= 10.3 Hz, H3′), 5.45 (1 H, dm, J = 17.0 Hz, H3′), 3.98 (1 H, ddm, J = 13.5, J = 6.3, H1′), 3.56 (1 H, ddm, J = 13.5, J = 8.5 Hz, H1′), 3.34 (1 H, s, H3), 2.70 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 2.18, 1.75, 1.50 (4 H, m, H5, H6), 1.03 (3 H, s, CH_3), 1.00 (3 H, s, CH_3), 0.94 (3 H, s, CH_3); ^{1}H NMR (minor isomer) δ 3.09 (1 H, s, H3); HRMS calcd for $C_{13}H_{20}O_2S$ 240.1184, found 240.1174.

Epimerization of the 3-*exo*-(Allylsulfinyl)isoborneols 31–34. (1*R*,2*S*,*R*$_S$)-*exo*-3-(Prop-2′-enylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (41). A melt of the S_S sulfoxide **31** (200 mg, 0.83 mmol) was heated at 140 °C for 1 h in a stoppered tube. The R_S sulfoxide **41** slowly crystallized out of the melt at this temperature. The reaction was followed by HPLC (1:99 ethanol:ethyl acetate, Brownlee SI 100, 4.6 mm i.e. × 25 cm 5-μm column at 600 psi, S_S sulfoxide, t_R 18 min, R_S sulfoxide, t_R 14.8 min). After epimerization was complete, the product was recrystallized from ethyl acetate/light petroleum ether to give the product (190 mg, 95%) as colorless cubes, mp 171–174 °C, $[\alpha]_D$ +92° (c 0.85, acetone): ^{1}H NMR δ 6.04 (1 H, m, H2′), 5.42 (2 H, m, H3′), 3.89 (1 H, ddm, J = 13.1, J = 6.7 Hz, H1′), 3.46 (1 H, ddm, J = 13.1, J = 8.5 Hz, H1′), 3.84 (1 H, dd, $J_{2,3}$ = 7.8, $J_{2,OH}$ = 4.8 Hz, H2), 3.02 (1 H, d, $J_{3,2}$ = 7.8 Hz, H3), 2.68 (1 H, d, $J_{OH,2}$ = 4.8 Hz, OH), 2.38 (1 H, d, $J_{4,5exo}$ = 4.4 Hz, H4), 1.90, 1.57, 1.08 (4 H, m, H5, H6), 1.31 (3 H, s, CH_3), 0.94 (3 H, s, CH_3), 0.87 (3 H, s, CH_3). Anal. Calcd for $C_{13}H_{22}O_2S$: C, 64.4; H, 9.2. Found: C, 64.6; H, 9.2.

(1*R*,2*S*,2′*E*,*R*$_S$)-*exo*-3-(But-2′-enylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (42). A melt of the S_S sulfoxide **32** was heated at 110 °C for 20 min. After this time complete crystallization of the sample was observed. The colorless needles of the product **42** so obtained (>95%) had the following: mp 175–177 °C, $[\alpha]_D$ +108° (c 1.0, acetone); ^{1}H NMR δ 5.83 (1 H, dqm, J = 15.3, J = 6.5 Hz, H3′), 5.66 (1 H, dtm, J = 15.3, J = 7.5 Hz, H2′), 3.83 (1 H, dd, $J_{2,3}$ = 7.8, $J_{2,OH}$ = 4.8 Hz, H2), 3.84 (1 H, m, H1′), 3.35 (1 H, dd, J = 13.0, J = 8.0 Hz, H1′), 3.20 (1 H, m, OH), 2.98 (1 H, d, $J_{3,2}$ = 7.8 Hz, H3), 2.36 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.78 (3 H, dm, J = 6.5 Hz, H4′), 1.88, 1.70, 1.56, 1.07 (4 H, m, H5, H6), 1.30 (3 H, s, CH_3), 0.94 (3 H, s, CH_3), 0.87 (3 H, s, CH_3). Anal. Calcd for $C_{14}H_{24}O_2S$: C, 65.6; H, 9.4. Found: C, 65.7; H, 9.2.

(1*R*,2*S*,*R*$_S$)-*exo*-3-[(3′-Methylbut-2′-enyl)sulfinyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (43). A melt of the S_S sulfoxide **33** was heated at 90° for 20 min or until complete crystallization had taken place to give colorless needles (>95%), mp 199–200 °C of the product **43**, $[\alpha]_D$ +127° (c 1.0, dichloromethane): ^{1}H NMR δ 5.45 (1 H, ddm, J = 8.3, J = 7.5 Hz, H2′), 3.88 (1 H, dd, J = 13.3, J = 7.5 Hz, H1′), 3.40 (1 H, dd, J = 13.3, J = 8.3 Hz, H1′), 3.86 (1 H, $J_{2,3}$ = 7.8, $J_{2,OH}$ = 4.5 Hz, H2), 3.01 (1 H, d, $J_{3,2}$ = 7.8 Hz, H3), 2.65 (1 H, d, $J_{OH,2}$ = 4.5 Hz, OH), 2.32 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.83 (3 H, s, CH_3), 1.74 (3 H, s, CH_3), 1.89, 1.57, 1.08 (4 H, m, H5, H6), 1.37 (3 H, s, CH_3), 0.94 (3 H, s, CH_3), 0.87 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{26}O_2S$: C, 66.6; H, 9.7. Found: C, 66.6; H, 9.4.

(1*R*,2*S*,2′*E*,*R*$_S$)-*exo*-3-(Oct-2′-enylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (44). The S_S sulfoxide **34** was heated at 110 °C for 2 h. The colorless oil so obtained was shown by ^{1}H NMR spectroscopy to consist of the R_S and S_S diastereomers **44** and **34** in a ratio of 9:1. Separation of this mixture could not be achieved and hence the substance was analyzed as a mixture, which had $[\alpha]_D$ +60° (c 2.0, acetone): ^{1}H NMR [R_S epimer] δ 5.82 (1 H, m, H2′), 5.66 (1 H, m, H3′), 3.84 (1 H, m, H1′), 3.39 (1 H, dd, J = 12.8, J = 8.0 Hz, Hu′), 3.82 (1 H, dd, $J_{2,3}$ = 7.6, $J_{2,OH}$ = 5.2 Hz, H2), 3.02 (1 H, d, $J_{3,2}$ = 7.6 Hz, H3), 2.39 (1 H, d, $J_{4,5exo}$ = 4.4 Hz, H4), 2.31 (1 H, d, $J_{OH,2}$ = 5.2 Hz, OH), 2.13 (2 H, dt, J = 7.2, J = 6.4 Hz, H4′), 1.89, 1.57, 1.38, 1.26, 1.06 (10 H, m, H5, H6, H5′, H6′, H7′), 1.31 (3 H, s, CH_3), 0.94 (3 H, s, CH_3), 0.87 (3 H, s, CH_3), 0.89 (3 H, t, J = 6.5 Hz, H8′); HRMS calcd for $C_{18}H_{31}OS$ 295.2096, found 295.2092.

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Supplementary Material Available: Characterization data, including IR, UV, $[\alpha]_D$, and mass spectral data for compounds **2–4**, **8–18**, **20–28**, **31–39**, and **41–44**; crystallographic data for **31** (14 pages). Ordering information is given on any current masthead page.

Cross-Conjugated and Pseudo-Cross-Conjugated Mesomeric Betaines. 1. Synthesis and Characterization†

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Reaction of pyrazoles, 1,2,3-triazoles, and 1,2,4-triazoles with aryl(chlorocarbonyl)ketenes, alkylmalonyl dichlorides, or carbon suboxide results in a series of cross-conjugated mesomeric betaines, characterized by the presence of distinct cationic and anionic segments. 1-Substituted imidazoles, suitably substituted 1,2,4-triazoles, and pyridine with the above reagents give rise to pseudo-cross-conjugated mesomeric betaines which, in addition to charge separation, are characterized by the presence of the 2-oxyallyl cation 1,3-dipole. Alternative syntheses of cross-conjugated mesomeric betaines which allow the introduction of more diverse substituents are also described.

Introduction

In a recent review of the chemistry of heterocyclic, mesomeric betaines (MB), Ollis, Stanforth, and Ramsden contrast[2a] the characteristics of conjugated mesomeric betaines (CMB), cross-conjugated mesomeric betaines (CCMB), and pseudo-cross-conjugated mesomeric betaines (PCCMB) and detail the known and potential dipolar cycloaddition characteristics of each family of mesomeric betaine. Although representatives of CMB are well-known, e.g., mesoionic compounds, pyridinium ylides, etc., only a few scattered reports of heterocycles that may be classified as CCMB or PCCMB have appeared. In our con-

† Dedicated to Prof. E. C. Taylor on the occasion of his 65th birthday.

