyridinyls,[4] and 2,2′,2″-terpyridinyls[5] and the application of pyridinium phenacylides or their salts in the synthesis of a wide variety of 2,4,6-trisubstituted pyridines.[6] This latter procedure has been applied to the synthesis of numerous substituted bi-, ter-, quater-, quinque-, sexi- and septipyridinyls, all of which are of interest as ligands for metal chelation. 2,2′-Bi- and 2,2′,2″-terpyridinyl have attracted the most attention in this respect,[7] and the 4′-(4-methoxyphenyl)terpyridinyl[8] and its sulfonated[9] derivative have been introduced in clinical chemistry for the estimation of Fe$^{2+}$. In general these oligopyridines are high melting products and are not easily soluble in the usual organic solvents, factors which have restricted somewhat their further development. We now describe

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(1) Supported in part by NSF Grant CHE 79-01704.
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Table I. Substituted Pyridines Derived from α-Ketoketene Dithioacetals **2**[11]
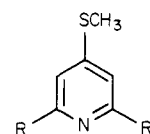


| R | R$^1$ | mp, °C | yield, % | M$^{+.a}$ |
|---|---|---|---|---|
| C$_6$H$_5$ | C$_6$H$_5$ | 105–107 | 81 | 277 |
| 4-CH$_3$OC$_6$H$_4$ | CH$_3$ | 69–70 | 70 | 245$^b$ |
| 4-BrC$_6$H$_4$ | 4-BrC$_6$H$_4$ | 115–116 | 85 | 435 |
| 4-CH$_3$OC$_6$H$_4$ | 4-CH$_3$OC$_6$H$_4$ | 90.5–91 | 48 | 337 |
| C$_6$H$_5$ | 2-C$_5$H$_4$N | 80–81 | 89 | 278 |
| 2-C$_5$H$_4$N | 2-C$_5$H$_4$N | 133–133.5 | 79 | 279 |
| 2-C$_5$H$_4$N | 2-C$_4$H$_3$S | 133–134 | 80 | 284 |
| 6-Br-2-C$_5$H$_3$N | 6-Br-2-C$_5$H$_3$N | 184–185 | 31 | 437 |
| 2-C$_4$H$_3$S | 2-C$_4$H$_3$S | 115–116 | 99 | 289 |
| 2-C$_4$H$_3$S | 5-Cl-2-C$_4$H$_2$S | 115–116 | 72 | 323 |
| 2-C$_4$H$_3$O | 2-C$_4$H$_3$O | 96–97 | 64 | 257 |
| 2-C$_4$H$_3$O | 2-C$_4$H$_3$S | 95–97 | 74 | 273 |

$^a$ Relative intensities, 100%.    $^b$ 93%.

a versatile, direct synthesis of a variety of substituted pyridines and oligopyridines with favorable solubility characteristics.

Our "one-pot", two-component procedure involves the in situ generation of unsaturated 1,5-diketones derived[10] by reaction of α-ketoketene dithioacetals and methyl ketone carbanions. Reaction of these enediones with ammonium acetate in hot acetic acid gives the 2,6-disubstituted-4-(methylthio)pyridines, a representative selection of which is shown in Table I. Alternatively, the 1,5-enedione may be isolated before conversion into the pyridine although, in general, this offers no advantages over the more direct procedure. The synthesis of 2,2′,2″-terpyridine (**4**, $R = R^1 = 2$-C$_5$H$_4$N; $R^2 = H$; $X = N$) illustrates the general procedure used.

2-Acetylpyridine (**1**, $R = 2$-C$_5$H$_4$N) was converted into 3,3-bis(methylthio)-1-(2-pyridinyl)-2-propen-1-one[11] (**2**; $R = 2$-C$_5$H$_4$N) by using NaH/Me$_2$SO, CS$_2$ and CH$_3$I and was obtained[10] as yellow needles (71%) from ethanol, mp 108–109 °C, $\nu_{CO}$ 1605 cm$^{-1}$, M$^+$· 225. This α-ketoketene dithioacetal (3.0 g, 0.013 mol) was added to a solution of 2-acetylpyridine (1.6 g, 0.013 mol) and potassium *tert*-butoxide (3.0 g, 0.027 mol) in dry THF (80 mL). After stirring for 3 h at room temperature, ammonium acetate (10.0 g, 0.13 mol) and glacial acetic acid (80 mL) were added to the above solution which was then heated for 2 h with continuous removal of THF. After cooling, addition of ice water resulted in the separation of 2,6-di(2-pyridinyl)-4-(methylthio)-pyridine (**4**, $R = R^1 = 2$-C$_5$H$_4$N; $R^2 = SCH_3$; $X = N$) which crystallized from ethanol–water as colorless needles, 2.0 g (79%), mp 120–121 °C, M$^+$· 279. Refluxing this product with an excess of Raney nickel (6 h) in ethanol gave 2,2′,2″-terpyridine (**4**, $R = R^1 = 2$-C$_5$H$_4$N; $R^2 = H$; $X = N$) as cream prisms (60%), mp 84–85 °C (lit.[12] mp 84–85 °C), M$^+$· 233.2735 (100%).

