$CH_3C_6H_4SO_2$) as colorless prisms, 1.0 g (68%), mp 189–192 °C dec (with gas evolution).

Hydrolysis of 11 (R = p-$CH_3C_6H_4SO_2$). A. With Methanol. The adduct (0.7 g, 0.0019 mol) was refluxed in dry methanol for 4 h. Solvent was removed in vacuo and the residue recrystallized from ethanol, affording 2-methoxycarbonyl-2-(*N*-benzoyl-*N*-methylamino)acet-*p*-toluenesulfonamide (**12**) as small, colorless, clustered needles: 0.55 g (57%); mp 157–159 °C; ir (KBr) 3000 (broad, CH), 1750, 1720 cm^{-1} (CO); λ_{max} (CH_3OH) 226 nm (log ϵ 4.45); NMR ($CDCl_3$) δ 10.93 (bs, 1, NH, exchanged with D_2O), 7.17–7.97 (m, 9, aromatic), 5.33 (s, 1, C_2 H, exchanged with D_2O), 3.73 (s, 3, OCH_3), 3.00 (s, 3, NCH_3), 2.42 (s, 3, aryl CH_3); M^+· 403 (2).

Anal. Calcd for $C_{19}H_{20}N_2O_6S$: C, 56.56; H, 4.75; N, 6.95. Found: C, 56.45; H, 4.73; N, 6.83.

B. With 10% Sodium Hydroxide Solution. The adduct (1.0 g, 0.0027 mol) was heated on a steam bath with 10% sodium hydroxide (15 ml) for 5 min. The reaction mixture was cooled, neutralized with 3 N HCl, and extracted with chloroform. The chloroform layer was separated, dried over sodium sulfate, and evaporated in vacuo, leaving a colorless, crystalline residue which recrystallized from 1,2-dichloroethane–anhydrous ether yielding 2-(*N*-benzoyl-*N*-methylamino)acet-*p*-toluenesulfonamide (**13**) as colorless prisms: 0.2 g (20%); mp 156–157°; ir (KBr) 3000 (broad), 1710, 1625 cm^{-1}; λ_{max} (CH_3OH) 226 nm (log ϵ 4.32); NMR ($CDCl_3$) δ 7.17–7.92 (m, 9, aromatic), 4.13 (bs, 2, CH_2), 3.02 (s, 3, NCH_3), 2.43 (s, 3, aryl CH_3); M^+· 346 (6).

Anal. Calcd for $C_{17}H_{18}N_2O_4S$: C, 58.94; H, 5.24; N, 8.09. Found: C, 58.86; H, 5.13; N, 8.25.

Hydrolysis of 12. Treatment of **12** with 10% sodium hydroxide on a steam bath for 15 min, extraction of the reaction with chloroform, and evaporation of the chloroform extract afforded a colorless, crystalline solid identical[23] with **13** above.

Acknowledgments. It is a pleasure to acknowledge the assistance of Dr. E. Williams, G. E. Corporate R & D Center, Schenectady, N.Y., in the determination of the ^{13}C NMR data.

Registry No.—**1** (R = Ph), 13288-67-0; **1** (R = p-ClC_6H_4), 52730-97-9; **6**, 57513-31-2; **7**, 57513-32-3; **8**, 57513-33-4; **9**, 2568-34-5; **12**, 57513-34-5; **13**, 57513-35-6; phenyl isothiocyanate, 103-72-0; phenyl isocyanate, 103-71-9; benzoyl isocyanate, 4461-33-0; *p*-chlorobenzoyl isocyanate, 4461-36-3; trichloroacetyl isocyanate, 3019-71-4; *p*-toluenesulfonyl isocyanate, 4083-64-1; *N*-chlorosulfonyl isocyanate, 1189-71-5; acetyl isothiocyanate, 13250-46-9.

References and Notes

(1) (a) Support of this work by U.S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged; (b) abstracted in part from the Ph.D. Thesis of J.B., 1973; (c) NSF Trainee.
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Mesoionic Compounds. XXXVI. Reaction of Mesoionic Systems with Diphenylcyclopropene Derivatives[1]

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anhydro-2,3-Diphenyl-4-hydroxythiazolium hydroxide and diphenylcyclopropenone at 80° gave a 1:1 cycloadduct shown to be 2,3,5,6-tetraphenyl-6-aza-8-thiabicyclo[3.2.1]oct-2-ene-4,7-dione which, on thermolysis, lost the elements of COS forming 1,4,5,6-tetraphenyl-2(1*H*)-pyridone. With diphenylcyclopropenethione at room temperature the corresponding 7-oxo-2,3,5,6-tetraphenyl-6-aza-8-thiabicyclo[3.2.1]oct-2-ene-4-thione was formed which, on thermolysis, gave 3,4,6-triphenyl-2*H*-thiopyran-2-thione and 4-oxo-2,3,6,7-tetraphenyl-2*H*-1,3-thiazocinium 8-thiolate. *anhydro*-2-*p*-Chlorophenyl-4-hydroxy-3-phenylthiazolium hydroxide gave an analogous series of *p*-chlorophenyl substituted products. *anhydro*-2,4-Diphenyl-5-hydroxy-3-methyl-1,3-oxazolium hydroxide, generated in situ from *N*-benzoyl-*N*-methyl-*C*-phenylglycine and Ac_2O, and diphenylcyclopropenone gave 1-methyl-2,3,5,6-tetraphenyl-4(1*H*)-pyridone, and the corresponding thione was formed with diphenylcyclopropenethione. Reaction with 1,2,3-triphenylcyclopropene gave 1-methyl-2,3,4,5,6-pentaphenyl-1,4-dihydropyridine. *anhydro*-5-Hydroxy-3-methyl-2-phenylthiazolium hydroxide and diphenylcyclopropenethione underwent reaction at room temperature giving 1-methyl-2,3,5-triphenyl-4(1*H*)-pyridinethione, whereas with diphenylcyclopropenone no reaction occurred. Chemical and spectral evidence used to establish these structures is described.

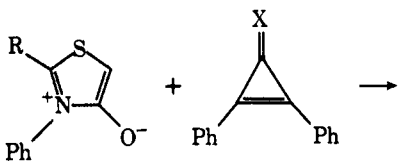
In the short time since the initial synthesis[2] of diphenylcyclopropenone, it has found applications as a versatile intermediate in organic synthesis.[3] As would be anticipated from its physical characteristics, it is a particularly interesting substrate in cycloaddition reactions and this property is shared to some degree by its thio analogue. Cycloadducts have been formed with carbonyl ylides,[4] heteroaromatic ring systems such as pyridine, pyridazine, etc.,[5] some 1,3-dipolar systems,[6] and also with enamines and other electron-rich olefinic systems.[7] Recently 1-azirines were

shown to react with diphenylcyclopropenone forming 4-pyridones.[8]

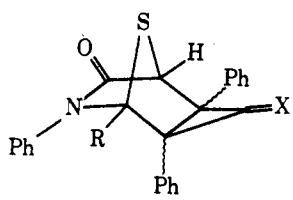
Previous papers in this series on mesoionic compounds described the reactions of the *anhydro*-2,3-disubstituted 4-hydroxythiazolium hydroxide system with acetylenic[9] and olefinic[10] dipolarophiles and, as a part of the study of the chemistry of mesoionic compounds,[11] we have investigated the reaction of this and several other mesoionic rings systems with diphenylcyclopropene derivatives.

anhydro-2,3-Diphenyl-4-hydroxythiazolium hydroxide (1, R = Ph) contains a "masked" thiocarbonyl ylide 1,3-dipole. Annelation of the three-carbon system of cyclopropene to the mesoionic ring offers the opportunity for a [3 + 3] cycloaddition with possible thermal ring expansions to six-membered and larger ring systems. Reaction of diphenylcyclopropenone with 1,3-dipoles has been observed to occur in three ways: addition across the carbonyl group;[6,12] addition across the carbon–carbon double bond;[13] a C–C insertion reaction such that the final product is an α,β-unsaturated ketone.[2c,4,7] The first two addition modes are usually accompanied by further skeletal rearrangement and, in the last, the initial reaction probably occurs at the C-2 atom of the three-membered ring.