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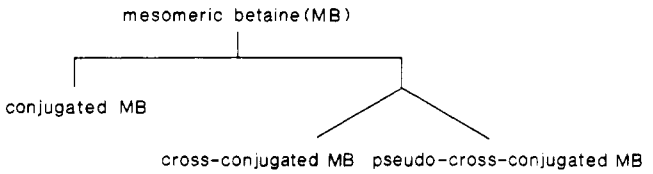
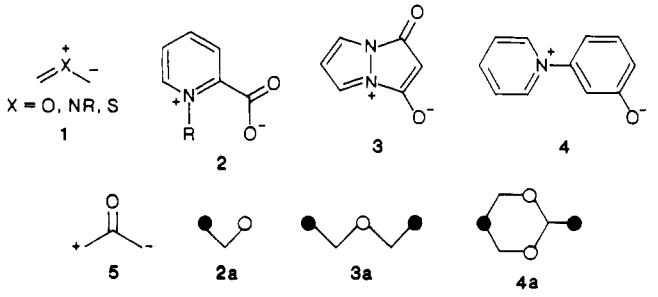
(2) (a) Ollis, W. D.; Stanforth, S. P.; Ramsden, C. *Tetrahedron* **1985**, *41*, 2239. (b) Ollis, W. D.; Ramsden, C. A. *Adv. Heterocycl. Chem.* **1976**, *19*, 1.

0022-3263/88/1953-2889$01.50/0

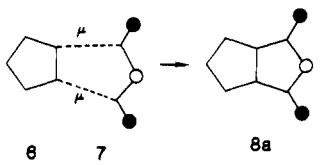
Scheme I



tinuing study of mesomeric betaines, we have developed general synthetic approaches to a number of CCMB and PCCMB, and our studies described in this paper provide experimental verification of some of the theoretical hypotheses advanced earlier.



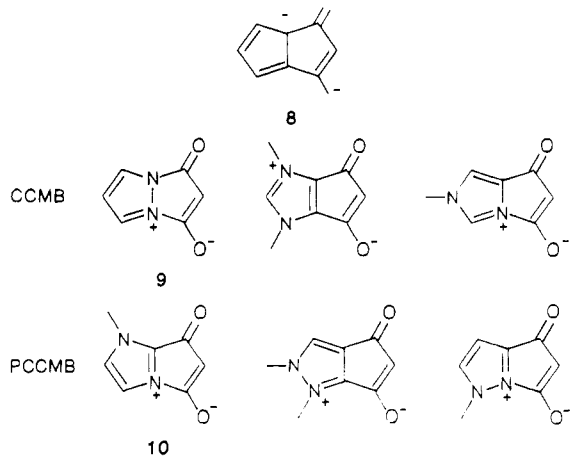
CMB, except for those with an element of symmetry, contain the masked 1,3-dipolar species **1**, and many undergo 1,3-dipolar cycloadditions[2b] to five-membered heterocycles. In sharp contrast, both CCMB and PCCMB contain isolated anionic and cationic segments, the anionic segment being isoconjugate with an odd alternant hydrocarbon anion. [The term isoconjugate, originally introduced by R. S. Mulliken, describes two molecules that have the same number of atoms and π-orbitals in the conjugated system (Platt, J. R. *J. Chem. Phys.* **1951**, *19*, 101).] Three such examples of the anionic segment are the carboxylate ion, illustrated by structure **2**, the β-dicarbonyl enolate in the betaine **3**, and the phenolate ion in structure **4**. "Union bonds" (designated as "u" in structures **6** and **7**) join the cationic fragment to the anionic fragment at atoms in the anionic fragment which are nodal positions (or the even-numbered atoms) in the HOMO of the corresponding odd, alternant hydrocarbon anion. These nodal positions are illustrated by structures **2a**, **3a**, and **4a**. While PCCMB contain the masked 2-oxyallyl cation 1,3-dipole **5**, an oxygen derivative of which is contained in structure **2**, CCMB do not contain a common dipolar species, and typical representations are structures **3** and **4**.



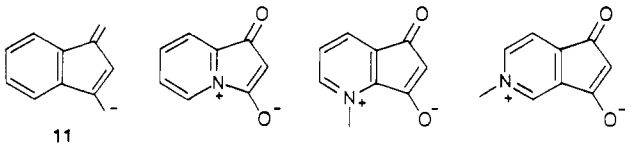
Slight modification of the original classification scheme suggested by Ollis and co-workers leads to a simplified classification of mesomeric betaines shown in Scheme I. A convenient, conceptual approach to determining structural types whose electron distribution is consistent with that proposed to be present in a CCMB and a PCCMB is to consider structures formed by union of cationic segments to anionic segments derived from odd, alternant hydrocarbon anions.[3] We have studied systems derived from union of **6** with the anion **7** leading to the 1,3-dimethylenepentalenyl dianion (**8**). The HOMO profile **8a**

(3) Potts, K. T.; Kuehnling, W. R. *J. Org. Chem.* **1984**, *49*, 3672.

Scheme II



Scheme III



and the corresponding zwitterion isoconjugate with the dianion of **8** are directly related to the HOMO profile of the anionic fragment of **7**. There are three CCMB and three PCCMB families which are derived from **8** by the introduction of two two-electron heteroatoms. These families are shown[4] in Scheme II. The synthesis and characterization of members of the family derived from structure **9**, and also from structure **10**, are described in detail below.

Other PCCMB may also be readily visualized by union of the anion **7** with, for example, benzene, which results in the 1,3-dimethyleneindenyl dianion (**11**). Similar HOMO profile relationships exist between **7** and **11** as between **7** and **8**. Three families of PCCMB, derived from **11** by the introduction of one two-electron heteroatom, are shown[5] in Scheme III. Substituting a one-electron heteroatom into the cationic or anionic portion of these families is not considered to generate a new family of CCMB or PCCMB. The insertion of two two-electron heteroatoms into **8** gives rise to CCMB and PCCMB and consequently defines the families of MB isoconjugate with **8**.

(a) Synthesis of CCMB

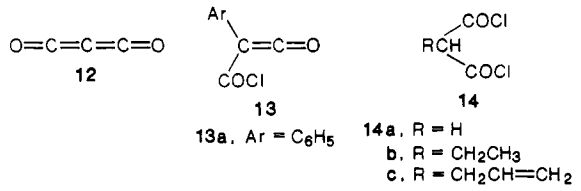
Several representative of CCMB and PCCMB have been described[6] in the literature as early as the 19th century, but their recognition as such has awaited the classification scheme proposed[2] by Ollis, Stanforth, and Ramsden. In our earlier studies of the use of heteroaromatic betaines in cycloaddition chemistry, we[7a] and others[7b] utilized these

(4) In this approach we consider systems differing by replacement of one or more carbon atoms by a one-electron nitrogen atom to be of the same type. Consequently, variation of the exocyclic oxygen atoms between S, Se, NR, and CR_2 in the six systems containing nitrogen shown in Scheme II results in 90 possible systems. When two-electron heteroatoms other than nitrogen, e.g., O, S, and Se, are included in the ring-fused skeleton, the total number of possible betaines is increased to 1035 systems. Practical syntheses of many of these present synthetic challenges of a high order.

(5) If the same atom substitutions as described in footnote 4 above were made, variation of the exocyclic substituents leads to 75 possible systems. Variation of the peripheral ring atoms in the above fashion increases the total number of possible systems to 225 systems. Only two have been synthesized to date.

(6) Hrnciar, P. *Chem. Zvesti* **1965**, *19*, 360.

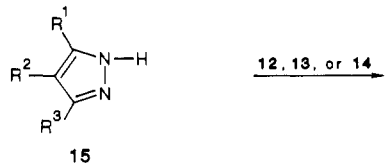
betaines as a source of 1,4-dipoles. These betaines are all CCMB, formally derived from the *m*-quinodimethane dianion.[8]



12 13 14

13a, Ar = C_6H_5

14a, R = H
b, R = CH_2CH_3
c, R = $CH_2CH{=}CH_2$



15

12, 13, or 14

	R^1	R^2	R^3
15a	H	H	H
b	CH_3	H	CH_3
c	$COOCH_3$	$COOCH_3$	H
d	$COOCH_3$	H	$COOCH_3$

16 18

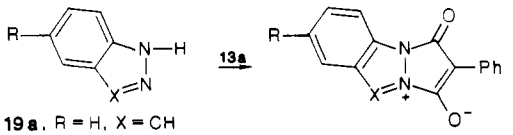
	R^1	R^2	R^3	R
16a	H	H	H	C_6H_5
b	H	H	H	H
c	CH_3	H	CH_3	H
d	CH_3	H	CH_3	$COCH_2COOCH_2CH_3$
e	CH_3	H	CH_3	CH_2CH_3
f	CH_3	H	CH_3	$CH_2CH{=}CH_2$
g	$COOCH_3$	$COOCH_3$	H	C_6H_5
h	$COOCH_3$	H	$COOCH_3$	C_6H_5
i	C_6H_5	H	C_6H_5	C_6H_5
j	C_6H_5	H	Cl	C_6H_5
k	C_6H_5	H	SCH_3	C_6H_5
l	CH_3	Cl	CH_3	C_6H_5

The CCMB and PCCMB already described in the literature have, as the most common anionic segment, that derived from a β-dicarbonyl enolate. These zwitterionic systems result when a 1,3-bielectrophile which is a synthetic equivalent of a malonic acid derivative is allowed to unite with a 1,2-binucleophile destined to be the cationic segment. These 1,3-bielectrophiles may be divided into three groups: carbon suboxide (**12**), aryl(chlorocarbonyl)ketenes (**13**), and substituted malonyl dichlorides (**14**).

