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Bimolecular chemistry of dimethylcarbene

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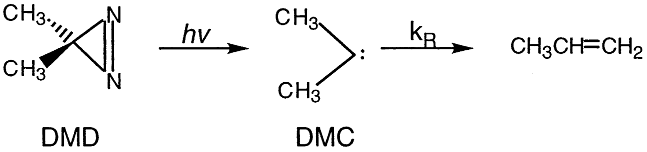
Abstract—A new non-nitrogenous precursor of dimethylcarbene has been synthesized. Photolysis of 10,10′-dimethyltricyclo[4.3.1.0^{1,6}]deca-2,4-diene in solution with 254 nm light produces dimethylcarbene. Previously unknown intermolecular reactions of dimethylcarbene have been observed.

Dimethylcarbene (DMC) is the simplest of all dialkylcarbenes. Examples of intermolecular reactions of simple alkyl and dialkylcarbenes are rare, however.[1] Historically, the absence of bimolecular chemistry of simple alkyl and dialkylcarbenes has been attributed to a very rapid competitive rate of rearrangement of DMC to propene.

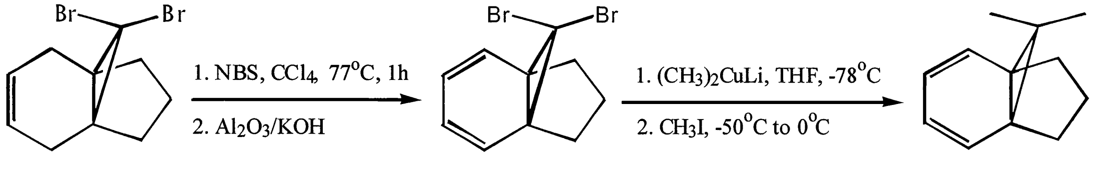


Recent kinetic and computational studies have revealed that DMC has a lifetime of several nanoseconds at ambient temperature. Thus, DMC should be sufficiently long-lived to allow bountiful bimolecular chemistry.[2] It was concluded that the low yields of bimolecular products obtained upon photolysis of dimethyldiazirine (DMD) was due to the inefficiency of carbene production from the precursor. It was proposed that an excited state of DMD suffers rearrangement to propene, without intervention of DMC.[2]

To discover bimolecular chemistry of DMC we synthesized 10,10′-dimethyltricyclo-[4.3.1.0^{1,6}]deca-2,4-diene **1** in 66% yield from 10,10-dibromotricyclo[4.3.1.0^{1,6}]deca-2,4-diene[3] by treatment with an excess of dimethylcopper lithium, following the approach developed by Jones, and co-workers for their precursor to dibromocarbene (Scheme 1).[4]

Precursor **1** is easier to handle than DMD, 2-diazopropane or dimethylketene, traditional precursors of DMC. It also has a built-in internal standard, the yield of indane product, against which yields of DMC adducts (as illustrated with cyclohexane as trap) can be quantified (Scheme 2).

Thus, **1** was photolyzed (254 nm, Rayonet reactor, quartz, 4°C) in a series of solvents. The yield of DMC was presumed to be equal to the yield of indane. The yield of adducts were measured by GC relative to indane using authentic materials for calibration. The results are given in Table 1.



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Scheme 1.

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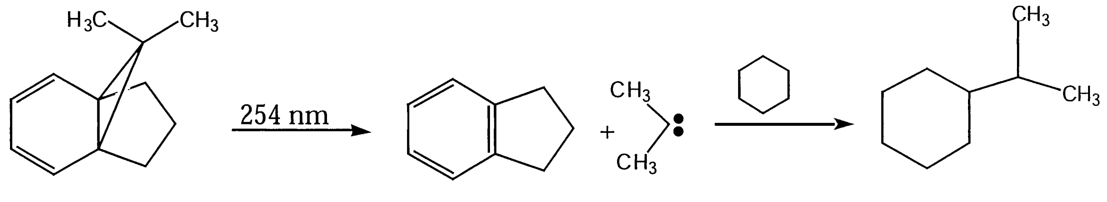

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Scheme 2.

