

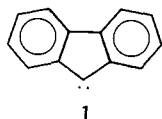
Chemistry of Fluorenylidene at Low Temperatures

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Abstract: Photolyses of 9-diazo fluorene were carried out in isobutene, *cis*-2-butene, and *trans*-2-butene at 0, -77, -100, -160, and -196 °C. In all cases, the products included the dimethylspiro[cyclopropane-1,9'-fluorene(s)] and the 9'-fluorenylalkene(s) appropriate to the addition and abstraction-recombination reactions, respectively, of fluorenylidene (**1**) with the substrate butene. For each substrate, the cyclopropane/9'-fluorenylalkene product ratio was studied as a function of temperature. In all cases, the relative yields of the 9'-fluorenylalkenes markedly increase at low temperatures. It is concluded that generation at low temperature favors reactions of triplet **1**, relative to those of singlet **1**, and that the energetically preferred reaction of triplet **1** with butenes is abstraction of allylic hydrogen, rather than addition to the double bond. The reaction of **1** with [1-¹³C]-2-methylpropene at 77 K was shown to afford 2-methyl-3-(9'-fluorenyl)propene with equal amounts of ¹³C at C(1) and C(3).

The triplet ground state of fluorenylidene (**1**) has been observed by electron spin resonance,¹ ENDOR,² and spin-



trapping techniques.³ Generated by the ambient-temperature photolysis of 9-diazo fluorene in solution, however, **1** behaves as a nonequilibrium mixture of singlet and triplet species. In contrast to the structurally related diphenylcarbene, for which singlet-triplet equilibration has been suggested to be faster than reactions of the carbene with C=C or C-H bonds,⁴ the rate of equilibration of fluorenylidene states is either slower than or comparable with the rates of many intermolecular reactions of the singlet. Consequently, in addition to alkenes, the relative yields of singlet and triplet addition products can be altered by dilution with hexafluorobenzene, which enhances triplet addition by affording an opportunity for singlet-triplet transitions secondary to molecular collisions of low productivity, or by dilution with 1,3-butadiene, which enhances singlet addition by selectively scavenging triplet fluorenylidene.⁵

Singlet and triplet fluorenylidene can also be differentiated by reaction with 1,1-dicyclopropylethylene, where the singlet gives the anticipated cyclopropane, but the triplet additionally affords a rearranged diene via an intermediate 1,3 diradical.⁶ This partition is sensitive to dilution with decalin or benzene.

Fluorenylidene "inserts" into the secondary C-H bonds of cyclohexane⁷ and the allylic C-H bonds of cyclohexene.^{8,9} In large part, these reactions appear to proceed by triplet hydrogen abstraction-radical pair recombination, and, in the case of cyclohexene, addition to the double bond and allylic hydrogen abstraction are competitive.⁹

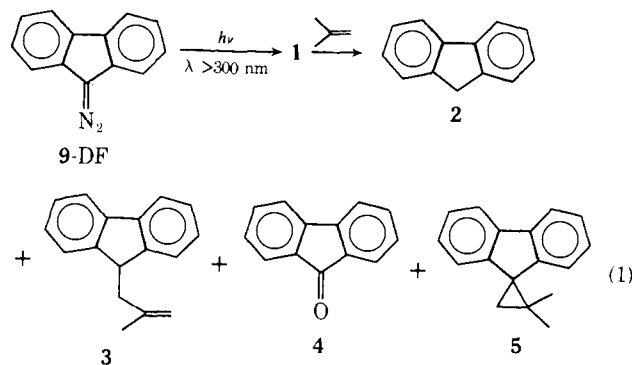
Until now, and despite the work of Baldwin and Andrist,⁸ the prevailing opinion has been "fluorenylidene, unlike diphenylcarbene, adds to π -systems without the complication of large amounts of hydrogen-abstraction".¹⁰ We were concerned that this generalization might only be applicable to ambient temperature reactions of **1**, because we had shown that abstraction reactions dominate addition reactions in the low temperature reactions of phenylcarbene,^{11,12} methylphenylcarbene,¹² and diphenylcarbene¹³ with simple alkenes. We therefore undertook a careful study of the reactions of **1** with *cis*-butene, *trans*-butene, and isobutene at temperatures ranging from 0 to -196 °C. Our enthusiasm was whetted by the suspicion that, because of its "slow" spin state equilibration,⁵ the temperature dependence of the reactions of **1** with

alkenes might be rather different from that of diphenylcarbene,^{4,13} for which spin state equilibration appears to be rapid relative to intermolecular reaction, and also different from the behavior of phenylcarbene,¹¹ for which rapid spin state equilibration has been suggested.¹⁴

The results, described below, demonstrate that the chemistry of **1** at low temperature does indeed involve a substantially enhanced triplet component, and that, in parallel with the behavior of other arylcarbenes,¹¹⁻¹³ the hallmark of low temperature triplet fluorenylidene chemistry is abstraction from rather than addition to alkenes.

Results

Photolyses in Isobutene. Dilute, degassed solutions of 9-diazo fluorene (**9-DF**) in isobutene, containing 13% (by weight) of dry diglyme were photolyzed in sealed Pyrex tubes ($\lambda > 300$ nm) according to the procedures detailed in the Experimental Section. GC analysis of the product mixture revealed the presence of fluorene (**2**), 2-methyl-3-(9'-fluorenyl)propene (**3**), fluorenone (**4**), and the anticipated cyclopropanation product, 2,2-dimethylspiro[cyclopropane-1,9'-fluorene] (**5**); cf. eq 1.



TLC analysis indicated the presence of fluorenone ketazine¹⁵ and bifluorenylidene.¹⁵ The identities of the latter compounds, as well as of **2** and **4**, were established by appropriate chromatographic comparisons with authentic samples. Cyclopropane **5** was isolated from a 0 °C photolytic experiment and identified by NMR and (exact) mass spectral determinations. Alkene **3** was identified by GC augmentation techniques, using an authentic sample prepared from 3-chloro-2-methylpropene and lithium 9-fluorenyl. Product distributions were determined by GC analysis using mechanical (Disc) integration, and appear in Table I.

