and 20 mL of pentane and filled with 125 mL of pentane. Dianion 1 (3.06 mmol, method A) in 4 mL of THF and the solution of the dialdehyde were simultaneously added, and the solution was stirred for 60 min and quenched with 2 mL of water. The solvents were removed under vacuum. A mixture of compounds 7 and 8 was isolated by preparative TLC on alumina with benzene but 7 and 8 were not separated from one another. Their structures were deduced from their spectral properties.

7: NMR δ 2.4 (d, J = 7 Hz, 4 H), 3.8 (b, variable, 2 H), 4.8 (s, 2 H), 5.15 (m, 2 H), 7.1–7.4 (m, 4 H).

8: NMR δ 1.8 (s, 3 H), 2.45 (d, J = 7 Hz, 2 H), 3.8 (b, variable, 1 H), 4.7 (s, 2 H), 5.15 (t, J = 7 Hz, 1 H), 6.3 (m, 1 H), 7.1–7.4 (m, 4 H).

Reaction of 1 with Epichlorohydrin. To a flask equipped with 2 septums and a 25-mL dropping funnel and filled with 100 mL of pentane and 50 mL of THF under argon at −78 °C were added simultaneously 2.68 mmol (0.99 mL) of epichlorohydrin in 25 mL of THF via the dropping funnel and 2.68 mmol (method A) of dianion 1 complex in 10 mL of THF by syringe. The mixture became blue and was stirred at 0 °C for 30 min, becoming turquoise. After 30 min of stirring it became yellow and remained so even after quenching with 1 mL of water. The solution was decanted, the residue was washed with ether, and the solvents were removed. The major product was 11, identified by comparison of spectral data with literature values.[13]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 1·2L$^+$, 53721-69-0; **2a**, 100-52-7; **2b**, 119-61-9; **2c**, 98-86-2; **2d**, 67-64-1; **3a**, 71370-00-8; **3b**, 71370-01-9; **3c**, 71370-02-0; **3d**, 71370-03-1; **4a**, 23092-23-1; **4b**, 71370-04-2; **4c**, 71370-05-3; **4d**, 19781-53-4; **5**·K$^+$, 64544-47-4; **6**, 643-79-8; **7**, 71370-06-4; **8**, 71370-07-5; **9**, 71370-08-6; **10**, 22508-64-1; **11**, 106-89-8; **12**, 29560-84-7; **13**, 60380-86-1; **14**, 4049-81-4.

Ring Annulation with Heterocyclic Ylides. Annulation of Pyridinones to the Imidazole and 1,2,4-Triazole Systems[1a]

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1-Methyl-2(3*H*)-imidazolethione and α-bromophenylacetyl chloride/Et_3N gave *anhydro*-3-hydroxy-7-methyl-2-phenylimidazo[2,1-*b*]thiazolium hydroxide which, with a variety of acetylenic and olefinic dipolarophiles in refluxing benzene, formed 1-methyl-6-phenyl-5*H*-imidazo[1,2-*a*]pyridin-5-ones. Methyl, *p*-tolyl, and *p*-methoxyphenyl isocyanate formed stable 1:1 cycloadducts with the ring-fused mesoionic system but no product was obtained with *p*-toluenesulfonyl isocyanate. Attempts to prepare *anhydro*-3-hydroxy-7-methylimidazo-[2,1-*b*]thiazolium hydroxide by cyclodehydration of (1-methylimidazol-2-yl)thioglycolic acid with DCC or Ac_2O always resulted in formation of the desired mesoionic system acylated in the 2-position with the precursor thioglycolic acid. *anhydro*-3-Hydroxy-7-methyl-2-phenylthiazolo[3,2-*b*][1,2,4]triazolium hydroxide was prepared from 4-methyl-3(4*H*)-1,2,4-triazolethione via cyclodehydration of the corresponding *S*-(4-methyl-1,2,4-triazol-3-yl)-phenylthioglycolic acid. Olefinic and acetylenic dipolarophiles reacted with this ring-fused mesoionic system in boiling xylene, the corresponding ring-fused α-pyridinone being formed by elimination of H_2S or S, respectively, from the initial 1:1 cycloadduct.

In a recent publication[2] the potential of heterocyclic ylides in ring annulation reactions was illustrated by the conversion of the *anhydro*-2- and -3-hydroxythiazolo-[2,3-*b*]benzothiazolium hydroxides into the pyrrolo[2,1-*b*]benzothiazole and the 1*H*-pyrido[2,1-*b*]benzothiazol-1-one ring systems, respectively. Isoelectronic ring systems such as *anhydro*-1-hydroxythiazolo[3,2-*a*]quinolinium hydroxide also underwent ready reaction, except that the anticipated ring-fused pyridinone was not isolated but rather the pyrrolo[1,2-*a*]quinoline system was formed[3] by extrusion of COS after initial rearrangement of the 1:1 adduct.

Numerous structures containing the thiocarbonyl ylide dipole are conceivable. Incorporation of the thiocarbonyl ylide dipole into a bicyclic heterocyclic system is possible by the conversion of the cyclic thione[4] 1 into the ring-fused mesoionic system 2. The thiocarbonyl ylide dipole **2a** would be expected to undergo cycloaddition with both olefinic and acetylenic electron-deficient dipolarophiles so that, after extrusion of hydrogen sulfide or sulfur, respectively, from the postulated, initial 1:1 cycloadducts, e.g., **2b**, the ring-fused pyridinone **3** is formed. Insufficient evidence is available to predict with any degree of certainty whether ring closure to the bicyclic system will occur and whether the resultant ring system will undergo cycloaddition reactions. In this and the accompanying paper attention is focussed on five-membered rings fused to the thiazole nucleus, and the heteroatom peri to the sulfur atom is varied between nitrogen and sulfur atoms. In subsequent publications our results with six-membered rings fused to the thiazole ring will be described.

