Reactions of Di- and Triphenylmethanes with Benzene and Acid Catalysts. Diphenylmethane and triphenylmethane were allowed to react with $AlCl_3$ or triflic acid for 1 or 2 h at temperatures of 25 °C or 60 °C in the presence or absence of benzene. The reaction workup and analysis were as described previously; the results are depicted in Table III.

Reactions of Diarylmethanols with Arenes and Acid Catalysts. Diphenylmethanol and *p*-anisylphenylmethanol were allowed to react for 1 or 6 h with $AlCl_3$ at temperatures of 25 °C or 60 °C with or without toluene as solvent. The reaction workup and analysis were as described previously. The results are depicted in Table IV.

Acknowledgment. Support for this work by the Robert A. Welch Foundation is gratefully acknowledged.

Notes

New 2-Pyridone Derivatives via 1,3-Dipolar Cycloadditions of Novel Mesoionic Compounds

D. Roger Moore and Lon J. Mathias*

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

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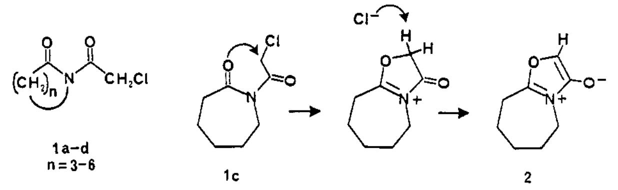
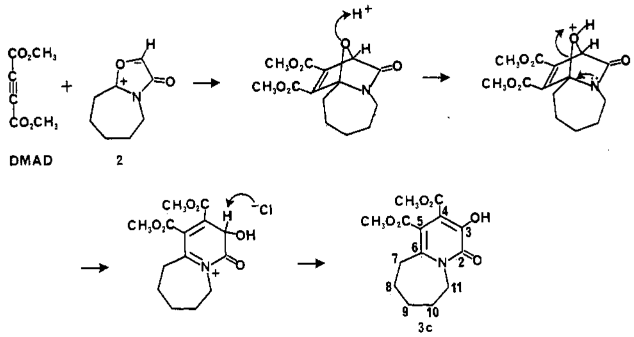
Mesoionic compounds were first reported in 1935[1] and were recently reviewed.[2] Isolable munchnones and isomunchnones were first described in 1964[3] and 1974,[4] respectively. Our interest in the chemistry of mesoionic compounds stems from the discovery of the polymerization of a new family of isomunchnones.[5] *N*-chloroacetyl lactams **1b–d** (but not **1a**) were found to spontaneously form low molecular weight polymers through the intermediacy of isomunchnone **2**.[6]



During our attempts to observe and trap this intermediate, we became intrigued by several aspects of the chemistry of this family of mesoionic heterocycles. They represent the first bicyclic isomunchnones as well as the first possessing only alkyl substituents; aryl substituents have been used routinely to stablize charge in isomunchnones as well as munchnones. The synthesis of **2** involved the readily available and inexpensive starting materials caprolactam and chloroacetyl chloride. Previous syntheses of isomunchnones involved carbene intermediates to effect the ring closure[4] or ring closure of *N*-benzoylphenylglyoxanilide using triphenyl phosphite.[7] Conventional ring-closure approaches to isomunchnones have proven unsuccessful due to various rearrangements,[8] and it was of interest to examine the synthetic utility of α-chloroacetimides as precusors to isomunchnones and their cycloadducts.

Scheme I



Results and Discussion

N-chloroacetyl lactams **1a–d** were examined for reaction with several dienophiles known to undergo 1,3-dipolar cycloadditions.[1] The pyrrolidone derivative **1a** was unexpectedly stable and failed to react even with prolonged heating at 150 °C. Compounds **1b** and **1c** reacted readily with both dimethyl acetylenedicarboxylate (DMAD) and *N*-phenylmaleimide (NPM), two of the more reactive dienophiles.[1] The products obtained resulted from rearrangement of the initially formed adduct by two distinct mechanisms, both of which are apparently catalyzed by the HCl liberated during formation of the isomunchnone; e.g., in the formation of **2** from **1c**. The proposed general mechanism for DMAD addition and rearrangement is given in Scheme I, while the overall process for reaction with NPM is outlined in Scheme II.

