alcohol **3** was (vide supra) ~75:25, the reaction is clearly highly stereoselective.

Monodecarbethoxylation of **7** with lithium chloride in aqueous Me_2SO[11] gave the mixture of esters **8**, $[\alpha]^{22}{}_D$ +9.5° (*c* 1.6, benzene). This gave a single peak on 5% FFAP at 140 °C, but was (^{13}C NMR) a trans-cis mixture, as expected. Oxidation of the mixture of stereoisomers with ruthenium oxide-sodium periodate in aqueous acetone[12] to the half ethyl ester of cyclopentane-1,2-dicarboxylic acid, $[\alpha]^{22}{}_D$ +21.2° (*c* 2.1, benzene), and hydrolysis (0.9 M potassium hydroxide in 1:1 THF-EtOH at room temperature) gave the desired cyclopentane-1,2-dicarboxylic acid **9**. The identity of the product thus obtained, a cis-trans mixture of cyclopentane-1,2-dicarboxylic acids, was established by comparison (as the dimethyl esters) with authentic racemic material.[13] The absolute configuration of the trans diacid **9** in the mixture could easily be established, since the cis isomer does not contribute to the rotation. The mixture of acids had $[\alpha]^{22}{}_D$ +17.2° (*c* 1.2, H_2O). This establishes the presence of an excess of the (1*S*,2*S*)-(+) trans isomer of the absolute stereochemistry shown in **9** since the (1*R*,2*R*)-(−) diacid antipode of **9** has been correlated with the (1*S*,2*S*)-(−) isomer of 1,2-cyclopentanediacetic acid.[14,15]

We conclude that the internal displacement with rearrangement ($S_{cN'}$) of a reactive ester of an allyl alcohol takes place anti to the departing carboxylate function when the displacing (cyclizing) group is a carbanion. This is the same stereochemistry which we had previously established for displacement by sulfide ion.[1] The apparent agreement with some recent theoretical proposals[16] is probably illusory because (a) some intermolecular displacements also involving negatively charged displacing groups have been shown to involve syn displacement;[17] (b) at least one intramolecular displacement, involving an allylic epoxide, seems to take place syn.[2a]

It is indeed likely that the nature of the counterion, of the departing group and of the medium will all be involved. It does however appear possible, in many cases, to delineate those systems which may be expected to lead to predictable chirality transfer. We intend to pursue this goal.

Acknowledgment. We thank the National Science Foundation for partial support of this work and also NATO and the French CNRS for Fellowship support to A.R.S.

References and Notes

(1) Stork, G.; Kreft, A. F. *J. Am. Chem. Soc.* **1977**, *99*, 3851–3853.

(2) Cf.: (a) Martel, J.; Blade-Font, A.; Marie, C.; Vivat, M.; Toromanoff, E.; Buendia, *J. Bull. Soc. Chim. Fr.* **1978**, *II*, 131–139. Buendia, J.; Vivat, M.; Toromanoff, E; Martel, J. *Ibid.* **1978**, *II*, 140–143. (b) See also: Chiche, L.; Coste, J.; Christol, H.; Plenat, F. *Tetrahedron Lett.* **1978**, 3251–3254. Uebel. J. J.; Milaszewski, R. F.; Art, R. E. *J. Org. Chem.* **1977**, *42*, 585–591.

(3) This would be especially attractive since (a) ethynylcarbinols are easily obtained in high optical purity by reduction of ethynyl ketones with chiral hydride reagents (Brinkmeyer, R. S.; Kapoor, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 8339–8341). (b) A given chiral ethynylcarbinol can lead to either absolute configuration in the ring compound **2**, depending on whether the ethynylcarbinol is reduced to a *cis*- or to a *trans*-vinylcarbinol before cyclization.

(4) It is unsatisfactory to refer to an internal $S_{N'}$ reaction as "internal S_N2'" since it cannot be second order. We suggest the symbol $S_{cN'}$, the c signifying that the reaction involves cyclization.

(5) *Inter*molecular S_N2' reactions often take place by syn displacement. See: Stork, G.; Kreft, A. F. *J. Am. Chem. Soc.*, **1977**, *99*, 3850–3851. Magid, R. M.; Fruchey, O. S. *Ibid.* **1977**, *99*, 8368–8370. Dobbie, A. A.; Overton, K. H. *J. Chem. Soc., Chem. Commun.* **1977**, 722–723. Oritani, T.; Overton, K. H. *Ibid.* **1978**, 454–455. Toromanoff, E. *Tetrahedron*, **1978**, *34*, 1665–1673. Also see ref 17.