***anhydro*-3-Hydroxyimidazo[2,1-*b*]thiazolium Hydroxide System (5).** 1-Methyl-2(3*H*)-imidazolethione (4) underwent ready reaction with α-bromophenylacetyl chloride/Et_3N to give *anhydro*-3-hydroxy-7-methyl-2-phenylimidazo[2,1-*b*]thiazolium hydroxide (**5a**) as yellow needles. Spectral and analytical data (Experimental Section), especially m/e 230 (M^+· 86), ν_{CO} 1610 (s) cm^{-1} and doublets at δ 6.83 and 7.47 (J = 2.0 Hz), confirmed the assigned structure. Although formation of the isomeric 2-hydroxy system **6** is not excluded by this spectral data, it need not be considered further as the cycloadditions described below would have yielded the pyrrole derivatives

(1) (a) Mesoionic Compounds. 49. (b) Partial support of this work by USPHS Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged. (c) On leave from Yamaguchi University, Japan.
(2) Potts, K. T.; Choudhury, D. R. *J. Org. Chem.* **1978**, *43*, 2697.
(3) Potts, K. T.; Choudhury, D. R. *J. Org. Chem.* **1978**, *43*, 2700.
(4) For a review see: (a) Patai, A. "The Chemistry of the Thiol Group"; Wiley-Interscience: New York, 1974. (b) "Organic Compounds of Sulphur, Selenium and Tellurium", Specialists Periodical Reports; The Chemical Society: London: Vol. 1–3.

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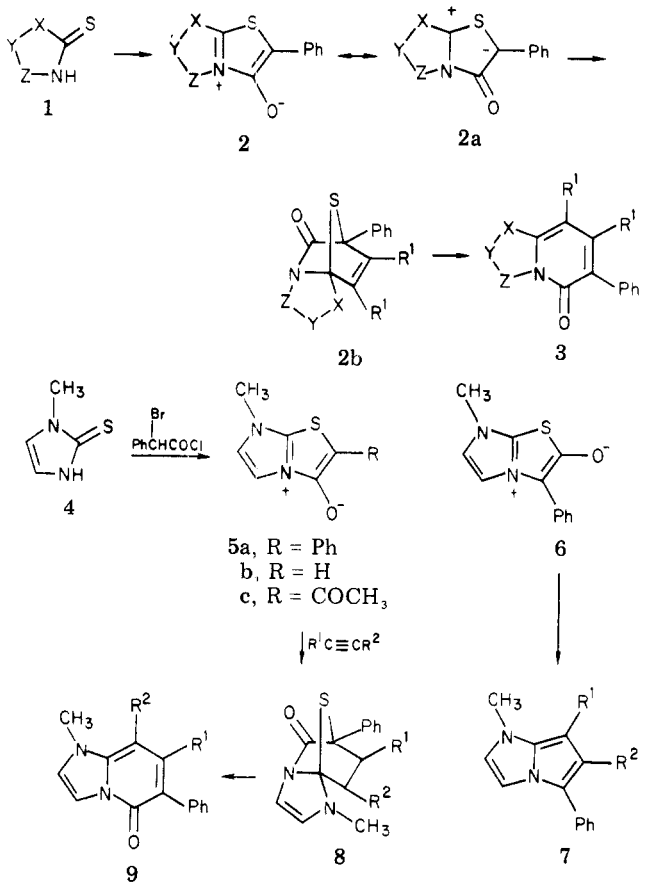
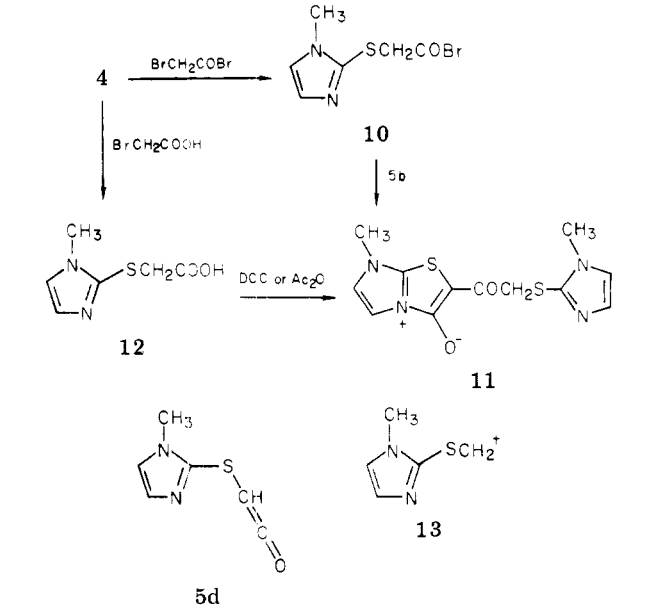


7 instead of the pyridinones **9**. Also, an ion at m/e 121 in the mass spectrum of **5a** consistent with $PhCS^+$ can only be accounted for on the basis of structure **5**.

Reactions of **4** with bromoacetyl bromide, however, did not yield **5b**. The mesoionic system was formed, but the 2-position was sufficiently reactive for condensation to occur with another molecule of the supposed intermediate **10**, and the product actually isolated was the acylated system **11**. This acylation of mesoionic systems has been



observed before[3,5] and often provides an excellent, qual-

(5) Potts, K. T.; Choudhury, D. R.; Elliott, A. J.; Singh, U. P. *J. Org. Chem.* **1976**, *41*, 1724. Greco, C. V.; Gray, C. P.; Grosso, V. G. *Ibid.* **1967**, *32*, 4101. Potts, K. T.; Husain, S. *Ibid.* **1971**, *36*, 3368.

Table I. Cycloadducts 9 Formed from *anhydro*-3-Hydroxy-7-methyl-2-phenylimidazo[2,1-*b*]thiazolium Hydroxide (5a) and Acetylenic and Olefinic Dipolarophiles