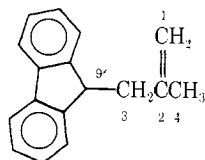
1-¹³C-labeled isobutene was prepared from acetone and triphenylphosphonium [¹³C]methylide and contained 12.4 ±

Table I. Product Distributions. Photolysis of 9-DF in Isobutene^a

Temp, °C	2	3	4	5	3/5
0 ^b	1.9	3.8	1.4	94.3	0.040
-77 ^c	tr ^d	6.0	1.9	94.0	0.064
-100 ^e	tr ^d	1.4	1.3	98.5	0.014
-160 ^{f,g}	6.3	8.4	11.6	85.2	0.098
-196 ^{f,h}	2.6	38.9	4.5	58.4	0.67

^a Data are averaged percent (based on duplicate runs) of products **2**, **3**, and **5**, normalized to 100%; the percent yield of fluorenone, **4**, is based on a *separate* normalization including **4**. ^b Average deviations were 0.0, 0.0, 0.4, and 0.0. ^c Average deviations were —, 0.2, 0.0, and 3.0. ^d Trace implies <1%. ^e Average deviations were —, 0.2, 0.5, and 0.2. ^f Solid matrix. ^g Average deviations were 1.1, 1.4, 0.5, and 2.3. ^h Average deviations were 0.8, 1.4, 3.3, and 2.2.

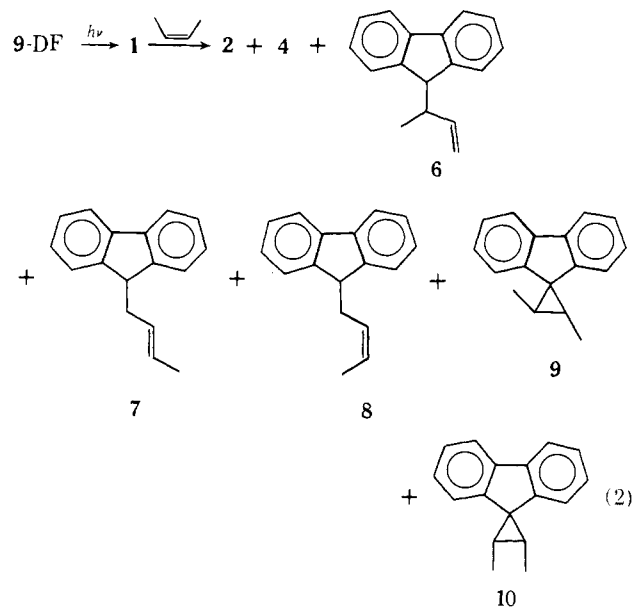
0.2 at. % ¹³C at C(1), according to integration of the H₂C(1) parent and satellite signals in its ¹H NMR spectrum. 9-DF was irradiated in the labeled isobutene for 30 h at -196 °C. After a normal workup, the ¹³C NMR spectrum of the product mixture was determined and compared with that of the pure alkene, **3'**, which exhibits (inter alia) absorptions at δ^{Me₄Si} 113.3



(C(1)), 143.4 (C(2)), 42.16 (C(3)), 22.54 (C(4)), and 44.88 (C(9')), with observed integral intensities of C(3) and C(1) in the ratio 1.05:1. In the spectrum of the photolysis product mixture obtained under identical spectrometer operating conditions, the signals of C(3) and C(1) were strongly enhanced, relative to the other absorptions of **3**, and were in the intensity ratio 1.00:1. No other ¹³C signals were within 5 ppm of these signals. Within a few per cent, then, the ¹³C label in carbene product **3** was equally distributed between C(1) and C(3).

The ¹³C NMR spectrum of a product mixture obtained by photolyzing 9-DF and normal isobutene at 0 °C (i.e., the product mixture was rich in **5**) was compared with the ¹³C NMR spectrum of pure **3**. Signals observed in the former spectrum did not overlap with the C(1) or C(3) resonances of **3**.

Photolyses in *cis*-Butene. Carried out as in the case of isobutene, these reactions afforded **2** and **4** as GC-detectable products, as well as 3-(9'-fluorenyl)-1-butene (**6**), *trans*-1-(9'-fluorenyl)-2-butene (**7**), *cis*-1-(9'-fluorenyl)-2-butene (**8**), *trans*-2,3-dimethylspiro[cyclopropane-1,9'-fluorene] (**9**), and *cis*-2,3-dimethylspiro[cyclopropane-1,9'-fluorene] (**10**); cf. eq 2. Products **6**, **7**, and **8** were identified by appropriate GC comparisons with authentic samples synthesized by reactions of lithium 9-fluorenyl with, respectively, 3-chloro-1-butene



and *trans*-crotyl bromide, and by a Wittig reaction of 9'-fluorenylacetaldehyde and the ylide derived from ethyltriphenylphosphonium bromide. Experimental details and spectral characterizations appear below.

Cyclopropanes **9**⁵ and **10**⁵ were GC collected from 0 °C photolytic runs and characterized by NMR and (exact) mass spectra. Isomer **10** was the major product of reaction 2 at 0 °C, as was previously reported for the 5 °C photolysis.⁵

The GC-determined product distributions appear in Table II for photolyses carried out at various temperatures. Fluorenone, though present, was not quantitatively determined in these reactions. Although there was poor reproducibility of alkene yields at -196 °C, there is no doubt that alkenes become the major products at this temperature. TLC analysis again revealed the presence of fluorenone ketazine and bifluorenylidene.

Photolyses in *trans*-Butene. Photolyses of 9-DF in *trans*-butene containing 13% (by weight) of diglyme were carried out similarly, and gave GC-detectable products which corresponded to those observed in the *cis*-butene reactions; cf. eq 2. Product identities were established by appropriate GC-augmentation experiments using authentic samples, and the product distributions as a function of temperature appear in Table III. Note that the reproducibility of the alkene distributions at -196 °C is quite satisfactory.