(6) Weidmann, R.; Schoofs, A. R.; Horeau, A. *Bull. Soc. Chim. Fr.* **1976**, 645–648. Olsson, L. I.; Claesson, A. *Acta Chem. Scand., Ser. B* **1977**, *31*, 614–618.

(7) Determined by the method of Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.

(8) All new compounds gave satisfactory infrared, as well as proton and carbon NMR spectra and chemical ionization mass spectra. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter.

(9) Stork, G.; White, W. N. *J. Am. Chem. Soc.* **1956**, *78*, 4609–4619.

(10) Fraser, R. R.; Petit, M. A.; Saunders, J. K. *Chem. Commun.* **1971**, 1450–1451.

(11) Krapcho, A. P.; Weimaster, J. F.; Eldridge, J. M.; Jahngen, E. G. E., Jr.; Lovey, A. J.; Stephens, W. P. *J. Org. Chem.* **1978**, *43*, 138–147.

(12) Pelletier, S. W.; Iyer, K. N.; Chang, C. W. J. *J. Org. Chem.* **1970**, *35*, 3535–3538.

(13) The trans isomer has the shorter retention time on 5% FFAP at ~150 °C.

(14) Inouye, Y.; Sawada, S.; Ohno, M.; Walborsky, H. M. *Tetrahedron* **1967**, *23*, 3237–3243.

(15) Bourn, P. M.; Klyne, W. *J. Chem. Soc.* **1960**, 2044–2046.

(16) Yates, R. L.; Epiotis, N. D.; Bernardi, F. *J. Am. Chem. Soc.* **1975**, *97*, 6615–6621.

(17) Kirmse, W.; Scheidt, F.; Vater, H.-J., *J. Am. Chem. Soc.* **1978**, *100*, 3945–3946.

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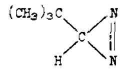
Received April 4, 1979

Roles of Multiplicity and Electronic Excitation on Intramolecular Reactions of Alkylcarbenes in Condensed Phase

Sir:

Little information exists as to the roles of multiplicity and electronic excitation in intramolecular reactions of alkylcarbenes in condensed phase. Such intermediates generated thermally have been presumed to rearrange and insert by singlet mechanisms.[1] Triplet alkylcarbenes have had little study but are theorized to resist rearrangement and concerted carbon-hydrogen insertion because the conversions into triplet products are unfavorable energetically.[2-4] Recently, thermal, photolytic, and photosensitized decompositions of 1-diazo-2-methyl-2-phenylpropane to 1-methyl-1-phenylcyclopropane, 2-methyl-1-phenylpropene, 2-methyl-3-phenylpropene, *cis*- and *trans*-2-phenyl-2-butenes, and 2-phenyl-1-butene have been interpreted to involve varying mixed singlet and triplet carbenic processes.[5] It is also not clear whether triplet alkylcarbenes undergo intramolecular carbon-hydrogen insertion by abstraction, spin inversion, and recombination.[6] Important further theory is that the more indiscriminate intramolecular gas-phase insertion and rearrangement reactions upon photolysis than by thermolysis of alkyldiazirines have been attributed to vibrationally excited carbenes (hot radicals) as generated photochemically.[7] A study is now reported of carbenic decomposition of 3-*tert*-butyldiazirine (**1**),[8a] 1-diazo-2,2-dimethylpropane (**2**),[8b] and 3-isopropyldiazirine (**3**)[8a] by various methods in condensed phase. Particular emphasis has been directed to the intramolecular triplet processes from **1–3**.



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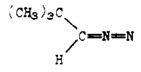

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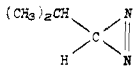

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Decompositions of **1–3** by thermal and photochemical methods occur efficiently by carbenic routes in environments which minimize cationic processes.[9] Thermolysis of **1** and **2** in decalin or cumene (Table I) at 130–180 °C in the presence of sodium hydride thus gives 1,1-dimethylcyclopropane (**4**, 87–91%) and 2-methyl-2-butene (**5**, 9–12%) in the indicated proportions. The 2-methyl-1-butene (**6**, 3.2%) from **2** is an initial contaminant of the diazo compound and is also formed by cationic decomposition of **2** upon warming. The similarities in the ratios of **4** and **5** from thermolyses of **1**[10] and **2** imply that common reaction intermediates are involved.