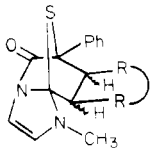
dipolarophile used[a]	yield, %	mp, °C	crystal form	crystn solvent[b]	formula[c,d]	IR (KBr) ν_{CO}, cm^{-1}	NMR ($CDCl_3$), δ
$CH_3OOCC{\equiv}CCOOCH_3$	28	202–203	yellow prisms	A	$C_{18}H_{16}N_2O_5$	1700, 1620	3.53 (s, 3, NCH_3 or OCH_3), 3.80 (s, 6, OCH_3 or NCH_3), 7.00 (d, 1, J = 2.4 Hz, C_2 H), 7.87 (d, 1, J = 2.4 Hz, C_3 H), 7.33 (s, 5, aromatic)
$PhCOC{\equiv}CCOPh$	19	288.5–289	yellow prisms	B	$C_{28}H_{20}N_2O_3$	1650,[e] 1620	3.33 (s, 3, NCH_3), 7.0–7.7 (m, 16, aromatic and C_2 H), 7.97 (d, 1, J = 2.4 Hz, C_3 H)
N-ethylmaleimide	83	248–249	orange prisms	C	$C_{18}H_{15}N_3O_3$	1745,[e] 1695, 1650, 1610	1.18 (t, 3, J = 6.7 Hz, NCH_2CH_3), 3.62 (q, 2, J = 6.7 Hz, NCH_2CH_3), 4.28 (s, 3, NCH_3), 6.95 (d, 1, J = 2.0 Hz, C_2 H), 7.78 (d, 1, J = 2.0 Hz, C_3 H), 7.38 (s, 5, aromatic)
N-phenylmaleimide	64	248.5	yellow needles	D	$C_{22}H_{15}N_3O_3$	1755,[e] 1700, 1630, 1620[e]	4.30 (s, 3, NCH_3), 7.00 (d, 1, J = 2.2 Hz, C_2 H), 7.85 (d, 1, J = 2.2 Hz, C_3 H), 7.2–7.5 (m, 10, aromatic)
maleic anhydride	51	216–216.5	yellow prisms	D	$C_{16}H_{10}N_2O_4$	1800,[e] 1750, 1650, 1600	4.37 (s, 3, NCH_3), 7.13 (d, 1, J = 2.2 Hz, C_2 H), 7.95 (d, 1, J = 2.2 Hz, C_3 H), 7.43 (s, 5, aromatic)
fumaronitrile	38	231–232	gold needles	C	$C_{16}H_{10}N_4O$	2200 (CN), 1660	4.10 (s, 3, NCH_3), 7.10 (d, 1, J = 2.0 Hz, C_2 H), 7.88 (d, 1, J = 2.0 Hz, C_3 H), 7.47 (s, 5, aromatic)
$CH_2{=}CHCN$	38	209–210	colorless needles	A	$C_{15}H_{11}N_3O$	2210 (CN), 1640	4.05 (s, 3, NCH_3), 6.98 (d, 1, J = 2.2 Hz, C_2 H), 7.90 (d, 1, J = 2.2 Hz, C_3 H), 7.3–7.8 (m, 5, aromatic), 7.82 (s, 1, C_7 H)
$CH_2{=}CHCOOEt$	29	191–192	colorless needles	A	$C_{17}H_{16}N_2O_3$	1700, 1640	1.37 (t, 3, J = 7.2 Hz, CH_2CH_3), 4.02 (s, 3, NCH_3), 4.32 (q, 2, J = 7.2 Hz, CH_2CH_3), 6.92 (d, 1, J = 2.0 Hz, C_2 H), 7.92 (d, 1, J = 2.0 Hz, C_3 H), 7.7–7.9 (m, 5, aromatic), 8.32 (s, 1, C_7 H)

[a] All required a 16-h reaction time except acrylonitrile where a 17-h period was necessary. [b] A = CH_3OH; B = CH_3COCH_3; C = $CH_3CHOHCH_3$; D = CH_3COOEt. [c] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in the table. [d] All products gave M^+. (100%). [e] Shoulder.

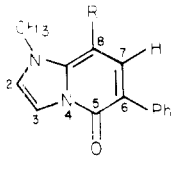
itative indication of the reactivity of the mesoionic system. The acyl derivatives themselves are stable and do not undergo cycloaddition reactions. Conversion of **4** into the thioglycolic acid **12** with bromoacetic acid followed by cyclodehydration with *N,N'*-dicyclohexylcarbodiimide or acetic anhydride also gave **11**. The structure of **11** was evident from its analytical and spectral data. The mass spectrum indicated its $M^{+\cdot}$ was at *m/e* 308, and an ion at *m/e* 128 is consistent with the ion **13**, formed from the thiomethylcarbonyl side chain as this type of fragmentation is not observed in the mass spectrum of **5a**. Carbonyl absorptions at 1560 and 1660 cm^{-1}, together with a methylene resonance at δ 4.28 and two sets of imidazole protons at δ 6.92, 7.22 and 7.77, 7.93, respectively, are in agreement with this structure. Attempts to trap **5b** by carrying out the cyclodehydration with DCC or Ac_2O in the presence of *N*-ethylmaleimide also resulted in the isolation of **11**. This indicated that the acylation was faster than cycloaddition of the dipolarophile to **5b** as the reaction conditions were sufficiently vigorous to induce elimination of H_2S from any initial 1:1 adduct formed. It also suggested that the formation of **11** involved addition of **5b** to its valence bond ketene isomer **5d**, evidently an extremely facile process, as no **5c** was isolated when Ac_2O was used as the cyclohydration agent.

Reaction with Acetylenic Dipolarophiles. Dimethyl acetylenedicarboxylate and dibenzoylacetylene reacted readily with **5a** in refluxing benzene. Sulfur was extruded from the postulated intermediate adduct **8**, the pyridinones **9** being isolated on chromatography of the crude reaction product. These pyridinones are described in Table I, the analytical and spectral data being consistent with the assigned structures. Reaction with a variety of electron-deficient acetylenic dipolarophiles would be anticipated to occur under analogous conditions to give appropriately substituted derivatives of **9**. It should be emphasized that these reaction conditions are relatively mild, indicative of a very reactive mesoionic ring system.

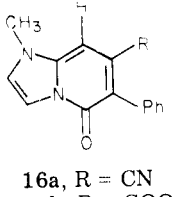
Reaction with Olefinic Dipolarophiles. Olefinic dipolarophiles such as *N*-ethyl- and *N*-phenylmaleimide, maleic anhydride, and fumaronitrile also underwent similar ready cycloaddition to **5a** in boiling benzene. Decomposition of the postulated, initial 1,1-cycloadduct **14** occurred under these mild reaction conditions with elimination of H_2S so that the pyridinones **9** (Table I) were isolated from the reaction mixture in variable yields. These products all exhibited an intense yellow-green fluorescence in solution, present to a reduced extent in **9** (R = $COOCH_3$, COPh). No reaction was observed with diethyl fumarate or dimethyl maleate.