Reaction of the mesoionic system 1 (R = Ph) and diphenylcyclopropenone in refluxing benzene gave a stable 1:1 adduct. Its molecular formula, $C_{30}H_{21}NO_2S$, established by analytical and mass spectral data, may be accommodated by structures **2**, **3**, **4**, or **5** (R = Ph; X = O), repre-



1 X = O,S



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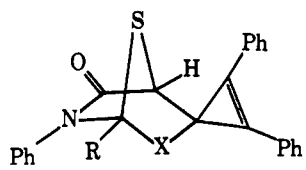

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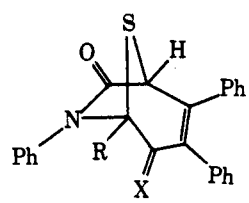

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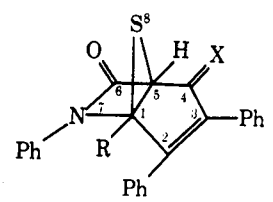

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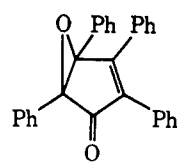


6

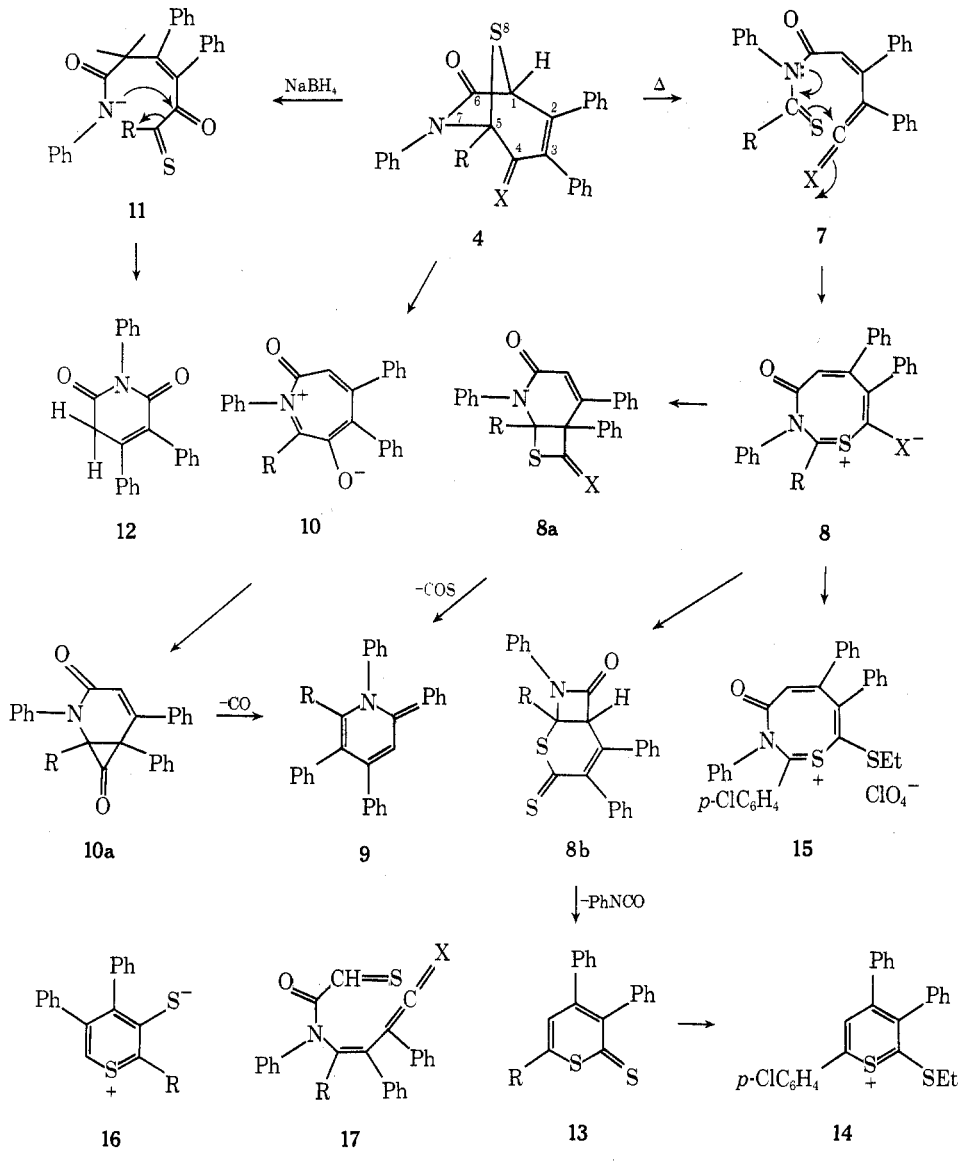
senting 1:1 adducts formed by the various addition modes described above. Structures **2** and **3** may be excluded immediately on the basis of the infrared spectral data. A carbonyl absorption at 1650 cm^{-1} attributed to the amide carbonyl group and an additional absorption at 1725 cm^{-1} are not consistent with a carbonyl group in a cyclopropane ring (for structure **2**, ν_{CO} ca. 1875–1800 cm^{-1})[14] nor with structure **3**. Structures **4** and **5** are, however, compatible with the additional carbonyl absorption at 1725 cm^{-1}, an analogous chromophore absorbing[15] at 1727 cm^{-1} in 4,5-epoxy-2,3,4,5-tetraphenylcyclopenten-1-one (**6**) and in 2,3-diphenylcyclopenten-2-one at 1681 cm^{-1}. This same chromophore in **6** has an ultraviolet absorption at 233 nm (log ϵ 4.23) and 338 (3.85), whereas the cycloadduct above exhibits its absorption maxima at 205 nm (log ϵ 4.64), 246 (4.45), 300 (4.26), and 353 (4.17). This shift to longer wavelength may be attributed to interaction of the bridge sulfur atom with the carbonyl chromophores of the amide and α,β-unsaturated ketone systems, a feature observed previously with adducts from 1 and heterocumulenes.[16]

A distinction between structures **4** and **5** can be made, however, on the basis of NMR data. In addition to the aromatic multiplet at δ 7.8–6.7 a singlet proton resonance was observed at δ 6.1 and this proton was not exchanged with D_2O–NaOD. This is more consistent with structure **4** than **5**, for in the latter this bridgehead proton would be expected to be at much lower field, being in the deshielding zones of the two flanking carbonyl groups. Though there is a change in the geometry of the bicyclo[3.2.1]octane system compared to the bicyclo[2.2.1]heptane system present in the cycloadducts from 1 and heterocumulenes,[16] it should not be sufficient to result in a chemical shift change from ca. δ 10 to δ 6.1.

