uct by column chromatography, it was dissolved in $CDCl_3$ and shaken repeatedly with deuterium oxide to ensure N-deuteration. The NMR spectrum of the resulting product no longer displayed any signals at 2.1 and 5.15 ppm, but the position and intensity of the other bands for **9** were unchanged. The results confirm that the acetylenic and amide protons of **9** were abstracted during the reaction with *n*-butyllithium, but that the allylic and vinylene protons were not. Consequently, no epimerization had occurred at the allylic C_3 and C_5 positions of the cyclopentene ring and, therefore, the sulfonamido and ethynyl groups in **9** are cis to each other.

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Registry No.—2, 42082-52-0; **6,** 53112-02-0; **7,** 58191-30-3; **8,** 58191-31-4; **9,** 58191-32-5; **10,** 58191-33-6; potassium *tert*-butoxide, 865-47-4; lithium aluminum hydride, 16853-85-3; pyridine-d_5, 7291-22-7; butyllithium, 109-72-8; methyllithium, 917-54-4.

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Carbene Multiplicity in Decompositions of 2-Methyl-2-phenyldiazopropane

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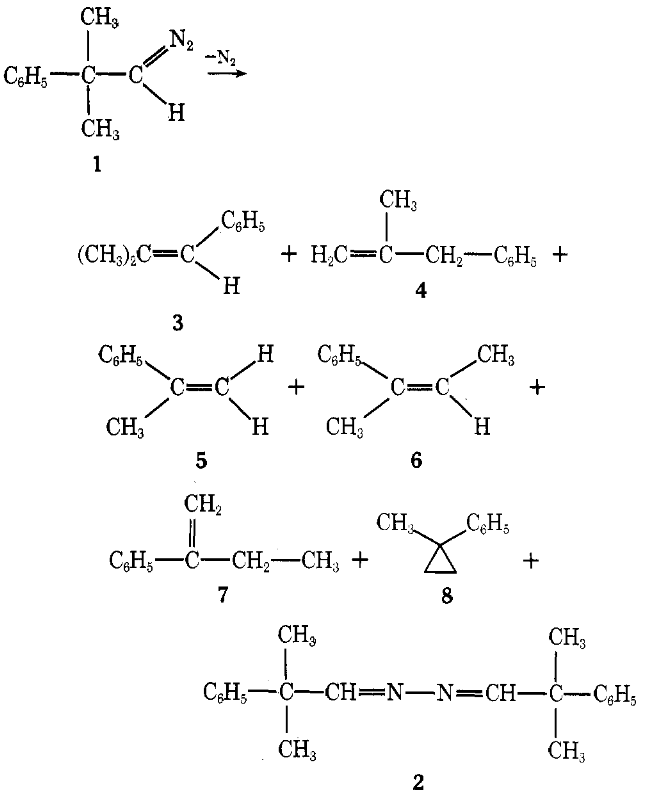
The literature of chemistry contains many examples of carbenes whose singlet and triplet states exhibit different chemical reactions.[1] A classical example of this phenomenon is seen in the addition of carbenes to cis or trans olefins. Singlet carbenes add predominantly stereospecifically, whereas triplet carbenes form cyclopropanes in a nonstereospecific manner.[2]

Some intramolecular carbene reactions are also dependent upon carbene multiplicity. When competing reactions are available, the rearrangements of hydrogen atoms[3] and phenyl groups[4] proceed more favorably to singlet rather than triplet carbenes. However, the experimental evidence does not exclude some triplet contribution to these rearrangement processes.