14



15a, R = CN
b, R = COOEt



16a, R = CN
b, R = COOEt

With the unsymmetrical dipolarophiles acrylonitrile and ethyl acrylate, the question of regioselectivity in the cycloaddition arises. The two products **15** and **16** are possible in these reactions. From the reaction with acrylonitrile in boiling benzene (17 h), 8-cyano-1-methyl-6-phenyl-5*H*-imidazo[1,2-*a*]pyridin-5-one (**15a**) was isolated. Infrared absorptions at 2210 (CN) and 1640 (CO) cm^{-1}, a mass spectral peak for $M^{+\cdot}$ at *m/e* 249 (100%), and analytical data confirmed the gross structure, and a distinction between **15a** and **16a** was possible from the NMR data. The C_7 H was observed as a sharp singlet at δ 7.82 and C_6 phenyl protons occurred as a multiplet at δ 7.8–7.3. However, in the fumaronitrile adduct **9** ($R^1 = R^2 = CN$), the C_6 phenyl protons occurred as a sharp singlet, suggesting that the C_6 phenyl group is out of the plane of the bicyclic system and accordingly experiences no ring-current effect. In all derivatives of **9** with a C_7 substituent and in which there are no other obscuring phenyl protons, the C_6 phenyl is found as a singlet.

Similarly, the adduct from ethyl acrylate, formed in an analogous manner, is represented by **15b**. In this case the aromatic protons of the C_6 phenyl group were better resolved, the meta and para protons being at δ 7.6–7.3 and the ortho protons at δ 7.9–7.7, respectively. These adducts are those anticipated on the basis of electronic considerations.

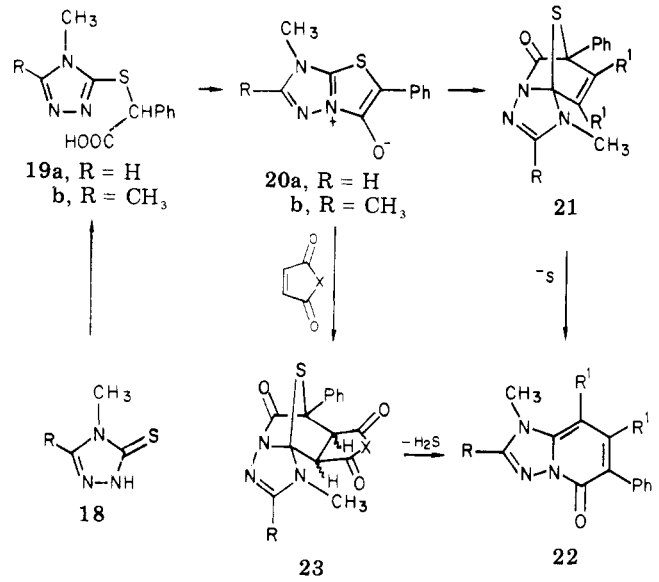
Reaction with Isocyanates. Methyl isocyanate reacted readily with **5a** in boiling benzene (17 h) to give a quantitative yield of a 1:1 adduct, isolated by evaporation of the reaction solvent. The molecular weight, *m/e* 287 ($M^{+\cdot}$, 45%), indicated that all the components of the reactants were retained in the adduct, and an ion at *m/e* 230 (30%) corresponded to that obtained in the mass spectrum of **5a**. This suggests that this adduct underwent either an electron impact or a thermally induced retrocycloaddition requiring a simple relationship of the addend and **5a**. This also excludes any thermally induced rearrangement occurring during the reaction with methyl isocyanate. Similar retrocycloadditions under comparable conditions have been observed[6] with isocyanate adducts derived from the *anhydro*-4-hydroxythiazolium hydroxide system. The ^{13}C NMR data, shown in Table II, confirmed the assigned structure **17**. The ^{13}C chemical shift of C_1 in similar cycloadducts is found in the range 120–126 ppm.

Both *p*-methoxyphenyl isocyanate and *p*-tolyl isocyanate underwent a similar ready reaction with **5a**, giving 1:1 adducts in quantitative yields. Their similar behavior to **17** and their spectral characteristics are indicative of structures analogous to that of **17**. This retention of the bridge sulfur atom is not too surprising, similar 1:1 adducts being obtained from analogous monocyclic systems and isocyanates,[6] and only in the case where the bridge sulfur atom is replaced by selenium does ready thermal extrusion of the bridge atom occur.[7] Under analogous reaction conditions, no cycloadduct was formed with *p*-toluenesulfonyl isocyanate.

***anhydro*-3-Hydroxythiazolo[3,2-*b*][1,2,4]triazolium Hydroxide System.** The more convenient route to this ring-fused mesoionic system involved cyclodehydration of the thioglycolic acid **19** derived from the 3(2*H*)-1,2,4-triazolethione **18**. Reaction of the thione **18** with α-bromophenylacetyl chloride proved to be unsatisfactory due to the instability of the mesoionic system **20** to water in the purification procedure. This susceptibility of **20** to hydrolysis was circumvented by the presence of a small amount of cyclodehydrating agent such as $(CF_3CO)_2O$ or Ac_2O in the solvent being used for recrystallization or spectral characterization.

Ring closure of the thioglycolic acid **19a** occurred readily with Ac_2O at 70–80 °C for 10 min. The mesoionic system **20a** was obtained as yellow needles in 89% yield and showed the characteristic ν_{CO} at 1610 cm^{-1}. Its NMR spectrum was consistent with the assigned structure as was its fragmentation pattern under electron impact. The

(6) Potts, K. T.; Baum, J.; Datta, S. K.; Houghton, E. *J. Org. Chem.* **1976**, *41*, 813.
(7) Potts, K. T.; Huang, F.; Khattak, R. K. *J. Org. Chem.* **1977**, *42*, 1644.



presence of an ion at m/e 121 (69%) attributable to the $PhCS^+$ ion is additional evidence in support of structure **5**. The presence of a 5-methyl substituent in **19b** facilitated this cyclodehydration as **20b** was obtained in 94% yield.

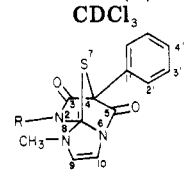
Reaction with Acetylenic Dipolarophiles. Cycloaddition of **20a** and **20b** with dimethyl acetylenedicarboxylate occurred readily in refluxing xylene (30 min). With dibenzoylacetylene, a 17-h reaction time was necessary to ensure complete reaction of the mesoionic system. Formation of the pyridinones **22** occurred in moderate yield by extrusion of S from the initial 1,1-cycloadduct **21** under these reaction conditions. Their characterization is described in Table III, and these data are consistent with those of the pyridinones described in Table I.

