refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 1.26/[\sigma(F)^2 + 0.0035F^2]$) was employed for calculating R_w and in least-squares refinement.

The structure was solved by using the automatic centrosymmetric direct methods program of SHELX-76. The total number of parameters varied was 205 for 1807 observations. The full-matrix least-squares refinement converged at $R = 0.0636$ and $R_w = 0.0739$. The final atomic coordinates and thermal parameters are available as supplementary material Table IX, and the list of bond distances and angles is available as supplementary material Table IV. The list of calculated and observed structure factors is available from the authors.

Crystal Structure of the Dimer 16. A. Data Collection. A crystal of the dimer **16** with approximate dimensions 0.6 × 0.6 × 0.5 mm was mounted on a glass fiber by using epoxy cement such that the longest crystal dimension, 0.6 mm, was approximately parallel to the fiber axis. Unit cell parameters were determined as described above. Fifteen reflections whose 2θ values ranged from 5.21 to 18.38° were machine centered and used in least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were $a = 11.544$ (4) Å, $b = 10.218$ (5) Å, $c = 6.425$ (3) Å, $\alpha = 104.26$ (3)°, $\beta = 104.15$ (3)°, $\gamma = 92.62$ (3)°, and $V = 707.7$ (5) Å^3. The calculated density of 1.27 g cm^{-3} for 2 formula units per unit cell agrees with the experimental density of 1.26 g cm^{-3} measured by the flotation method using a mixture of $ZnCl_2$ and H_2O. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.2°, indicating a satisfactory mosaic spread for the crystal. Axial photographs indicated that the crystal belonged to the triclinic system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences. No systematic absences were observed, consistent only with space groups $P1$ or $P\bar{1}$ (No. 1 or 2).[13] Successful refinement in $P\bar{1}$ confirmed our initial choice of that space group.

Intensity data were collected by using θ–2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate of from 2.93 to 29.3°/min was used, and a scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (500, 040, 002) monitored every 97 reflections. Intensities were calculated as described above. From a total of 2498 reflections collected in a complete hemisphere of data out to $2\theta = 50°$, 2255 were accepted as statistically above background on the basis that F was greater than $3\sigma(F)$. Lorentz and polarization corrections were made in the usual way.

B. Solution and Refinement of the Structure. Computations were performed as described above. In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 3.902\ [\sigma(F)^2 + 0.002F^2]$) was employed for calculating R_w and in least-squares refinement.

The structure was solved by using the automatic centrosymmetric direct methods program of SHELX-76. The total number of parameters varied was 205 for 2255 observations. The full-matrix least-squares refinement converged at $R = 0.0540$ and $R_w = 0.0738$. The final atomic coordinates and thermal parameters are available as supplementary material Table X, and the list of bond distances and angles is available as supplementary material Table V. The list of calculated and observed structure factors is available from the authors.

Registry No. 1, 71370-30-4; **2b**, 66077-98-3; **2c**, 20498-02-6; **3**, 6674-22-2; **5**, 71370-25-7; **7**, 66921-79-7; **9**, 71423-34-2; **10**, 71423-35-3; **11**, 71370-26-8; **12**, 71423-36-4; **13**, 71370-27-9; **14**, 71370-28-0; **15**, 71370-29-1; **16**, 71423-37-5; $CH_3COCH_2CO_2Et$, 141-97-9; cyclohexenone, 930-68-7; PBr_3, 7789-60-8; EtO_2CNHNH_2, 4114-31-2; furan, 110-00-9; p-$BrC_6H_4SO_2NHNH_2$, 2297-64-5; $HONH_3Cl$, 5470-11-1.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters (Tables VI–X) and tables of bond distances and bond angles (Tables I–V) (14 pages). Ordering information is given on any current masthead page.

Reactions of 2-Methyleneallyl Dianion with Aldehydes, Ketones, Epoxides, and Allyl Halides

Robert B. Bates,* William A. Beavers, and Bernard Gordon III

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Nancy S. Mills

Department of Chemistry, Carleton College, Northfield, Minnesota 55057

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Reactions of 2-methyleneallyl dianion with aldehydes, ketones, ethylene oxide, and allyl chloride gave diaddition products in 49–76% yield, always accompanied by some monoadduct (5–37% yield). Elimination was the only reaction observed with epichlorohydrin. Phthalaldehyde gave a cyclic diaddition product in 9% yield, but none was obtained from benzil or quinone. Attempts to obtain a mixed diadduct in good yield by reacting the dianion with two different electrophiles failed. An improved procedure is given for the preparation of the dianion.

