

LOW TEMPERATURE KETENE PREPARATIONS USING NITROSYLTETRACARBONYLCHROMIUM (-II) ANION

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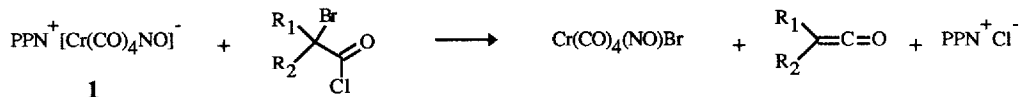
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Abstract: Methylene and cyclopropyl ketenes can be generated at -100°C by the dehalogenation of α -bromoacylhalides using nitrosyltetracarbonylchromium (-II) anion. This facilitates the trapping of these ketenes with more stable ketenes to give mixed ketene dimers.

Although ketenes can be produced by a great variety of methods¹, some of the more general procedures are not overly convenient for synthetic purposes, e.g. pyrolysis, photolysis etc. Also, since many ketenes dimerize rapidly at ordinary temperatures, matrix isolation techniques are commonly involved. There are of course many practical instances where ketenes can be generated *in situ* in the presence of a desired trapping agent but in this work we have sought a methodology in which reactive ketenes themselves can be simply and conveniently generated in solution at very low temperatures.

The reaction of $\text{Mn}(\text{CO})_5^-$ and α -bromoacyl halides, to form ketenes and $\text{Mn}(\text{CO})_5\text{Br}$, is one approach which has been successful^{2,3}. However, this reaction generally becomes sluggish below about -50°C . The manganese reagent is also reasonably expensive (based on $\text{Mn}_2(\text{CO})_{10}$) for a stoichiometric reagent.

It has now been found that the isoelectronic chromium nitrosyltetracarbonyl anion, $\text{Cr}(\text{CO})_4\text{NO}^-$, **1**, reacts in a similar way to $\text{Mn}(\text{CO})_5^-$.



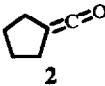
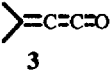
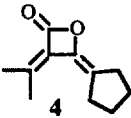

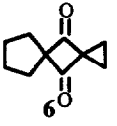
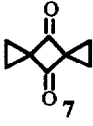

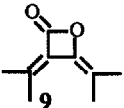
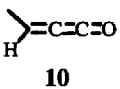
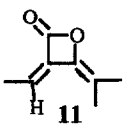
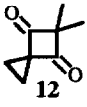
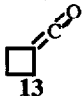
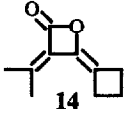
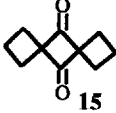
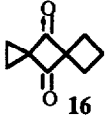
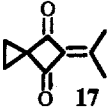
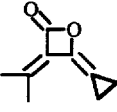
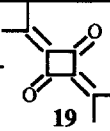
However, **1** has a number of advantages (and a few disadvantages) compared to $\text{Mn}(\text{CO})_5^-$:

1. reactions with α -bromoacyl halides are virtually instantaneous at -100°C ;
2. the reagent, as the easily-handled crystalline PPN salt, can be prepared in a simple one-pot reaction, as described by Gladfelter *et al.*⁴, from $\text{Cr}(\text{CO})_6$ and $\text{PPN}^+\text{NO}_2^-$. Additionally, $\text{Cr}(\text{CO})_6$ is less expensive than $\text{Mn}_2(\text{CO})_{10}$.
3. the deep red color of **1** changes to essentially colorless $\text{Cr}(\text{CO})_4\text{NOBr}$ on reaction, permitting the course of the reaction to be easily monitored. In the $\text{Mn}(\text{CO})_5^-$ reactions, a light orange color changes to a deeper orange, but the change is quite gradual and not easy to follow.

The disadvantages of **1** include a more complex inorganic chemistry. The initial inorganic product in either case is an organometallic bromide, $\text{Cr}(\text{CO})_4\text{NOBr}$ vs. $\text{Mn}(\text{CO})_5\text{Br}$. Both are reasonably soluble in nonpolar solvents but $\text{Cr}(\text{CO})_4\text{NOBr}$ is relatively unstable at ambient temperatures, losing carbon monoxide and presumably forming low oxidation state chromium nitrosyl species which could conceivably react with the dimeric ketene products also present, although we have no specific indication that this occurs. Another slight disadvantage of **1** compared to $\text{Mn}(\text{CO})_5^-$, is that **1** is somewhat more air sensitive. It can however be weighed in air, although for extended storage **1** must be kept under an inert atmosphere.

The reactions of **1** can be carried out in THF or methylene chloride solvent under nitrogen, but chloroform solvent appears to react with **1**. One can either add the solution of **1** to the cold acid chloride solution or in the

Table 1

Entry	First Formed Ketene	Reactive Ketene	Mixed Dimer(s)	Other
(1)				
(2)	2			
(3)		3		
(4)	8			
(5)	8	5		7
Co-generated				
(6)		3		
(7)	13	5		7, 15
(8)	5	3	 	7 + 



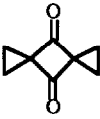
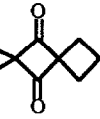
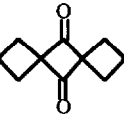
Yields: (1):76%; (2):72% 6,7% 7; (3):81%; (4):15%; (5):20% 12,19% 7; (6):78% 14,5% 15; (7):75% 16,3% 7,2% 15; (8):39% 17,21% 7,13% 18,8% 19. Yields were determined using GC, isolated yields were lower primarily because of volatility problems.

reverse manner. In the former case, as mentioned earlier, the rate of the reaction can be easily monitored by the near instantaneous disappearance of the dropwise added deep red anion color.