Table 1. Yields of dimethylcarbene and its insertion products

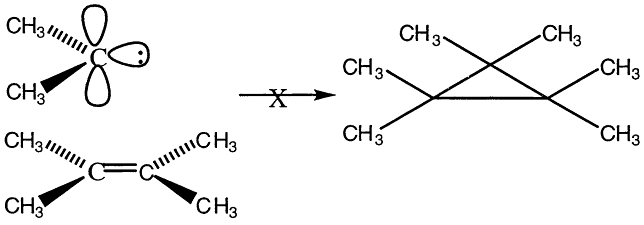
Solvent	Yield of DMC (%)[a]	Insertion product	Yield (%)
Cyclohexane	15–20[a]	Isopropylcyclohexane	4[b]
Benzene	13–15	Cumene	0.1[b]
Cyclohexylamine	6	Isopropylcyclohexyl amine	80[b]
Isopropanol	10	Diisopropyl ether	70[b]
Isobutylene	7	1,1,2,2-Tetramethylcyclopropane	33[c]

[a] The yield of dimethylcarbene was determined by measuring amounts of indane formed upon irradiation.

[b] Yields of insertion products relative to dimethylcarbene were calculated from GC data using calibration with the corresponding reference compounds.

[c] Yield calculated by NMR.

Diene **1** is clearly not an efficient precursor of DMC and dimethylcarbene reacts in cyclohexane and benzene to give adducts in only very low yields. Adduct formation is modest in isobutylene solvent and is significant in both cyclohexylamine and in 2-propanol. Interestingly, DMC does not react with tetramethylethylene (TME) to form an adduct under standard conditions. We speculate that steric interactions in the cycloaddition of DMC are more severe with TME than with isobutylene and retard the rate of this process.



This type of steric argument has been used to explain the fact that fluorenylidene adds to butenes to form cyclopropanes efficiently, but diphenylcarbene does not.[5]

The results demonstrate that DMC is sufficiently long-lived to be efficiently intercepted with a nucleophilic trapping agent. This is consistent with previously reported kinetic studies.[2]

References

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3. **10,10′-Dimethyltricyclo[4.3.1.0^{1,6}]deca-2,4-diene**

   A solution of methyllium in ether (1.4 M, 48 mL) was added dropwise under argon at −50°C to a magnetically stirred solution of copper(I) iodide (6.4 g, 33.6 mmol) in dry THF (120 mL). The mixture was allowed to warm up to 0°C, stirred for 5 min, and cooled to −60°C. Then a solution of 10,10′-dimethyltricyclo[4.3.1.0^{1,6}]deca-2,4-diene (0.96 g, 3.3 mmol) in dry THF (20 mL) was added dropwise over 5 min. The mixture was stirred at −40°C for 3 h then iodomethane (4.35 mL, 70 mmol) was added dropwise. The mixture was allowed to warm up to 1–5°C and was stirred at this temperature for 16 h, concentrated on the rotary evaporator at room temperature, poured into a 15% solution of ammonium hydroxide (150 mL), extracted with light petroleum ether, washed with water, dried over magnesium sulfate, evaporated and decolorized by passing through a short silica gel column using light petroleum ether as the eluent. Yield 0.352 g (66.3%), colorless liquid: ^{1}H NMR (500 MHz, C_6D_6) δ 0.53 (s, 3H), 1.26 (s, 3H), 1.40 (m, 1H), 1.74 (m, 3H), 1.99 (m, 2H), 5.85 (dd, $J=7.3$, 2.7 Hz, 2H), 5.91 (m, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 16.70, 16.77, 17.17, 27.15, 33.39, 47.75, 120.91, 127.52; λ_{max} 250 nm; IR, cm^{-1} (neat) 3026, 2949, 2871, 1640, 1452, 1374, 1385, 757; HRMS calcd for $C_{12}H_{16}$ 160.1252, found 160.1298.

   Dimethylcarbene trapping experiments

   Solutions of 10,10′-dimethyltricyclo[4.3.1.0^{1,6}]deca-2,4-diene (3–6 mg) in dry deoxygenated solvents (0.25 mL) under argon were irradiated with 254 nm light in a rayonet reactor at 4–8°C until complete conversion of the starting material as confirmed by GC (2–26 h). Yields of dimethylcarbene were determined from calibrated GC data by measuring the yield of indane formed upon irradiation.

Yields of insertion products were based on the yield of dimethylcarbene as calculated from the GC data using calibration with the corresponding reference compounds purchased from Aldrich.

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