A variety of monoprotonic, heterocyclic binucleophiles undergo ready reaction with the above reagents, leading to the CCMB related to **9** described in Scheme II. Reaction of pyrazole (**15a**) in THF with (chlorocarbonyl)phenylketene (**13a**) resulted in ready formation of violet prisms of anhydro-1-hydroxy-3-oxo-2-phenylpyrazolo[1,2-*a*]pyrazolium hydroxide (**16a**), which was also obtained, but in much reduced yield, by the acid-catalyzed condensation of malonaldehyde diethyl acetal with 4-phenyl-3,5-pyrazolidinedione (**17**).

Structure **16a** was established as follows: analytical and mass spectral data showed the molecular formula to be $C_{12}H_8N_2O_2$, thus excluding dicondensation of two molecules of the pyrazole with the bielectrophile, and in the mass spectrum, an ion, *m/z* 145 (39%), with a metastable ion at *m/z* 97.8, was consistent with the phenyl(carbonyl)ketene radical cation, formed by loss of the pyrazole radical from the molecular ion, i.e., cleavage of the betaine at the "union bonds". The valence tautomer **18** was eliminated from consideration as the structure of the product by the absence of a ketene absorption in the IR (ν_{CO} 1680, 1650 cm^{-1}), as well as by the symmetry of the molecule, which was reflected in its ^1H NMR spectrum [δ H_5,H_7 = 8.73 (d); δ H_6 = 6.93 (tr)] and ^{13}C NMR spectrum (δ C_5,C_7 = 129.4; δ C_6 = 112.0; δ C_1,C_3 = 157.7; δ C_2 = 80.0). The structure **16a** was confirmed[9] by single-crystal X-ray analysis. A variety of pyrazoles underwent ready reaction with (chlorocarbonyl)phenylketene (**13a**) under analogous conditions to give the substituted analogues of **16** described in Table I. All of these products are characterized by the spectral data described in Table I, by their intense colors, and by being stable in air. The majority were insoluble in water, and on the addition of a little acetone or alcohol, hydrolysis readily occurred with bleaching of the aqueous system.

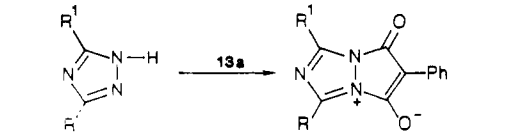
This approach to CCMB synthesis may be applied to a variety of heterocycles containing the =NNH functional group as part of their ring system. Thus, indazole (**19a**) gave **20a** (Table I), and the corresponding 5-nitroindazole (**19b**) gave **20b**. Similarly, 3,5-diphenyl-1*H*-1,2,4-triazole (**21a**) gave the 6-aza analogue **22a** of **16** as maroon needles, and 3-phenyl-1*H*-1,2,4-triazole (**21b**) gave **22b** as red needles (Table I). Benzotriazole (**19c**), upon treatment with **13a**, gave **20c** as blue-black needles (Table I).



19a, R = H, X = CH
b, R = NO_2, X = CH
c, R = H, X = N

13a

20a, R = H, X = CH
b, R = NO_2, X = CH
c, R = H, X = N



21a, R = R^1 = C_6H_5
b, R = H, R^1 = C_6H_5

13a

22a, R = R^1 = C_6H_5
b, R = H, R^1 = C_6H_5

Carbon suboxide (**12**) as the 1,3-bielectrophile and pyrazole (**15a**) (Et_2O, −78 °C) gave the parent ring system anhydro-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium hydroxide (**16b**), obtained as yellow prisms, mp 55–65 °C dec, which was very sensitive to minute traces of moisture. Mass spectral and spectroscopic data readily established the structure of **16b**, especially ν_{CO} 1745, 1695 cm^{-1}, δ H_2 = 4.22 (d), δ H_6 = 6.72 (sextet), and δ H_5,H_7 = 7.99 (d) together with δ C_1,C_3 = 144.9, δ C_2 = 41.4, δ C_5,C_7 = 128.6, and δ C_6 = 110.8; (M + 1), *m/z* 137 (15%). Introduction of methyl substituents into the 5- and 7-positions of **16** by

(7) (a) Potts, K. T.; Dery, M. O. *J. Chem. Soc., Chem. Commun.* **1986**, 563. Potts, K. T.; Ehlinger, R.; Nichols, W. M. *J. Org. Chem.* **1975**, *40*, 2596. Potts, K. T.; Sorm, M. *J. Org. Chem.* **1971**, *36*, 8. Potts, K. T.; Sorm, M. *J. Org. Chem.* **1972**, *37*, 1422. Potts, K. T.; Hsia, R. C. *J. Org. Chem.* **1973**, *38*, 3485. (b) Kappe, T.; Golser, W.; Hariri, M.; Stadlbauer, E. *Chem. Ber.* **1979**, *112*, 1585. Kappe, T.; Gosler, W. *Synthesis* **1972**, 312. Hagemann, H.; Ley, K. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 1012. Coburn, R. A.; Bhooshan, B. *J. Org. Chem.* **1973**, *38*, 3868. Stadlbauer, W.; Kappe, T. *Chem. Ber.* **1976**, *109*, 3661. Greco, C. V.; Gala, K. J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 331. Kappe, T.; Pocivalnik, D. *Heterocycles* **1983**, *20*, 1367. Friedrichsen, W.; Schmidt, R.; van Hummel, G. J.; van dem Ham, D. M. W. *Liebigs Ann. Chem.* **1981**, 521. Friedrichsen, W.; Kujath, E.; Liebezeit, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 222.

(8) Friedrichsen, W.; Kappe, T.; Bottcher, A. *Heterocycles* **1982**, *19*, 1083.

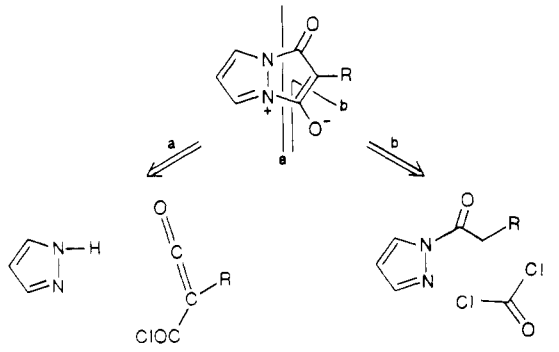
(9) Raston, C. L.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 2577.

Table I. CCMB Containing Pyrazoles and 1,2,3- and 1,2,4-Triazoles

							spectral data			
no.	method	yield %	mp, °C	crystal habit, solvent	molecular formula	$M^{\cdot+}$ [a] (rel int)	ν_{CO} (KBr), cm^{-1}	λ_{max} (solvent)	^1H NMR, [b] δ	^{13}C NMR, [b] ppm
16a	A; THF, 25 °C	77	247–248	violet prisms, MeOH	$C_{12}H_8N_2O_2$	212 (100)	1680, 1650	434 (CH_3CN)	8.73 (d, 2, C_5/C_7-H), 6.93 (t, 1, C_6-H), 8.2–8.0 (m, 2, aromatic), 7.5–7.1 (m, 3 aromatic)	157.7, 132.2, 129.4, 127.9, 123.8, 123.3, 112.0, 80.0
16b	A; ether, −78 °C	58	55–65 dec	yellow needles, cold THF/hexane	$C_6H_4N_2O_2$	137 (15) CI	1745, 1695	378 (CH_2Cl_2)	7.99 (d, 2, J = 2.41, C_5/C_7-H), 6.72 (s, 1, J = 2.41, 1.03, C_6-H), 4.22 (d, 1, J = 1.03, C_2-H)	144.9, 128.6, 110.8, 41.4
16c	A; ether, −78 °C	66	96–110 dec	yellow needles, cold THF/hexane	$C_8H_8N_2O_2$	164 (45)	1755, 1700	369 (CH_2Cl_2)	6.16 (s, 1, C_6-H), 4.16 (s, 1, C_2-H), 2.63 (s, 6, 2 CH_3)	161.4, 142.7, 111.4, 68.9, 11.0
16d	B; CH_3CN	70	194–197 dec	yellow needles, EtOAc	$C_{13}H_{14}N_2O_5$	278 (19)	1735, 1705	349 (CH_3CN)	6.33 (s, 1, C_6-H), 4.19 (q, 2, J = 7.0, CH_2CH_3), 3.80 (s, 2, CH_2), 2.71 (s, 6, 2 CH_3), 1.26 (t, 3, J = 7.0, CH_2CH_3)	
16e	B; EtOAc	75	171–173	yellow prisms, EtOH	$C_{10}H_{12}N_2O_2$	192 (67)	1700, 1675	397 (CH_3CN)	6.09 (s, 1, C_6-H), 2.61 (s, 6, 2 CH_3), 2.21 (q, 2, J = 7.4, CH_2CH_3), 1.14 (t, 3, J = 7.4, CH_2CH_3)	
16f	B; EtOAc	95	167–169 dec	orange prisms, CH_2Cl_2/ether	$C_{11}H_{12}N_2O_2$	204 (37)	1755, 1660	398 (THF)	6.11 (s, 1, C_6-H), 5.8–6.0 (m, 1, alkene), 4.9–5.2 (m, 2, alkene), 2.93 (d, 2, CH_2), 2.61 (s, 6, 2 CH_3)	
16g	A; THF, 25 °C	47	210–212	red needles, cold THF	$C_{16}H_{12}N_2O_6$	328 (100)	1735, 1700	448 (THF)	9.55 (s, 1, C_7-H), 7.9–7.1 (m, 5, aromatic), 4.05 (s, 3, OCH_3), 3.88 (s, 3, OCH_3)	169.4, 159.0, 132.9, 132.8, 130.6, 129.9, 128.2, 128.1, 124.5, 123.6, 116.7, 79.6, 52.9, 52.2
16h	A; THF, 0 °C	*c*	*c*	red prisms, cold THF	$C_{16}H_{12}N_2O_6$	328 (31)	1735, 1700	482 (THF)	*c*	*c*
16i	A; THF, 25 °C	79	226–228	violet spears, $CHCl_3$	$C_{24}H_{16}N_2O_2$	364 (100)	1679		8.13–7.86 (m, 6, aromatic), 7.62–7.3 (m, 9, aromatic), 6.75 (s, 1, C_6-H)	147.3, 110.5 [d]
16j	A; THF, 25 °C	89	181	red prisms, acetone	$C_{18}H_{11}ClN_2O_2$	322 (100)	1700		8.27–6.98 (m, aromatic)	
16k	A; THF, 25 °C	80	198 dec	orange leaves, $CHCl_3$	$C_{19}H_{14}N_2O_2S$	334 (100)	1689, 1663		8.01 (m, 4, aromatic), 7.38 (m, 6, aromatic), 6.41 (s, 1, C_6-H), 2.62 (s, 3, SCH_3)	158.9, 106.7 [d]
16l	*e*	43	232–233	scarlet prisms, EtOAc	$C_{14}H_{11}ClN_2O_2$	274 (84)	1680	427 (CH_3CN)	8.20–7.95 (m, 2, aromatic), 7.57–7.10 (m, 3, aromatic), 2.62 (s, 6, CH_3)	159.0, 139.9, 131.6, 128.1, 124.5, 124.2, 114.8, 80.5, 9.2
20a	A; THF, 25 °C	67	224–225	purple prisms, THF	$C_{16}H_{10}N_2O_2$	262 (100)	1730, 1655	505 (CH_2Cl_2)	8.2–7.9 (m, aromatic)	
20b	A; THF, 25 °C	68	265–266 dec	reddish brown prisms, acetone	$C_{16}H_9N_3O_4$	307 (64)	1650	*f*	*f*	*f*
20c	A; ether, 25 °C	64	123 dec	blue-black needles, cold THF/ether	$C_{15}H_9N_3O_2$	263 (50)	1745, 1710	*c*	*c*	*c*
22a	A; THF, 25 °C	85	220–223 dec	maroon prisms, THF	$C_{23}H_{15}N_3O_2$	365 (100)	1710, 1660	477 (CH_2Cl_2)	8.3–7.9 (m, aromatic)	
22b	A; ether, 25 °C	35	110–112 dec	red needles, THF/ether	$C_{17}H_{11}N_3O_2$	289 (40)	1710, 1665	*c*	*c*	*c*