The carbene produced by the decomposition of 2-methyl-2-phenyldiazopropane (**1**) is suited to the study of three competing intramolecular reactions: phenyl rearrangement, methyl rearrangement, and C–H insertion. The thermal decomposition of **1** in dry hexane at 59 °C has been reported[5] to yield an azine ($C_{20}H_{24}N_2$), **2**, and six products of formula $C_{10}H_{12}$: 2-methyl-1-phenylpropene (**3**); 2-methyl-3-phenylpropene (**4**); *cis*-2-phenyl-2-butene (**5**); *trans*-2-phenyl-2-butene (**6**); 2-phenyl-1-butene (**7**); and 1-methyl-1-phenylcyclopropane (**8**). Products **3** and **4** are formed by phenyl rearrangement; olefins **5**, **6**, and **7** are methyl migration products; and cyclopropane **8** is a product of intramolecular C–H insertion. The object of the present study was to determine how the relative yields of these products might be affected by reaction conditions which would selectively favor carbene reaction from either the singlet or triplet state.



The ground state of alkylcarbenes appears to be the triplet.[6] However, the thermal or direct photochemical decomposition of diazoalkanes initially produces the excited singlet state of the carbene.[1] Methods of inducing triplet behavior in the carbene include the use of triplet photosensitizers to directly produce the triplet carbene, and the use of heavy atom solvents to quench the initially formed singlet to the ground state triplet.[7] The products of the decomposition of **1** under varying reaction conditions are summarized in Tables I and II.

While the origins of individual products in Table II are open to speculation, certain trends in migratory aptitudes and C–H insertion are evident. In comparing thermal decompositions I and II with reaction III, it is seen that the use of a heavy atom solvent decreases the relative amounts of methyl rearrangement and cyclopropane formation. The same trend is noted when comparing direct photolysis IV with photosensitized decompositions V and VI. Triplet sensitization increases phenyl migration at the expense of the competing intramolecular processes.

It is possible that phenyl rearrangement, methyl rearrangement, and C–H insertion all proceed to both the singlet and triplet states of the carbene. In any case, reaction conditions which favor triplet carbene production decrease the relative rates of methyl migration and C–H insertion while increasing the relative rate of phenyl rearrangement. The distinction between singlet and triplet behavior may be blurred by rapid intersystem crossing.[4b]

Tetraphenylethylene-catalyzed diazo decompositions have recently been reported by Ho, Conlin, and Gaspar.[8] The relative product yields of the tetraphenylethylene-catalyzed decomposition of **1** (reactions VII and VIII) resemble product yields from triplet carbene reactions (III, V, and VI) more closely than they resemble singlet carbene product yields (I, II, and IV). An explanation for this obser-

Table I. Reaction Conditions and Product Yields from Decompositions of 2-Methyl-2-phenyldiazopropane

Reaction no.[a]	Solvent	Temp, °C	Additive	Mode of decomposition	% N_2[b]	% $C_{10}H_{12}$[b]	% azine[b]
I	Hexane	69	None	Thermal	67	52	30
II	Benzene	69	None	Thermal	70	56	37
III	1-Bromonaphthalene	69	None	Thermal	78	57	c
IV	Benzene	25–29	None	Photolytic	64	54	38
V	Benzene	25–29	500% benzil	Photosensitized	66	48	c
VI	Benzene	25–29	500% fluorenone	Photosensitized	60	51	c
VII[d]	Hexane	−196 to 25	5% tetraphenylethylene	Catalytic	c	66	c
VIII[d]	Benzene	−196 to 25	10% tetraphenylethylene	Catalytic	c	62	c

[a] Averages of three to five reactions. Internal consistency among reactions was high. [b] Based on the amount of urethan used to prepare the diazo. [c] Not determined. [d] Degassed six times by freeze–pump–thaw.