Metalating systems such as n-butyllithium/tetramethylethylenediamine (TMEDA) and n-butyllithium/potassium *tert*-butoxide have yielded a variety of delocalized polyanions[1-3] not readily accessible through other routes such as halogen–metal exchange. Because of the availability of these polylithiated species, we are interested in exploring their synthetic utility. Delocalized carbanions have recently been used in the preparation of terpenoids.[4]

We chose to examine the reactions of 2-methyleneallyl dianion (**1**) because of the simplicity of its product mixtures and because of current interest in the "aromaticity" of cross-conjugated polyanions possessing a Hückel number of electrons.[5] Reactions of **1** with mono-[2] and dihaloalkanes[6] have been described. We now report the results

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[1] J. Klein and A. Medlik, *J. Chem. Soc., Chem. Commun.*, 275 (1973).

[2] R. B. Bates, W. A. Beavers, M. G. Greene, and J. H. Klein, *J. Am. Chem. Soc.*, **96**, 5640 (1974).

[3] T. Clark and P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 789 (1976).

[4] S. R. Wilson and L. R. Phillips, *Tetrahedron Lett.*, 3047 (1975); S. R. Wilson, K. M. Jernberg, and D. T. Mao, *J. Org. Chem.*, **41**, 3209 (1976).

[5] P. Gund, *J. Chem. Educ.*, **49**, 100 (1972); J. Klein, A. Medlik-Balan, A. Y. Meyer, and M. Chorev, *Tetrahedron*, **32**, 1839 (1976); J. Klein and A. Medlik-Balan, *Tetrahedron Lett.*, 279 (1978).

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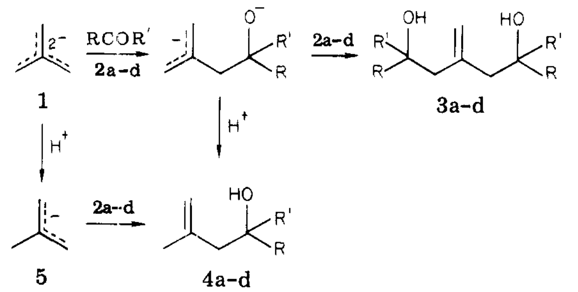
Table I. Percent Yields in Reactions of Carbanions with Monofunctional Carbonyl Compounds

	2a	2b	2c	2d
n-BuLi[7]	100	73[a]	81[b]	80[c]
allyllithium[8]	80			
5		65[d]	42[d]	46[d]

	3a	4a	3b	4b	3c	4c	3d	4d
1 (method A)	76	17	69	28	49	37	60	12
1 (method B)			68[d]	6[d]				

[a] Plus 26% Ph_2CHOH (reduction). [b] Plus 20% Ph(CO)-Me (enolization) and 1% PhCH(OH)Me (reduction). [c] Plus 16% Me_2CO (enolization). [d] Yield from butyllithium; other yields are from 1.

Chart I



a, R = Ph; R′ = H
b, R = R′ = Ph
c, R = Ph; R′ = Me
d, R = R′ = Me

of reactions of 1 with ketones, aldehydes, epoxides, and allyl halides.

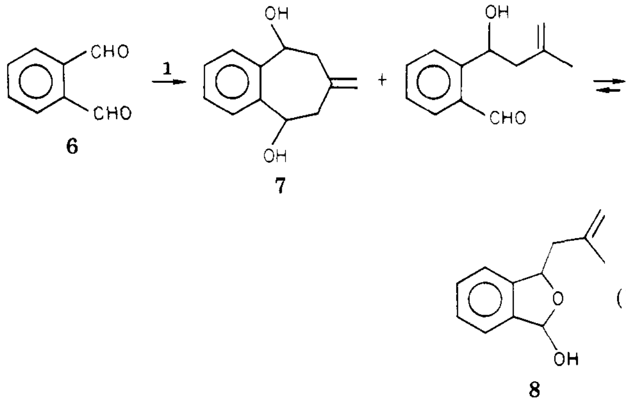
Results and Discussion

Dianion 1 was prepared previously as the crystalline dilithium salt with *n*-butyllithium/TMEDA (method A).[6] This procedure required several days and appears to offer no advantage over a new way (method B) employing *n*-butyllithium/potassium *tert*-butoxide and requiring only a few minutes.

The reactions of dianion 1 with simple carbonyl compounds are summarized in Table I along with the results of addition of some monocarbanions to the same carbonyl compounds. The desired diadducts **3a–d**, obtained in 49–76% yield, were accompanied in all cases by lesser amounts of monoadducts **4a–d** (authentic samples of **4b–d** were prepared from monoanion **5** in the yields indicated in Table I).