[a] EI mass spectra unless otherwise noted; CI is chemical ionization with methane as the ionizing gas. [b] $CDCl_3$ unless otherwise noted. [c] CCMB is too sensitive to moisture for accurate determination of spectra and other physical constants. [d] C_1, C_2, and C_3 atoms only. [e] Prepared from 3-chloro-2,4-pentanedione and 3,5-dihydroxy-4-phenylpyrazole. [f] Insoluble in $CHCl_3$, DMSO-d_6.

Scheme IV



reaction of 3,5-dimethylpyrazole (**15b**) and carbon suboxide (**12**) under analogous conditions resulted in **16c**, yellow irregular prisms, mp 96–100 °C dec. Accurate mass data (calcd for $C_8H_8N_2O_2$ m/z 164.0586, found 164.0585) and compatible spectral data (Table I) were consistent with this structure. In both the above reactions, small amounts of products corresponding to the addition of 2 equiv of the pyrazole to carbon suboxide were isolated. These products are described in the Experimental Section.

These two compounds represent the first pyrazolium CCMB having hydrogen in the 2-position. Attempts to prepare the same compounds by using malonyl dichloride (**14a**) and triethylamine were unsuccessful, the 2-position apparently undergoing ready electrophilic attack by a second equivalent of malonyl dichloride. Reaction workup involving ethanol resulted in **16d** (R = $COCH_2COOEt$) (Table I). However, substituted malonyl dichlorides (**14**; R = Et, $CH_2CH{=}CH_2$) and 3,5-dimethylpyrazole (**15b**) in the presence of Et_3N resulted in the correspondingly substituted derivatives **16e** and **16f**. The interesting spectral characteristics of the parent member of this group of CCMB and its dimethyl-substituted derivative are discussed in detail in the following paper.

Although the above approach enables one to vary the cationic segment in CCMB over a range of heterocyclic cations, its principle limitation is lack of variation in the exocyclic atoms and the 2-substituent of the anionic segment. The same limitation also exists in the alternative approach involving the condensation[10] of **17** with β-diketones similar to malonaldehyde diethyl acetal. To remedy these limitations we have developed an alternative procedure shown in Scheme IV. The approach used above is represented by pathway a. Disconnection along pathway b suggests use of the 1-(substituted acetyl)pyrazole and reactive one-carbon fragments such as phosgene, thiophosgene, etc. Our application of this latter route greatly increasing the substitution pattern in CCMB is described below. 1-(Substituted acetyl)pyrazole derivatives **23** are readily prepared[11] from 1,3-dicarbonyl compounds and substituted acetylhydrazides in the presence of acid, or by acylation of pyrazoles with acyl chlorides.[12] The former procedure was found to be more satisfactory for our purposes, leading to **23a–c**. Treatment of **23b** with NaH/benzene, followed by the addition of a cold benzene solution of phosgene (**25a**), gave **24a** in 36% yield, identical with the product obtained from 3,5-dimethylpyrazole (**15a**)

Table II. CCMB Derivatives from Acylpyrazoles and $Cl_2C{=}X$

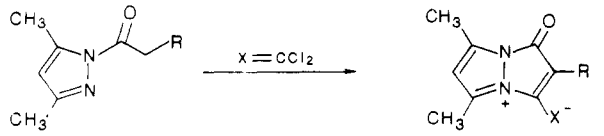
						spectral data			
no.	reagent[a] $Cl_2C{=}X$	yield %	mp, °C	crystal habit, solvent	molecular formula	$M^{+\cdot}$[b] (rel int)	ν_{CO} (KBr), cm^{-1}	λ_{max}[c]	^1H NMR,[d] δ	^{13}C NMR,[d] ppm
24a	$COCl_2$	36	217–218	orange prisms, CH_3CN	$C_{14}H_{12}N_2O_2$	240 (100)	1750, 1680	421	8.2–8.0 (m, 2, aromatic), 7.5–7.0 (m, 3, aromatic), 6.06 (s, 1, C_6H), 2.61 (s, 6, 2 CH_3)	159.2, 143.2, 132.3, 128.0, 124.2, 124.1, 111.7, 82.0, 11.0
24b	$CSCl_2$	23	155–157	purple plates, CCl_4	$C_{14}H_{12}N_2OS$	256 (100)	1720	489	8.4–8.0 (m, 2, aromatic), 7.6–7.0 (m, 3, aromatic), 6.18 (s, 1, C_6H), 2.89 (s, 3, CH_3), 2.65 (s, 3, CH_3)	174.7, 159.6, 145.2, 140.7, 131.1, 127.9, 127.6, 126.3, 112.6, 108.6, 14.4, 10.8
24c	$TOSN{=}CCl_2$	31	196–200 dec	orange-red prisms, CH_3CN	$C_{21}H_{19}N_3O_3S$	393 (54)	1725	428	7.6–7.1 (m, 9, aromatic), 6.20 (s, 1, C_6H), 2.63 (s, 3, CH_3), 2.51 (s, 3, CH_3), 2.36 (s, 3, CH_3)	159.1, 152.9, 146.0, 144.0, 141.7, 141.2, 131.3, 129.2 128.9, 127.9, 127.5, 126.0, 112.5, 91.5, 21.4, 12.9, 11.0
24d	$Cl_2C{=}C(CN)_2$	38	152–155 dec	purple needles, CCl_4	$C_{17}H_{21}N_4O$	288 (100)	1730	497	7.5–7.3 (m, 5, aromatic), 6.47 (s, 1, C_6H), 2.78 (s, 6, 2 CH_3)	155.8, 153.2, 150.9, 148.8, 130.5, 128.5, 128.2, 127.5, 116.5, 115.3, 102.0, 40.9, 16.6, 11.5
24e	$COCl_2$	10	222–223	yellow prisms, CH_3CN	$C_9H_7N_3O_2$	189 (100)	1785, 1760	360	6.36 (s, 1, C_6H), 2.70 (s, 6, 2 CH_3)	157.5, 145.5, 118.0, 113.4, 112.6, 11.5
24f	$CSCl_2$	10	241–242	orange needles, EtOAc	$C_9H_7N_3OS$	205 (50)	1730	428	6.43 (s, 1, C_6H), 2.87 (s, 3, CH_3), 2.72 (s, 3, CH_3)	179.5, 157.3, 147.3, 144.5, 115.0, 113.8, 85.8, 13.5, 10.6

[a] All prepared by using method D (Experimental Section). [b] EI mass spectra. [c] All measured in CH_3CN as solvent. [d] $CDCl_3$ as solvent.

(10) For example, see: Zvilichovsky, G.; David, M. *J. Org. Chem.* **1982**, *47*, 295.

