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CYCLOPROPYLPHENYLCARBENE - THERMAL CONTROL OF INTERMOLECULAR ADDITION

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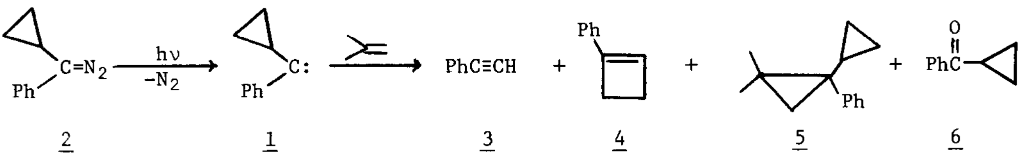
Summary. At 25°, photolytically generated cyclopropylphenylcarbene affords phenylcyclobutene (63%, by ring expansion), phenylacetylene (16%, by fragmentation), and only traces (<3%) of the adduct to isobutene; at lower temperatures, however, the latter compound becomes the major product.

It has been reported that cyclopropylphenylcarbene (1) generated photolytically from diazoalkane 2 in "unsaturated hydrocarbons [at 25°] resulted in nearly quantitative conversion into 1-phenylcyclobutene" (3).[1] We find, however, that intermolecular additions of 1 become prominent and, at least in one case, dominant reactions at lower temperatures.

Cyclopropylphenyldiazomethane[2] was irradiated (Rayonet reactor or Oriel focussed lamp, NH_3-washed Pyrex vessels, $\lambda>3000$ nm) in isobutene at various temperatures. A preparative run (5.1 mmol of 2 in 15 ml of isobutene and 1.5 ml of pentane) at -77° afforded four products, isolated by gc on Carbowax 20M at 150°; eq. (1). Products 3,[3] 4,[1,4] and 6 were identified by nmr spectroscopy and (3 and 6) comparisons to authentic samples. Major product 1,1-dimethyl-2-cyclopropyl-2-phenylcyclopropane, 5, was characterized by a satisfactory elemental analysis and its definitive nmr spectrum.[5]



(1)

Table I records mean absolute product yields for reaction (1) at various temperatures, as well as mean values of the ratios of intramolecular rearrangement to intermolecular addition [4/5]. Yields of ketone 6 were quite low when $T \geq -40°$, but rose to ~8% at -77°. Accordingly, reaction mixtures for $T \leq -77°$ runs were degassed before irradiation. Photolyses were generally carried to completion (bleaching of the red color of 2); interrupted reactions, quenched with maleic anhydride, afforded similar 4/5 ratios.[6]

Yields of 3 and 4 decrease, whereas that of 5 increases as solution reaction temperatures are lowered. The 4/5 distribution shifts by an overall factor of ~94, from strongly in favor of 4 (25°) to moderately in favor of 5 (-128°). These trends are reversed at -150° and -196°, with 4 once again dominant. In -196° (matrix) reactions, we suspect that mobility restrictions imposed upon the carbene[7] disfavor intermolecular addition, relative to intramolecular rearrangement.[8] A similar phenomenon may operate in the -150° runs, where crystallites of isobutene (mp -140°) doped with 2 may exist in suspension in propane. Importantly, we observed no *new* products in the -196° matrix reactions, so that 1 differs markedly from phenylmethylcarbene,[8] diphenylcarbene,[9] and fluorenylidene,[10] all of which afford mainly abstraction-recombination intermolecular products in -196° isobutene matrices.

Analysis of the 4/5 ratios (Table I) reveals a satisfactory Arrhenius relation between ring expansion and addition reactions: ln[4/5] vs. 1/T is linear for the 7 solution points, r = 0.965, significant at the 99.9% confidence level, with slope ($\Delta E^a_{apparent}$) = -1.34 kcal/mol. This suggests that the partition between 4 and 5 results from competitive reactions with different activation energies. We can readily conceive of three competitive situations.

(a) Products 4 and 5 arise from competitive intramolecular and intermolecular reactions of singlet 1. The data require E^a for ring expansion to exceed E^a for addition by ~1.3 kcal/mol. This is not impossible, but we note that $E^a_{expansion}$ itself should be quite low; a value of 3.8 kcal/mol has been calculated for the parent singlet cyclopropylcarbene.[11]

(b) Cyclobutene 4 stems from ring expansion of singlet 1, whereas 5 mainly forms from addition reactions of *triplet* 1. Ring expansion can certainly be associated with singlet 1.[11] Moreover, the ground states of phenylcarbene[12] and (probably) cyclopropylcarbene[11,13] are triplets, so that the ground state of 1 may well also be triplet. If an equilibrium is rapidly established between singlet and triplet 1,[14] then as long as the ΔE^a between triplet addition and singlet ring expansion is less than the difference in energy between singlet and triplet 1, addition will gain, relative to expansion, as temperature decreases; the increase in triplet population will more than offset the higher activation energy needed for addition.