Irradiation (Table I) of **1**[11] at 25 and −80 °C in solvents containing tetramethylguanidine or sodium hydride yields **4** (45–46%) and **5** (54–55%). Similarly, photolyses (phot) of **2** in tetrahydrofuran at 25 and −80 °C give **4** (46.5 and 51.9%)

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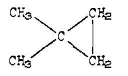
Table I. Decomposition of 3-*tert*-Butyldiazirine (**1**) and 1-Diazo-2,2-dimethylpropane (**2**)

reactant	method, temp in °C	solvent[a]	**4**, %	**5**, %	**6**, %	no. of expt
1	180	$C_{10}H_{18}$[b]	88.4 ± 1.0	11.6 ± 1.0	0	3
1	145	$PhCH(CH_3)_2$	87.6 ± 1.3	12.4 ± 1.3	0	3
2	130	$C_{10}H_{18}$[b]	86.8 ± 1.0	9.9 ± 1.0	3.2	3
1	phot, 25	C_6H_6	44.7 ± 1.6	55.3 ± 1.6	0	4
1	phot, 25	C_6H_6(TMG)[c]	45.1	54.9	0	1
1	phot, 25	$PhCH(CH_3)_2$	45.9 ± 1.5	54.1 ± 1.5	0	3
1	phot, −80	THF	46.0	54.0	0	1
2	phot, 25	THF	46.5	46.7	6.7	2
2	phot, −80	THF	51.9	45.6	2.5	2
1	PS, TXO,[d] 25	C_6H_6(TMG)[c]	90.8 ± 1.2	9.2 ± 1.2	0	6
1	PS, TXO,[d] 25	$PhCH(CH_3)_2$[e]	88.7 ± 1.5	10.4 ± 1.8	0	3
1	PS, TXO,[d] 25, 2MP[f]	C_7H_{16}[g]	no change in **1**			
1	PS, BPO,[h] 25	C_6H_6	88.4 ± 2.0	11.6 ± 2.0	0	3
1	PS, *p*-MAPO,[i] 25	$PhCH(CH_3)_2$[j]	86.1 ± 1.3	10.8 ± 0.5	2.1 ± 0.9	2
1	PS, *p*-MAPO,[i] −80	THF	89.5 ± 1.2	10.5 ± 1.2	0	2
1	PS, Phen,[k] 25	C_7H_{16}[l]	47.3	52.7		1
1	PS, Phen,[k] 25, 2MP[f]	C_7H_{16}[m]	46.8	53.2	0	1
1	PS, Anth,[n] 25	C_7H_{16}[o]	no change in **1**			
2	PS, TXO,[d] 25	C_6H_6	87.5	7.8	4.7	4
2	PS, *p*-MAPO,[i] −80	THF	87.5	11.0	1.6	2

[a] Unless noted, sodium hydride was present to minimize cationic processes. [b] Decalin. [c] Tetramethylguanidine. [d] 10-Thioxanthone (E_T = 65.5 kcal/mol). [e] Neopentane (0.8 ± 0.1%) was also formed. [f] 2-Methyl-*trans*-1,3-pentadiene. [g] Photolysis of **1** (0.0258 M), TXO (0.025 M), and 2MP (0.11 M) in heptane. [h] Benzophenone (E_T = 69 kcal/mol). [i] *p*-Methoxyacetophenone (E_T = 71 kcal/mol). [j] Neopentane (1.0 ± 0.1%) was also produced. [k] Phenanthrene. [l] Photolysis of **1** (0.036 M) and Phen (0.112 M) in heptane. [m] Irradiation of **1** (0.026 M), Phen (0.110 M), and 2MP in heptane. [n] Anthracene. [o] Photolysis of **1** (0.032 M) and Anth (0.115 M) in heptane.

and **5** (46.7 and 45.6%) along with **6** (6.7 and 2.5%). Since **2** undergoes some cationic decomposition while being photolyzed, the results lead to the conclusion that **1** and **2** react by essentially identical carbenic processes.[12] Neither **4** nor **5** is altered after formation and the wavelength of the light for photolysis, from 302.5 to 334 nm and at >348 nm, has no effect on the composition of the products formed. Irradiation of **1** and **2** results in much more methyl migration to **5** and less insertion to **4** than does thermolysis. Further, the product proportions from photolysis of **1** and **2** in solution at −80 to 25 °C are similar to that (**4**/**5**, ~1) from irradiation of **1** in the gas phase[7c] in the presence of diluents at sufficient pressures to deactivate collisionally the **4** and **5** produced.[13]



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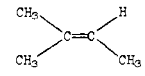