Reaction with Olefinic Dipolarophiles. *N*-Ethyl- and *N*-phenylmaleimide and maleic anhydride underwent cycloaddition with the mesoionic systems **20a** and **20b** in refluxing xylene (16 h), both reaction temperature and reaction time being critical for complete cycloaddition to occur. The initial 1:1 cycloadduct **23** was not isolated, H_2S being readily eliminated to give the pyridinone **22**, this elimination occurring to some extent in refluxing benzene even at 80 °C. The ring-fused pyridinones prepared by this route are described in Table III.

Discussion

Although isoelectronic with the *anhydro*-3-hydroxythiazolo[3,2-*a*]pyridinium hydroxide system,[3] the *anhydro*-3-hydroxyimidazo[2,1-*b*]thiazolium hydroxide system **5** underwent cycloadditions with olefinic and acetylenic dipolarophiles with exceptional ease. This is in marked contrast to the former mesoionic system which was unreactive under analogous reaction conditions. Both underwent ready acylation when the 2-position was unsubstituted. The mesoionic system **5** readily reverted to its precursor thioglycolic acid on hydrolysis, the pyridinium system being more stable to hydrolysis. Introduction of an additional nitrogen atom into the imidazole ring to give **20** not only resulted in a ring system more susceptible to hydrolysis but also reduced the reactivity of the fused-ring mesoionic system in comparable cycloaddition reactions. The destabilizing effect of adding the additional sp^2 nitrogen atom may be attributed to the inductive effect exerted by this atom with a subsequent increase in the susceptibility of the fused-ring system to hydrolytic attack at the C_3 carbonyl group.

Table II. ^{13}C Chemical Shifts (δ) for 17 (R = CH_3) in $CDCl_3$



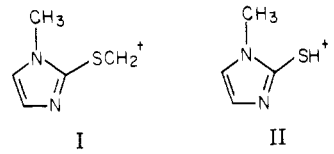
atom no.	δ	atom no.	δ
3,5	168.6	10 or 9	130.7
4	74.0	1′	134.9
2 (NCH_3) or 8 (NCH_3)	25.0	3′	126.8
1	124.8	2′	129.2
8 (NCH_3) or 2 (NCH_3)	34.1	4′	129.6
9 or 10	130.5		

Experimental Section[8]

***anhydro*-3-Hydroxy-7-methyl-2-phenylimidazo[2,1-*b*]thiazolium Hydroxide (5a).** 1-Methyl-2(3*H*)-imidazolethione (3.42 g, 0.03 mol) in dry $CHCl_3$ (75 mL) was treated with α-bromophenylacetyl chloride[9] (7.02 g, 0.03 mol) at room temperature and the reaction mixture then heated under reflux for 30 min. The colorless product that separated (7.5 g) was treated with cold, aqueous K_2CO_3 solution, giving a halogen-free product which crystallized from acetone as colorless needles and, after being dried on the steam bath, crystallized from ethyl acetate as yellow needles: 5.0 g (72%); mp 188–189 °C dec; IR (KBr) ν_{CO} 1610 cm^{-1}; NMR ($CDCl_3$) δ 3.50 (s, 3, NCH_3), 6.83 (d, 1, J = 2.0 Hz, C_5 H), 7.47 (d, 1, J = 2.0 Hz, C_6 H), 6.9–7.4 (m, 3, aromatic), 7.65 (brd, 2, aromatic); mass spectrum, m/e (rel intensity) 230 (M^+·, 86).

Anal. Calcd for $C_{12}H_{10}N_2OS$: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.71; H, 4.35; N, 12.19.

***anhydro*-3-Hydroxy-2-[(((1-methylimidazol-2-yl)thio)methyl)carbonyl]-7-methylimidazo[2,1-*b*]thiazolium Hydroxide (11). A. From 4 and Bromoacetyl Bromide.** 1-Methyl-2(3*H*)-imidazolethione (4; 2.28 g, 0.02 mol) in dry $CHCl_3$ (50 mL) was treated dropwise at room temperature with bromoacetyl bromide (4.40 g, 0.02 mol). After 10 min Et_3N (2.02 g) in dry $CHCl_3$ (10 mL) was added followed by an additional 2.02 g of Et_3N after the reaction mixture was kept for 30 min at room temperature. The reaction mixture was then heated under reflux for 2 h. After removal of volatile material, the residue was washed with water, giving a beige product which crystallized from acetone as beige plates: 1.4 g (23%); mp 206.5–207.5 °C dec; IR (KBr) 1560, 1660 (CO) cm^{-1}; mass spectrum, m/e (rel intensity) 308 (M^+·, 2), 128 (I, 8), 114 (II, 100).



I II

Anal. Calcd for $C_{12}H_{12}N_4O_2S_2$: C, 46.76; H, 3.92; N, 18.18. Found: C, 46.98; H, 3.97; N, 18.10.

B. From (1-Methylimidazol-2-yl)thioglycolic acid (12). 1-Methyl-2(3*H*)-imidazolethione (2.28 g, 0.02 mol) in dry $CHCl_3$ (25 mL) was treated with bromoacetic acid (2.78 g, 0.02 mol). After 10 min at room temperature, Et_3N (2.02 g) was added and stirring continued for 1.5 h. The Et_3N·HBr was filtered off and the filtrate evaporated leaving a pale yellow residue. This was extracted with boiling acetone and the acetone then evaporated to give a resinous product which solidified on treatment with Et_2O. Recrystallization from 2-propanol afforded colorless, irregular prisms: 3.20 g (90%),

(8) Spectral characterizations were carried out with the following instrumentation: IR, Perkin-Elmer Model 337 spectrophotometer; NMR, Varian T-60, Bruker WP60 spectrometers using Me_4Si as internal standard; mass spectra, Hitachi-Perkin Elmer RMU-6E mass spectrometer at 70 eV using the direct-insertion probe at about 120 °C. Evaporations were done under reduced pressure by using a Rotovap apparatus, and melting points were determined in capillaries. Analyses were by Instranal Laboratories, Inc., Rensselaer, NY.