Relative Product Ratios. In discussing the product distributions cited in Tables I-III, it will be helpful to use relative yields in place of absolute yields, and, moreover, to employ them in semiquantitative estimates of rate constant ratios for competing reactions. We have chosen to use relative yields because the photolyses reactions are rather inefficient, particularly at low temperature, and the reactions were generally

Table II. Product Distributions. Photolysis of 9-DF in *cis*-Butene^a

Temp, °C	2	6	7	8	9	10	9	
							9 + 10	6 + 7 + 8 9 + 10
0 ^b	5.0	2.1	tr ^c	6.7	32.6	53.1	0.38	0.10
-77 ^d	tr ^c	1.1	tr ^c	4.0	41.5	53.5	0.44	0.054
-100 ^e	2.6	0.8	tr ^c	2.6	43.3	50.6	0.46	0.036
-160 ^{f,g}	10.0	5.7	3.3	18.4	22.7	35.7	0.39	0.47 ^h
-196 ^{f,i}	13.2	9.7	9.3	47.8	4.5	15.4	0.23	3.4 ^j

^a Data are averaged percent (based on duplicate runs) of products **2** and **6**-**10**, normalized to 100%. ^b Average deviations were 0.4, 0.1, —, 0.2, 0.2, and 0.7. ^c Trace implies <1%. ^d Average deviations were —, 0.0, —, 0.2, 0.1, and 0.3. ^e Single run. ^f Solid matrix. ^g Average deviations were 0.6, 1.1, 0.2, 2.0, 1.5, and 3.4. ^h 0.64, if **2** is included in numerator. ⁱ Average of six runs, with average deviations 4.0, 2.3, 7.6, 10.0, 0.7, and 1.9. ^j 4.0 if **2** is included in numerator.

Table III. Product Distributions. Photolysis of 9-DF in *trans*-Butene^a

Temp, °C	2	4	6	7	8	9	10	10		6 + 7 + 8	
								9 + 10	9 + 10	9 + 10	9 + 10
0 ^b	6.2	6.0	2.5	8.0	4.0	73.0	6.2	0.078	0.18		
-77 ^c	tr ^d	9.5	tr	3.3	tr	84.5	11.5	0.12	0.034		
-100 ^e	tr	9.0	tr	8.2	tr	86.5	5.2	0.057	0.089		
-160 ^{f,g}	7.5	17.2	4.9	34.5	4.9	41.1	7.0	0.15	0.92 ^h		
-196 ^{f,i}	3.1	<i>j</i>	5.2	67.	10.7	11.9	2.1	0.15	5.9 ^k		

^a Data are averaged percent (based on duplicate runs) of products **2** and **6–10**, normalized to 100%; the percent yield of fluorenone (**4**) is based on a separate normalization. ^b Average deviations were 0.9, 2.4, 0.3, 0.5, 0.2, 2.0, and 0.2. ^c Average deviations were —, 2.0, —, 0.7, —, 4.0, and 3.5. ^d Trace implies <1%. ^e Average deviations were —, 0.4, —, 0.4, —, 0.4, and 0.0. ^f Solid matrix. ^g Average deviations were 3.4, 0.0, 0.5, 0.8, 1.3, 0.3, and 0.5. ^h 1.1 if **2** is included in the numerator. ⁱ Average deviations were 0.2, —, 0.6, 0.3, 1.0, 0.3, and 0.1. ^j Quantitatively determined (in only one run) as 2.3%, based on a separate normalization. ^k 6.1 if **2** is included in numerator.

carried only to low conversions (<50%) before termination and destruction of the remaining diazofluorene with maleic anhydride (see Experimental Section).

The use of relative yields is justifiable, however, if *all* products of **1** and the olefins are accounted for in each reaction. We have carefully synthesized and identified all observed products of **1** and the three butene olefin substrates. In the GC traces used to generate the quantitative data shown in Tables I–III, *all* observed products of **1** and the butenes were determined and included in the normalizations upon which the relative distributions rest.

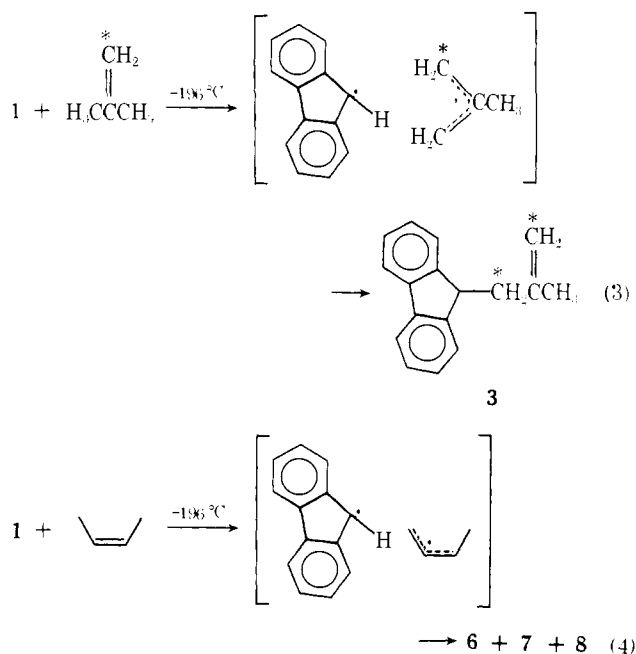
Discussion

The observed behavior of **1** toward *cis*- or *trans*-butene at 0 °C is in agreement with the description, by Jones and Rettig,⁵ of these reactions at 5 °C. Alkenes are minor products at 0 °C (cf. Tables II and III), and the extents of nonstereospecific cyclopropanation by **1** were 1.62 **10/9** from *cis*-butene and 0.085 from *trans*-butene, which compare reasonably well with 1.95 and 0.06, the corresponding reported⁵ product ratios.

Further reference to the tables, however, shows that the yields of fluorenylalkenes **3** (from isobutene) and **6–8** (from the 2-butenes) are markedly enhanced at low temperature, particularly at -196 °C. Alkene formation is strongly augmented in the low temperature reaction of **1** and isobutene; the ratio (**3/5**) increases from 0.04 at 0 °C to 0.67 at -196 °C (Table I). In the low temperature reactions of **1** with *cis*- or *trans*-butenes, fluorenylalkenes become the *major* products; the product ratio (**6 + 7 + 8**)/(**9 + 10**) increases from 0.10 or 0.18 (0 °C) to 3.4 or 5.9 (-196 °C), respectively. One notes that the major alkene product formed from either 2-butene corresponds to formal C-H "insertion" at C(1), with predominant retention of geometry at the double bond.