The mass spectrum of **4** (R = Ph; X = O) is particularly informative. A fragmentation of the molecular ion, *m/e* 459.1291, involves the loss of CO giving an ion $C_{29}H_{21}NOS$ (*m/e* 431.1396) corresponding to the product anticipated from the reaction of **1** (R = Ph) and diphenylacetylene. The cycloreversion of this process was observed with the formation of the diphenylacetylene ion $C_{14}H_{10}$ (*m/e* 178.0803) and the ion corresponding to 1 (R = Ph), $C_{15}H_{11}NOS$ (*m/e* 253.0580).[17] These processes can only be interpreted in terms of structures **4** or **5**. Additional evidence in support of **4** comes from the formation of 1,4,5,6-tetraphenyl-2(1*H*)-pyridone (**9**, R = Ph) on thermolysis of **4** (R = Ph; X = O). Cleavage of the 4,5 bond in **4** to the intermediate ketene **7** (R = Ph; X = O), followed by rearrangement through the resonance-stabilized betaine **8** (R = Ph; X = O) and its valence tautomer **8a** (R = Ph; X = O), provides a satisfactory explanation for the formation of **9** (R = Ph). An alternative route, initiated by loss of S from **4** to give an intermediate betaine **10** (R = Ph) followed by rearrangement to **10a** (R = Ph) with subsequent loss of CO, is relatively unlikely. Experience has shown that loss of S from adducts such as **4** only occurs readily when an aromatic ring system is formed in the process.[10,16] This thermal rearrangement dictates against the alternative formulation of the adduct as structure **5**. Although cleavage of the 4,5 bond in **5** would give rise to a ketene intermediate **17** (X = O) that, by ring closure and elimination of COS as above, would give the pyridone **9**, the intermediate **17** would be anticipated to be an extremely unstable product with little tendency to undergo ring closure to an intermediate analogous to **8** (X = O).

The structure of the pyridone **9** was assigned on the basis of analytical and spectral data. Mass spectrometry and analytical data established the molecular formula as $C_{29}H_{21}NO$ and, in addition to the aromatic proton multiplet at δ 7.1–7.8 in the NMR spectrum, a sharp singlet occurred at δ 6.4. The analogous 3 proton in 2-pyridone has been observed[18] at δ 6.57, substituents in the ring having only minor effects on this chemical shift.

Reaction of *anhydro*-2-*p*-chlorophenyl-4-hydroxy-3-phenylthiazolium hydroxide (**1**, R = *p*-ClC_6H_4) with diphenylcyclopropenone gave rise to the 5-*p*-chlorophenyl



analogue of **4** (R = p-ClC_6H_4) with spectral characteristics consistent with those of **4** (R = Ph).

The action of $NaBH_4$ on **4** (R = Ph or p-ClC_6H_4; X = O) gave a product of molecular formula $C_{23}H_{17}NO_2$, requiring loss of the C_5 atom as some combination of RCS. The isolation of a small amount of sulfur-containing polymeric substance indicates that this species was most likely the appropriate thioaldehyde. Structure **12** readily accommodates two carbonyl groups at 1740 and 1670 cm^{-1}, and may be formed by hydride ion attack at the C_1 bridgehead position in preference to the more sterically hindered C_5 position with formation of **11**, followed by ring closure to **12**. In agreement with this structure, the NMR spectrum of **12**, 1,3,4-triphenyl-2,6-dioxo-1,2,5,6-tetrahydropyridine, showed a two-proton singlet at δ 4.00 in addition to the aromatic protons at δ 6.87–7.60.

Diphenylcyclopropenethione also reacted readily with **1** forming 1:1 cycloadducts at room temperature in anhydrous benzene over 18 h, these adducts being assigned the structure of 7-oxo-2,3,5,6-tetraphenyl-6-aza-8-thiabicyclo[3.2.1]oct-2-ene-4-thione (**4**, R = Ph; X = S). The chemical shift of the C_1 bridgehead proton was observed at δ 6.2, a chemical shift inconsistent with the alternative structure **5** (R = Ph; X = S) in which the bridgehead proton would be in the deshielding zone of both the C_7 carbonyl group and the C_2 thiocarbonyl group. Absorptions consistent with a C=S group were observed in the 1020–1250-cm^{-1} region and an absorption at 1650 cm^{-1} may be attributed to the C_7 carbonyl group.

On thermoylsis, **4** (R = Ph, p-ClC_6H_4; X = S) formed two brilliant-red products. The first product isolated from chromatography of the reaction mixture was identified as 6-aryl-3,4-diphenyl-2*H*-thiopyran-2-thione (**13**, R = Ph, p-ClC_6H_4). Its spectral characteristics, especially the NMR data and ultraviolet absorption, were consistent with data reported for analogous structures in the literature, and the 3,4,6-triphenyl derivative **13** (R = Ph) was synthesized by an alternative route utilizing the reaction of 1-(benzoylmethyl)pyridinium bromide and diphenylcyclopropenone[19] to give the 3,4,6-triphenyl-2*H*-pyran-2-one which was converted into the 2-thione with P_4S_{10}–pyridine, and the 2*H*-pyran-2-thione isomerized[20] to the corresponding 2*H*-thiopyran-2-one which finally with P_4S_{10}–pyridine gave the 2*H*-thiopyran-2-thione **13** (R = Ph). Reaction with Meerwein's reagent gave the corresponding 2-ethylthio derivative **14**.

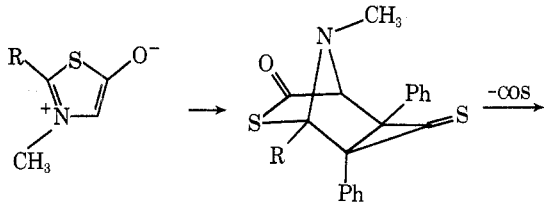
The second product formed in the thermolysis was isomeric with **4** (R = Ph, p-ClC_6H_4; X = S). Structure **8** (R = Ph, p-ClC_6H_4; X = S), 2-aryl-4-oxo-3,6,7-triphenyl-2*H*-1,3-thiazocinium 8-thiolate, was consistent with its chemical and spectral properties, and it reacted readily with Meerwein's reagent to give the corresponding SEt product **15**. The chemical shift of the methylene protons at δ 3.3 (qt) correlates well with an SEt group adjacent to a posi-

tively charged sulfur atom rather than with those of an OEt group.[21]

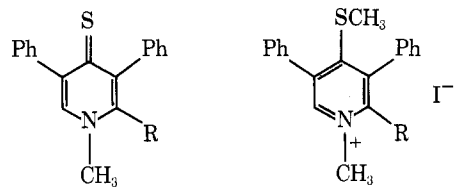
In the thermolysis of 4 (X = O, S), the intermediate ketene 7 (X = O) and thioketene 7 (X = S) satisfactorily explain all the observed products. Ring closure to 8 (X = O) ultimately leads[22] to the pyridone 9 whereas in 8 (X = S) an alternative valence isomerization to 8b and subsequent loss of phenyl isocyanate give the thiopyranthione 13. A product 16 isomeric with 13 could conceivably be derived by elimination of PhNCO from 4 (X = S) but, as shown above, this retrocycloaddition is not favored in this thermolysis over fission of the 4,5 bond. Similarly the intermediacy of the ketene 17 (X = O) or thioketene (X = S) derived from 5 can be excluded by the above results.