This reaction sequence is also useful for pyridine ring annulation to a variety of cycloalkyl ketones. Reaction of **2** ($R = 4$-CH$_3$OC$_6$H$_4$) with cyclohexanone under the above conditions gave **5** ($X = N$) as colorless needles (10%), mp 105–106 °C, M$^+$· 285 (100%). In addition quinquepyridines may also be obtained by this route. Reaction of **6** (3.0 g, 0.013 mol) with 2-acetylpyridine (1.09 g, 0.0066 mol) and potassium *tert*-butoxide (3.0 g, 0.027 mol) in dry THF as above gave 2,6-bis[2′-(4′-methylthio)-6′-(2″-pyridinyl)pyridinyl]pyridine (**7**) as colorless flakes from DMF: 1.5 g (53%), mp 265–266 °C, M$^+$· 479.6271 (100%).

These 1,5-enediones also provide a ready entry into a variety of substituted pyrylium salts. This new procedure overcomes the

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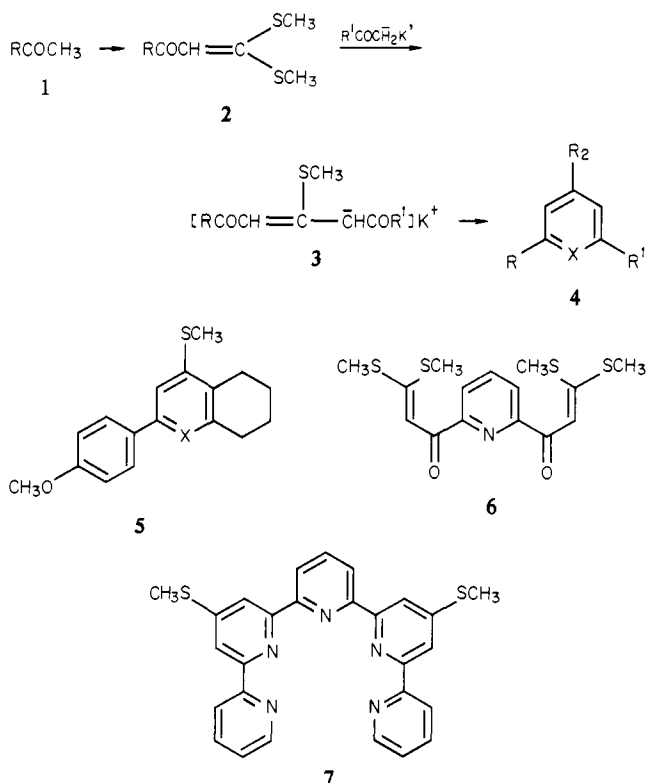
majority of the disadvantages of current procedures[13] and approaches the goal of a general synthesis. It is illustrated by the preparation of 2-methyl-4-(methylthio)-6-(4-methoxyphenyl)pyrylium tetrafluoroborate (**4**, R = 4-$CH_3OC_6H_4$; $R^1$ = $CH_3$; $R^2$ = $SCH_3$; X = $O^+BF_4^-$). Potassium *tert*-butoxide (5.04 g, 0.045 mol) was added to a stirred mixture of acetone (1.2 g, 0.02 mol) and the ketene dithioacetal **2** (R = 4-$CH_3OC_6H_4$; 5.0 g, 0.02 mol). An initial yellow suspension changed over a 16-h reaction period into a dense green precipitate of **3** (R = 4-$CH_3OC_6H_4$; $R^1$ = $CH_3$). This was collected and added to an ice-cold 4% HCl solution (200 mL), giving[10] the corresponding 1,5-diketone as a thick suspension which was collected and then stirred in dichloromethane (40 mL) with $HBF_4$ (20 mL of 48% solution) for 4 h at 50 °C. The yellow pyrylium salt separated during this period, and after addition of water (20 mL), the pyrylium salt was collected. It crystallized from acetic acid as light yellow needles (70%), mp 207–210 °C dec. Use of cyclohexanone as the ketonic component in the above reaction gave 2-(4-methoxyphenyl)-4-(methylthio)-5,6,7,8-tetrahydrobenzopyrylium tetrafluoroborate (**5**, X = $O^+BF_4^-$) as yellow-green needles (40%) from acetic acid, mp 246–250 °C dec. Aromatic substituents were readily introduced into the 2,6-positions; e.g., use of 4-methoxyacetophenone (**1**; $R^1$ = 4-$CH_3OC_6H_4$) in the above reaction gave 2,6-bis(4-methoxyphenyl)-4-(methylthio)pyrylium tetrafluoroborate (**4**, R = $R^1$ = 4-$CH_3OC_6H_4$; $R^2$ = $SCH_3$; X = $O^+BF_4^-$) as yellow prisms (53%) from acetic acid, mp 288–290 °C dec. In some cases the yield approaches quantitative as in the formation of 2,6-diphenyl-4-(methylthio)-pyrylium tetrafluoroborate (**4**, R = $R^1$ = $C_6H_5$; $R^2$ = $SCH_3$; X = $O^+BF_4^-$) which was isolated as pale-green needles (93%) from 1,2-dichloroethane, mp 253–255 °C. The variety of aryl and heterocyclic ketones,[14] either as the α-ketoketene dithioacetal component or the ketonic component, which take part in this reaction allows the introduction of a wide variety of substituents in the 2 and 6 positions.