What is the origin of the fluorenylalkenes observed at low temperature? The reaction of **1** with ¹³CH₂=C(CH₃)₂ at -196 °C gave **3** in which the label was equally divided between C(3) and C(1) (see above). This is only consistent with an abstraction-recombination (a-r) mechanism for the formation of **3** (cf. eq 3) and implies that the **1** + *cis*- or *trans*-butene reactions proceed similarly at -196 °C (cf. eq 4).¹⁶ Analogous results have been obtained upon photogeneration of phenylcarbene in solid *cis*-butene at -196 °C.¹¹

The formation of 3-(9'-fluorenyl)cyclohexene in 54% yield from fluorenylidene and cyclohexene (at 17 °C) has been attributed to a triplet **1** initiated a-r reaction on the basis of labeling experiments which employed 3-deuteriocyclohexene as a substrate.⁸ If triplet **1** is indeed responsible for fluorenylalkene formation here, it is even more likely to be responsible for the formation of alkenes **3** and **6–8** in -196 °C olefinic matrices; the ground state of **1** is known to be a triplet and relatively stable in fluorolube glasses at -196 °C,¹⁷ making it reasonable to expect the formation of substantial amounts of triplet **1** in olefinic glasses at liquid nitrogen temperature.



Supportive analogies emerge from the work of Roth and Manion with acetylcarbene¹⁸ and vinylcarbene.¹⁹ Acetylcarbene, generated in cyclohexene-*d*₁₀ by the photosensitized decomposition of diazoacetone, afforded CIDNP spectra for product 3-acetylcyclohexene which supported a *triplet* a-r mechanism of formation.¹⁸ Presumably, an analogous mechanism holds for the formation of 3-allylcyclohexene via the photosensitized decomposition of vinyl diazomethane in cyclohexene.¹⁹

Accepting a triplet a-r mechanism for the formation of alkenes in the low temperature reactions between **1** and the butene olefins,²⁰ we must still inquire *how* the decrease in reaction temperature suppresses the ambient temperature addition reactions of **1** in favor of the low temperature a-r reactions. Two aspects must be considered: (a) the effect of decreasing reaction temperature alone; (b) possible matrix effects.

The reaction of diphenylcarbene and isobutene, for example, is also subject to a strong temperature effect,^{13,22} with the alkene/cyclopropane product ratio changing from 0.24 (0 °C) to 44.6 (-196 °C). In this case, the logarithm of the product ratio varies linearly with *T*⁻¹. Noting that singlet-triplet equilibration of diphenylcarbene is faster than reactions of the carbene with alkenes,⁴ analysis¹³ indicates that the activation energy for triplet abstraction is greater by ~2 kcal/mol than the activation energy for singlet addition. However, this difference is smaller than the energy difference between the singlet and triplet states of diphenylcarbene (≤3 kcal/mol⁴). Thus, as the reaction temperature is lowered, triplet abstraction gains, relative to singlet addition. Moreover, product ratios

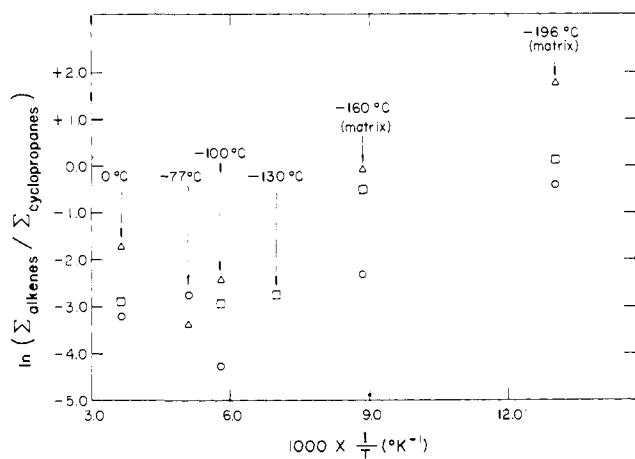


Figure 1. \ln (total alkene product/total cyclopropane product) for the reactions of fluorenylidene and isobutene (O), fluorenylidene and *trans*-butene (Δ), and phenylcarbene and *cis*-butene (\square) vs. T^{-1} (K^{-1}).

determined in either isobutene solutions or isobutene matrices obey the same Arrhenius relation, so that the shift from addition to abstraction products can be explained simply as a temperature effect, without recourse to a "matrix effect".^{23,24a}

The behavior of **1** and isobutene, however, is different. The logarithm of the product ratio (3/5) is not simply related to T^{-1} (cf. Figure 1) and this situation does not change appreciably if the yield of fluorene (counted as a triplet product) is added to the yield of **3**. Similar results obtain in the formation of **6-8** from the reactions of **1** with either *trans*-butene (Figure 1) or *cis*-butene (not illustrated), and in the formation of the analogous olefinic products from the reaction of phenylcarbene with *cis*-butene¹¹ (presented in Figure 1 for comparison).