In contrast to the ready reaction of 1 with diphenylcyclopropenone and diphenylcyclopropenethione, the 5-phenyl derivative of 1 did not undergo any reaction, an observation also noted by others.[23]

The isomeric thiazole mesoionic system 18 and diphenylcyclopropenone in refluxing benzene did not form a cycloadduct. Instead the diphenylcyclopropenone dimer was isolated. In view of the reaction reported recently[23] for its 4-phenyl derivative, this failure to isolate a product is probably due to the thermal instability of 18, a not uncommon occurrence in cycloadditions with this ring system. However, with diphenylcyclopropenethione, 18 (R = Ph, p-ClC_6H_4), readily gave a product in benzene at room temperature identified as 2-aryl-3,5-diphenyl-1-methyl-4(1H)-pyridinethione (20, R = Ph, p-ClC_6H_4). The most direct route to this product involves an intermediate such as 19 (see below) which loses COS to form the observed product.



18 19

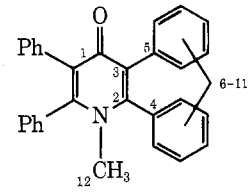


20 21

The following spectral data for 20 are consistent with a thiopyridone structure. In the infrared spectrum a C=C absorption at 1610 cm^{-1} and absorption maxima in its ultraviolet spectrum [360 nm (log ϵ 3.96), 267 (3.71), and 226 (4.13)] were analogous to those reported for the thiopyridone 24 (X = S). The C_6 H was masked in the aromatic multiplet between δ 7.00 and 8.00 in the NMR spectrum, and the mass spectrum gave a fragmentation pattern analogous to that obtained for 24 (X = S). When 20 was converted into a methylated derivative 21 with methyl iodide, the C_6 proton was shifted downfield to δ 8.74.

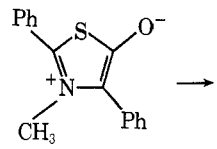
The different modes of cycloaddition of the isomeric thiazolium mesoionic systems suggested extension of these studies to other mesoionic systems. 3-Phenyl- and 3-methylsydnone were found to be unreactive with diphenylcyclopropenone and its thione but *anhydro*-2,4-diphenyl-5-hydroxy-3-methyl-1,3-oxazolium hydroxide (22) reacted readily. This mesoionic system can be utilized most effectively

Table I. ^{13}C Chemical Shifts of 1-Methyl-2,3,5,6-tetraphenyl-4-pyridone[25b]



Assigned carbon	Chemical shift, ppm	Assigned carbon	Chemical shift, ppm
1	189.7	5	134.9
2	175.3	6–11	126.2–131.3
3	149.5	12	41.3
4	135.5		

by generation *in situ* from *N*-benzoyl-*N*-methyl-*C*-phenylglycine and acetic anhydride[24] and when this mixture was heated at 85°C for 10 min with diphenylcyclopropenone, 1-methyl-2,3,5,6-tetraphenyl-4(1H)-pyridone (24, X = O) was obtained as colorless needles. The reaction may proceed through the intermediacy of a cyclopropanone 23 (X = O) with concomitant loss of CO_2 to the pyridone 24 (X = O). However, alternative modes of addition to 22 are possible, and would result in the formation of the isomer, *anhydro*-3-hydroxy-1-methyl-2,4,5,6-tetraphenylpyridinium hydroxide (25, X = O). Spectral data (Experimental Section), especially ν_{CO} 1620 cm^{-1}, do not allow an unambiguous assignment of structure but favor structure 24 over 25.



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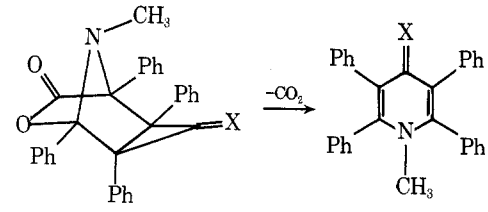
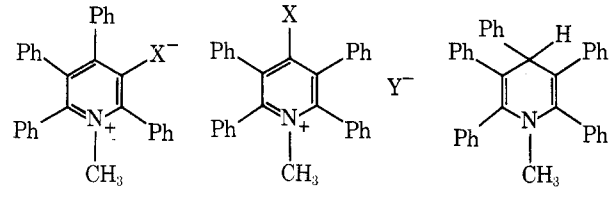


23 24



25 26 27

The simplicity of the ^{13}C PFT spectrum of the product is indicative of the symmetry within 24 which theoretically should give rise to a 12-line spectrum. Chemical shifts (downfield from Me_4Si) and carbon assignments are shown in Table I. The pyridone 24 (X = O) was characterized further by conversion with Meerwein's reagent into 4-ethoxy-1-methyl-2,3,5,6-tetraphenylpyridinium tetrafluoroborate (26, X = OEt; Y = BF_4) whose spectral data are fully consistent with this structural assignment. An interesting feature of the mass spectrum of the salt 26 (X = OEt; Y = BF_4) was the incorporation of fluorine into the pyridine ring. It may be speculated that, after initial, thermal loss of BF_3, the residual fluorine covalently bonds with the pyridine ring, most likely at the 2 position, and accounts for a

series of ions, $C_{32}H_{28}FNO$, *m/e* 461 (11), $C_{32}H_{29}FNO$, *m/e* 460 (5), and $C_{30}H_{23}FNO$, *m/e* 432 (2).

Confirmation of the structure of the product from **22** and diphenylcyclopropenone as **24** (X = O) was obtained by its synthesis by an alternative route from 2,3,5,6-tetraphenyl-4(4*H*)-pyrone and methylamine.[25a]

When diphenylcyclopropenethione and *N*-benzoyl-*N*-methyl-*C*-phenylglycine were heated in acetic anhydride at 40 °C for 5 min, a product crystallized from solution and corresponded to the loss of CO_2 from a primary cycloadduct. Ambiguity in structural assignment exists in this case as well, depending upon the mode of cycloaddition to **22.** If C=C addition to **22** had occurred, then 1-methyl-2,3,5,6-tetraphenyl-4(1*H*)-pyridinethione (**24,** X = S) would result. If C–CS insertion had occurred, then *anhydro*-3-mercapto-1-methyl-2,4,5,6-tetraphenylpyridinium hydroxide (**25,** X = S) would be formed. That C=C addition had occurred was demonstrated by the synthesis of **24** (X = S) from **24** (X = O) and P_4S_{10} in refluxing pyridine. This reaction, and that of **18** with diphenylcyclopropenethione, represent the first examples of addition to the C=C bond of diphenylcyclopropenethione, insertion between C_1–C_2 being the usual mode of reaction. The spectral data, consistent with this structure, are described in the Experimental Section. The thione was readily converted into the corresponding *S*-methyl product **26** (X = CH_3S; Y = I) with methyl iodide and alkylated with triethyloxonium tetrafluoroborate to 4-ethylthio-1-methyl-2,3,5,6-tetraphenylpyridinium tetrafluoroborate (**26,** X = EtS; Y = BF_4).[26]