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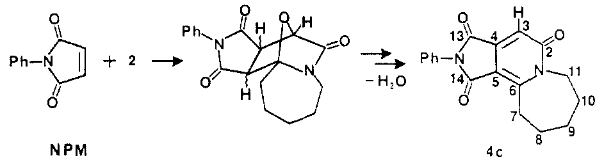
Table I. Properties of 2-Pyridones[a]

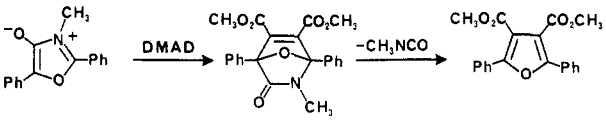
compd	mp, °C	% yield	IR (KBr), cm^{-1}	UV [EtOH], λ_{max} (ϵ)
3b	166–167	<10	3234, 2595, 1742, 1729, 1641, 1439, 1412, 1264, 1214	311 (2.5×10^4), 285 (2.7×10^4), 219 (3.6×10^4)
3c	200–201	16.7	3213, 2945, 2924, 2860, 1732, 1641, 1611, 1439, 1248, 1229	315 (9.2×10^3), 277 (9.1×10^3), 220 (1.5×10^4)
4b	265–266	42.7	3058, 2952, 2875, 1710, 1671, 1600, 1409, 1373, 1111, 763	353 (1.5×10^4), 281 (6.8×10^4), 214 (7.4×10^4)
4c	184–185	42.7	3044, 2924, 2854, 1721, 1663, 1606, 1420, 1360, 1111, 766	351 (8.0×10^3), 281 (4.2×10^4), 207 (5.9×10^4)
4d	192–194	39.1	2931, 2854, 1715, 1671, 1600, 1428, 1373, 1116, 761	352 (1.2×10^4), 282 (6.2×10^4), 216 (6.3×10^4)
5	304–305	9.7	3030, 1729, 1669, 1387, 1368, 753, 689	292 (4.4×10^4), 244 (3.6×10^4), 216 (7.4×10^4)

[a] Satisfactory analyses (±0.4 for C, H, N) were reported for all compounds except **5** (calcd, C, 72.15; found; C, 70.67).

Scheme II



Scheme III

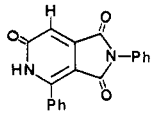


Identification of compounds **3b–c** and **4b–d** involved mainly spectroscopic data. Carefully purified **3c** was the first compound to be characterized and was found to possess a unique hydroxy pyridone structure compared to other DMAD adducts of various mesoionic compounds.[1] Previously reported 1,3-dipolar cycloadducts of isomunchnones with acetylenic compounds yielded furans through thermal extrusion of methyl isocyanate as shown in Scheme III.[9]

Heteronuclear COSY results were used to support the proposed structures **3b** and **3c**. Important connectivities (for **3c**, for example) established with this method involve coupling of the 3-hydroxyl hydrogen to carbons 2, 3, and 4, coupling of position 7 hydrogens to carbons 5 and 6, and coupling of position 11 hydrogens to carbons 2 and 6. When combined with IR data, the UV spectrum, proton and carbon chemical shifts and multiplicities, proton integration ratios, and carbon DEPT results, structure **3c** is confirmed. Similar spectral data confirmed structure **3b**.

Identification of **4b–d** was based on results reported for similar compounds[12] and by comparison with the spectral data for **3b,c**. Complete characterization of all compounds is given in Tables I and II. Previous reports of 1,3-dipolar cycloadducts of isomunchnones with a variety of ethylenic compounds indicated good stability of the initially formed cycloadducts and high reactivity toward even strained olefins such as norbornadiene.[10] Isomunchnone **2** failed to give cycloadducts with dimethyl fumarate and maleate, ethyl acrylate, and dicyanocyclobutene. A polymer was formed instead in a competitive process. Reactions of **2** with *p*-nitroacetophenone and *p*-tolylisocyanate yielded apparent copolymers.