(11) Gilman, H.; Spatz, S. M. *J. Org. Chem.* **1951**, *16*, 1485. See also: Reid, W.; Meyers, A. *Chem. Ber.* **1957**, *90*, 2841. Reid, W.; Konigstein, F.-J. *Justus Liebigs Ann. Chem.* **1959**, *622*, 37.

(12) See, e.g.: Seidel, F.; Thier, W.; Uber, A.; Dittmer, J. *Ber. Dtsch. Chem. Ges.* **1935**, *68*, 1913. Staab, H. A. *Justus Liebigs Ann. Chem.* **1959**, *622*, 31. Reid, W.; Konigstein, F.-J. *Justus Liebigs Ann. Chem.* **1959**, *622*, 37.



23a, R = H
b, R = C_6H_5
c, R = CN

25a, X = O
b, X = S
c, X = N-tosyl
d, X = $C(CN)_2$

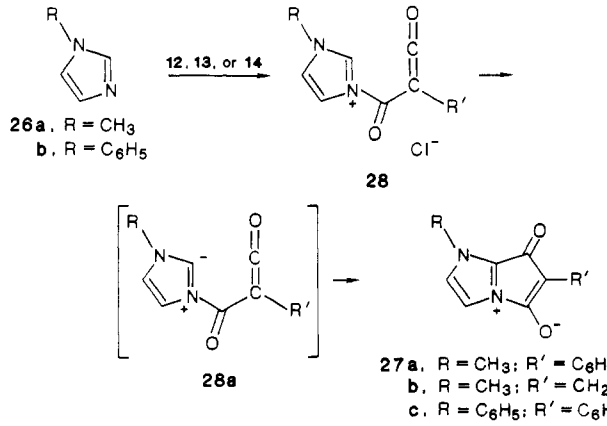
24a, R = C_6H_5, X = O
b, R = C_6H_5, X = S
c, R = C_6H_5, X = N-tosyl
d, R = C_6H_5, X = $C(CN)_2$
e, R = CN, X = O
f, R = CN, X = S

and (chlorocarbonyl)phenylketene (**13a**). Replacement of the phosgene with thiophosgene (**25b**) gave **24b** as lustrous purple plates, mp 155–157 °C, whose spectral characteristics are described in Table II. Similar reactions carried out on **23a** were unsuccessful, leading to decomposition of the product under these reaction conditions.

Variation of the one-carbon electrophile enabled us to introduce other exocyclic groups at C_3. Thus reaction of **23b** with *N*-(dichloromethylidene)-4-methylbenzenesulfonamide[13] (**25c**) as above gave **24c**, described in Table II. Similarly, **23b** and **25d** gave **24d** (Table II). Variation of the substituted acetyl group in **23** provided a means of varying the 2-substituent in **24**. Thus, **23c** and phosgene (**25a**) gave **24e**, and with thiophosgene (**25b**), the corresponding sulfur analogue **24f** was obtained (Table II).

(b) Synthesis of PCCMB

The synthesis of PCCMB requires the generation of reactive intermediates capable of forming both a C–C and a C–N "union bond" from a CH=N group and a 1,3-bielectrophile. 1-Methylimidazole (**26a**) and (chlorocarbonyl)phenylketene (**13a**) in THF at room temperature in the presence of Et_3N gave, in an extremely facile reaction, anhydro-1-hydroxy-7-methyl-3-oxo-2-phenylpyrrolo[1,2-*a*]imidazolium hydroxide (**27a**) as red spears, mp 188–189 °C dec; ν_{CO} 1730, 1625 cm^{-1}; $M^{\bullet+}$ 226 (100%). In addition to the spectroscopic data (Table III) in support of structure **27a**, additional evidence was obtained when 1,2-dimethylimidazole and (chlorocarbonyl)phenylketene (**13a**) were reacted as above, unchanged starting material being obtained in this instance.



26a, R = CH_3
b, R = C_6H_5

28

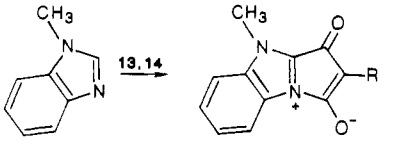
28a

27a, R = CH_3; R′ = C_6H_5
b, R = CH_3; R′ = CH_2CH_3
c, R = C_6H_5; R′ = C_6H_5

The reaction to form **27a** occurred via the initial formation of a quaternary N_3-acylated imidazole **28** which could be isolated as a cream solid on mixing the reactants; when Et_3N/THF was added to this insoluble salt, a deep-red colored solution developed and Et_3N·HCl separated. The ready removal of the C_2-H in the imidazole nucleus to give the transient ylide **28a** is due to the quaternization of N_3. Similar ylidic intermediates have been postulated[14] to account for the ready deuterium exchange of the imidazole C_2 hydrogen atom. Similarly, reaction of **26a** with ethylmalonyl dichloride (**14b**)/Et_3N/THF readily gave **27b**, which was also obtained as red needles, mp 82–86 °C (Table III). Replacement of the *N*-methyl group in **26** with a phenyl group had no effect on the overall reaction, **26b** being readily converted into **27c**.

In contrast to pyrazole above, the imidazole **26a** and carbon suboxide (**12**) (Et_2O, −78 °C) failed to yield an isolable product. Although a yellow color characteristic of a CCMB without a 2-phenyl substituent developed in the reaction medium, no clearly identifiable product was finally isolated. However, the mass spectrum of the isolated material showed an ion, *m/z* 150 (12%), consistent with the molecular weight of the desired product, but the ^1H NMR data were not sufficiently definitive to exclude 1:2 adducts from consideration.

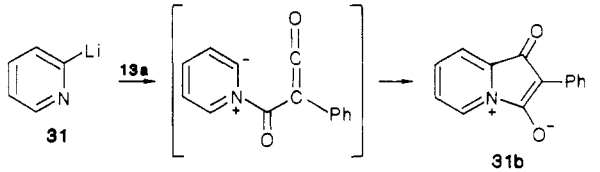
As anticipated, 1-methylbenzimidazole (**29**) and (chlorocarbonyl)phenylketene (**13a**) readily underwent reaction in the presence of Et_3N/THF, giving **30a** in greater than 98% yield. Data consistent with this structure are reported in Table III. Substituted malonyl dichlorides **14b** and **14c** also underwent reaction with **29**, giving **30b** and **30c**, respectively (Table III).



29

30a, R = C_6H_5
b, R = CH_2CH_3
c, R = $CH_2CH{=}CH_2$

The reaction conditions required to generate PCCMB containing two five-membered rings are in direct contrast to those necessary to form analogous PCCMB containing a six-membered ring. Direct reaction of pyridine with the 1,3-bielectrophiles **12**, **13**, or **14**, with or without Et_3N present, was unsuccessful, starting material being recovered. For a successful PCCMB synthesis derived from **11**, it was necessary to remove the C_2 pyridinyl proton by generating 2-pyridyllithium (**31**) formed[15] in the usual way from 2-bromopyridine and *n*-BuLi. Although it was not possible to obtain direct experimental evidence, it is likely that the ylidic intermediate **31a** is formed from **31** and



31

31a

31b

(chlorocarbonyl)phenylketene (**13a**), with subsequent ring closure occurring to anhydro-1-hydroxy-3-oxo-2-phenylpyrrolo[1,2-*a*]pyridinium hydroxide (**31b**), purple plates, mp 264–268 °C (Table III). In addition to the spectroscopic data, definitive structural proof for **31b** was obtained by a single-crystal X-ray analysis described in the following paper. As one would anticipate from the well-established reactivity of 2-pyridyllithium (**31**), use of carbon suboxide (**12**) or the malonyl dichlorides **14** led to intractable reaction mixtures.

(13) Neideln, R.; Hausmann, W.; Heukelbach, E. *Chem. Ber.* **1966**, *99*, 1253.

(14) Elvidge, J. A.; Jones, J. R.; O'Brien, C.; Evans, E. A.; Sheppard, H. C. *Adv. Heterocycl. Chem.* **1974**, *16*, 5.

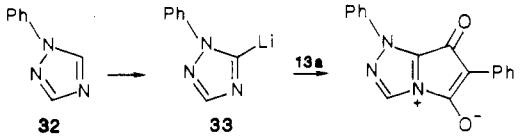
(15) Gilman, H.; Spatz, S. M. *J. Org. Chem.* **1951**, *16*, 1485.