To analyze these results, we must first ask whether there is a greater proportion of *total* triplet product formed at low temperature than at 0 °C, and then examine the *distribution* of triplet products as a function of temperature.^{24b} Studies of **1** reacting with *cis*-butene, diluted with hexafluorobenzene, indicate that triplet **1** affords **10** and **9** in the ratio 0.25:1 at 5 °C.⁵ If, in the reaction of *cis*-butene and **1** at 0 °C (Table II) we attribute the 32.6% **9** exclusively to triplet **1**, and consider that some of the 53% yield of cyclopropane **10** ($0.25 \times 32\% = 8\%$) also comes from triplet **1**, then $\sim 41\%$ of the total product represents triplet **1** derived cyclopropanes and $\sim 45\%$ represents singlet derived cyclopropanes. The remaining $\sim 14\%$ of the product (**2** + **6** + **8**) can be considered largely triplet derived,²⁰ making the overall triplet/singlet product ratio $\sim 55/45$ or ~ 1.2 . An analogous treatment of the 0 °C **1** + *trans*-butene data (Table III) gives a triplet/singlet product ratio of 51/49, or ~ 1.0 . These results agree with the estimate of Jones et al.⁹

Now, if similar product assignment analyses are applied to the -196 °C data of Tables II and III, assuming that the **10/9** distribution from triplet **1** and the 2-butenes remains 0.25/1, and counting fluorene (**2**) and alkenes **6-8** as triplet products, then the low temperature triplet/singlet product ratios are $\sim 85/15$ (~ 5.7) for **1** + *cis*-butene and $\sim 96/4$ (~ 24) for **1** + *trans*-butene. We conclude that the products formed at -196 °C reflect larger contributions of triplet **1** than the products formed at 0 °C.

Why is the triplet contribution enhanced at -196 °C? The rate of singlet-triplet interconversion of **1** is slower than or comparable with the rates of its intermolecular reactions with alkenes at 5 °C,^{5,25} and ambient temperature photolysis of **9-DF** affords $\sim 50:50$ mixtures of singlet and triplet **1**, with the triplet arising either from spin inversion of the photoexcited **9-DF** prior to nitrogen loss, or from spin inversion of singlet

1 competitive with its intermolecular reactions. It is tempting, but by no means unavoidable, to *postulate* the operation of a matrix effect in the -196 °C (and -160 °C) photolyses of **9-DF** in the butene olefins; viz., photolysis of **9-DF** initially leads to an approximately equal mixture of singlet and triplet **1**, but the singlet, restricted in the matrix, decays to triplet faster than it can react with the matrix. Accordingly, the triplet contribution to product formation would be enhanced at -196 °C.

Consider now the fates of triplet **1** at 0 and -196 °C. About 55% of **1** generated at 0 °C in *cis*-butene reacts as the triplet (see above) and affords mainly cyclopropanes **9** and **10**, rather than abstraction-initiated products, fluorene (**2**) and alkenes **6-8**; the abstraction/addition ratio, (**2** + **6** + **7** + **8**)/(**9** + **10**), for triplet **1** and *cis*-butene is ~ 0.34 at 0 °C. At -196 °C, however, the same ratio is ~ 14 . A similar analysis of the (more reliable) *trans*-butene data gives the triplet **1** abstraction/addition ratio as ~ 0.9 at 0 °C and ~ 8.6 at -196 °C. Clearly, the reactivity of triplet **1** toward the 2-butenes has changed from predominant addition at 0 °C to predominant abstraction at -196 °C.

A priori this could reflect either a "matrix effect" or a temperature effect. A consistent explanation can be constructed on the latter basis, however, so that there is *no need to invoke a matrix effect here*. In particular, if the activation energy for triplet addition of **1** to *cis*-butene marginally *exceeds* that for triplet abstraction by **1** from *cis*-butene,^{26a} but the ratio of preexponential factors, $A_{\text{addn}}/A_{\text{abstn}}$, is considerably larger than unity,^{26b} then addition of **1** will predominate at 0 °C, but abstraction reactions will predominate at -196 °C.

Indeed, from the "observed" triplet **1**-*cis*-butene abstraction/cyclopropanation ratios at 0 and -196 °C (0.34 and 14, see above), we estimate ($E_{\text{addn}}^a - E_{\text{abstn}}^a$) to be ~ 790 cal/mol and $A_{\text{addn}}/A_{\text{abstn}} \sim 12.7$. Similar estimates follow from the triplet **1**-*trans*-butene data.²⁷ Comparison of these values with the analogous triplet diphenylcarbene-*cis*-butene parameters²⁶ indicates that the two triplet carbenes are quite similar in competitive abstraction-addition reactions with *cis*-butene. We suggest that an energetic preference for abstraction rather than addition may be general in the reactions of arylcarbenes and aliphatic olefins.

The apparent gross reactivity differences between diphenylcarbene and **1** (e.g., the discontinuities observed in graphs of \ln (abstraction/addition) vs. T^{-1} for **1**; cf. Figure 1) are largely traceable to the absence of rapid singlet-triplet equilibration in the latter case. Once this is circumvented, the two systems are seen to behave similarly. In cases where spin equilibration is faster than available intermolecular reactions, a matrix effect of the kind suggested for **1** (above) would be by-passed, but it might then be necessary to postulate a *second* kind of matrix effect to rationalize the phenylcarbene-*cis*-butene matrix photolysis¹¹ in which, assuming spin state equilibration to be rapid at ambient temperatures,¹⁴ there appears to be a matrix-induced enhancement of triplet a-r products at the expense of singlet addition; cf. Figure 1. We have previously suggested a *modus operandi* for such a matrix effect.¹²

It is, perhaps, worth noting that, if the proposal of rapid spin state equilibration for phenylcarbene were *incorrect*, then the temperature and matrix dependence of phenylcarbene reactivity would become entirely analogous to that of **1**, and subject to the analysis presented above. Coincidentally, a recent MINDO/3 calculation gives the singlet-triplet splitting of phenylcarbene as at least 22 kcal/mol,^{28a} which, although probably too high, may be suggestive of a relatively large splitting. This would suggest a low rate of spin state equilibration because the rate of this process is inversely related to the state separation.^{28b}

On the other hand, we note the recent reports of Tomioka et al. concerning OH vs. CH insertion reactions of carbenes generated in alcohol solutions or in frozen alcohol matrices.^{29,30} In particular, the generation of phenylcarbene (by photolysis of phenyldiazomethane) in methanol, ethanol, or 2-propanol led mainly to the respective alkylbenzyl ethers (OH insertion) at 0 °C, but increasingly to the respective α (or to a lesser extent, β) CH "insertion" product at -72, -110, and -196 °C.³⁰ The ethers were attributed to OH insertion by singlet phenylcarbene and the CH insertion products were attributed to *matrix-enhanced* a-r reactions of triplet phenylcarbene. However, the published experimental data do not force the conclusion that a matrix effect operates. If the logarithms of the CH insertion product yields,³¹ relative to the ether yields, are plotted against T^{-1} , a reasonable linearity is observed for the 2-propanol data, whereas, with methanol and ethanol, *less* triplet product is observed at -196 °C than would be expected on the basis of the higher temperature results. Viewed in this way, the results of Tomioka³⁰ can be taken as reflecting a temperature effect¹³ operating on an *equilibrated* singlet and triplet phenylcarbene system. Whatever matrix effect may operate, it does not enhance triplet a-r reactions.