In order to demonstrate the potential for isomunchnone generation from α-chloroacetimides, *N*-(chloroacetyl)benzamide was prepared as previously described.[11] Reaction of this compound with NPM resulted in the formation of *N*,6-diphenyl-1,2-dihydro-2-oxopyridine-4,5-dicarboximide **5**. This compound was prepared previously from the reaction of NPM with 2-phenyl-4(5*H*)-oxazolone (**6**),[12] which was obtained from reaction of diazomethane with benzoyl isocyanate.[13] This oxazolone was also obtained from the reaction of *N*-(chloroacetyl)benzamide with sodium hydride in THF.[11] It is interesting to note that pyridone **5** was obtained under both neutral and basic conditions when **6** was reacted with NPM,[12] which indicates that these rearrangements do not neccessarily require acid catalysis.



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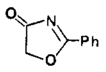

6

Experimental Section

Melting points were determined in capillaries and are uncorrected. Microanalyses were performed by MicAnal, Tuscon, AZ. FTIR spectra were obtained on a Nicolet 5DX spectrometer and UV spectra with a Perkin-Elmer 320 interfaced to the Nicolet 5DX computer. ^1H NMR spectra were determined on a Varian EM360, and ^{13}C NMR spectra were obtained on a JEOL FX90Q. The heteronuclear COSY spectra were obtained by M. Appel and M. Goeckel of Bruker Instruments, Billerica, MA, and their assistance is gratefully acknowledged.

Reaction of *N*-(Chloroacetyl)caprolactam with DMAD. Freshly prepared *N*-(chloroacetyl)caprolactam (**1c**) (6.00 g; 0.0317 mol) was heated with 6.75 g (0.0475 mol) of DMAD for 2 h at 80 °C under 2 mmHg vacuum. Trituration with diethyl ether and recrystallization of the resulting solids yielded 1.56 g of 7,8,9,10,11-pentahydro-3-hydroxy-4,5-bis(methoxycarbonyl)cyclohepta[*a*]pyridin-2-one (**3c**). Compound **3b** was prepared in similar fashion, while the reaction of *N*-(chloroacetyl)enantholactam (**1d**) with DMAD gave a complex mixture of compounds from which no pyridone could be isolated.

Reaction of *N*-(Chloroacetyl)caprolactam with *N*-Phenylmaleimide. Freshly prepared *N*-(chloroacetyl)caprolactam (5.48 g, 0.0289 mol) and 5 g (0.0289 mol) of *N*-phenylmaleimide were combined with 5 mL of dimethylformamide (DMF) and heated at 90 °C for 2 h. After removal of the DMF under vacuum, the crude solid was triturated with methanol, at which point analytically pure crystals of 2-oxo-*N*-phenyl-2,7,8,9,10,11-hexahydrocyclohepta[*a*]pyridine-4,5-dicarboximide **4c** separated from the solution. Yield on filtration and drying was 3.80 g. Compounds **4b** and **4d** were obtained in similar fashion.

Reaction of *N*-(Chloroacetyl)benzamide with *N*-Phenylmaleimide. *N*-(Chloroacetyl)benzamide (1.50 g, 0.00759 mol) and 1.58 g (0.00912 mol) of *N*-phenylmaleimide were combined with 10 mL of DMF and heated for 14 h at 100 °C. The reaction mixture was poured into a large excess of water, and the resulting solids were dissolved in a large volume of ethanol. Crystalline *N*-phenyl-1,2-dihydro-2-oxopyridine-4,5-dicarboximide (**5**) (0.23 g) was obtained from this solution on cooling.

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Table II. NMR Data (δ) for 2-Pyridones