1,2,3-Triphenylcyclopropene reacted in an analogous fashion with **22,** giving 1-methyl-2,3,4,5,6-pentaphenyl-1,4-dihydropyridine (**27**), this product being reported recently as having been prepared from an isolated sample of **22** and the cyclopropene.[27]

Experimental Section[28]

2,3,5,6-Tetraphenyl-6-aza-8-thiabicyclo[3.2.1]oct-2-ene-4,7-dione (4, R = Ph; X = O). *anhydro*-2,3-Diphenyl-4-hydroxythiazolium hydroxide (**1**, R = Ph) (5.0 g, 0.02 mol) and diphenylcyclopropenone (4.0 g, 0.02 mol) in dry benzene were refluxed for 30 min. The solvent was removed in vacuo and the residue chromatographed on Kieselgel G (benzene) using $CHCl_3$ as eluent. Crystallization from chloroform–cyclohexane afforded yellow needles of **4** (R = Ph; X = O): 2.0 g (27%); mp 198–200 °C; ir (KBr) 1725, 1650 cm^{-1} (CO); λ_{max} (CH_3OH) 353 nm (log ϵ 4.17), 300 (4.26), 246 (4.45); NMR ($CDCl_3$) δ 6.71–7.83 (m, 20, aromatic), 6.10 (s, 1, C_4 H); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 459.1291 (0.34), $[M - CO]^{\cdot+}$ 431.1396 (2).

Anal. Calcd for $C_{30}H_{21}NO_2S$: C, 78.41; H, 4.61; N, 3.05. Found: C, 78.49; H, 4.66; N, 2.94.

5-*p*-Chlorophenyl-2,3,6-triphenyl-6-aza-8-thiabicyclo-[3.2.1]oct-2-ene-4,7-dione (4, R = *p*-ClC_6H_4; X = O) was prepared from **1** (R = *p*-ClC_6H_4) in a similar manner. It crystallized from benzene–anhydrous ether as yellow needles: mp 137–139 °C dec; ir (KBr) 1720, 1660 cm^{-1} (CO); NMR ($CDCl_3$) δ 6.70–7.62 (m, 19, aromatic), 6.10 (s, 1, C_4 H).

Anal. Calcd for $C_{30}H_{20}ClNO_2S$: C, 72.94; H, 4.05; N, 2.84. Found: C, 72.59; H, 4.62; N, 2.71.

Thermolysis of 2,3,5,6-Tetraphenyl-6-aza-8-thiabicyclo[3.2.1]oct-2-ene-4,7-dione (4, R = Ph; X = O). The above cycloadduct (500 mg) was heated at 200 °C (1 mm) for 20 min. After melting and gas evolution (~15 min) the oil solidified. This product was chromatographed on Kieselgel G (benzene) using chloroform as eluent. 1,4,5,6-Tetraphenyl-2(1*H*)-pyridone (**9**, R = Ph) crystallized from chloroform–ether as colorless needles: 350 mg (80%); mp 279–281 °C; ir (KBr) 1650 cm^{-1} (CO); λ_{max} (CH_3OH) 340 nm (log ϵ 4.05), 243 (4.28); NMR ($CDCl_3$) δ 7.14–7.81 (m, 2, aromatic), 6.40 (s, 1, C_3 H); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 399 (100).

Anal. Calcd for $C_{29}H_{21}NO$: C, 87.19; H, 5.30; N, 3.51. Found: C, 86.57; H, 5.26; N, 3.27.

Sodium Borohydride Reduction of 4 (R = Ph; X = O). The cycloadduct **4** (R = Ph; X = O) (500 mg) in ethanol (100 ml) was treated with a solution of $NaBH_4$ (120 mg) in ethanol (20 ml). After 4 h at room temperature, the solvent was removed, water added, and the aqueous solution extracted with $CHCl_3$ (2 × 50 ml). After drying (Na_2SO_4) the chloroform extract was evaporated to dryness and the residue chromatographed on Kieselgel G (benzene) using $CHCl_3$ as eluent. The product **12** crystallized from chloroform–petroleum ether or benzene–petroleum ether (bp 35–60 °C) as colorless needles: 250 mg, mp 228–230 °C; ir (KBr) 3050 (CH), 1740, 1670 cm^{-1} (CO); λ_{max} (CH_3OH) 356 nm (log ϵ 4.07), 246 sh (4.19); NMR ($CDCl_3$) δ 6.87–7.60 (m, 15, aromatic), 4.00 (s, 2, CH_2); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 339.1284 (44), $[M - PhNCO]^{\cdot+}$ 220.0889 (100).

Anal. Calcd for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13. Found: C, 81.55; H, 5.13; N, 3.88.

5-*p*-Chlorophenyl-2,3,6-triphenyl-6-aza-8-thiabicyclo[3.2.1]oct-2-ene-4,7-dione (**4**, R = *p*-ClC_6H_4; X = O) was treated with $NaBH_4$ as above. The product isolated was identical[29] with **14.**

Reaction of *anhydro*-2-Aryl-4-hydroxy-3-phenylthiazolium Hydroxide (1) with Diphenylcyclopropenethione. The mesoionic compound **1** (R = *p*-ClC_6H_4) (2.8 g, 0.01 mol) and diphenylcyclopropenethione (2.2 g, 0.01 mol) were stirred in dry benzene (200 ml) for 18 h. The solvent was removed in vacuo, and the residue chromatographed on silica gel (chloroform). The first band was collected, solvent removed in vacuo, and the red, oily residue dissolved in anhydrous ether, from which orange needles of 5-*p*-chlorophenyl-7-oxo-2,3,6-triphenyl-6-aza-8-thiabicyclo[3.2.1]oct-2-ene-4-thione (**4**, R = *p*-ClC_6H_4; X = S) separated on standing overnight: 2.5 g (43%); mp 163–165 °C dec; ir (KBr) 1650 cm^{-1} (CO); λ_{max} (CH_3OH) 427 nm (log ϵ 4.05), 294 (4.43), 237 sh (4.41); NMR ($CDCl_3$) δ 6.83–7.66 (m, 19, aromatic), 6.23 (s, 1, C_4 H).

Anal. Calcd for $C_{30}H_{20}ClNOS_2$: C, 70.64; H, 3.95; N, 2.75. Found: C, 70.79; H, 4.01; N, 2.75.

Similarly, 7-oxo-2,3,5,6-tetraphenyl-6-aza-8-thiabicyclo[3.2.1]-oct-2-ene-4-thione (**4**, R = Ph; X = S) crystallized from benzene–petroleum ether (bp 60–80°) as orange prisms: 30%, mp 170–172 °C; ir (KBr) 1650 cm^{-1} (CO); λ_{max} (CH_3OH) 425 nm (log ϵ 4.01), 293 (4.38), 239 (4.32); NMR ($CDCl_3$) δ 7.8–6.7 (m, 20, aromatic), 6.29 (s, 1, C_4 H); mass spectrum *m/e* $M^{\cdot+}$ 475.1063, $[M - PhNCO]^{\cdot+}$ 356.0643.

Anal. Calcd for $C_{30}H_{21}NOS_2$: C, 75.78; H, 4.45; N, 2.95. Found: C, 75.69; H, 4.38; N, 2.88.