(9) Fischer, E.; Schmidlin, J. *Justus Liebigs Ann. Chem.* **1905**, *304*, 191.

Table III. Cycloadducts 22 Formed from *anhydro*-3-Hydroxy-7-methyl-2-phenylthiazolo[3,2-*b*][1,2,4]triazolium Hydroxide (20) and Acetylenic and Olefinic Dipolarophiles

R	dipolarophile used	reaction time, h	yield, %	mp, °C	crystal form	crystallization solvent[a]	formula[b,c]	IR (KBr) ν_{CO}, cm^{-1}	NMR ($CDCl_3$), δ
H	$CH_3OOCC{\equiv}CCOOCH_3$	1	34	272–274	cream prisms	A	$C_{17}H_{15}N_3O_5$	1720, 1650	3.52 (s, 3, NCH_3), 3.80 (s, 3, OCH_3), 3.92 (s, 3, OCH_3), 7.35 (s, 5, Ph), 8.10 (s, 1, C_2 H)
CH_3	$CH_3OOCC{\equiv}CCOOCH_3$	0.5	63	251–252	colorless prisms	A	$C_{18}H_{17}N_3O_5$	1720, 1650	2.57 (s, 3, CCH_3), 3.52 (s, 3, NCH_3), 3.72 (s, 3, OCH_3), 3.80 (s, 3, OCH_3), 7.33 (s, 5, Ph)
CH_3	PhCOC CCOPh	16	39	330 dec	yellow prisms	B	$C_{28}H_{21}N_3O_3$	1640, 1590	2.58 (s, 3, CCH_3), 3.28 (s, 3, NCH_3), 7.0–7.6 (m, 15, aromatic)
H	*N*-ethylmaleimide	16	45	264–265	orange-yellow prisms	A	$C_{17}H_{14}N_4O_3$	1750, 1700,[d] 1670, 1630	1.18 (t, 3, J = 7.3 Hz, CH_2CH_3), 3.62 (q, 2, J = 7.3 Hz, CH_2CH_3), 4.25 (s, 3, NCH_3), 7.43 (s, 5, Ph), 8.25 (s, 3, C_2H)
CH_3	*N*-ethylmaleimide	16	67	275	yellow needles	C	$C_{18}H_{16}N_4O_3$	1740, 1695,[d] 1660, 1630	1.18 (t, 3, J = 6.8 Hz, CH_2CH_3), 2.53 (s, 3, CCH_3), 3.47 (q, 2, CH_2CH_3), 4.22 (s, 3, NCH_3), 7.42 (s, 5, Ph)
CH_3	*N*-phenylmaleimide	48	76	285–286	yellow needles	C	$C_{22}H_{16}N_4O_3$	1750, 1705, 1660, 1620	2.57 (s, 3, CCH_3), 4.25 (s, 3, NCH_3), 7.0–7.5 (m, 10, aromatic)
CH_3	maleic anhydride	0.5	84	332–333	yellow-green prisms	B	$C_{16}H_{11}N_3O_4$	1820, 1760, 1650	2.80 (s, 3, CCH_3), 4.40 (s, 3, NCH_3), 7.50 (br s, 5, Ph)

[a] A = CH_3OH; B = CH_3NO_2; C = EtOH. [b] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in this table. [c] All products gave M^+. (100%). [d] Shoulder.

mp 86–87.5 °C. Crystallization from benzene gave colorless prisms of the same melting point: IR (Nujol) 1700 (br, CO) cm^{-1}.

Anal. Calcd for $C_6H_8N_2O_2S$: C, 41.86; H, 4.68; N, 16.28. Found: C, 41.68; H, 4.60; N, 16.14.

The above acid (0.34 g, 0.02 mol), *N*-ethylmaleimide (0.25 g, 0.02 mol), and DCC (0.43 g, slight excess) in dry CH_2Cl_2 (15 mL) were heated under reflux for 1 h. The reaction mixture turned a bright yellow, and the urea separated on the walls of the flask. After being cooled, the precipitate was filtered and washed with CH_2Cl_2, and the solvent then evaporated, leaving an oil which solidified on trituration with Et_2O. Recrystallization from ether gave **11**. Heating the acid **12** in Ac_2O at 70–80 °C for 3 min gave a yellow reaction mixture from which, on cooling, **11** separated.

Reaction of 5a with Acetylenic and Olefinic Dipolarophiles. General Procedure. The mesoionic system (0.46 g, 2 mmol) and dimethyl acetylenedicarboxylate (0.3 g, slight excess) in dry benzene (10 mL) were refluxed for 16 h. Removal of the benzene left a dark residue which was chromatographed on silica gel with chloroform as eluent. Methyl 1-methyl-6-phenyl-5-oxoimidazo[1,2-*a*]pyridine-7,8-dicarboxylate (**9**; $R^1 = R^2 = COOCH_3$) crystallized from methanol as yellow prisms: 0.19 g (25%), mp 202–203 °C (see Table I).

Reaction of 5a with Methyl Isocyanate. The mesoionic system **5a** (0.23 g, 1 mmol) and methyl isocyanate (0.5 mL, excess) in dry benzene (20 mL) were heated under reflux for 17 h. Removal of the solvent and unreacted methyl isocyanate in vacuo gave a colorless viscous oil which solidified on trituration with petroleum ether (bp 40–60 °C). The 1:1 adduct **17** (R = CH_3) crystallized from benzene as colorless needles: 0.28 g (98%); mp 103.5–104.5 °C; IR (KBr) 1740 (CO) cm^{-1}; NMR ($CDCl_3$) δ 2.70 (s, 3, NCH_3), 3.73 (s, 3, NCH_3), 7.02 (d, 1, J = 1.0 Hz, imidazole H), 7.15 (d, 1, J = 1.0 Hz, imidazole H), 7.3–7.5 (m, 3, aromatic), 7.6–7.8 (m, 2, aromatic); mass spectrum, m/e (rel intensity) 287 (M^+·, 45), 230 (M^+· – CH_3NCO, 30), 121 ($PhCS^+$, 100).

Anal. Calcd for $C_{14}H_{13}N_3O_2S$: C, 58.53; H, 4.56; N, 14.63. Found: C, 58.71; H, 4.52; N, 14.51.