Experimental Section

Instruments. IR spectra were recorded on a Perkin-Elmer Model 137 spectrometer. ¹H NMR spectra were recorded on a Varian Model T-60 spectrometer as CCl₄ solutions with an internal (CH₃)₄Si standard; ¹³C NMR spectra were recorded under similar conditions using a Varian Model CFT-20 spectrometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-7 instrument. Melting points were obtained with a Mel-Temp apparatus and are uncorrected. All GC work was done on a Varian Model 1720 instrument, fitted with a 11.5 ft × 0.25 in. 3.5% Carbowax 20M + 2.5% SE-30 on 60/80 GCR column; operating conditions included injector, 250; detector, 260; and column 210 °C. The He flow rate was 70 mL/min. Product distributions were determined with a Disc integrator.

9-Diazo fluorene (9-DF). To a 100-mL flask was added 4.0 g (22 mmol) of fluorenone hydrazone,³² 60 mL of dry ether, 1 g of anhydrous Na₂SO₄, and 1 mL of saturated ethanolic KOH solution. Yellow mercuric oxide (15 g) was added and the reaction mixture was stirred magnetically in the dark for 6 h. After filtration and concentration of the filtrate, cooling (5 °C) afforded 2.1 g (11 mmol, 50%) of solid 9-DF, mp 98–99 °C (lit.³³ mp 94–95 °C).

[1-¹³C]-Isobutene. In a 500-mL round-bottom flask was placed 300 mL of dry ether, 2.0 g of 90 at. % [¹³C]methyl iodide (Merck Sharp & Dohme), 16.0 g of methyl iodide (126 mmol), and 40.0 g of triphenylphosphine (Aldrich, 153 mmol). The solution was stirred at 25 °C for 5 days; the resulting phosphonium salt was filtered and dried under vacuum, affording 47.3 g (93%) of methyltriphenylphosphonium iodide (~12.9% ¹³C by ¹H NMR), mp 184–186 °C (lit.³⁴ mp 184–186 °C).

The above phosphonium salt and 300 mL of dry ether were added to a three-neck 500-mL flask equipped with a condenser, nitrogen inlet, rubber septum, and magnetic stirrer. With stirring, 60 mL (125 mmol) of 2.1 M *n*-butyllithium in hexane (Alfa) was slowly added via syringe at 25 °C under nitrogen. After addition, stirring was continued for 4 h. Then ether was removed under reduced pressure, and 30 mL of dioxane (distilled from sodium) was added. After 20 min of stirring, dioxane and residual ether were removed under reduced pressure. An additional 60 mL of dry dioxane was added, the top of the condenser was connected to a cold trap (-78 °C) which terminated in a gas bubbler, and 15 mL of dry acetone was slowly syringed into the stirred reaction mixture. A slow stream of nitrogen was passed over the reaction mixture, and, after 2 h, an additional 5 mL of acetone was added. Stirring was continued for 5 more h. About 3.3 g (50%) of isobutene collected in the cold trap. ¹H NMR indicated the presence of traces of ether. The ¹⁻¹³C content was determined to be 12.4 ± 0.2 at. % by repetitive integration of the ¹²CH₂ signal (centered at δ 4.62 in the ¹H NMR) and of its satellite at δ 5.92.

trans-1-(9'-Fluorenyl)-2-butene (7). A 250-mL, three-neck flask was equipped with a condenser, addition funnel, nitrogen inlet, and magnetic stirrer. To the flamed and nitrogen-blanketed flask was added 5.0 g (30 mmol) of fluorene (Aldrich) and 100 mL of dry

hexane. The solution was heated to reflux and 30 mmol of *n*-butyllithium in hexane was added slowly; reflux was continued for 3 h. Then a solution of 5 g (37 mmol) of technical grade crotyl bromide (Aldrich, 80% crotyl bromide and 20% 3-bromo-1-butene) in 10 mL of hexane was slowly added, and reflux was continued overnight. The resulting slurry was washed with 75 mL of water, and the organic phase was concentrated. The oily yellow product was analyzed by GC; fluorene, fluorenone, and olefins **6**, **7**, and **8** were present. The major olefinic product was **7**, which was preparatively collected. The overall yield of olefins was ~50%. NMR; δ 1.60 (crude d, 3 H, CH₃), 2.57 (m, 2 H, allylic CH₂), 3.87 ("t", J = 6 Hz, 9'-H), 5.00–5.77 (m, 2 H, vinylic), 7.00–7.80 (m, 8 H, aromatic). Calcd for C₁₇H₁₆: *m/e* 220.1252. Found: *m/e* 220.1231.

3-(9'-Fluorenyl)-2-methylpropene (3). This alkene was prepared from 3-chloro-2-methylpropene (Aldrich) and 9-fluorenyl anion using a procedure analogous to that used for the preparation of **7**. The crude product mixture contained fluorene, fluorenone, and **3**, which was GC collected. NMR: δ 1.87 (s, 3 H, CH₃), 2.53 (d, J = 7 Hz, 2 H, allylic CH₂), 4.08 (t, J = 7 Hz, 1 H, 9'-H), 4.85 (d, J = 8 Hz, 2 H, =CH₂), 7.10–7.96 (m, 8 H, aromatic). The ¹³C NMR spectrum is described above. Calcd for C₁₇H₁₆: *m/e* 220.1252. Found: *m/e* 220.1276.