Thermolysis of 4 (R = *p*-ClC_6H_4; X = S). The 1:1 adduct **4** (R = *p*-ClC_6H_4; X = S) (1.0 g, 0.002 mol) was heated under vacuum (ca. 25 mm) to 170 °C and left at that temperature for 10 min until the gas evolution subsided. The dark residue was chromatographed on silica gel (benzene). The first dark band was collected, the solvent removed in vacuo, and the dark-red residue recrystallized from ethanol forming a three-component product. This product was chromatographed on preparative silica gel (chloroform), the first band isolated, and recrystallized from ethanol yielding deep-red, irregular prisms of 6-*p*-chlorophenyl-3,4-diphenyl-2*H*-thiopyran-2-thione (**13**, R = *p*-ClC_6H_4): 150 mg (21%); mp 148–155 °C dec; ir (KBr) 3050 cm^{-1} (CH); λ_{max} (CH_3OH) 477 nm (log ϵ 3.90), 338 sh (4.07), 312 (4.23), 250 (4.45); NMR ($CDCl_3$) δ 7.00–7.66 (m, aromatic).

Anal. Calcd for $C_{23}H_{15}ClS_2$: C, 70.66; H, 3.87. Found: C, 70.77; H, 3.87.

The second dark band was collected, solvent removed in vacuo, and the residue recrystallized from benzene yielding 2-*p*-chlorophenyl-4-oxo-3,6,7-triphenyl-3*H*-1,3-thiazocinium 8-thiolate (**8**, R = *p*-ClC_6H_4) as dark brown needles: 300 mg (30%); mp 249–251 °C; ir (KBr) 3080 (CH), 1670 (CO), 1630 cm^{-1} (C=N); λ_{max} (CH_3OH) 460 nm (log ϵ 3.68), 328 (3.95), 244 (4.39); NMR ($CDCl_3$) δ 6.50–7.46 (m, aromatic); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 509 (25).

Anal. Calcd for $C_{30}H_{20}ClNOS_2$: C, 70.64; H, 3.95; N, 2.75. Found: C, 70.58; H, 3.87; N, 2.59.

Similarly, thermolysis of **4** (R = Ph; X = S) gave 3,4,6-triphenyl-2*H*-thiopyran-2-thione (**13**, R = Ph) as deep maroon needles from benzene–petroleum ether: 27%; mp 160–162 °C; ir (KBr) 1560, 1460, 1205, 752, 695 cm^{-1}; λ_{max} (CH_3OH) 480 nm (log ϵ 4.14), 330 sh (4.30), 308 (4.44), 245 (4.63); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 356 (70), $[M - 1]^+$ 355 (100).

Anal. Calcd for $C_{23}H_{16}S_2$: C, 77.49; H, 4.52. Found: C, 77.83; H, 4.53.

The second product from this thermolysis, 4-oxo-2,3,6,7-tetraphenyl-3*H*-1,3-thiazocinium 8-thiolate (**8**, R = Ph), was likewise obtained as deep maroon prisms: 20%; mp 248–250 °C; ir (KBr)

1650, 1600, 1540, 1440, 1050, 750, 685 cm^{-1}; λ_{max} (CH_3OH) 463 nm (log ϵ 3.88), 328 (4.11), 240 (4.56); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 475 (100), $[M-1]^+$ 474 (63), $[M-93]^+$ 382 (89).

Anal. Calcd for $C_{30}H_{21}NOS_2$: C, 75.75; H, 4.45; N, 2.95. Found: C, 75.34; H, 4.31; N, 2.81.

Reaction of 6-*p*-Chlorophenyl-3,4-diphenyl-2*H*-thiopyran-2-thione (13, R = *p*-ClC_6H_4) with Triethyloxonium Tetrafluoroborate. The above thione (0.3 g, 0.0008 mol) in dry methylene chloride (20 ml) was treated with an excess of triethyloxonium tetrafluoroborate added in small portions at room temperature. After 5 days anhydrous Et_2O was added causing an orange solid to separate. Recrystallization from ethanol afforded 6-*p*-chlorophenyl-3,4-diphenyl-2-ethylthio-2*H*-thiopyrylium tetrafluoroborate (14) as rust-colored plates: 0.25 g (27%); mp 204–207 °C dec; ir (KBr) 1350, 1050 cm^{-1} (BF_4^-); λ_{max} (CH_3OH) 436 nm (log ϵ 4.04), 304 (4.06), 253 (4.29); NMR ($CDCl_3$) δ 8.17 (s, 1, C_6 H), 7.73 (A_2B_2 qt, 4, *p*-ClC_6H_4), 7.30 (bs, 10, aromatic), 3.45 (qt, 2, SCH_2CH_3), 1.47 (t, 3, SCH_2CH_3).

Anal. Calcd for $C_{25}H_{20}BClF_4S_2$: C, 59.24; H, 3.98. Found: C, 59.07; H, 3.93.

Reaction of 2-*p*-Chlorophenyl-4-oxo-3,6,7-triphenyl-3*H*-1,3-thiazocinium 8-Thiolate (8, R = *p*-ClC_6H_4) with Triethyloxonium Tetrafluoroborate. The thiolate (0.25 g, 0.005 mol) in dry methylene chloride (40 ml) was treated with triethyloxonium tetrafluoroborate (0.4 g, 0.002 mol) added in small portions with an immediate lightening in color of the reaction mixture. Stirring was continued for 30 min, anhydrous ether (100 ml) added, and excess triethyloxonium tetrafluoroborate filtered off. Evaporation of the solvent left a yellow oil that was dissolved in EtOH (10 ml) and treated with perchloric acid (20 ml, 70%). The resultant yellow solid crystallized from ethanol, giving 2-*p*-chlorophenyl-8-ethylthio-4-oxo-3,6,7-triphenyl-3*H*-1,3-thiazocinium perchlorate (15) as yellow-orange prisms: 0.7 g (74%); mp 160–165 °C dec; ir (KBr) 1690 cm^{-1} (C=N^+–); λ_{max} (CH_3OH) 428 nm (log ϵ 3.63), 305 sh (3.64), 244 (4.14); NMR ($CDCl_3$) δ 9.05 (s, 1, C_5 H), 7.00–8.06 (m, 19, aromatic), 3.37 (qt, 2, OCH_2CH_3), 1.55 (t, 3, OCH_2CH_3).

Anal. Calcd for $C_{32}H_{25}Cl_2NO_5S_2$: C, 60.18; H, 3.95; N, 2.19. Found: C, 60.33; H, 3.95; N, 2.19.

Reaction of *anhydro*-5-Hydroxy-3-methyl-2-phenylthiazolium Hydroxide (18) with Diphenylcyclopropenethione. At room temperature, a mixture of the mesoionic compound 18 (R = Ph) (1.2 g, 0.005 mol), diphenylcyclopropenethione (1.4 g, 0.005 mol), and dry benzene (25 ml) was stirred for 12 h. Filtration of the precipitated solid, chromatography on preparative silica gel (ethyl acetate), and crystallization from chloroform–petroleum ether (bp 60–90 °C) gave 1-methyl-2,3,5-triphenyl-4(1*H*)-pyridinethione (20, R = Ph) as yellow needles: 450 mg (20%); mp 240–245 °C dec; ir (KBr) 3030 (CH), 1610 cm^{-1} (C=C); λ_{max} (CH_3OH) 360 nm (log ϵ 3.96), 267 (3.71), 226 (4.13); NMR ($CDCl_3$) δ 7.00–8.00 (m, 16, aromatic and C_6 H), 3.40 (s, 3, NCH_3); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 353 (58), 352 (100), M^{2+} 176.5 (5).