The following preparations seem particularly suited to the low temperature generation of ketenes:

- the one-pot preparation of unsymmetrical ketene dimers. The results of this study are summarized in Table 1 (entries (1)-(5)). The basic premise is that one generates a stable ketene at low temperatures and then sequentially follows this with the slow generation of a more reactive ketene, resulting in a mixed ketene dimer as the major product.⁸ The "stable ketene" need not be very stable, as shown in Table 2 for cyclobutyl and cyclopropyl ketene. At -40°C , the first formed cyclobutyl ketene dimerizes *before* one can add the cyclopropyl ketene precursor. At -112°C , the cyclobutyl ketene does not self dimerize and the mixed dimer is formed in good yield. Entries (6),(7), and (8) illustrate another feature of these reactive ketenes, viz. a propensity to form mixed dimers. These experiments involve the addition of a *ca.* 1:1 molar mixture of the two acyl chloride precursors to a solution of **1**. The predominant formation of the mixed dimer illustrates two things: (a) an obvious kinetic preference for mixed dimer formation and (b) evidence that **1** is so reactive and *non-selective* that both ketenes are co-generated at the same time. Entry (8) illustrates (b). The self dimerization reactions of solutions of pure **3** or **5** are known to be extremely rapid. Under mixed conditions, if **3** or **5** were to be generated at significantly different rates, one would probably have found mainly self-dimers, contrary to what is seen. Entry (7) illustrates that the sequential addition technique shown in Table 2 was unnecessary in this particular case, although the Table 2 data still illustrate an important point.

Table 2

	+		→		+		+	
13		5		7		16		15
		Temp. ($^{\circ}\text{C}$)		Yield (%)				
				7	16	15		
		-112		10	52	1		
		-78		21	19	20		
		-40		31	0	33		

- the preparation of pure solutions of simple ketenes, such as methyl ketene⁶, are easily accomplished. The preparation is carried out at -80°C in methylene chloride solvent, which is subsequently distilled together with the formed methyl ketene *en vacuo* bulb-to-bulb at *ca.* -40°C . Distilled yields of this reactive ketene are about 75%.
- like $\text{Mn}(\text{CO})_5^-$, **1** reacts with tertiary γ -bromocrotonoyl chlorides to give methyl-substituted vinyl ketenes in good yield. For example ketene **20** was prepared as a distilled methylene chloride solution in 80% yield starting from **1** and the γ -bromocrotonoyl chloride **21**.



However, unlike $\text{Mn}(\text{CO})_5$, **1** has not yielded the more reactive unsubstituted vinyl ketene using the parent γ -bromocrotonoyl chloride.²

In conclusion, we point out that methylene ketenes in particular have not been easy to generate in a preparatively useful way and we believe that the reactions of **1** described in this paper help to open up the chemical possibilities for utilizing this reactive class of ketenes.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for generous financial support.

References and Notes

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- An abbreviated list of physical and spectroscopic data for **4**, **6**, **11**, **12**, **14**, **16**, **17**, and **18** are given below:
4: ¹H-N.M.R.: 2.55 (2H); 2.44(2H); 2.15 (3H); 2.06 (3H); 1.74 (4H). I.R.(CH₂Cl₂): 1839(m); 1725(m); 1689(m). Mpt.: 63°C.
6: ¹H-N.M.R.: 2.06(4H); 1.97(4H); 1.78(4H). I.R.(CH₂Cl₂): 1738(m). Mpt.:56.0°C. **11**: ¹H-N.M.R.: 6.31(1H); 2.07(3H); 1.94(3H); 1.81(3H). I.R.(CH₂Cl₂): 1852(m); 1729(m); 1689(w). **12**: ¹H-N.M.R.: 1.94(4H); 1.33(6H). I.R.(CH₂Cl₂): 1741(m).
14: ¹H-N.M.R.: 2.96(2H); 2.84(2H); 2.13(2H); 2.11(3H); 1.93(3H). I.R.(CH₂Cl₂): 1845(sh); 1841(m); 1735(m); 1703(w). Mpt.:46-48°C. **16**: ¹H-N.M.R.: 2.52(4H); 1.98(2H); 1.95(4H). I.R.: 1742(m). Mpt.:47°C. **17**: ¹H-N.M.R.: 2.26(6H); 1.77(4H). I.R.(CH₂Cl₂): 1716(m); 1656(m). **18**: ¹H-N.M.R.: 2.15(3H); 2.06(3H); 1.47(4H). I.R.(CH₂Cl₂): 1859(w); 1783(s); 1714(m).
 Compounds **7**, **9**, **15** and **19** are known.^{9,10,11}
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- All of the precursors for the simple ketenes were the corresponding α -bromoacyl chlorides, while α -bromoacryloyl chlorides were used to generate methylene ketenes.
- In a typical experiment, two equivalents of **1** (*ca.* 0.3 mmole) was dissolved in methylene chloride or THF and cooled to minus 78°C. A solution of the acyl chloride precursor for the "stable ketene" was then added over *ca.* two minutes, stirred for one minute, and then a solution of the precursor for the reactive ketene was added dropwise over five minutes. Where the reaction was carried out in THF, pentane was added and the mixture was filtered. The inorganic products decomposed on warming and exposure to air. In methylene chloride most of the inorganic material could be removed by adding pentane at -78°C and then decanting the supernatant from the oil which forms. The products were purified by either flash chromatography/crystallization or sublimation.
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