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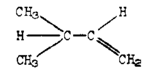

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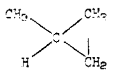
Photosensitization (PS) of **1**[14] and **2** is revealing (Table I). Decomposition of **1** and **2** in base-protected solvents at −80 and 25 °C with ketone sensitizers (10-thioxanthone,[15a] benzophenone,[15b] and *p*-methoxyacetophenone[15c]) of triplet energies ranging from 65.5 to 71 kcal/mol gives results essentially identical with those of thermolyses at 130-180 °C: discriminating insertion to **4** (86-91%), minor methyl migration to **5** (9-12%), and little evidence for **6**.[16] Photolytic decomposition of **1**, however, does not occur in the presence of 10-thioxanthone containing 2-methyl-*trans*-1,3-pentadiene; formation of 2-methyl-*cis*-1,3-pentadiene is indicative of quenching triplet 10-thioxanthone during radiation. Triplet derivatives of **1** and **2** are thus presumably formed in the above photosensitizations with ketones.

Phenanthrene (E_T = 62 kcal/mol; E_S = 83.0 kcal/mol) effects different photosensitization of **1** and **2** than do aromatic ketones. Photolyses of **1** in heptane containing phenanthrene and with phenanthrene containing 2-methyl-*trans*-1,3-pentadiene yield **4** and **5** (Table I) in identical composition as those for photolysis in the absence of phenanthrene. Since the 2-methyl-*trans*-1,3-pentadiene quenches triplet phenanthrene and is converted into its cis isomer, the photosensitization of **1** apparently arises from excited singlet phenanthrene. In the presence of anthracene (E_T = 42.5 kcal/mol; E_S = 75.5 kcal/mol) photolytic decomposition of **1** does not occur.

Study has been extended to **3**. Thus, thermolysis (180 °C in decalin) and photosensitization (25 °C, 10-thioxanthone in benzene and *p*-methoxyacetophenone in benzene or cumene) of **3** yield methylcyclopropane (**7**, 49.1-46.6%), isobutene (**8**, 49.7-51.1%), *cis*-2-butene (**9**, 0.5-0.6%), and *trans*-2-butene (**10**, 0.7-0.6%). The photolysis reactions (25 °C, benzene) of



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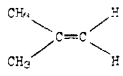

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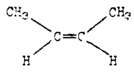

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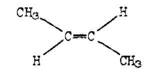
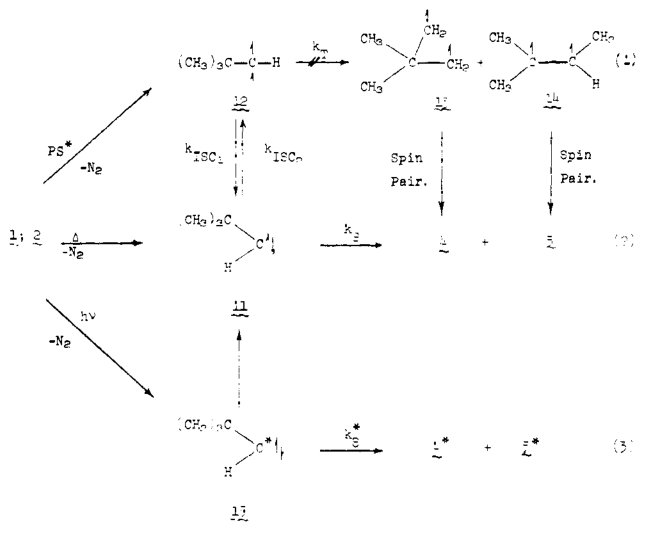


10

3 are much more indiscriminate, however, in that **7** (35.4 ± 1.1%), **8** (45.1 ± 2.9%), **9** (7.5 ± 1.4%), and **10** (12.0 ± 0.6%) are formed. The overall response of **3** to thermolysis, triplet photosensitizers, and photolysis is thus analogous to that of **1** and **2**.

The present study thus reveals that (1) triplet photosensitization of **1**-**3** becomes identical with thermolysis, (2) direct photolysis and singlet photosensitization result in identical but much more indiscriminate rearrangement and insertion processes than do thermolyses and triplet photosensitization, and (3) the mechanistic behaviors of **1**-**3**, 1-diazo-2-methyl-2-phenylpropane,[5] (2-*n*-butylphenyl)diazomethane,[2c] and methyl (2-diazo-*trans,trans*-2,3-dimethyl-1-cyclopropyl)acetate[2b] are decidedly different.