Table III. PCCMB Derived from 1-Methylimidazole, 1,2,4-Triazoles, and Pyridine

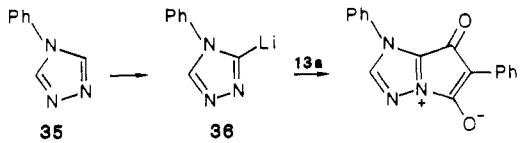
							spectral data			
no.	method	yield, %	mp, °C	crystal habit, solvent	molecular formula	$M^{+\cdot}$ [a] (rel int)	ν_{CO} (KBr), cm^{-1}	λ_{max} (solvent)	^1H NMR,[b] δ	^{13}C NMR,[b] ppm
27a	B; THF	31	188–190 dec	red prisms, EtOAc	$C_{13}H_{10}N_2O_2$	226 (100)	1730, 1625	469 (CH_3CN)	7.4–7.0 (m, 5, aromatic), 7.22 (d, 1, J = 1.8, C_5-H), 6.88 (d, 1, J = 1.8, C_6-H), 3.99 (s, 3, CH_3)	169.0, 161.6, 143.9, 133.5, 128.0, 124.6, 124.4, 124.1, 113.3, 94.6, 34.5
27b	B; EtOAc	59	82–86	red prisms, CCl_4	$C_9H_{10}N_2O_2$	178 (23)	1740, 1630	423 (CH_2Cl_2)	7.19 (br s, 1, C_5-H), 6.93 (br s, 1, C_6-H), 4.01 (s, 3, CH_3), 2.25 (q, 2, CH_2CH_3), 1.10 (t, 3, CH_2CH_3)	170.3, 163.2, 144.7, 127.9, 125.0, 96.2, 33.6, 14.8, 13.9
27c	B; THF	52	265–267	blue-black needles, CH_2Cl_2/ether	$C_{18}H_{12}N_2O_2$	288 (100)	1710, 1625	507 ($CHCl_3$)	8.1–7.1 (m, aromatic)	
30a	B; THF	98	225–227	purple prisms, CH_2Cl_2/ether	$C_{17}H_{12}N_2O_2$	276 (100)	1710, 1625	530 (CH_2Cl_2)	8.2–6.9 (m, 10, aromatic), 4.17 (s, 3, CH_3)	
30b	B; THF	68	204–206	red needles, CH_2Cl_2/ $ClCH_2CH_2Cl$	$C_{13}H_{12}N_2O_2$	228 (24)	1750, 1623	474 (CH_2Cl_2)	8.1–7.5 (m, 4, aromatic), 4.23 (s, 3, CH_3), 2.30 (q, 2, CH_2CH_3), 1.13 (t, 3, CH_2CH_3)	168.4, 165.0, 150.2, 136.1, 128.5, 126.6, 125.3, 114.2, 112.5, 100.2, 31.3, 14.9, 13.7
30c	B; THF	18	202–203	red plates, CH_2Cl_2/ether	$C_{14}H_{12}N_2O_2$	240 (2)	1755, 1625	457 (THF)	8.0–7.4 (m, 4, aromatic), 5.8–6.0 (m, 1 alkene), 5.2–4.9 (m, 2, alkene), 4.23 (s, 3, CH_3), 3.03 (dt, 2, CH_2)	
31b	C	9	264–268 dec	purple plates, CH_3CN	$C_{14}H_9NO_2$	223 (100)	1760, 1735	513 (CH_3CN)	7.19 (tt, 1, para phenyl), 7.40 (dd, 2, meta phenyl), 7.83 (dt, 1, C_6-H), 7.90 (dd, 1, C_8-H), 8.28 (dd, 2, ortho phenyl), 8.42 (dt, 1, C_7-H), 8.71 (dd, 1, C_5-H)	178.2, 164.2, 149.8, 141.3, 133.0, 132.5, 128.1, 127.8, 124.0, 116.8, 89.2 (DMSO-d_6)
34	C	77	121–123 dec	red needles, cold ether	$C_{17}H_{11}N_3O_2$	289 (15)	1740, 1600	487 (CH_2Cl_2)	8.39 (s, 1, C_5-H), 7.6–7.1 (m, 10, aromatic)	
37	C	63	67 dec	purple needles, cold THF/ether	$C_{17}H_{11}N_3O_2$	289 (5)	1700, 1615	530 (CH_2Cl_2)	[c]	[c]

[a] EI mass spectra. [b] $CDCl_3$ unless otherwise noted. [c] PCCMB too sensitive to moisture to accurately measure.

Although incorporation of additional nitrogen atoms into the imidazole ring increases the acidity of the ring system and enhances ease of removal of a carbon proton, the resultant triazole anion is a weak nucleophile with reduced basicity. Thus, both 1-substituted and 4-substituted 1,2,4-triazole derivatives had to be converted into their corresponding lithio derivatives for reaction with (chlorocarbonyl)phenylketene (**13a**) to yield the corresponding PCCMB. 1-Phenyl-1*H*-1,2,4-triazole (**32**) and *n*-BuLi have been reported[16] to give the 5-lithio-1-phenyl-1*H*-1,2,4-triazole (**33**). Addition of (chlorocarbonyl)phenylketene (**13a**) to an Et_2O solution of **33** at −78 °C resulted in the instant formation of a dark-red precipitate of anhydro-2,7-diphenyl-1-hydroxy-3-oxopyrrolo[1,2-*d*]-1,2,4-triazolium hydroxide (**34**), finally obtained as red needles, mp 121–123 °C dec (Table III). Similarly, 4-phenyl-4*H*-1,2,4-triazole (**35**), via the 3-lithio derivative **36**, and (chlorocarbonyl)-phenylketene (**13a**) gave anhydro-2,7-diphenyl-1-hydroxy-3-oxopyrrolo[1,2-*b*]-1,2,4-triazolium hydroxide (**37**), purple needles, mp 67 °C dec (Table III). In comparison with the PCCMB **27a**, the addition of an extra nitrogen atom to the cationic fragment as in **34** and **37** resulted in appreciable destabilization of the ring systems, reflected in the relative ease of decomposition of these betaines.

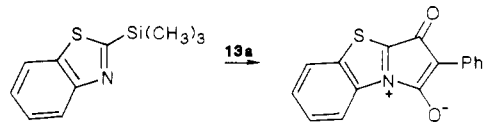


32 **33** **34**



35 **36** **37**

Incorporation of sulfur into the cationic portion of CCMB and PCCMB would result in systems of special interest. Our synthetic efforts which resulted in sulfur-containing PCCMB are described below. Thiazole or benzothiazole did not undergo reaction with (chlorocarbonyl)phenylketene (**13a**) alone, or in the presence of Et_3N. Conversion into their 2-lithio derivatives[17] and subsequent reaction with **13a** did not yield identifiable products, decomposition being the predominant pathway. However, 2-(trimethylsilyl)benzothiazole[18] (**38**) and **13a** in

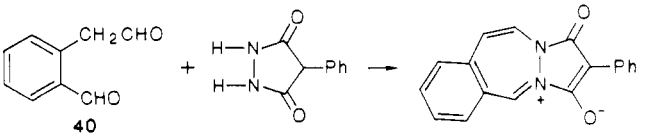


38 **39**

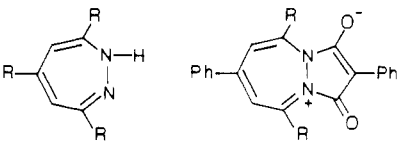
the absence of solvent resulted in a dark-red, amorphous product whose mass spectrum showed *m/z* 279 (9%) corresponding to the $M^{\bullet+}$ of **39** and with a fragmentation pattern consistent with structure **39**. This product was sensitive to minute traces of moisture, and even with rigorously dried solvents, decomposition occurred on dissolution in NMR solvents. The corresponding 2-(trimethylsilyl)thiazole also underwent reaction with **13a** generating the characteristic deep-red solution color of the PCCMB. Attempts to isolate a solid product from this solution were unsuccessful.

(c) Syntheses of CCMB Containing Seven-Membered Rings

The synthetic efforts described above always resulted in CCMB and PCCMB whose cationic segments contained $(4n + 2)$ π-electrons and which were all aromatic. It was of interest to prepare a cationic segment containing $(4n)$ π-electrons, i.e., an antiaromatic system, to evaluate its overall influence on the stability of the betaine. We believe that the stability of the cationic segment is a limiting factor in the overall stability of the betaine and, consequently, a betaine containing a $(4n)$ π cationic segment should be less stable than one containing a $(4n + 2)$ π cationic segment.



40 **17** **41**



42 **43**

Reaction of homophthalaldehyde[19] (**40**) with the pyrazolidinedione **17** in anhydrous THF/$MgSO_4$ resulted in the rapid development of a deep-purple colored solution from which a high-melting, purple product was isolated. Its high-resolution mass spectrum showed *m/z* 288.0907 (calcd for $C_{18}H_{12}N_2O_2$: 288.0899) and a fragmentation pattern consistent with betaine **41** formation. Attempts at solution characterization were unsuccessful due to rapid decomposition of **41**. The betaine derived from glutacondialdehyde and **17** was also obtained as an unstable, deep-purple product, which immediately decomposed in solution. Attempts to form an isolable betaine from the diazepine **42** (R = Ph, 4-$CH_3OC_6H_4$) with (chlorocarbonyl)phenylketene (**13a**) were also unsuccessful, although a deep-purple product was obtained in this instance. A molecular ion, consistent with **43**, was not obtained, and immediate decomposition of the product occurred in solution.