Alternatively, this synthesis may be accomplished in a one-pot reaction. In this case the 1,5-diketone is not isolated, and the

tetrafluoroboric acid is merely added to the initial THF reaction mixture. The product is contaminated with $KBF_4$ which may be removed by washing with hot water, resulting in a reduced yield of the pyrylium salt. This procedure is best with aromatic substituents in the 2 and 6 positions. The 4-methylthio group in **4** (X = $O^+BF_4^-$), similar to the 4-chloro[15] and 4-methoxy groups,[16] is susceptible to displacement by nucleophiles such as secondary amines.

This synthesis offers many advantages over those currently used[17] for the preparation of the corresponding 4-(substituted-thio)pyrylium salts. As pyrylium salts of the corresponding 1,5-diketones are readily converted into thiopyrylium[18] and selenopyrylium[19] salts, these ring systems are now readily available with similarly diverse substitution patterns. Further extensions and applications of these syntheses are currently being studied in our laboratory.

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## Laser Flash Photolysis with NMR Detection. Submicrosecond Time-Resolved CIDNP: Kinetics of Triplet States and Biradicals
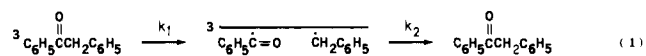
G. L. Closs* and R. J. Miller

*Department of Chemistry, The University of Chicago Chicago, Illinois 60637*

*Received March 5, 1981*

Recently we described a time-resolved CIDNP investigation of the laser flash photolysis of benzyl phenyl ketone.[1] The time resolution of those experiments ($1 \times 10^{-6}$ s) was sufficient to discriminate between the geminate radical pair process and the much slower formation of random phase products on the time scale of diffusion-controlled encounters. The purpose of the present paper is to report attainment of a time resolution of $1 \times 10^{-7}$ s by employing a high-power, broad-band pulse amplifier and active switching of the quality factor of the single coil probe circuitry.[2] This improvement makes NMR detection applicable to a greater diversity of dynamic phenomena. The results of experiments conducted on two ketones that react by Norrish type I cleavage shall serve as illustrative examples.

The investigation of benzyl phenyl ketone has been extended to the submicrosecond time domain. The results reported previously establish that any time dependency observable over the range of hundreds of nanoseconds must be attributable solely to the geminate recombination reaction (eq 1).[1] Singlet–triplet

$$^3C_6H_5\overset{O}{\overset{\|}{C}}CH_2C_6H_5 \xrightarrow{k_1} {}^3\overline{C_6H_5\dot{C}=O \quad \dot{C}H_2C_6H_5} \xrightarrow{k_2} C_6H_5\overset{O}{\overset{\|}{C}}CH_2C_6H_5 \quad (1)$$

intersystem crossing in the n,π* state of the ketone is taken to be very fast, and parallel decay routes for the excited state ketone are neglected. Further, it is assumed that the dynamics describing the evolution of the spin states in the geminate radical pair and the chemical kinetics characterizing σ-bond formation to diamagnetic product can be consolidated into one phenomenological, first-order rate coefficient, $k_2$. The development of the signal from the emissively polarized benzyl protons of benzyl phenyl ketone is depicted in Figure 1. The large data scatter results from the poor signal-to-noise ratios obtained in this particular system. A

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