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Reactions of atomic carbon with acyl chlorides

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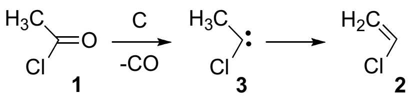
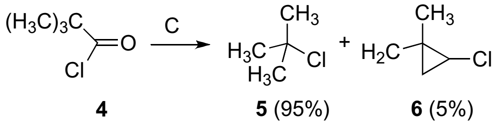
ABSTRACT

Reactions of arc-generated carbon atoms with acyl chlorides proceed by two distinct mechanistic pathways depending on the nature of the alkyl group in the substrate. Acetyl chloride affords vinyl chloride from the putative chloromethylcarbene produced by deoxygenation, whereas pivaloyl chloride gives *t*-butyl chloride as the predominant product via a chain reaction from the initially generated pivaloyl radical. When the alkyl group is isopropyl, both pathways are implicated.

The deoxygenation of carbonyl compounds by atomic carbon is an effective way of generating carbenes whose chemistry is untainted by precursor reactions.[1] Although the C atom deoxygenation of phosgene yields dichlorocarbene,[2] there have been no reports of the generation of alkylchlorocarbenes by the deoxygenation of acyl chlorides. This investigation explores the feasibility of generating these carbenes by C atom deoxygenation.

When acetyl chloride, **1**, is co-condensed with arc-generated C at 77 K at 10^{-4}–10^{-5} torr,[3] the formation of CO is indicated by a pressure rise to 10^{-2}–10^{-3} torr and vinyl chloride, 2, is produced. We feel that **2** is the result of an intramolecular hydrogen shift in the chloromethylcarbene intermediate, **3**.[4] Attempts to trap an intermediate chloromethylketene by the addition of methanol were unsuccessful.[5,6]

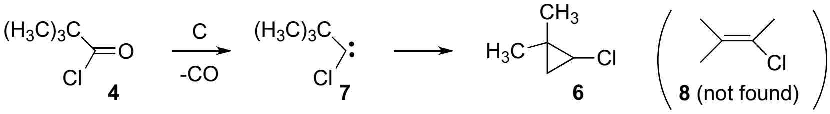




The reaction of pivaloyl chloride, **4,** with atomic carbon follows a quite different course giving *tert*-butyl chloride, **5**, as the major product along with a small amount of 2-chloro-1,1-dimethylcyclopropane, **6**. We attribute the formation of **6** to the known intramolecular C–H insertion in *tert*-butylchlorocarbene, **7**,[7] which presumably results from the deoxygenation of **4** by carbon (Scheme 1). We were not able to detect any 2-chloro-3-methyl-2-butene, **8**, which often,[7] but not always,[8] accompanies the generation of **7** from its diazirine precursor. It has been suggested that the 1,2-methyl shift in **7** to form **8** is a process that is not generally favorable, although it could occur to a small extent at elevated temperatures.[7b,c] An earlier report by Skell and Harris indicates that the reaction of atomic carbon with *tert*-butyl chloride, **5**, produces **7** by carbon atom insertion into the C–Cl bond, which then rearranges to give **6** and **8** in a 9:1 ratio.[9]

We propose that **6** results from the free radical chain reaction in Scheme 2. Thus, an initial abstraction of chlorine from **4** by atomic carbon produces the pivaloyl radical **9** and C–Cl. Loss of carbon monoxide from **9** generates the stable *tert*-butyl radical **10.**[10] Abstraction of chlorine from **4** by **10** gives rise to the product **5** and regenerates the radical **9**, which carries the chain.

Observations made during the reaction of **4** with atomic carbon are consistent with this hypothesis. When the arc is struck at 10^{-4}–10^{-5} torr, there is an increase in pressure to about 10^{-2}–10^{-3} torr) reflecting the formation of CO. However, when the arc was stopped, the pressure took an unusually long time to return to



Scheme 1.

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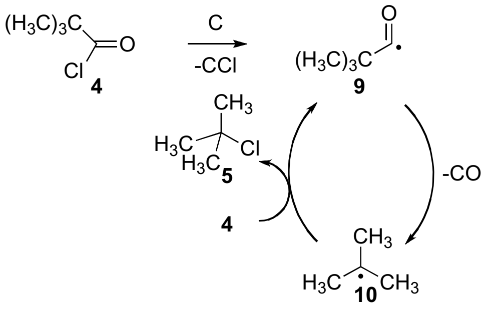
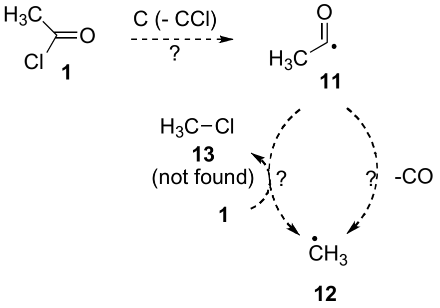


Scheme 2.



Scheme 3.

the previous lower levels. This lends credence to the notion that CO was being released even when there was no arc. An analogous free radical mechanism in the reaction of **1** with atomic carbon would have produced chloromethane, **13**, via the acetyl radical **11** and methyl radical **12** (Scheme 3). We were, however, unable to find any chloromethane in the reaction mixture of **4** + C. Further, when **1** is used as the substrate, in marked contrast to the behavior of **4**, the pressure rises when the arc is struck but falls quickly after it is stopped. Control experiments show that **9** does not result from pyrolysis of **4** in the arc.