Experimental Section[20]

General Considerations. Four different sets of reaction conditions were employed in the synthesis of CCMB and PCCMB. Most heterocyclic precursor–1,3-bielectrophile combinations gave satisfactory results with one or more of these methods. **Method A** involved combining the heterocycle and the 1,3-bielectrophile in an anhydrous solvent and is effective with **12** and **13**, the 1 equiv of HCl evolved during the reaction remaining in solution. In **Method B**, the 1,3-bielectrophile was added to the heterocycle in the presence of Et_3N. The base facilitated the removal of HCl,

(16) Micetich, R. G.; Hall, T. W.; Spevak, P.; Bains, B. K. *Heterocycles* **1985**, *23*, 1645.
(17) Pinkerton, F. H.; Thames, S. F. *J. Heterocycl. Chem.* **1971**, *8*, 257.
(18) Dondoni, A.; Fogagnalo, M.; Fantin, G. *J. Chem. Soc., Chem. Commun.* **1981**, 655.
(19) Potts, K. T.; Robinson, R. *J. Chem. Soc.* **1955**, 2675.
(20) Melting points were obtained with a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 298 spectrometer. NMR spectra were recorded on either Perkin-Elmer R600, Varian XL-200, or Bruker 100 spectrometers. Chemical shifts (^1H or ^{13}C) are reported in parts per million (ppm) downfield from $(CH_3)_4Si$. Mass spectra were recorded on a Hewlett-Packard GC–MS system Model 5987-A spectrometer by electron impact or chemical ionization with CH_4 as the ionizing gas. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. All commercial reagents were ACS reagent grade and used without further purification. Anhydrous solvents (benzene, THF, ether) were dried by continuous reflux over sodium benzophenone ketal in a nitrogen atmosphere.

though yields can be lower due to byproduct formation from the addition of two heterocyclic systems to one bielectrophile, affording a substituted malonic acid derivative. **Method C** involved quenching the α-lithio derivative of the heterocycle with the bielectrophile at −78 °C. Weaker bases either failed to exchange the α-proton completely or required a more reactive nucleophile to ensure PCCMB formation. **Method D** involved treatment of **23** with **25** to afford **24**. A variety of exocyclic substituents have been introduced into **24** with this procedure. The following syntheses illustrate the general procedures used.

Method A: Anhydro-5,7-dimethyl-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium Hydroxide (16c). A solution of carbon suboxide[21] (1.0 g, 14.7 mmol) in diethyl ether (100 mL) and THF (30 mL) was treated with a solution of 3,5-dimethylpyrazole (**15b**) (1.40 g, 14.6 mmol) in THF (75 mL) at −78 °C under nitrogen over 10 min. After the reaction mixture was stirred for 15 min, anhydrous hexane (200 mL) was added over 15 min. The resultant mixture was filtered under nitrogen to afford the product as an amorphous yellow solid: yield 1.57 g (66%); mp 96–110 °C dec (Table I); mass spectrum, *m/z* (relative intensity) $M^{\cdot+}$ 164 (45), 165 (5), 136 (12), 96 (41), 95 (100), 81 (11), 69 (24); high-resolution mass spectrum calcd for $C_8H_8N_2O_2$ *m/z* 164.0586, found 164.0585 ($\Delta m/z$ = 1 ppm).

Method B: Anhydro-1-hydroxy-7-methyl-3-oxo-2-phenylpyrrolo[1,2-*a*]imidazolium Hydroxide (27a). 1-Methylimidazole (**26a**) (0.82 g, 10 mmol) was added dropwise to a stirred solution of (chlorocarbonyl)phenylketene[22] (**13a**) (1.81 g, 10 mmol) in freshly distilled THF (50 mL). A yellow precipitate formed instantly. Upon addition of Et_3N (1.1 g, 10 mmol), the mixture turned deep-red with some evolution of heat. After the mixture was stirred for 72 h, the Et_3N·HCl was removed and the filtrate evaporated under reduced pressure. The resulting red paste was purified by flash column chromatography (5:1 CH_2Cl_2/acetone) and the product finally obtained as small red prisms from EtOAc: 0.7 g (31%); mp 188–190 °C dec (Table III); mass spectrum, *m/z* (relative intensity) $M^{\cdot+}$ 226 (100), 227 (15) (M + 1), 225 (32), 170 (14), 169 (18), 155 (10), 109 (43), 89 (10).

Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.12; H, 4.52; N, 12.32.

Method C: Anhydro-1-hydroxy-3-oxo-2-phenylpyrrolo-[1,2-*a*]pyridinium Hydroxide (31b). A stirred solution of *n*-BuLi (1.5 M solution in hexane; 6.7 mL, 11 mmol) in absolute Et_2O (40 mL) was cooled to −40 °C in a dry ice/acetone bath. Upon rapid addition of 2-bromopyridine (1.58 g, 10 mmol) in absolute Et_2O (5 mL), a deep-red color formed and some precipitate appeared. The cooling bath was removed, and the mixture was stirred for 10 min, during which time the temperature reached −30 °C. Upon rapid addition of (chlorocarbonyl)phenylketene (1.81 g, 10 mmol) in absolute Et_2O (5 mL), a brown precipitate formed. The mixture was stirred at room temperature for 14.5 h, and then partitioned between $CHCl_3$ (150 mL) and H_2O (150 mL). The organic layer was separated, dried over Na_2SO_4, and filtered and the filtrate evaporated under reduced pressure. The residual brown oil was separated by HPLC (10:1 $CHCl_3$/acetone) and the product **31** finally obtained as purple plates by recrystallization from CH_3CN: 0.20 g (9%); mp 264–268 °C dec (Table III); mass spectrum *m/z* (relative intensity) $M^{\cdot+}$ 223 (100), 224 (16) (M + 1), 167 (21), 156 (32), 155 (22), 106 (10), 89 (10), 78 (52).

Anal. Calcd for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27. Found: C, 75.10; H, 4.11; N, 6.27.

Method D: Anhydro-5,7-dimethyl-1-hydroxy-3-oxo-2-phenylpyrazolo[1,2-*a*]pyrazolium Hydroxide (24a). A solution of phosgene (1.40 g, 14 mmol) in dry benzene (50 mL) was prepared by bubbling phosgene through ice-cooled benzene for 15 min. A stirred solution of 3,5-dimethyl-1-(phenylacetyl)pyrazole (**23b**) (2.5 g, 12 mmol) in dry benzene (75 mL) was treated with NaH (50% dispersion) (0.62 g, 13 mmol). After 30 min, the previously prepared phosgene solution was added dropwise and the mixture stirred for 3 h. CH_3OH was added to destroy any unreacted phosgene and the mixture filtered to remove the NaCl formed. The filtrate was evaporated under reduced pressure and the residue recrystallized from CH_3CN to afford the product as orange-red prisms: 1.2 g (36%); mp 215–217 °C. Spectral data were identical in all respects with those listed for this compound prepared from 3,5-dimethylpyrazole and (chlorocarbonyl)-phenylketene (Table II).

1,3-Bis(3,5-dimethylpyrazolyl)-1,3-propanedione. A solution of carbon suboxide (1.27 g, 18.7 mmol) in ether (100 mL) and THF (50 mL) was treated with solid 3,5-dimethylpyrazole (**15b**) (3.61 g, 37.4 mmol) at −78 °C under nitrogen. The mixture was stirred for 4 h as the temperature rose to 25 °C. The colorless solid was removed by filtration, and the filtrate was evaporated and treated with water. The additional solid formed was collected, and the combined solids were washed with water. Recrystallization from cold ethanol/water afforded colorless prisms: 3.62 g (74%); mp 90–91 °C; IR (KBr) 1720 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.97 (s, 1, pyrazole C_5-*H*), 4.83 (s, 1, CH_2), 2.55 (d, 3, pyrazole C_5-CH_3), 2.20 (s, 3, pyrazole C_3-CH_3); mass spectrum, *m/z* (relative intensity) $M^{\cdot+}$ 260 (0.1), 232 (0.2), 165 (53.9), 164 (51.9), 97 (100), 96 (56.3), 95 (56.9), 81 (8.2), 69 (15.8).

Anhydro-1-hydroxy-3-oxo-2-phenylpyrrolo[2,1-*b*]benzothiazolium Hydroxide (39). (Chlorocarbonyl)phenylketene (0.63 g, 3.5 mmol) was added to 2-(trimethylsilyl)benzothiazole[18] (0.71 g, 3.4 mmol), the addition being carried out in a N_2 atmosphere. After 30 min, a dark red color formed, at which point the mixture was cooled to −78 °C. The positive pressure of nitrogen was closed, the system was attached to a vacuum (1 mmHg), and after 15 min the cooling bath was removed. After 3 h, the product remained as a red oil, which was very air and/or moisture sensitive: mass spectrum, *m/z* (relative intensity) $M^{\cdot+}$ 279 (9), 223 (7), 162 (26), 145 (4), 134 (100), 121 (35), 117 (3), 108 (33), 89 (82), 77 (32).

Reaction of 4-Phenyl-3,5-pyrazolidinedione[23] (17) with Homophthalaldehyde (40). A stirred mixture of freshly distilled homophthalaldehyde (0.9 g, 6.1 mmol) and anhydrous $MgSO_4$ (1.0 g, 8.3 mmol) in freshly distilled THF (15 mL) was treated with 4-phenyl-3,5-pyrazolidinedione (1.07 g, 6.1 mmol). A deep purple color developed instantly. After 18 h, the $MgSO_4$ was removed by filtration and the filtrate evaporated under reduced pressure. The residue was separated by using flash column chromatography (CH_2Cl_2/THF/AcOH) affording an unstable purple solid thought to be **41**: 0.6 g; mp 300 °C; UV λ_{max} (DMF) 496 nm; mass spectrum, *m/z* (relative intensity) $M^{\cdot+}$ 288 (30), 261 (10), 260 (17), 255 (13), 254 (10), 230 (15), 229 (55), 228 (16), 227 (11), 216 (17), 214 (22), 202 (11), 176 (25), 171 (45), 170 (15), 153 (10), 145 (16), 144 (15), 142 (10), 135 (10), 130 (10), 129 (73), 128 (60), 126 (10), 119 (13), 118 (52), 117 (27), 116 (22), 115 (43), 114 (20), 105 (22), 104 (20), 103 (27), 102 (34), 101 (23), 100 (10), 92 (24), 91 (82), 90 (58), 89 (100), 88 (15), 87 (17), 86 (12), 85 (16), 81 (10).