Anal. Calcd for $C_{24}H_{19}NS$: N, 3.96. Found: N, 4.01.

It was characterized further by reaction with methyl iodide in methanol at room temperature for 6 h. Concentration of solvent under reduced pressure and addition of anhydrous ether precipitated a yellow solid which was filtered, washed with several portions of anhydrous ether, and recrystallized from ethanol–anhydrous ether affording yellow needles of 4-methylthio-1-methyl-2,3,5-triphenylpyridinium iodide (21, R = Ph): 72%; mp 207–210 °C dec; ir (KBr) 3060 (CH), 1610 cm^{-1} (C=N); λ_{max} (CH_3OH) 325 nm (log ϵ 3.56), 271 (3.77), 219 sh (4.05); NMR ($CDCl_3$) δ 8.74 (s, 1, C_6 H), 7.10–7.92 (m, 15, aromatic), 4.04 (s, 3, NCH_3), 1.72 (s, 3, SCH_3).

Anal. Calcd for $C_{25}H_{22}INS$: C, 60.61; H, 4.48; N, 2.83. Found: C, 60.87; H, 4.45; N, 2.92.

Similarly, reaction of *anhydro*-2-*p*-chlorophenyl-5-hydroxy-3-methylthiazolium hydroxide (18, R = *p*-ClC_6H_4) and diphenylcyclopropenethione afforded 2-*p*-chlorophenyl-3,5-diphenyl-1-methyl-4(1*H*)-pyridinethione (20, R = *p*-ClC_6H_4) as yellow needles: 34%; mp 265–268 °C dec; ir (KBr) 3050 (CH), 1630 cm^{-1} (C=N); λ_{max} (CH_3OH) 359 nm (log ϵ 4.01), 287 (3.95), 247 (4.27); NMR ($CDCl_3$) δ 7.00–7.71 (m, 15, aromatic and C_6 H), 3.38 (s, 3, NCH_3); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 387 (74), 386 (100), M^{2+} 193.5 (2).

Anal. Calcd for $C_{24}H_{18}ClNS$: N, 3.61. Found: N, 3.32.

It was characterized as above by conversion into 2-*p*-chlorophenyl-3,5-diphenyl-4-methylthio-1-methylpyridinium iodide (21, R = *p*-ClC_6H_4) obtained as yellow, irregular prisms from ethanol–anhydrous ether: 65%; mp 204–207 °C dec; ir (KBr) 1610 cm^{-1} (C=N); λ_{max} (CH_3OH) 325 nm (log ϵ 4.09), 272 (4.16), 218 sh (4.57); NMR ($CDCl_3$) δ 8.73 (s, 1, C_6 H), 7.17–8.00 (m, 14, aromatic), 4.03 (s, 3, NCH_3), 1.75 (s, 3, SCH_3).

Anal. Calcd for $C_{25}H_{21}ClINS$: C, 56.66; H, 4.00; N, 2.64. Found: C, 56.52; H, 3.87; N, 2.61.

Alkylation of 2-*p*-Chlorophenyl-3,5-diphenyl-1-methyl-4-pyridinethione (20, R = *p*-ClC_6H_4) with Triethyloxonium Tetrafluoroborate. The title compound (0.6 g, 0.0016 mol) in methylene chloride (25 ml) was treated with an excess of triethyloxonium tetrafluoroborate, and the reaction mixture stirred at room temperature for 24 h. Addition of excess anhydrous ether, filtration, and recrystallization from ethanol gave 2-*p*-chlorophenyl-3,5-diphenyl-4-ethylthio-1-methylpyridinium tetrafluoroborate as yellow needles: 0.8 g (100%); mp 198–200 °C dec; ir (KBr) 3050, 2975, 2940 (CH), 1620 cm^{-1} (CN); λ_{max} (CH_3OH) 326 nm (log ϵ 3.96), 276 (4.08), 237 sh (4.25); NMR ($CDCl_3$) δ 8.23 (s, 1, C_6 H), 6.97–7.90 (m, 14, aromatic), 3.90 (s, 3, NCH_3), 2.07 (qt, 2, CH_2CH_3), 0.85 (t, 3, CH_2CH_3).

Anal. Calcd for $C_{26}H_{23}BClF_4NS$: C, 61.98; H, 4.60; N, 2.78. Found: C, 62.10; H, 4.62; N, 2.81.

Reaction of *anhydro*-2,4-Diphenyl-5-hydroxy-3-methyloxazolium Hydroxide (22) with Diphenylcyclopropenone. *N*-Benzoyl-*N*-methyl-*C*-phenylglycine (3.6 g, 0.013 mol), diphenylcyclopropenone (2.4 g, 0.012 mol), and acetic anhydride (50 ml) were stirred and heated to 85 °C. After 10 min a colorless solid separated and heating was discontinued. Recrystallization from chloroform–anhydrous ether gave 1-methyl-2,3,5,6-tetraphenyl-4(1*H*)-pyridone (24, X = O) as colorless needles: 1.4 g (29%); mp 309–310 °C (lit.[25a] mp 309–310 °C, sealed tube 317–318 °C); ir (KBr) 3050 (CH), 1620 cm^{-1} (CO); λ_{max} (CH_3OH) 276 nm (log ϵ 4.12), 236 sh (4.36); NMR ($CDCl_3$) δ 7.23 (s, 10, aromatic), 7.07 (s, 10, aromatic), 3.03 (s, 3, NCH_3); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 413 (58), $[M-1]^+$ 412 (100), M^{2+} 206.5 (5).

Anal. Calcd for $C_{30}H_{23}NO$: C, 87.14; H, 5.60; N, 3.39. Found: C, 87.07; H, 5.56; N, 3.26.

Alkylation of 24 (X = O) with Triethyloxonium Tetrafluoroborate. The pyridone (0.5 g, 0.0012 mol) in methylene chloride (25 ml) was treated with an excess of triethyloxonium tetrafluoroborate and stirred at room temperature for 48 h. Anhydrous ether was added and the resultant precipitate recrystallized from ethanol, forming colorless needles of 4-ethoxy-1-methyl-2,3,5,6-tetraphenylpyridinium tetrafluoroborate (26, X = OEt; Y = BF_4): 0.65 g (100%); mp 275–278 °C dec; ir (KBr) 3050, 2980 (CH), 1610 cm^{-1} (C=N); λ_{max} (CH_3OH) 290 sh nm (log ϵ 3.94), 243 (4.41); NMR ($CDCl_3$) δ 7.00–7.73 (m, 20, aromatic), 3.63 (s, 3, NCH_3), 3.55 (qt, 2, CH_2CH_3), 0.67 (t, 3, CH_2CH_3); mass spectrum *m/e* (rel intensity) 412 (100).

Anal. Calcd for $C_{32}H_{28}BF_4NO$: C, 72.60; H, 5.33; N, 2.65. Found: C, 72.51; H, 5.35; N, 2.53.