Reaction of 5a with *p*-Methoxyphenyl Isocyanate. Formation of 17 (R = *p*-$CH_3OC_6H_4$). The mesoionic system **5a** (0.23 g, 1 mmol) and *p*-methoxyphenyl isocyanate (0.15 g, 1 mmol) in dry benzene (10 mL) were heated under reflux for 5 h. Reaction workup as above gave **17** (R = *p*-$CH_3OC_6H_4$) as colorless prisms from benzene–petroleum ether: 0.38 g (100%); mp 111–112 °C; IR (KBr) 1740 (CO) cm^{-1}; NMR ($CDCl_3$) δ 3.77 (s, 6, NCH_3 and OCH_3), 6.97 (d, 1, J = 1.0 Hz, imidazole H), 7.20 (d, 1, J = 1.0 Hz, imidazole H), 6.8–7.9 (m, 9, aromatic); mass spectrum, m/e (rel intensity) 149 ([*p*-$CH_3OC_6H_4NCO$]$^+$, 100).

Anal. Calcd for $C_{20}H_{17}N_3O_3S$: C, 63.32; H, 4.52; N, 11.08. Found: C, 63.69 H, 4.51; N, 11.06.

Reaction of 5a with *p*-Tolyl Isocyanate. Formation of 17 (R = *p*-$CH_3C_6H_4$). The mesoionic compound **5a** (0.69 g, 3 mmol) and *p*-tolyl isocyanate (0.42 g, slight excess) in dry benzene (20 mL) were heated under reflux for 3.5 h, resulting in a clear, light violet solution. Removal of the solvent and trituration of the residue with petroleum ether gave a crystalline product which separated from benzene–petroleum ether as colorless prisms: 1.05 g (96%); mp 103–104 °C dec; IR (KBr) 1740 (CO) cm^{-1}; NMR ($CDCl_3$) δ 2.28 (s, 3, CCH_3), 3.72 (s, 3, NCH_3), 6.9–7.8 (m, 11, imidazole and aromatic); mass spectrum, m/e (rel intensity) 230 ([M^+· – *p*-$CH_3C_6H_4NCO$], 6), 133 [*p*-$CH_3C_6H_4NCO$]$^+$, 100).

Anal. Calcd for $C_{20}H_{17}N_3O_2S$: C, 66.11; H, 4.72; N, 11.57. Found: C, 66.55; H, 5.09; N, 11.89.

***S*-(4-Methyl-1,2,4-triazol-3-yl)phenylthioglycolic Acid (19a).** Sodium hydride (1.0 g, 50% oil suspension) was added in portions to a solution of 4-methyl-3(4*H*)-1,2,4-triazolethione[10] (**18**, R = H; 1.15 g, 10 mmol) in dry DMF (15 mL). After 5 min, α-bromophenylacetic acid (2.15 g, 10 mmol) was added in small portions at room temperature, an exothermic reaction resulting. The reaction mixture was heated at 50–60 °C for 1 h and, after cooling, poured into water (ca. 20 mL). The aqueous solution was acidified to pH 5 with concentrated HCl and then kept overnight at 0 °C. The precipitate was collected and washed with water, followed by petroleum ether (bp 40–60 °C); 2.3 g (92%). It crystallized from ethanol as colorless prisms: mp 183–184 °C dec;

(10) Freund, M. *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 2483. Goerdeler, J.; Galinke, J. *Chem. Ber.* **1957**, *90*, 202.

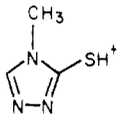
IR (KBr) 1680 (br, s, CO) cm^{-1}; NMR (CF_3COOH) 3.90 (s, 3, NCH_3), 5.72 (s, 1, CH), 7.50 (s, 5, Ph), 9.60 (s, 1, C_5 H); mass spectrum, *m/e* (rel intensity) 249 ($M^{+\cdot}$, 14), 205 ($M^{+\cdot} - CO_2$, 46), 121 ($PhCS^+$, 100).

Anal. Calcd for $C_{11}H_{11}N_3O_2S$: C, 53.01; H, 4.45; N, 16.86. Found: C, 53.14; H, 4.46; N, 16.74.

Under analogous conditions 4,5-dimethyl-3(4*H*)-triazolethione[11] (**18**; R = CH_3) gave *S*-(4,5-dimethyl-1,2,4-triazol-3-yl)phenylthioglycolic acid (**19b**) as colorless prisms (77%). It formed colorless prisms from methanol: mp 187 °C dec; IR (Nujol) 1680 (br, s, CO) cm^{-1}; NMR (CF_3COOH) δ 2.78 (s, 3, CCH_3), 3.73 (s, 3, NCH_3), 5.67 (s, 1, CH), 7.48 (s, 5, Ph); mass spectrum, *m/e* (rel intensity) 263 ($M^{+\cdot}$, 8), 219 ($M^{+\cdot} - CO$, 54), 121 ($PhCS^+$, 45).

Anal. Calcd for $C_{12}H_{13}N_3O_2S$: C, 54.75; H, 4.98; N, 15.96. Found: C, 54.82; H, 4.90; N, 15.61.

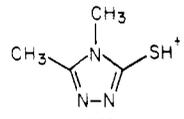
***anhydro*-3-Hydroxy-7-methyl-2-phenylthiazolo[3,2-*b*]-[1,2,4]triazolium Hydroxide (20a).** A mixture of the thioglycolic acid (**19a**; 1.7 g, 6.8 mmol) and Ac_2O (5 mL) was warmed on a steam bath at 70–80 °C for 10 min, during which time the reaction mixture assumed a yellow color. When the mixture was cooled at 0 °C, yellow crystals of **20** (R = H) separated. These were collected, washed with anhydrous Et_2O, dried at 80 °C for 3 h, and finally recrystallized from CH_3NO_2 containing a few drops of Ac_2O, giving yellow needles: 1.40 g (89%); mp 175–176 °C dec; IR (KBr) 1610 (CO) cm^{-1}; NMR [CF_3COOH + $(CF_3CO)_2O$] δ 4.25 (s, 3, NCH_3), 7.58 (s, 5, Ph), 8.82 (s, 1, C_6 H); mass spectrum, *m/e* (rel intensity) 231 ($M^{+\cdot}$, 27), 121 ($PhCS^+$, 69), 115 (III, 100).



