

Solvent Perturbs the Reactivity of *tert*-Butylcarbene¹

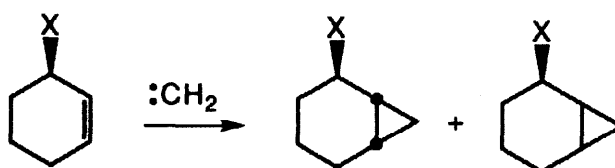
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Abstract: Two different sources of *tert*-butylcarbene are used to generate this reactive intermediate in a variety of solvents. Two products, 1,1-dimethylcyclopropane and 2-methyl-2-butene are formed. Solvents able to form an ylid or complex with the carbene strongly favor the alkene product. © 1998 Elsevier Science Ltd. All rights reserved.

The determination of the influence of complexation with nucleophiles on the intermolecular chemistry of carbenes has been the object of much effort, but has been attended by only sporadic hints of success. The most impressive result is that of Tomioka, Ozaki, and Izawa, who discovered that 1,4-dioxane altered the ratio of insertion of phenylcarbene into the O-H bonds of pairs of alcohols, and changed the ratio of addition to insertion when mixtures of alkenes and alcohols were used.² Other ethers were without substantial effect. More typical are the results of DeLuca, *et al.*, who needed heroic efforts to uncover small differences in the *syn/anti* ratio when methylene was allowed to react with cyclohexenes such as **1**.³ Here we report systematic solvent-induced changes on the intramolecular chemistry of *tert*-butylcarbene.



1, X = OCH₃, Cl

That ylids are formed from carbenes and all manner of heteroatom-containing molecules is not in doubt, as many rearrangements, fragmentations, and other reactions have been detected.⁴ Indeed, Ando and his coworkers have even isolated a number of stable sulfur ylids from reactions of carbenes.⁵ Platz, Jackson, and others have used the capture of carbenes by pyridine to visualize "invisible" carbenes through ylide formation and provide much quantitative data on carbene reaction rates.⁶ The trick is apparently to find the right balance; unstabilized carbenes such as methylene form weakly bound⁷ complexes that can reveal little, as no intramolecular reaction is possible in the old carbene fragment. On the other hand, the carbenes substituted with the anion-stabilizing groups that are typically used apparently produce too-stable ylids; further intermolecular reaction is not observed, and the substitution pattern has left little chance for intramolecular chemistry to occur in the old carbene fragment.

We have studied intramolecular reactions of *tert*-butylcarbene, 2, in a variety of nucleophilic solvents and found dramatic changes in product ratio. Duplicate runs lead to differences of no more than 3% in the ratios. In this case, apparently, intramolecular reaction of the ylid (or complex) competes successfully with free carbene chemistry. We have used two sources of 2, the hydrocarbon 3 and thermal decomposition of *tert*-butyl diazomethane, 4. Photolysis of *tert*-butyl diazomethane leads to much intramolecular reaction of the excited diazo compound, but the thermal reaction appears to give the carbene quite cleanly.⁸ Little difference between the products formed from 3 and 4 is found (Table).

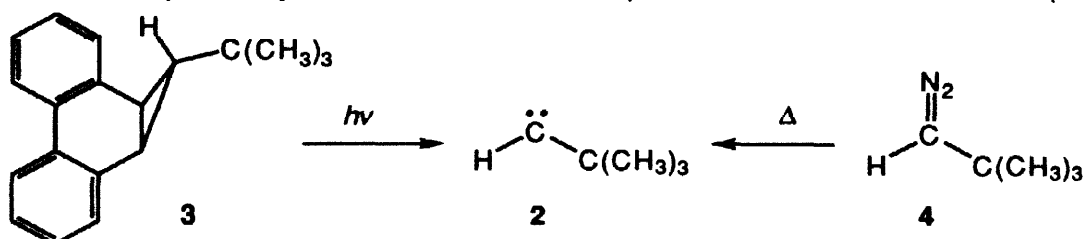
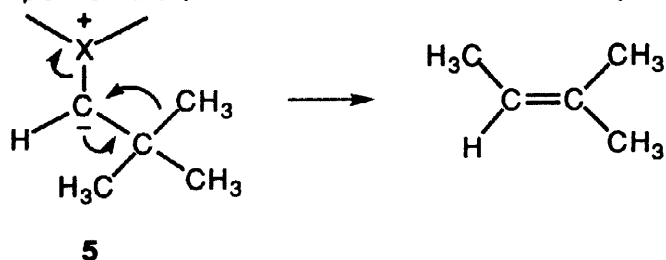