Reaction of 3,5,7-Triphenyl-4*H*-1,2-diazepine[24] (42) with (Chlorocarbonyl)phenylketene. A stirred solution of (chlorocarbonyl)phenylketene (0.87 g, 5 mmol) in anhydrous THF (50 mL) was heated with 3,5,7-triphenyl-4*H*-1,2-diazepine (1.55 g, 50 mmol). A deep purple color developed instantly. The reaction mixture was stirred for 2 h, and the solvent was then removed under reduced pressure. The residue was triturated with absolute Et_2O and the resulting black solid, thought to be **43**, collected and dried in vacuo: 2.2 g; mp 180–182 °C; IR (KBr) 1675 (CO) cm^{-1}; mass spectrum, *m/z* (relative intensity) 410 (6), 333 (7), 322 (11), 307 (19), 306 (44), 221 (17), 220 (100), 219 (14), 191 (13), 77 (7).

Acknowledgment. We express our thanks to Drs. S. Kanemasa, G. Zvilichovosky, and R. Cody for their experimental assistance in the early part of this work and to Prof. W. D. Ollis and Dr. C. A. Ramsden for helpful discussions. Grants from the National Science Foundation and the U.S. Public Health Service for the purchase of the major equipment used in these studies are gratefully acknowledged; P.M.M. thanks IBM for the award of a Fellowship.

Registry No. **12**, 504-64-3; **13a**, 17118-70-6; **14a**, 1663-67-8; **14b**, 55552-69-7; **14c**, 96088-97-0; **15a**, 288-13-1; **15b**, 67-51-6; **15c**, 114505-83-8; **15d**, 4077-76-3; **15i**, 1145-01-3; **15j**, 93233-17-1; **15**,

(21) Ziegler, E.; Kappe, T. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 491.
(22) Nakanishi, S.; Butler, K. *Org. Prep. Proced. Int.* **1975**, *7*, 155.
(23) Braeuniger, H.; Moede, R. *Pharm. Zentralhalle* **1969**, *108*, 615 and ref 10.
(24) Buchardt, O.; Pedersen, C. L.; Svanholm, U. *Acta Chem. Scand.* **1969**, *23*, 3136.

55752-63-1; **16a**, 75526-82-8; **16b**, 97938-47-1; **16c**, 102860-35-5; **16d**, 114505-84-9; **16e**, 76426-55-6; **16f**, 114492-39-6; **16g**, 114505-85-0; **10h**, 114505-86-1; **16i**, 79815-55-7; **16j**, 114505-87-2; **16k**, 114505-88-3; **16l**, 114492-31-8; **17**, 23876-79-1; **19a**, 271-44-3; **19b**, 5401-94-5; **19c**, 95-14-7; **20a**, 114505-89-4; **20b**, 114505-90-7; **20c**, 114505-91-8; **21a**, 2039-06-7; **21b**, 3357-42-4; **22a**, 114505-92-9; **22b**, 114505-93-0; **23a**, 10199-63-0; **23b**, 36140-84-8; **3c**, 36140-83-7; **24a**, 76434-58-7; **24b**, 114505-94-1; **24c**, 114505-95-2; **24d**, 91994-38-6; **24e**, 91994-39-7; **24f**, 114505-96-3; **25a**, 75-44-5; **25b**, 463-71-8; **25c**, 1886-67-5; **25d**, 10472-00-1; **26a**, 616-47-7; **28b**, 7164-98-9; **27a**, 91994-35-3; **27b**, 114492-26-1; **27c**, 114505-26-9; **28** (R = CH_3, R' = C_6H_5), 114505-97-4; **29**, 1632-83-3; **30a**, 114492-42-1; **30b**, 114492-27-2; **30c**, 114492-43-2; **31b**, 91994-41-1; **32**, 13423-60-4; **34**, 114532-37-5; **35**, 16227-12-6; **37**, 114505-98-5; **38**, 32137-73-8; **39**, 114505-99-6; **40**, 25705-34-4; **41**, 114506-00-2; **42**, 78948-36-4; **43**, 114506-01-3; $(C_2H_5O)_2CHCHO$, 6367-37-9; $CHCl(COCH_3)_2$, 1694-29-7; 2-bromopyridine, 109-04-6; 1,3-bis-(3,5-dimethylpyrazol-1-yl)-1,3-propanedione, 31705-94-9.

Cross-Conjugated and Pseudo-Cross-Conjugated Mesomeric Betaines. 2. Structure and Reactivity†

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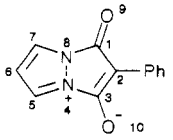
A theoretical and experimental study of cross-conjugated (CCMB) and pseudo-cross-conjugated (PCCMB) mesomeric betaines shows that they are best represented as containing distinct cationic and anionic segments which comprise a common π-electron system. The PCCMB differ from the CCMB in that they all contain a 2-oxyallyl cation 1,3-dipole. The behavior of these betaines under electrophilic and nucleophilic reaction conditions has been established.

In the preceding paper, synthetic methods leading to a variety of cross-conjugated (CCMB) and pseudo-cross-conjugated (PCCMB) mesomeric betaines have been described. We now report our theoretical and physical organic chemical studies which provide support for the classification of these cross-conjugated mesomeric betaines, establish the reactivity of these betaines under a variety of conditions, and by defining structural parameters, enable predictions to be made regarding further development of this concept.

X-ray Data. A single-crystal X-ray study of anhydro-1-hydroxy-3-oxo-2-phenylpyrazolo[1,2-*a*]pyrazolium hydroxide (**1**), a CCMB, showed[2] that the molecule is pseudoplanar with a 2-fold axis of symmetry and that the 2-phenyl substituent is twisted 7.3° out of the plane. Of particular interest is the N(8)–C(1) bond length of 1.49 Å, a "union bond" which approximates a normal N–C single bond, while the C(1)–O(9) bond length is 1.22 Å, consistent with a normal C=O bond length. These data are in agreement with negative charge delocalization over the β-diketone enolate and the phenyl ring and the positive charge being delocalized over the pyrazolium ring.



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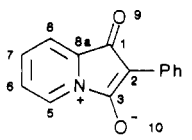

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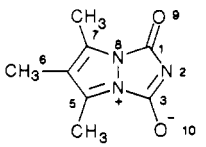

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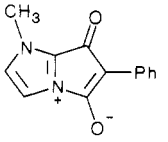

4

The X-ray structure of a PCCMB, anhydro-1-hydroxy-3-oxo-2-phenylpyrrolo[1,5-*a*]pyridinium hydroxide (**2**), was similar in many respect to that of **1** above. In particular, the C(8a)–C(1) bond length was 1.51 Å and the N(4)–C(3) bond length was 1.52 Å, again signifying no appreciable π-overlap between the pyridinium ring and the β-diketone system. The 2-phenyl substituent was twisted 13.0° from the plane of the bicyclic system. The C(1)–O(9) bond length of 1.24 Å approximates that of a normal carbonyl group. The data for **2** shows a pseudo 2-fold axis of symmetry, resulting in some disorder in the crystal. The X-ray data for structure **2** is shown in Figure 1, and further details are provided in the supplementary material.

It is particularly interesting that the X-ray data of the CCMB **3**, anhydro-1-hydroxy-3-oxo-5,6,7-trimethylpyrazolo[1,2-*a*]-1,2,4-triazolium hydroxide, shows[3] remarkable consistency with the bond lengths of **1** and **2**. For example, the N(8)–C(1) bond length is 1.49 Å and the C(1)–O(9) bond length is 1.18 Å. The consistency in the "union bonds" approximating single bonds is also observed in the X-ray data of several six-membered CCMB containing a pyrimidine[4] and a 1,3-oxazine[5] nucleus.

Dipole Moments. The hypothesis advanced to rationalize the structures of CCMB and PCCMB requires a high degree of charge separation which would be reflected in the dipole moment. Figure 2 shows the experimental[6]

† Dedicated to Prof. E. C. Taylor on the occasion of his 65th birthday.

(1) Abstracted from the Ph.D. theses of W. R. K. (1984) and P. M. M. (1987), Rensselaer Polytechnic Institute; acknowledgement is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this work (PRF Grant 13306-AC4). Part of this work appeared in a Preliminary Communication. Potts, K. T.; Murphy, P. M. *J. Chem. Soc., Chem. Comm.* **1986**, 144.

(2) Raston, C. L.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 2577.

(3) Friedrichsen, W.; Bottcher, A.; Debaerdemeker, T. *Heterocycles* **1983**, *20*, 23.

(4) Kratky, Ch.; Kappe, T. *J. Heterocycl. Chem.* **1981**, *18*, 881.

(5) Debaerdemeker, T.; Friedrichsen, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 217.

(6) Guggenheim, E. A. *Trans. Faraday Soc.* **1951**, *47*, 573. Smith, J. W. *Trans. Faraday Soc.* **1950**, *46*, 394.

0022-3263/88/1953-2898$01.50/0