III

Anal. Calcd for $C_{11}H_9N_3OS$: C, 57.14; H, 3.92; N, 18.18. Found: C, 56.83; H, 3.93; N, 17.89.

Similarly, a mixture of **19b** and Ac_2O afforded a 94% yield of *anhydro*-6,7-dimethyl-3-hydroxy-2-phenylthiazolo[3,2-*b*][1,-2,4]triazolium hydroxide (**20b**), likewise obtained as yellow needles from CH_3NO_2 and a few drops of Ac_2O: mp 210 °C dec; IR (KBr) 1620 (CO) cm^{-1}; NMR [CF_3COOH + $(CF_3CO)_2O$] δ 2.80 (s, 3, CCH_3), 4.07 (s, 3, NCH_3), 7.53 (s, 5, Ph); mass spectrum, *m/e* (rel intensity) 245 ($M^{+\cdot}$, 16), 129 (IV, 100), 121 ($PhCS^+$, 39).



IV

Anal. Calcd for $C_{12}H_{11}N_3OS$: C, 58.77; H, 4.52; N, 17.14. Found: C, 58.95; H, 4.40; N, 17.27.

General Procedure for Reaction of 20. A. With Acetylenic Dipolarophiles. The mesoionic system (**20a**) (0.46 g, 2 mmol) and dimethyl acetylenedicarboxylate (0.3 g, slight excess) in dry xylene (10 mL) were heated under reflux for 1 h. After the mixture was cooled to ca. 5 °C, the beige precipitate which separated was collected and washed with methanol; 0.23 g (34%). Products obtained in this way are described in Table III.

B. With Olefinic Dipolarophiles. The mesoionic system (**20b** 0.02 mol), *N*-ethylmaleimide (0.25 g, 0.02 mol), and dry xylene (10 mL) were heated together under reflux for 16 h. When the mixture was cooled, the yellow crystalline product was filtered and washed with Et_2O; 0.45 g (67%). Use of a lower reaction temperature (80 °C) or a shorter reaction time always resulted in a mixture of the cycloadduct and the initial mesoionic ring system.

Registry No. 4, 60-56-0; **5a**, 71370-34-8; **9** (R^1 = R^2 = $COOCH_3$), 71370-35-9; **9** (R^1 = R^2 = COPh), 71370-36-0; **9** (R^1, R^2 = –CON(Et)CO–), 71370-37-1; **9** (R^1, R^2 = –CON(Ph)CO–), 71370-38-2; **9** (R^1, R^2 = –COOCO–), 71370-39-3; **9** (R^1 = R^2 = CN), 71370-40-6; **9** (R = CN), 71371-25-0; **9** (R = COOEt), 71371-26-1; **11**, 71370-41-7; **12**, 71370-42-8; **15a**, 71370-43-9; **15b**, 71370-44-0; **17** (R = CH_3), 71370-45-1; **17** (R = *p*-$CH_3OC_6H_4$), 71370-46-2; **17** (R = *p*-$CH_3C_6H_4$), 71370-47-3; **18** (R = H), 24854-43-1; **18** (R = CH_3), 38942-50-6; **19a**, 71370-48-4; **19b**, 71370-49-5; **20a**, 71370-50-8; **20b**, 71370-51-9; **22** (R = H; R^1 = $COOCH_3$), 71370-52-0; **22** (R = CH_3; R^1 = $COOCH_3$), 71370-53-1; **22** (R = CH_3; R^1 = COPh), 71370-54-2; **22** (R = H; R^1, R^1 = –CON(Et)CO–), 71370-55-3; **22** (R = CH_3; R^1, R^1 = –CON(Et)CO–), 71370-56-4; **22** (R = CH_3; R^1, R^1 = –CON(Ph)CO–), 71370-57-5; **22** (R = CH_3; R^1, R^1 = –COOCO–), 71370-58-6; α-bromophenylacetyl chloride, 19078-72-9; bromacetyl bromide, 598-21-0; bromoacetic acid, 79-08-3; acrylonitrile, 107-13-1; ethyl acrylate, 140-88-5; methyl isocyanate, 624-83-9; *p*-methoxyphenyl isocyanate, 5416-93-3; *p*-tolyl isocyanate, 622-58-2; α-bromophenylacetic acid, 4870-65-9; dimethyl acetylenedicarboxylate, 762-42-5; dibenzoylacetylene, 1087-09-8; *N*-ethylmaleimide, 128-53-0; *N*-phenylmaleimide, 941-69-5; maleic anhydride, 108-31-6; fumaronitrile, 764-42-1.

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Ring Annulation with Heterocyclic Ylides. Annulation of Pyridinones to the Thiazole and 1,3,4-Thiadiazole Systems[1a]

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2(3*H*)-Thiazolethione and its 4-methyl derivative and α-bromophenylacetyl chloride/NEt_3 readily gave *anhydro*-3-hydroxy-2-phenylthiazolo[2,3-*b*]thiazolium hydroxide and its 5-methyl derivative. This ring-fused mesoionic system underwent cycloaddition in refluxing toluene with acetylenic and olefinic dipolarophiles to form substituted 5*H*-thiazolo[3,2-*a*]pyridin-5-ones. α-Bromophenylacetyl chloride also reacted readily with 5-methyl-2(3*H*)-1,3,4-thiadiazolethione to form the *anhydro*-5-hydroxy-2-methyl-6-phenylthiazolo[2,3-*b*][1,-3,4]thiadiazolium hydroxide system. In this instance cycloaddition with olefinic and acetylenic dipolarophiles occurred in refluxing benzene, a variety of substituted 5*H*-1,3,4-thiadiazolo[3,2-*a*]pyridin-5-ones being obtained.

In the preceding paper,[2] use was made of cycloaddition reactions with the *anhydro*-3-hydroxyimidazo[2,1-*b*]thiazolium hydroxide and the *anhydro*-3-hydroxythiazolo-[3,2-*b*][1,2,4]triazolium hydroxide ring systems formed from the corresponding cyclic thiones to effect annulation of the pyridinone ring to the imidazole and 1,2,4-triazole

(1) (a) Mesoionic Compounds. 50. (b) Partial support of this work by U.S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged. (c) On leave from Yamaguchi University, Japan.

(2) Potts, K. T.; Kanemasa, S. *J. Org. Chem.*, preceding paper in this issue.

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