		position																
compd	NMR	2	3	4	5	6	7	8	9	10	11	12	12a	12b	13	13a	13b	14	phenyl
3b[a]	^{13}C	158.0	141.1	119.0	105.8	141.6	25.2	17.7	20.7	42.1			165.7	52.1		165.7	52.2		
	^1H		9.76 (s, 1 H)				2.95 (t, 2 H, J = 6 Hz)	1.83-1.69 (m, 4 H)		4.00 (t, 2 H, J = 6 Hz)				3.75 (s, 3 H)			3.69 (s, 3 H)		
3c[a]	^{13}C	157.9	142.0	117.9	107.2	143.8	28.8	27.0	28.2	28.2	43.8		165.4	52.3		166.3	52.2		
	^1H		9.85 (s, 1 H)				2.94 (m, 2 H)	1.65 (m, 6 H)			4.37 (m, 2 H)			3.75 (s, 3 H)			3.69 (s, 3 H)		
4b[b]	^{13}C	167.5	119.3	147.3	110.0	159.3	23.1	18.3	29.6	52.6					169.7			168.6	130-134
	^1H		7.40 (s, 1 H)				3.60 (t, 2 H, J = 8 Hz)	2-2.3 (m, 4 H)		4.32 (t, 2 H, J = 8 Hz)									7.5-7.3 (m, 5 H)
4c[c]	^{13}C	162.9	112.8	139.9	103.9	157.4	28.2	27.1	25.5	29.5	44.0				165.4			164.5	131-127
	^1H		6.91 (s, 1 H)				3.52 (t, 2 H, J = 4.5 Hz)	1.84-1.74 (m, 6 H)			4.40 (t, 2 H, J = 4.5 Hz)								7.5-7.3 (m, 5 H)
4d[c]	^{13}C	163.7	113.3	141.1	104.5	158.2	29.5	26.9	21.0	25.2	31.7	43.9			167.7			166.8	133-127
	^1H		6.85 (s, 1 H)				3.38 (t, 2 H, J = 10 Hz)	1.85-1.45 (m, 8 H)				4.25 (t, 2 H, J = 10 Hz)							7.5-7.29 (m, 5 H)

[a] In Me_2SO-d_6. [b] In CF_3COOH. [c] In $CDCl_3$.

Acknowledgment. Grateful acknowledgment is made to 3M for continued funding of this research and to Dr. Steve Heilmann of 3M Corporate Research for helpful discussions.

Registry No. **1a**, 43170-60-1; **1b**, 98303-90-3; **1c**, 98303-85-6; **1d**, 98303-92-5; **2**, 106420-73-9; **3b**, 106420-69-3; **3c**, 98303-86-7; **4b**, 106420-71-7; **4c**, 106420-70-6; **4d**, 106420-72-8; **5**, 68475-24-1; DMAD, 762-42-5; NPM, 941-69-5; (E)-$H_3CO_2CCH{=}CHCO_2CH_3$, 624-49-7; (Z)-$H_3CO_2CCH{=}CHCO_2CH_3$, 624-48-6; $H_2C{=}CHCO_2CH_2CH_3$, 140-88-5; 4-$O_2NC_6H_4COCH_3$, 100-19-6; 4-$H_3CC_6H_4NCO$, 622-58-2; $ClCH_2CONHCOC_6H_5$, 7218-27-1; dicyanocyclobutene, 3716-97-0.

Supplementary Material Available: Figure containing heteronuclear COSY spectrum for compound **3c** (1 page). Ordering information is given on any current masthead page.

Michael Additions of Nitroalkanes to α,β-Unsaturated Carbonyl Compounds Using KF/Basic Alumina

David E. Bergbreiter* and James J. Lalonde

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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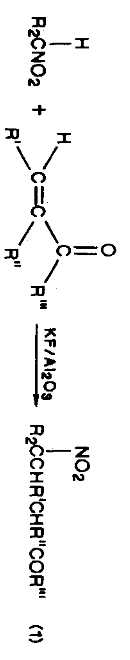
Catalysts and reagents supported on inorganic substrates have received increasing attention in recent years as a means to develop more convenient or selective catalysts or reagents.[1-3] In this context, potassium fluoride adsorbed on various sorts of alumina has commonly been used as a base. Such heterogeneous bases have been shown to be effective in both aldol condensations and Michael addition reactions. Adsorbing KF on neutral alumina greatly enhances the activity of this basic catalyst.[4,5] Other workers have also noted that the use of basic alumina as a support for KF leads to moderate yields of Michael addition products when reactions are carried out in the absence of solvent.[6] However, poor yields and low selectivity were obtained in the latter case for reaction of nitromethane and 3-buten-2-one. In the course of studying the chemistry of nitroparaffins and their derivatives, we have developed procedures using KF/basic alumina which are very effective at promoting Michael-type reactions between nitroparaffins and reactive Michael acceptors such as acrylate esters and α,β-unsaturated carbonyl compounds (eq 1). Unlike the procedures used by Rosini,[6] these



(1)

reactions proceed in the presence of a solvent (THF) and can be carried out on large scale. Our results resemble those obtained by Clark[5] using neutral alumina. However, while KF/neutral alumina forms mono-Michael adducts with *sec*-nitroalkanes as nucleophiles, the reaction of

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