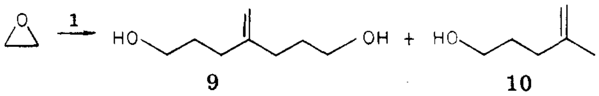
Two possible routes to the monoadduct byproducts **4a–d** are shown in Chart I. The proton source can be at least partly ketone in the cases of methyl ketones **2c** and **2d**, which enolize to the extent of 16–20% in their reaction with *n*-butyllithium, as indicated in Table I.[7] This source was confirmed in the present work by quenching with D_2O and recovering monodeuterated acetophenone (**2c**) in 11% yield and monodeuterated acetone (**2d**) in 21% yield. Benzaldehyde (**2a**) and benzophenone (**2b**) are nonenolizable, so monoadducts **4a** and **4b** must arise in other ways which probably operate in the cases of **4c** and **4d** as well. These include traces of monoanion **5**[8] in the dianion preparation, traces of moisture entering during the reaction, and electron transfer from anions to carbonyl compounds; the latter should be most serious with benzophenone and least serious with acetone.[7]

Because the reaction of 1 with carbonyl substrates was so facile, we examined the formation of rings from dicarbonyl compounds. Phthalaldehyde (**6**) reacted with 1 to give an 18% yield of a 1:1 mixture of diadduct **7** and monoadduct **8** (eq 1). Attempts to separate the mixture by distillation or chromatography were unsuccessful. An attempt was made to oxidize the hemiacetal **8** to the lactone by the use of Ag^+, but although formation of a silver mirror indicated some oxidation, the reaction never removed more than 50% of **8**. Precedent for the low yield of cyclized product exists both in the reaction of 1 with a 1,4-disubstituted electrophile and in the reaction of phthalaldehyde (**6**) with a delocalized carbanion: Bates and co-workers[6] found that methylenecycloheptane was formed in 15% yield from the reaction of 1 with 1,4-dibromobutane; Cantrell and Shechter[9] found that phthalaldehyde reacted with cyclooctatetraene dianion to form a diadduct but in only 3.6% yield.



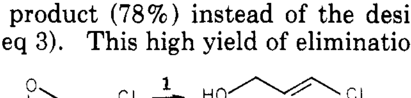
(1)

Dianion 1 gave no observed product with benzoquinone or benzil. Benzoquinone acted as an electron sink, yielding hydroquinone and intractable products. Benzil in reactions with other organolithium compounds has been observed to act as an electron acceptor, yielding benzoin rather than the diol adduct;[9] although some benzoin (~20%) was produced in the reaction of 1 with benzil, the remainder of the product was again intractable. Ethylene oxide reacted smoothly with dianion 1 to give 4-methylene-1,7-heptanediol (**9**, 80% yield) and 2-methyl-1-penten-5-ol (**10**, 5%) (eq 2); the latter had been prepared in 72% yield from the reaction of ethylene oxide with anion **5**.[10]



(2)

The reaction of 1 with epichlorohydrin (**11**) in THF/pentane at -78 °C gave (*E*)-3-chloro-2-propen-1-ol (**12**) as the major product (78%) instead of the desired cyclic products (eq 3). This high yield of elimination product



(3)

is more analogous to the result with *n*-butyllithium (90% elimination, 0% displacement) than that with allyllithium (43% elimination, 48% displacement).[11] As expected with the good metal-complexing agents TMEDA and THF present, we observed only the *E* stereoisomer.[12]

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[6] J. J. Bahl, R. B. Bates, W. A. Beavers, and N. S. Mills, *J. Org. Chem.*, 41, 1620 (1976).

[7] J. D. Buhler, *J. Org. Chem.*, 38, 904 (1973).

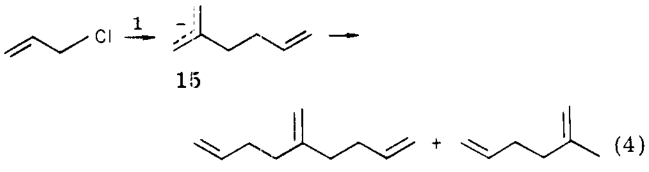
[8] S. Akiyama and J. Hooz, *Tetrahedron Lett.*, 4115 (1973).

[9] T. S. Cantrell and H. Shechter, *J. Am. Chem. Soc.*, 89, 5877 (1967).

[10] M. Schlosser and J. Hartmann, *Angew. Chem., Int. Ed. Engl.*, 12, 508 (1973).

[11] H. J. Fabris, *J. Org. Chem.*, 32, 2031 (1967).