Thus, the reaction of C with **4** appears to follow two pathways, initial chlorine abstraction and deoxygenation. The fact that the former initiates a chain reaction makes it difficult to estimate the relative importance of the competing initial C atom reactions. It is certainly possible that chlorine abstraction is a minor pathway in which products are considerably amplified by the chain reaction. While the decarbonylation of acyl radicals is endothermic, it is less so when the product is **10** (ΔH = 9.7 kcal/mol)[11] rather than **12** (ΔH = 11.9 kcal/mol).[11] While these differences in enthalpies of decarbonylation are not dramatic, they may be sufficient to slow the decarbonylation of **11** enough that an observable chain reaction is not initiated. Thus, it could be that **11**, if produced, simply does not decarbonylate fast enough to initiate a viable chain. A search of the reaction mixture for biacetyl, in the unlikely event that **11** dimerizes,[12] and acetaldehyde, which could arise from hydrogen abstraction by **11**,[13] was unsuccessful. It is also conceivable that **11** and **1** can simply interconvert by a degenerate chlorine exchange before the radical is eventually destroyed.

The abstraction of chlorine by atomic carbon to generate C–Cl has been observed in the reactions of C with CCl_4 and chlorofluorocarbons.[14] In these reactions, the C–Cl can be trapped with cyclohexene. Since attempts to trap the C–Cl with cyclohexene in the present reactions were not successful, we conclude that only a small amount of chlorine abstraction occurs and the majority of **5** is the result of the chain reaction.

Given the fact that decarbonylation to a methyl radical does not manifest itself in these reactions while decarbonylation producing a tertiary radical does, it was of interest to react C with isobutyryl chloride, **14**, in which chlorine abstraction followed by decarbonylation would generate a secondary radical. As illustrated in Scheme 4, the product mixture from the reaction of **14** + C showed the presence of both isopropyl chloride **15**, attributed to the chlorine abstraction mechanism, and 1-chloro-2-methylpropene **16**, from the known 1,2-H shift in the chloroisopropylcarbene, **17**,[15] in a 1:2 ratio. Thus, products resulting from Cl abstraction and decarbonylation to an isopropyl radical (ΔH = 9.9 kcal/mol)[11] are less important than those in the corresponding pathway involving a *tert*-butyl radical. It is also possible that steric effects could be involved with the bulky *tert*-butyl group directing the C atom away from the oxygen toward the sterically accessible Cl atom. We feel that these results demonstrate that C atoms will deoxygenate acid chlorides to chlorocarbenes in a manner similar to the deoxygenation of aldehydes and ketones. However, a competing Cl abstraction followed by decarbonylation renders carbene formation inefficient when the decarbonylation leads to a stable radical. Since alkylchlorocarbenes are ground state singlets[16] and the analogous carbonyl deoxygenations generate singlet carbenes,[11] we feel that the carbenes formed here are in the singlet state.

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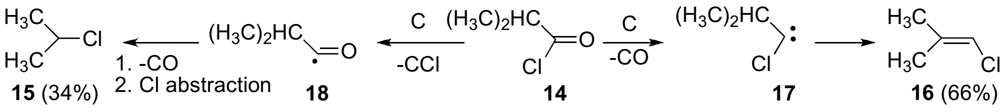
References and notes

1. For a recent review, see: Shevlin, P. B. In *Reactive Intermediate Chemistry;* Moss, R. A., Platz, M. S., Jones, Jr., M., Eds.; Wiley-Interscience: Hoboken, NJ, 2004; Chapter 10, p 463.
2. Skell, P. S.; Plonka, J. H. *J Am. Chem. Soc.* **1970**, *92*, 2160.
3. The reactor is modeled after the one described in: Skell, P. S.; Wescott, LDJr; Golstein, J. P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.
4. Moss, R. A.; Mamantov, A. *J. Am. Chem. Soc.* **1970**, *92*, 6951.
5. Ketenes have been proposed and trapped in the reaction of C with 2-butanone: (a) Dewar, M. J. S.; Nelson, D. J.; Shevlin, P. B.; Biesiada, K. A. *J. Am. Chem. Soc.* **1981**, *103*, 2802; (b) Biesiada, K. A.; Shevlin, P. B. *J. Org. Chem.* **1984**, *49*, 1151.
6. For an example of an alcohol adding to chloromethylketene, see: Tandon, V. K. *Tetrahedron Lett.* **2001**, *42*, 5985.
7. (a) Ishitsuka, M. O.; Niino, Y.; Wakahara, T.; Akasaka, T.; Liu, M. T. H.; Kobayashi, K.; Nagase, S. *Tetrahedron Lett.* **2004**, *45*, 6321; (b) Moss, R. A.; Liu, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1597; (c) Moss, R. A.; Ho, G.-J. *J. Am. Chem. Soc.* **1990**, *112*, 5642.
8. Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 4123.
9. Skell, P. S.; Harris, R. F. *J. Am. Chem. Soc.* **1965**, *87*, 5807.
10. (a) Jensen, C. M.; Lindsay, K. B.; Tanning, R. H.; Karaffa, J.; Hansen, A. M.; Skrydstrup, T. *J. Am. Chem. Soc.* **2005**, *127*, 6544; (b) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200.



Scheme 4.

11. Viskolcz, B.; Bérces, T. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5430–5436.
12. Gandini, A.; Hackett, P. A. *J. Am. Chem. Soc.* **1977**, *99*, 6195.
13. For a discussion of acyl radicals abstracting hydrogen, see: Chatgilialoglu, C.; Ferreri, C.; Lucarini, M.; Pedrielli, P.; Pedulli, G. F. *Organometallics* **1995**, *14*, 2672.
14. (a) LaFrancois, C. J.; Shevlin, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 9405; (b) LaFrancois, C. J. Ph.D. Dissertation, Auburn University, Auburn, AL, 1996.
15. LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877.
16. Jones, Jr., M.; Moss, R. A. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, Jr., M., Eds.; Wiley-Interscience: Hoboken, NJ, 2004; p 278.