The thermal and triplet photosensitization reactions of a diazirine or a diazoalkane such as **1** and **2** are interpretable on the basis that thermolysis generates the lowest energy singlet carbene **11** whereas triplet photosensitization yields **12**, the ground-state triplet which spin inverts to **11**;[17] **4** and **5** (eq 2) rather than intermediates **13** and **14** then form. For such a mechanism involving **12**, the barrier to singlet **11** must not be a very severe kinetic hurdle. Unless the rates of conversion of **11** into singlet products are enormously greater than for **12**, the triplet-singlet gap for **12** to **11** is probably considerably less than the 19.5 ± 0.7 kcal/mol value recently reported for methylene.[18] Conversion of **3** via triplet photosensitization into



8 as a major product strongly supports the presumption that intersystem crossing of **12** to **11** occurs.[19] It would thus appear that, along with rearrangement, insertion results from reaction of **11**. Without further information, however, it can not be concluded that conversion into **4** and **5** is the exclusive province of singlet **11**.[19]

Direct photolysis and singlet photosensitization of **1** and **2** occur with absorption of $\sim$82-90 kcal/mol of energy. Electronically excited singlets **1-2*** and/or possibly excited **15*** are thus highly energetic and their conversions into **4*** and **5*** are spin allowed. Rearrangement to **5*** is now extensive and the product does not undergo alteration as occurs when derived from vibrationally excited intermediates in the gas phase.[7e] Finally, triplet photosensitization of diazo compounds and diazirines as in the present systems may give advantage over thermolysis and direct photolysis for specific synthesis.

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged.

References and Notes

(1) (a) C. D. Gutsche, E. F. Jason, R. S. Coffey, and H. E. Johnson, *J. Am. Chem. Soc.*, **80**, 5756 (1958); (b) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959); (c) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (d) P. B. Sargeant and H. Shechter, *Tetrahedron Lett.*, 3957 (1964); (e) H. Zimmerman and J. H. Munch, *J. Am. Chem. Soc.*, **90**, 187 (1968); (f) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N.Y., 1971, pp 236–260 and 457–497; (g) M. Jones, Jr., and R. A. Moss, "Carbenes", Vol. I, Wiley, New York, N.Y., 1973, pp 1–151.

(2) (a) I. Moritani, Y. Yamamoto, and S.-I. Murahashi, *Tetrahedron Lett.*, 5697 (1968); (b) R. R. Gallucci and M. Jones, Jr., *J. Am. Chem. Soc.*, **98**, 7704 (1976); (c) T. A. Baer and C. D. Gutsche, *ibid.*, **93**, 5180 (1971); (d) see also M. Jones, Jr., and R. A. Moss, "Carbenes", Vol. II, Wiley, New York, N.Y., 1973, pp 207–362.

(3) (a) D. C. Montague and F. S. Rowland, *J. Phys. Chem.*, **72**, 3705 (1968); (b) H. M. Frey and L. Walsh, *Chem. Commun.*, 158 (1969).

(4) The photolysis reactions of (2-*n*-butylphenyl)diazomethane[2c] and methyl α-diazo(*trans,trans*-2,3-dimethyl-1-cyclopropyl)acetate[2b] are not altered by triplet photosensitization. In these systems the barriers for conversions of the *conjugated* excited singlet and the *conjugated* triplet carbenes generated to their lowest energy singlets are presumed to be so small that the intramolecular processes are totally completed by singlet mechanisms.

(5) J. J. Havel, *J. Org. Chem.*, **41**, 1464 (1976).

(6) H. Tomioka and Y. Izawa, *J. Am. Chem. Soc.*, **99**, 6128 (1977), indicate that intermolecular insertion reactions of triplet carbenes are more prevalent than previously suspected.

(7) (a) H. M. Frey and I. D. R. Stevens, *J. Am. Chem. Soc.*, **84**, 2647 (1962); (b) H. M. Frey, *J. Chem. Soc.*, 2293 (1962); (c) H. M. Frey and I. D. R. Stevens, *ibid.*, 3514 (1963); (d) *ibid.*, 4700 (1964); (e) *ibid.*, 3101 (1965); (f) H. M. Frey, *Pure Appl. Chem.*, **9**, 527 (1964); (g) A. M. Mansoor and I. D. R. Stevens, *Tetrahedron Lett.*, 1733 (1966).