Table. Products from *tert*-Butylcarbene in Various Solvents

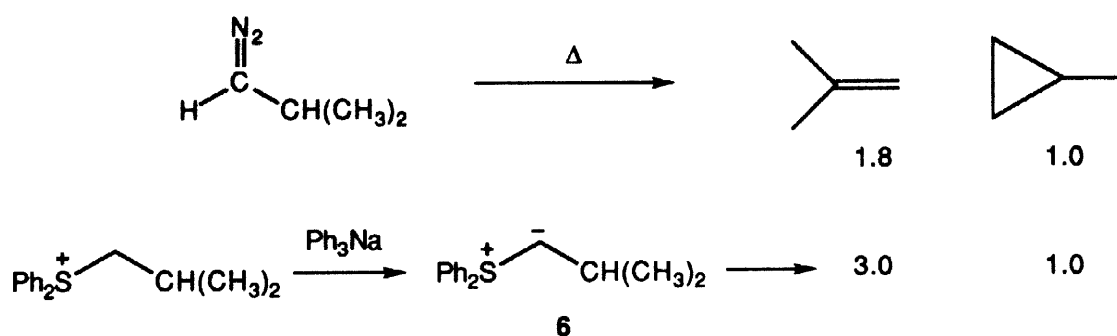
entry	solvent	carbene source	cyclopropane	alkene
1	decane	3, $h\nu$	90	10
2	decalin	4, 130 °C	89	11 ^{7a}
3	cyclohexene	3, $h\nu$	85	15
4	cyclohexene	3, $h\nu$	90	10 ^{7b}
5	<i>tert</i> -butylbenzene	3, $h\nu$	80	20
6	α,α,α -trifluorotoluene	3, $h\nu$	81	19
7	toluene	3, $h\nu$	77	23
8	benzene	3, $h\nu$	71	29
9	cyclohexylamine	3, $h\nu$	66	34
10	THF	3, $h\nu$	59	41
11	THF	4, 125 °C	58	42
12	anisole	3, $h\nu$	61	39
13	anisole	4, 125 °C	55	45
14	benzonitrile	3, $h\nu$	63	37
15	benzonitrile	4, 125 °C	51	49
16	acetonitrile	3, $h\nu$	53	47
17	pyridine	3, $h\nu$	50	50
18	DMF	3, $h\nu$	40	60
19	PhN(CH ₃) ₂	3, $h\nu$	51	49
20	PhN(Bu) ₂	3, $h\nu$	73	27
21	HN[CH(CH ₃) ₂]	3, $h\nu$	63	37
22	CH ₃ CH ₂ N[CH(CH ₃) ₂]	3, $h\nu$	80	20
23	dibutyl ether	3, $h\nu$	79	21

tert-Butylcarbene gives two products, 1,1-dimethylcyclopropane through carbon-hydrogen insertion and 2-methyl-2-butene through carbon-carbon insertion.⁹ In decane, at room temperature, their ratio is 90:10 (entry 1, Table). We reproduce earlier work in alkanes exactly (entry 2). In cyclohexene, the ratio drops to 90-85:10-15 (entries 3,4), and in several aromatic solvents, the ratio is between 71:29 and 81:19 (entries 5-8). The amount of 2-methyl-2-butene climbs sharply to ca. 40% when many solvents containing lone pair electrons are used (entries 9-15), and still further to ca. 50-60% in DMF, pyridine, or acetonitrile (entries 16-18).

We suggest that a series of ylids **5** is formed, and leads to 2-methyl-2-butene through a process resembling the Wolff, Curtius, or another of this well-known series of related rearrangements.¹⁰ Notice that there is no correlation with dipole moment (entries 5 and 6) or dielectric constant (entries 17 and 19). On the other hand, if the amount of 2-methyl-2-butene depends on ease of complex formation, then steric effects should influence the product ratio, and they do.



For examples, see entries 19 and 20, dimethylphenylamine (51:49) and dibutylphenylamine (73:27), or entries 21 and 22, diisopropylamine (63:37) and diisopropylethylamine (80:20).¹¹ In each case the sterically more encumbered amine leads to the smaller percentage of alkene, and the case for ylids or complexes is strengthened. There is at least one suggestive reaction in the literature that indicates that our interpretation may be correct. When isobutyl diazomethane is decomposed thermally (140-180 °C) in hexadecane, isobutene and methylcyclopropane are formed in a ratio of 1.8:1.¹² When ylid **6** is formed in dipentyl ether, the ratio changes to 3:1.¹³ The percentage of alkene is increased. In the original paper,¹³ a carbene was proposed, but the same intermediate(s) cannot be involved in both reactions. Were the sulfonium ylid **6** to undergo the Wolff-like rearrangement we propose, this time of hydrogen, the "extra" alkene becomes understandable.



The solvents chosen were picked so as to make the usual reactions of ylids formed from carbenes, alkyl migration and fragmentation,⁴ impossible, or at least unfavorable. When *tert*-butylcarbene is generated in dibutyl ether, such reactions should return. Once again, they do, as butyl neopentyl ether¹⁴ is formed. If the steric explanation proposed earlier is correct, the ratio of cyclopropane to alkene in dibutyl ether should be higher than that found in THF. As entries 10, 11, and 23 show, it is.

Is the intermediate we propose, 5, better described as an ylid as written, or a "long range complex,"⁶ as has been suggested? Surely the effect of the simple aromatic substrates is best described in terms of a complex, but the situation is less clear with the stronger nucleophiles. It seems that such a question is best resolved by resuming the theoretical investigation of these reactions and reactive intermediates.

We find that alkenes have little or no effect on the intramolecular chemistry of 2 (entries 3, 4), although aromatic compounds are more effective. There has been a dispute over the role of alkene complexes when diazo compounds or diazirines are photolyzed in alkenes.¹⁵ Our evidence would indicate that, at least in this case, alkenes produce little effect. Nor do our complexes seem competent to cyclopropanate alkenes. We are neither able to trap *tert*-butylcarbene in neat alkene, nor in alkene-THF mixtures.

References:

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