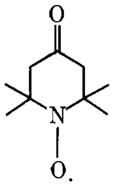
Table II. Relative Hydrocarbon Yields from Decompositions of 2-Methyl-2-phenyldiazopropane

Reaction no.	Relative yield, % 3	4	5	6	7	8	Ph~/Me~	Σ olefins/ cyclopropane
I	32.4	10.4	3.6	2.5	2.4	48.6	10.1	1.1
II	42.4	12.5	6.1	2.3	2.5	34.2	10.1	1.9
III	56.8	20.9	4.1	1.9	1.6	14.7	20.4	5.8
IV	25.7	25.6	9.7	6.3	4.4	28.3	5.0	2.5
V	49.9	22.1	2.9	2.3	2.8	20.0	18.0	4.0
VI	66.4	19.2	1.9	2.4	3.3	6.8	22.5	13.7
VII	66.0	6.8	3.7	1.5	1.3	20.7	22.4	3.8
VIII	51.0	12.8	4.8	2.0	1.7	27.7	15.0	2.6

[a] Ph~/Me~ = (3 + 4)/(5 + 6 + 7) ÷ 2.

vation may lie in the initial formation of a diazo–tetraphenylethylene charge-transfer complex, which subsequently dissociates to nitrogen, the triplet carbene, and triplet tetraphenylethylene (a spin conserving process). Tetraphenylethylene is an efficient triplet quencher (effective E_T = 45.4–47.3 kcal).[9]

Another method which was used to attempt to induce triplet carbene behavior was thermolysis of 1 in hexane at 69 °C in the presence of 10 mol % of the stable free radical, 4-oxo-2,2,6,6-tetramethylpiperidinooxy (9). It was expected that the stable free radical would promote spin inversion to form the ground state triplet carbene. Experimentally, the presence of the free radical had no effect upon absolute product yields or relative hydrocarbon yields (reaction I).



9

Experimental Section

2-Methyl-2-phenyldiazopropane (1) was prepared by the reaction sequence outlined by Hogan and Keating (urethane → *N*-nitrosourethane → diazo).[5,10] Diazo solutions were approximately 0.1 M for all decompositions. The NMR spectrum of the diazo solution (in benzene) shows no absorptions due to vinyl or cyclopropyl protons. NMR and ir spectroscopy indicate that conversion of the *N*-nitrosourethane to the diazo is quantitative. Reactions were performed under nitrogen in rigorously dried solvents. Photolytic and photosensitized reactions were carried out according to the procedures of Pomerantz and Witherup.[7] The tetraphenylethylene-catalyzed decomposition was induced by degassing through six freeze–pump–thaw cycles.[8]

In general, reactions were worked up by rotary evaporation of most of the solvent, removal of $C_{10}H_{12}$ materials under high vacuum, and recrystallization of the residual azine, 2, from hexane (mp 68–70 °C). Authentic samples of olefinic products 3–7 were prepared by dehydration of appropriate alcohols. Cyclopropane 8 was prepared by the Simmons–Smith procedure.[11] All products were stable to the conditions of reactions and analysis.

Hydrocarbon products were analyzed by VPC on a 15-ft column of 20% diethylene glycol succinate at 110 °C. Known amounts of isopropylbenzene were added to the hydrocarbon product mixtures as an external standard for determination of $C_{10}H_{12}$ yields. Retention times of the standard and products follow: isopropylbenzene, 7.3 min; 6, 10.5; 4, 11.6; 8, 12.6; 7, 13.9; 3, 16.1; and 5, 20.2. The relative molar VPC response of each $C_{10}H_{12}$ product was determined by VPC collection of the individual products and reinjection of each product as a mixture of known composition with isopropylbenzene. The relative molar VPC responses of all $C_{10}H_{12}$ products were nearly identical (1.05 ± 0.01 vs. isopropylbenzene standard as 1.00).

In several control experiments, a known amount of isopropylbenzene was added to a crude reaction mixture before work-up. VPC analysis before solvent removal, after solvent removal, and after high vacuum pumping showed that no appreciable changes in $C_{10}H_{12}$ absolute or relative yields occurred during work-up.

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Registry No.—**1**, 19217-61-9; **2**, 58208-01-8; **3**, 768-49-0; **4**, 3290-53-7; **5**, 768-00-3; **6**, 767-99-7; **7**, 2039-93-2; **8**, 2214-14-4.

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