(8) (a) E. Schmitz and R. Ohme, *Chem. Ber.*, **95**, 795 (1962); (b) G. M. Kaufman, J. A. Smith, G. G. Vander Stouw and H. Shechter, *J. Am. Chem. Soc.*, **87**, 935 (1965).

(9) Diazirines are of advantage because they are readily purified and protected against cationic decomposition.

(10) In the gas phase (250 mm) at 160 °C, **1** also thermolyzes to **4** (92%) and **5** (8%).[7g]

(11) Effected at 302.5, 313, and 334 nm with a Hanovia lamp (679A) through Pyrex.

(12) In diglyme containing lithium *tert*-butoxide, **2** photolyzes at 20 °C to **4** (51.6%), **5** (46.6%), and **7** (1.8%).

(13) Extension of subsequent theory of this manuscript raises the question that such gas-phase decompositions involve electronically excited intermediates.

(14) 10-Thioxanthone effects efficient photosensitization of larger ring azo analogues of **1** and **3**: P. S. Engel, *J. Am. Chem. Soc.*, **91**, 6903 (1969).

(15) (a) Hanovia 679A lamp, Corning 7380 filter; 10-thioxanthone, ϵ 2800 (349 nm). (b) Reaction mixtures were samples at <20% conversion. (c) Hanovia 679A lamp, potassium chromate filter.

(16) Neopentane ($\sim$1%) formed upon photosensitizations in cumene possibly arises by hydrogen abstraction by **12** and then the neopentyl radical.

(17) Isomerizations of **12** with spin preservation to **13** and **14** apparently are higher energy demanding processes.[2d]

(18) (a) P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbert, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.*, **98**, 3731 (1976).[18b] (b) Prior experimental values for the triplet-singlet energy gap for methylene range from 6 to 10 kcal/mol.[18c] (c) H. M. Frey, *J. Chem. Soc., Chem. Commun.*, 1024 (1972); W. L. Hase, R. J. Phillips and J. W. Simons, *Chem. Phys. Lett.*, **12**, 161 (1971); F. S. Rowland, C. McKnight, and E. K. C. Lee, *Ber. Bunsengess*, **72**, 236 (1968).

(19) (a) R. C. Friedmann of this laboratory has observed that photosensitization of 4-methyl-1-pyrazoline with benzophenone and with 10-thioxanthone in tetrahydrofuran at −78 to 25 °C yields **7** (97.0–98.0%) and **8** (1.5–2.8%). Direct photolysis of 4-methyl-1-pyrazoline in tetrahydrofuran at −78 to 25 °C results in **7** (84.4–88.0%), **8** (10.0–15.4%), and 1-butene (0.3–1.0%). The behavior of 4-methyl-1-pyrazoline and its presumed photolytic intermediates,[19b] triplet and singlet 2-methyl-1,3-propane diradicals, is quite different from that for photosensitization, thermolysis, and photolysis of **3** and argues strongly (1) against triplet and singlet β-C–H abstraction reactions for 2-methyl-1-propylidenes from **3** as a major source of **8** (and probably **7**) and (2) for spin inversion of triplet to singlet 2-methyl-1-propylidene and then to **8** (and probably **7**). Further, triplet photosensitization of 4,4-dimethyl-1-pyrazoline to give **4** (94–98%) and 2-methyl-1-butene (trace) as the only intramolecular products supports the conversion of **12** from **1** into **11** and then **5** (and probably **4**). (b) For summary of the experimental results and the theory of decomposition of various 1-pyrazolines, see G. Koga, N. Koga, and J.-P. Anselme and R. J. Drewer in "The Chemistry of the Hydrazo, Azo, and Azoxy Groups, Part 2", S. Patai, Ed., Wiley, New York, 1978, Chapters 19 and 20.

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Received November 21, 1978

Total Synthesis of Tryptoquivaline G

Sir:

A strain of the fungus *Aspergillus clavatus* collected from mold damaged rice produced a group of toxic, tremor inducing metabolites with novel structures. Tryptoquivaline (**1**) was found to be the major metabolite, and a transformation product containing a δ-lactone ring was used to determine its structure and relative configuration by X-ray crystallography.[1] Comparison of circular dichroism and ^{1}H NMR spectra with those of nortryptoquivaline[2] suggested structure **2** for this companion metabolite. Tryptoquivaline G (**3**) is a representative of a more recently discovered group of mycotoxins produced by *Aspergillus fumigatus*.[3-5] It, as well as tryptoquivaline L (**17**), an artefact, lacks the isobutyl side chain. The total synthesis of tryptoquivaline G (**3**) outlined here confirms the proposed