Because we wanted triene **13** for other purposes, the reaction of **1** with allyl chloride was explored (eq 4). The

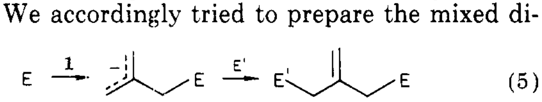


15

13 14

desired diadduct **13** was formed in 50% yield along with 11% of monoadduct **14**. No cyclized products from the initial intermediate **15** (e.g., methylenecyclohexane or 3-methylene-1-methylcyclopentane) were found, nor were cyclopropyl derivatives seen, in contrast to the reaction of phenyllithium with allyl chloride.[13]

Dianion **1** would be a much more versatile synthon if it could be reacted successively with two electrophilic reagents E and E′ to give a mixed diadduct **16** in good yield (eq 5). We accordingly tried to prepare the mixed di-



17 16

adduct **16** (E = PhCH(OH) and E′ = $HOCH_2CH_2$) by using 1 equiv of benzaldehyde (**2a**) followed by ethylene oxide, by using 1 equiv of ethylene oxide followed by benzaldehyde (**2a**), and by using both electrophiles simultaneously. In no case did the yield of mixed diadduct **16** exceed 27%, and considerable amounts of the symmetrical diadducts **3a** and **9** were formed in each case. The problem appears to be the large resonance stabilization of dianion **1**,[5] which results in similar rates for reaction of **1** and **17** with electrophiles. Hopefully, this will not be a problem with dianions with less resonance stabilization than **1**.

Experimental Section

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. NMR spectra were recorded on a Varian T-60 spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane. Elemental analyses were performed by Chemalytics, Inc.

Dianion 1. Method A. The procedure of ref 6 was used; the solid obtained, assumed to be entirely dianion·$2Li^+ \cdot 2(TMEDA)$, was dissolved in dry tetrahydrofuran (THF) for the reactions below.

Method B. To a mixture of 2.24 g (20 mmol) of KO-*t*-Bu, 20 mL of pentane, and 9.6 mL (20 mmol) of 2.2 M *n*-BuLi in hexane (Alfa, Ventron Corp.) in an argon-filled, round-bottomed flask was added dropwise via a dropping funnel or syringe over 5 min with stirring 1 mL (10 mmol) of isobutylene in 20 mL of pentane. After 10 min of further stirring, the dianion **1** salt was allowed to settle, the supernatant was removed via syringe, and the solid was blown dry with argon. For reactions, it was suspended in 20 mL of dry THF. This dianion preparation proceeds in about 80% yield.

Reaction of Dianion 1 with Monofunctional Electrophiles. To an argon-filled, septum-capped, 250-mL round-bottomed flask equipped with a magnetic stirring bar at −78 °C were added 100 mL of pentane, 50 mL of dry THF, and 2 equiv of electrophile. The reaction was conducted with rapid stirring at −78 °C by dropwise addition of the dianion solution via syringe through the septum cap. After 30–60 min of stirring, the reaction mixture was quenched with 1 mL of water. The organic layer was decanted and the residue discarded after being extracted with 2 × 30 mL of ether. Low-boiling solvents were removed by distillation through a 3-ft tantalum-wire column. Higher boiling solvents were removed by vacuum distillation, except the allyl chloride reaction mixture was flash distilled under vacuum and then purified by preparative GC. After solvent removal, the products were purified by preparative TLC on silica gel or basic alumina, using ether, methylene chloride, or 10% ether/methylene chloride as eluents. The product from the reaction with ethylene oxide was also purified by vacuum distillation in a micro-Hickman still (bath temperature 120 °C (1 mm)). Products **3b–d** were isolated as oils which crystallized upon standing and were recrystallized from benzene/petroleum ether to give **3b** (mp 122–124 °C), **3c** (mp 96–100 °C[14]), and **3d** (mp 77–78 °C).

The structures of **4a**,[15] **12**,[12] and **14**[16] were confirmed by comparison with spectral data from the literature.

The structure of **3a** was deduced from its spectral properties: NMR δ 2.5 (~d, *J* = 7 Hz, 4 H), 3.2 (b, variable, 2 H), 4.8 (t, *J* = 7 Hz, 2 H), 4.94 (s, 1 H),[17] 5.05 (s, 1 H),[17] 7.0–7.4 (m, 10 H). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.35; H, 7.34.

3b: NMR δ 2.8 (s, 4 H), 3.15 (b, variable, 2 H), 4.8 (s, 2 H), 7.2 (~s, 20 H). Anal. Calcd for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 85.62; H, 6.81.