Formation of 1-Methyl-2,3,5,6-tetraphenyl-4(1*H*)-pyridinethione (24, X = S). *N*-Benzoyl-*N*-methyl-*C*-phenylglycine (1.5 g, 0.0056 mol) was dissolved in acetic anhydride (20 ml) and to this solution at 40 °C was added diphenylcyclopropenethione (1.24 g, 0.0056 mol). Within 5 min an orange solid had precipitated and was filtered after stirring for 2 h. Recrystallization from chloroform–anhydrous ether afforded 24 (X = S) as yellow-orange, irregular prisms: 2.9 g (68%); mp 320–322° dec; ir (KBr) 3040 (CH), 1605 cm^{-1} (C=N); λ_{max} (CH_3OH) 360 nm (log ϵ 4.18), 272 sh (3.80), 238 (4.18); NMR ($CDCl_3$) δ 7.10, 7.23, 7.27 (3, s, 20, aromatic), 3.05 (s, 3, NCH_3); mass spectrum *m/e* (rel intensity) $M\cdot^+$ 429 (60), $[M-1]^+$ 428 (100), M^{2+} 214.5 (5).

Anal. Calcd for $C_{30}H_{23}NS$: C, 83.88; H, 5.40; N, 3.26. Found: C, 83.89; H, 5.29; N, 3.07.

Treatment of 1-methyl-2,3,5,6-tetraphenyl-4(1*H*)-pyridone (24, X = O) with a 1.5-fold excess of P_4S_{10} in refluxing pyridine afforded, after preparative thin layer chromatography, a product identical[29] with 1-methyl-2,3,4,5-tetraphenyl-4(1*H*)-pyridinethione (24, X = S) obtained above.

Alkylation of 24 (X = S) with Methyl Iodide. The thione (1.0 g, 0.0023 mol) was stirred with an excess of methyl iodide in dry methanol (25 ml) overnight at room temperature. Filtration and recrystallization from ethanol gave 4-methylthio-1-methyl-2,3,5,6-tetraphenylpyridinium iodide (26, X = SCH_3; Y = I) as yellow needles: 1.1 g (83%); mp 240–242 °C dec; ir (KBr) 3050 (CH), 1600 cm^{-1} (CN); λ_{max} (CH_3OH) 323 nm (log ϵ 3.93), 248 (4.02); NMR ($CDCl_3$) δ 7.00–7.84 (m, 20, aromatic), 3.60 (s, 3, NCH_3), 1.63 (s, 3, SCH_3).

Anal. Calcd for $C_{31}H_{26}NIS$: C, 65.14; H, 4.59; N, 2.45. Found: C, 64.97; H, 4.38; N, 2.70.

Alkylation of 24 (X = S) with Triethyloxonium Tetrafluoroborate. The thione (0.65 g, 0.0015 mol) in methylene chloride (25 ml) was treated with an excess of triethyloxonium tetrafluoroborate with stirring at room temperature. After 42 h excess anhydrous ether was added. The product was filtered, washed with several portions of anhydrous ether, and recrystallized from ethanol, giving light-yellow needles of 4-ethylthio-1-methyl-2,3,5,6-tetraphenylpyridinium tetrafluoroborate (**26**, X = SEt; Y = BF_4): 0.8 g (100%); mp 293–295 °C; ir (KBr) 3080, 2990, 2950 (CH), 1610 cm^{-1} (C=N); λ_{max} (CH_3OH) 322 nm (log ϵ 4.06), 248 (4.18); NMR ($CDCl_3$) δ 7.00–7.83 (m, 20, aromatic), 3.60 (s, 3, NCH_3), 1.97 (qt, 2, CH_2CH_3), 0.80 (t, 3, CH_2CH_3); mass spectrum *m/e* (rel intensity) 428 (100).

Anal. Calcd for $C_{32}H_{28}NBF_4S$: C, 70.46; H, 5.17; N, 2.57. Found: C, 70.62; H, 5.18; N, 2.55.

Reaction of *N*-Benzoyl-*N*-methyl-*C*-phenylglycine with Triphenylcyclopropene. To *N*-benzoyl-*N*-methyl-*C*-phenylglycine (1.0 g, 0.005 mol) dissolved in acetic anhydride (15 ml) at 40 °C was added triphenylcyclopropene (1.0 g, 0.004 mol) and the reaction mixture heated to 132 °C for 5.5 h. The reaction mixture was cooled, poured into water, and extracted with chloroform. The chloroform layer was extracted in turn with 10% sodium bicarbonate and water, dried over sodium sulfate, and evaporated in vacuo. The residue was either recrystallized from chloroform–ethanol or sublimed (203 °C 1 mm) to yield yellow prisms of 1-methyl-2,3,4,5,6-pentaphenyl-1,4-dihydropyridine (**27**): 0.25 g (14%); mp 206–207 °C (lit.[27] mp 209 °C); ir (KBr) 3050, 2930 cm^{-1} (CH); λ_{max} (CH_3OH) 343 sh nm (log ϵ 3.81), 275 (4.13); NMR ($CDCl_3$) δ 6.93–7.75 (m, 25, aromatic), 4.40 (s, 1, C_4 H), 2.53 (s, 3, NCH_3); mass spectrum *m/e* (rel intensity) $M^{\cdot+}$ 475 (8).

Anal. Calcd for $C_{36}H_{29}N$: C, 90.91; H, 6.15; N, 2.94. Found: C, 90.83; H, 6.19; N, 2.80.

Registry No.—**1** (R = Ph), 13288-67-0; **1** (R = *p*-ClC_6H_4), 52730-97-9; **4** (R = Ph; X = O), 57550-38-6; **4** (R = *p*-ClC_6H_4; X = O), 57550-39-7; **4** (R = Ph; X = S), 57550-40-0; **4** (R = *p*-ClC_6H_4; X = S), 57550-41-1; **8** (R = Ph), 57587-13-0; **8** (R = *p*-ClC_6H_4), 57550-42-2; **9** (R = Ph), 57550-43-3; **12**, 57550-44-4; **13** (R = Ph), 57550-45-5; **13** (R = *p*-ClC_6H_4), 57550-46-6; **14**, 57550-48-8; **15**, 57550-50-2; **18** (R = Ph), 1280-28-0; **18** (R = *p*-ClC_6H_4), 51787-62-3; **20** (R = Ph), 51787-66-7; **20** (R = *p*-ClC_6H_4), 51787-68-9; **21** (R = Ph), 51787-67-8; **21** (R = *p*-ClC_6H_4), 51808-61-8; **22**, 13712-75-9; **24** (X = O), 51787-63-4; **24** (X = S), 51787-64-5; **26** (X = OEt; Y = BF_4), 51808-60-7; **26** (X = SMe; Y = I), 51787-65-6; **26** (X = SEt; Y = BF_4), 57550-52-4; **27**, 39235-55-7; diphenylcyclopropenone, 886-38-4; $NaBH_4$, 16940-66-2; diphenylcylopropenethione, 2570-01-6; 2-*p*-chlorophenyl-3,5-diphenyl-4-ethylthio-1-methylpyridinium tetrafluoroborate, 57550-54-6; *N*-benzoyl-*N*-methyl-*C*-phenylglycine, 28544-45-8; methyl iodide, 74-88-4; triphenylcyclopropene, 16510-49-9.

References and Notes

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(29) Criteria for establishing product identity were superimposable infrared spectra, no depression in mixture melting point, and identical R_f values in two different solvent systems.