3-(9'-Fluorenyl)-1-butene (6). This alkene was prepared from 3-chloro-1-butene (Aldrich) and 9-fluorenyl anion, in a manner analogous to the preparation of **7**. The crude product mixture contained all of the products observed in the preparation of **7**, but **6** was the major olefinic component and was GC collected. NMR: δ 0.68 (d, J = 7 Hz, 3 H, CH₃), 2.83–3.33 (m, 1 H, CHCH₃), 4.00 (d, J = 4 Hz, 1 H, 9'-H), 4.93 and 5.10 (m's, 2 H, =CH₂), 5.70–6.27 (m, 1 H, CH=CH₂), 7.07–7.80 (m, aromatic); traces of fluorene were present in this sample. Calcd for C₁₇H₁₆: *m/e* 220.1252. Found: *m/e* 220.1270.

cis-1-(9'-Fluorenyl)-2-butene (8). A 250-mL, three-neck flask was equipped with an addition funnel, reflux condenser, nitrogen inlet, and magnetic stirrer, and charged with 5 g (30 mmol) of fluorene and 30 mL of dry hexane. The solution was brought to reflux and 32 mmol of *n*-butyllithium in hexane was slowly added. After 3 h at reflux 50 mL of tetrahydrofuran was added to dissolve the lithium fluorenyl. The resulting red solution was transferred, under nitrogen, to a fresh addition funnel, and subsequently added to a solution of 6.6 g (33.5 mmol) of bromoacetaldehyde diethyl acetal (Aldrich) in 25 mL of tetrahydrofuran. The reaction mixture was stirred for 10 h and then diluted with 50 mL of water. The organic phase was separated, dried (CaCl₂), and stripped of solvent, affording an oil which was purified by chromatography on a 2.5 × 48 cm silica gel column. Elution with 10:1 hexane-ether gave 9'-fluorenylacetaldhyde in the third and fourth 50-mL fractions. Removal of solvent gave 250 mg (4.3%) of the aldehyde. The IR spectrum (neat) showed the aldehydic CH at 2800 and a carbonyl absorption at 1720 cm⁻¹. The NMR spectrum, despite contamination with ether and hexane, revealed δ 2.73 ("d", J = 7 Hz, 2 H, CH₂C(=O)H); an additional 1-Hz splitting of each component was visible), 4.32 (t, J = 7 Hz, 1 H, 9'-H), 7.0–7.7 (m, aromatic), and 9.57 (t, J = 1 Hz, 1 H, CH₂C(=O)H). The aldehyde was converted to **8** without further purification.

A 250-mL, three-neck flask, equipped with a septum, nitrogen inlet, and magnetic stirrer, was charged with 3.7 g (10 mmol) of ethyl triphenylphosphonium bromide in 15 mL of hexane. *n*-Butyllithium (10 mmol) in hexane was added (syringe), and the solution was stirred for 4 h at 25 °C. Then, via a glass tube containing a filter frit, the solution was transferred to a 25-mL, three-neck flask which was fitted with an addition funnel, condenser, nitrogen inlet, and magnetic stirrer. (The filtration effected here provides salt-free ylide and optimizes the yield of *cis*-alkene.³⁵) To the salt-free ylide solution was added 1.5 g (7.7 mmol) of 9'-fluorenylacetaldhyde, prepared as above, in 10 mL of ether. The solution was kept at reflux for 10 h; the green supernatant was then decanted, washed with 15 mL of water, and dried over MgSO₄. Filtration, removal of solvents, and GC analysis revealed the presence of olefins **7** and **8**. The latter was the major component, and was preparatively collected. NMR: δ 1.50 (d, J = 4 Hz, 3 H, CH₃), 2.50–3.00 (m, 2 H, CH₂), 3.90 (t, J = 6 Hz, 1 H, 9'-H), 5.23–5.53 (m, 2 H, vinylic), 7.07–8.00 (m, aromatic). Calcd for C₁₇H₁₆: *m/e* 220.1252. Found: *m/e* 220.1254.

2,2-Dimethylspiro[cyclopropane-1,9'-fluorene] (5). This material was prepared by photolysis of 9-DF in isobutene at 0 °C (see below) and purified by GC. NMR: δ 1.43 (s, 6 H, CH₃'s), 1.72 (s, 2 H, CH₂), 7.00–7.40 and 7.57–7.87 (m's, 8 H, aromatic). Calcd for C₁₇H₁₆: *m/e* 220.1252. Found: *m/e* 220.1268.

trans-2,3-Dimethylspiro[cyclopropane-1,9'-fluorene] (9). This

compound was prepared by photolysis of **9**-DF in *trans*-butene at 0 °C and was purified by GC. NMR: δ 1.40 ("d", $J = 4$ Hz, CH₃'s) and 1.50–1.97 (m, cyclopropyl H's), 6.83–7.47 and 7.57–7.90 (m's, aromatic). The aggregate integral areas were in a ratio of 1:1. Calcd for C₁₇H₁₆: *m/e* 220.1252. Found: *m/e* 220.1221.

cis-**2,3-Dimethylspiro[cyclopropane-1,9'-fluorene]** (**10**). This compound was prepared by photolysis of **9**-DF in *cis*-butene at 0 °C and was purified by GC. NMR: δ 1.33 ("d", $J = 6$ Hz, 6 H, CH₃'s), 1.70–2.27 (m, 2 H, cyclopropyl H's), 6.67–7.47 and 7.47–7.93 (m's, 8 H, aromatic). Calcd for C₁₇H₁₆: *m/e* 220.1252. Found: *m/e* 220.1279.

Photolytic Procedures. In the general procedure, 50 mg (0.26 mmol) of **9**-DF was added to 15 mL of the appropriate olefin (containing 13%, by weight, of diglyme³⁶) in a 14 × 30 mm Pyrex tube. The sample was then degassed using three freeze-thaw cycles (nitrogen), and the sample tube was sealed under vacuum. The samples were warmed to 0 °C in the dark, shaken, and transferred to a quartz-tailed Dewar flask which contained coolants at the appropriate temperatures (see below).

Samples were irradiated by placing the tail of the Dewar in the center of a Rayonet reactor fitted with 16 300-nm lamps. Photolyses of olefinic solutions (0, –77, and –100 °C) were carried out for 9 h. Irradiations of olefinic matrices (–160 and –196 °C) were extended to total times of 24–32 h, but the matrices were thawed (in the dark) for 15–20 min at –77 °C every 2.5 h in order to homogenize them.