4b: NMR δ 1.3 (s, 3 H), 2.8 (b, variable, 1 H), 2.9 (s, 2 H), 4.6 (m, 1 H), 4.7 (m, 1 H), 7.0–8.4 (m, 10 H). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.67; H, 7.57.

3c: NMR δ 1.49 (s, 3 H),[17] 1.51 (s, 3 H),[17] 2.5 (~s, 4 H), 3.4 (b, variable, 2 H), 4.7 (s, 1 H),[17] 4.8 (s, 1 H),[17] 7.3 (~s, 10 H). Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.75; H, 8.12.

4c: NMR δ 1.48 (s, 3 H), 1.52 (s, 3 H), 2.6 (s, 2 H), 4.55 (m, 1 H), 4.65 (m, 1 H), 5.5 (b, variable, 1 H), 7.0–7.4 (m, 5 H). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.62; H, 9.40.

3d: NMR δ 1.1 (s, 12 H), 2.4 (s, 4 H), 2.6 (b, variable, 2 H), 4.8 (s, 2 H). Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.59; H, 11.80.

4d: NMR δ 1.2 (s, 6 H), 1.8 (s, 3 H), 2.4 (s, 2 H), 2.5 (b, variable, 1 H), 4.7 (m, 1 H), 4.8 (m, 1 H). Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.40; H, 12.60.

9: NMR δ 1.7 (m, 4 H), 2.1 (m, 4 H), 3.5 (t, *J* = 6 Hz, 4 H), 4.3 (b, variable, 2 H), 4.7 (s, 2 H). Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.33; H, 10.88.

10: NMR δ 1.5 (m, 2 H), 1.7 (s, 3 H), 2.0 (m, 2 H), 3.45 (t, *J* = 6 Hz, 2 H), 4.55 (~s, 2 H), 5.0 (b, variable, 1 H).

13: NMR δ 2.2 (~s, 8 H), 4.85 (s, 2 H), 5.0 (dd, *J* = 10, 2 Hz, 2 H), 5.1 (dd, *J* = 17, 2 Hz, 2 H), 5.8 (ddt, *J* = 17, 10, 6 Hz, 2 H). Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.94; H, 12.01.

Monoadducts 4b–d from Monoanion 5. The potassium salt of monoanion **5** was prepared by adding 4.5 mL (10 mmol) of 2.2 M *n*-BuLi in hexane dropwise to a stirred solution of 1.12 g (10 mmol) of KO-*t*-Bu, 20 mL of pentane, and 5 mL (fivefold excess) of isobutylene in a stirred argon-filled, 250-mL round-bottomed flask. After 10 min of stirring, the suspension was transferred via syringe to argon-filled centrifuge tubes and centrifuged, the liquid was removed, and the solid was blown dry in an argon stream. The solid was dissolved in dry THF for use.

The ketones **2b–d** were dissolved in THF under argon and 1 equiv of the above anion solution was added slowly at −78 °C. The solution was allowed to warm to 25 °C, quenched with water, washed with saturated NaCl, dried, and evaporated. The yields shown in Table I for **2b–d** were estimated by integration of the NMR spectra of the resulting solutions; in each case, an analytically pure sample was obtained by preparative GC. **2c** and **2d** were liquids, but one preparation of **2b** crystallized with a melting point of 52–54 °C.

Reaction of 1 with Phthalaldehyde. A 250-mL round-bottomed flask was equipped with a 25-mL dropping funnel containing 3.06 mmol (0.556 g) of phthalaldehyde in 2 mL of THF

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[12] D. F. Hoeg, J. E. Forrette, and D. I. Lusk, *Tetrahedron Lett.*, 2059 (1964).

[13] D. E. Applequist and E. G. Saurborn, *J. Org. Chem.*, 37, 1676 (1972).

[14] Recrystallized **3c** was either the meso form or the racemate; its NMR spectrum had peaks at δ 1.51 and 4.8 but not at δ 1.49 and 4.7.

[15] J. M. Watson, J. L. Irvine, and R. M. Roberts, *J. Am. Chem. Soc.*, 95, 3348 (1973).

[16] "Sadtler Standard NMR Spectra", Vol. 33, Sadtler Research Laboratories, No. 21372.

[17] Both **3a** and **3c** are, as expected, composed of approximately equal amounts of meso form and the racemate, as evidenced in each case by terminal methylene protons absorbing at different locations and, in the case of **3c**, methyl peaks with slightly different chemical shifts.

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]

Kevin T. Potts* and S. Kanemasa[1c]

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

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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 ($M^{+\cdot}$ 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

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[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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