To test triplet involvement in the formation of 5, diazoalkane 2 was photolyzed in *trans*- and *cis*-butene at -77°. Phenylcyclobutene was the major product in both cases,[15] but the appropriate cyclopropanes were also formed.[16] Addition of 2 to *trans*-butene was stereospecific, but *cis*-butene afforded 7.5% of the *trans*-butene adduct (relative to the total of cyclopropane products). Diazoalkane 2 was also photolyzed in *trans*-dichloroethene (diluted with pentane) at -40° and -65°. Gc and nmr analyses indicated the formation of cyclopropanation product but *not* of the rearranged olefins (*i.e.*, RR'C = $CHCHCl_2$) anticipated for triplet additions to dichloroethene.[17] Finally, we note again the absence of abstraction-recombination product from 1 and

Table I. Products from the Photolysis of Diazoalkane 2 in Isobutene[a]

Temp. (°C)	Runs	Yield (%)[b]				Total yield of volatiles	[4/5][c]
		3	4	5	6		
25	2	16	63	2.8	2.5[d,e]	86[d]	22.5 ± 1.1
0	3	16	57	4.8	2.7[d,e]	89[d]	11.9 ± 0.4
-18	2	16	52	7.4	3.3[d,e]	85[d]	7.1 ± 0.2
-40	2	12	52	15	4.9[d,e]	90[d]	3.4 ± 0.05
-77	3+5[f]	3.9	27	34	1.9[g]	69	0.76 ± 0.08
-95	1	7.0	18	39	1.7[g]	66	0.46
-128	3	4.4	10	42	3.3[g]	60	0.24 ± 0.003
-150[h]	3	1.3	9.9	3.4	3.0[g]	18	3.1 ± 0.9
-196[i]	2	j	j	j	j	j	9.0 ± 0.5

[a] Photolyses were carried out on solutions of 90 mg of 2 in 10-11 g of isobutene. Quantitative gc analysis: 2 m x 6.35 mm, 5% Carbowax 20M on 60/80 GCR column, 125° (inj., 115°; det., 170°), He flow, 50 ml/min. Retention times (min) were: 3, 5; 4, 14; 5, 16.8; and naphthalene (internal std.), 28. Ketone 6 was eluted by temperature programming (20°/min to 200°) after elution of naphthalene. Absolute yields of volatiles were determined against naphthalene by gc integration. Relative peak areas (corrected for detector response) were reproducible to 2-4%. [b] Mean values of absolute yields of the indicated number of reactions. [c] Mean values of [4/5] yield ratios of all reactions at this temperature; errors are average deviations. [d] Single experiment. [e] Reaction mixture not degassed. [f] Three experiments were photolyzed to completion; 5 experiments were interrupted at various times. Yields are based only on completed experiments, but the reported [4/5] ratio is an average of all 8 experiments. [g] Reaction mixtures were freeze-thaw degassed. [h] Samples were diluted with 38-40% (wt.) of propane. [i] Solid matrix of isobutene. [j] Absolute yields were not determined.

isobutene [*i.e.*, *c*-$C_3H_5PhCHCH_2C(CH_3)=CH_2$] under *any* of the reaction conditions of Table I, despite the rather typical formation of such products from triplet arylcarbenes and alkenes at very low temperatures or in olefinic matrices.[8-10,21]

The overall weight of evidence does not seem to support a *mainly* triplet origin for the adducts of **1**. The observed non-stereospecificity in addition to *cis*-butene is in keeping with some triplet intervention at -77°, but the data do not permit us to quantify this. The lack of olefin formation from **1** and dichloroethene, together with the absence of abstraction-recombination product in the matrix experiments, suggest that triplet involvement is limited.

(c) Finally, there is the possibility that **4** arises largely by rearrangement of photoexcited singlet **1**, whereas **5** stems from addition of conventional singlet **1** (and perhaps some triplet **1**). Presently, there is no evidence for or against these suggestions, but we note recent invocations of excited state participants in such typical carbene reactions as intramolecular insertion,[18] 1,2-dimethyl migration,[19] and even intermolecular addition.[20] We are continuing our studies of cyclopropylphenylcarbene, hoping to further clarify the mechanistic details of its chemistry.

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(15) The gc ratios (conditions of Table I) of **4** to addition products were 1.9:1 (*trans*-butene) and ~5:1 (*cis*-butene). *Cis*-butene afforded a pair of *syn*-phenyl and *anti*-phenyl cyclopropane isomers in a distribution of 1.3:1.

(16) These cyclopropanes were characterized by acceptable elemental analyses and structurally consistent nmr spectra.

(17) Reaction of $^3Ph_2C$ with *trans*-dichloroethene gives mainly $Ph_2C=CHCHCl_2$, as well as a cyclopropane: P. P. Gaspar, B. L. Whitsel, M. Jones, Jr., and J. B. Lambert, *J. Am. Chem. Soc.*, in press.

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(21) A referee has asked whether the low temperature reactivity of **1** differs significantly from that of $PhCCH_3$.[8] Key differences include: the absence of abstraction-recombination (a-r) products from **1** and isobutene in an isobutene matrix at -196°C, whereas a-r is the dominant intermolecular process of $PhCCH_3$ under these conditions. Also, $PhCCH_3$ adds to isobutene with ~constant efficiency from -40° to -120°C,[8] whereas the addition efficiency of **1** increases 14-fold (relative to ring expansion) over a comparable temperature range.

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