After irradiation, samples were brought to –196 °C, the reaction tube was opened, and the samples were then permitted to thaw at 0 °C. After olefin had evaporated, the residue was taken up in 20 mL of ethyl ether containing 5% (by weight) of maleic anhydride. After 15 min, the ethereal solution was washed twice with 20 mL of 10% aqueous KOH and once with 20 mL of water and then dried over CaCl₂. Filtration and removal of ether by rotary evaporation afforded a slurry of products derived from **1** and the olefinic substrate (liquid), and also ketazine¹⁵ and bifluorenylidene¹⁵ (both red solids). Appropriate control experiments demonstrated that removal of the ether under reduced pressure had not altered the relative ratios of **1** + olefin products. The final product slurry was diluted with a little pentane and submitted to GC analysis.

The identities of all volatile products were established by GC augmentation using authentic samples synthesized as described above. Fluorenone ketazine and bifluorenylidene were identified by TLC comparisons with authentic compounds¹⁵ on silica gel plates using 25:1 hexane-ether as the developing solvent.

Control Experiments. (a) Product mixtures were prepared from authentic materials, dissolved in the appropriate olefin–13% diglyme solution, frozen at –196 °C, and irradiated for 24 h. Analyses of the mixtures before and after irradiation indicated that components were not interconverted. (b) The *cis*- and *trans*-butene used in the **9**-DF photolyses were analyzed before and after irradiation experiments by capillary GC (100-ft SF-96 Golay column, –50 °C); in each case, the alkene's purity was >99%. (c) A sample of **9**-DF in isobutene and diglyme was prepared and worked up immediately, including destruction of the **9**-DF with maleic anhydride. GC analysis indicated traces of fluorene and fluorenone, but neither **3** nor **5** were present. This control implies that "carbene-olefin" products are produced only by the photolytic procedure and not adventitiously during workup.

Acknowledgments. We are indebted to the National Science Foundation and to the Public Health Service (Grant CA-14912 from the National Cancer Institute) for support of this research. We are grateful to Dr. D. Z. Denney for determining the ¹³C NMR spectra.

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- The origin of the *trans*-butenyl product, **7** (from the reaction of **1** and *cis*-butene), is uncertain, because the thermal isomerization of the intermediate *cis*-butenyl radical would be expected to be extremely slow at –196 °C. The matter is under further investigation.
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- See ref 9 and below.
- cis*-Butene + diphenylcarbene reactions behave similarly: G. L. Closs, L. E. Closs, and B. E. Rabinow, unpublished work; we thank Professor Closs for a summary of this work.
- A matrix effect was noted, however, on the equilibration of label in reactions of diphenylcarbene and [¹³C]isobutene.¹³
- (a) A similar conclusion may also hold for reactions of phenylmethylcarbene and isobutene, in which alkene formation first becomes detectably competitive with cyclopropanation at –120 °C.¹² (b) A referee has questioned whether the reactions carried out in the matrices really occur while the reaction mixtures are frozen, or whether they are not instead occurring at the thawing stage. Inspection of Tables I–III and Figure 1 will show that there are very large differences in product distributions, in each case, between –196 °C matrix reactions and –160 °C matrix reactions. If reactions were *not* occurring in the –196 °C matrices, it is very difficult to see why the product distributions should be so different from those obtained in –160 °C matrices. One would expect very similar distributions from *both* matrices if the reactions actually occurred at the thaw temperature, because this temperature would be the same for each matrix. In addition, the melting point of *trans*-butene is ca. –105 °C. Table III, however, shows large differences in product distributions between –160 °C matrix reactions and –100 °C solution reactions. Were the –160 °C reactions not really occurring until the thawing temperature, the product distributions ought to have resembled the –100 °C distributions.
- Not only are the foregoing differences between solution and matrix experiments apparent in reactions of **1** and butene olefins, but analogous differences have been observed for reactions of phenylcarbene,¹¹ phenylmethylcarbene,¹² and diphenylcarbene.¹³ In the latter case, not only were there product distribution differences between solution reactions (0, –77, –130 °C) and matrix reactions (–155, –196 °C) of diphenylcarbene and isobutene, but these distributions could be quantitatively fitted to a single Arrhenius relation, with good correlation (see above). The relation held over the entire range of solution and (both) matrix temperatures. Not only do these experiments¹³ indicate the absence of a specific matrix effect on the temperature-dependent (i.e., kinetic) competition which determines the ratio of abstraction–recombination to addition products in the diphenylcarbene/isobutene reaction, but they also demonstrate that the competitive reactions occur smoothly over the *entire* investigated temperature range, including the two lowest (matrix) temperatures.
- This contrasts with the behavior of diphenylcarbene, where the interconversion of singlet and triplet is rapid,⁴ and may be a consequence of a rather large energy difference between singlet and triplet **1**. A recent INDO calculation gave ($E_S - E_T$) for **1** as 21 kcal/mol; J. Metcalfe and E. A. Halevi, *J. Chem. Soc., Perkin Trans. 2*, 634 (1977); the companion calculation for diphenylcarbene gave ($E_S - E_T$) = 4 kcal/mol, whereas the experimental value⁴ is ≤ 3 kcal/mol.
- For triplet diphenylcarbene and *cis*-butene, (a) ($E_{\text{addn}}^{\text{tr}} - E_{\text{abstrn}}^{\text{tr}}$) ~ 870 cal/mol and (b) $A_{\text{addn}}/A_{\text{abstrn}} \sim 19$.²²
- Analysis of the comparable data for reactions of triplet **1** and *trans*-butene affords ($E_{\text{addn}}^{\text{tr}} - E_{\text{abstrn}}^{\text{tr}}$) ~ 480 cal/mol and $A_{\text{addn}}/A_{\text{abstrn}} \sim 2.7$. These estimates are derived from "two-point" Arrhenius relations, using the addition/abstraction product ratios at 0 and –196 °C.
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