(11 g, 27 mmol). The final reaction mixture was 14% (v/v) Me_2SO. Calcium carbonate was used in the preparation of calcium *p*-chloromandelate. The overall yield was 26% (based on (*p*-chlorophenyl)glyoxal) and the product was composed of a 76% ee of the *R* enantiomer. The recovered GX-I and GX-II had 3% and 59%, respectively, of their initial activities.

Mandelic Acid. An aqueous suspension of phenylglyoxal (65 mmol in 350 mL of H_2O, pH 6.3) was converted in a "simultaneous" process with immobilized enzymes to mandelic acid (7.4 g, 49 mmol; 91% ee *R*; 75% based on phenylglyoxal). The recovered enzymes were not active.

***p*-Methoxymandelate.** A "simultaneous" procedure, using soluble GX-I and GX-II, converted 256 mL of an aqueous solution of (*p*-methoxyphenyl)glyoxal (11 mmol) to the corresponding α-hydroxy acid. Calcium *p*-methoxymandelate (1.9 g, 4.6 mmol; 94% ee *R*; 84% based on (*p*-methoxyphenyl)glyoxal) was isolated with calcium carbonate. No enzymatic activity remained upon completion of the reaction.

Lactate. Methylglyoxal solutions are known to contain significant amounts of acid, persumably lactic acid.[4] A steam-distilled solution (450 mL of 2.97 M methylglyoxal, 0.48 M acid) was treated with 16 portions of Dowex-1 × 8/50 (OH^-) (15-mL portions, 20 min each) to give a solution (380 mL) of 1.62 M methylglyoxal and 8.7 mM acid. A "simultaneous" procedure, using immobilized enzymes, converted 200 mL of this solution (324 mmol methylglyoxal) to lactic acid, which was isolated as the zinc salt (7.9 g, 28 mmol; 97% ee *R*; 17% based on methylglyoxal), using zinc carbonate. No enzymatic activity was recovered.

Determination of Enantiomeric Compositions. D- and L-lactate were measured by using enzymatic assays.[26] The same value of enantiomeric excess was found for the lactate present in the reaction mixture before workup and for the zinc lactate isolated as product. This observation indicates that no enantiomeric enrichment occurs during workup. Assays for other materials were based on Mosher's method,[27,28] chemical shifts for the OCH_3 protons of the diasteromeric forms of $RCH(OCOC^*(CF_3)(OCH_3)Ph)CO_2CH_3$ differed by ~0.1 ppm, and those for the CO_2CH_3 group by ~0.03 ppm. At 250 MHz, the latter gave base line separations and were used to determine enantiomeric excess. The absolute configurations of the compounds were assigned by comparison with spectra of compounds derived from resolved or enriched α-hydroxy methyl esters. The methyl esters used were prepared by using a procedure described below for methyl 2-hydroxypentanoate. Control experiments carried out with the methyl esters of mandelic and *p*-chloromandelic acids showed that the procedure for the determination of the enantiomeric compositions does not result in enantiomeric enrichment.

Methyl 2-Hydroxypentanoate. The ester was prepared by placing the barium salt (0.5 g) of 2-hydroxypentanoic acid in MeOH (20 mL), adding acetyl chloride (0.5 mL), and heating the mixture under reflux for 30 min. The mixture was cooled, filtered to remove $BaCl_2$, and concentrated under reduced pressure. Ether (10 mL) was added, residual $BaCl_2$ removed by filtration, and solvent removed under vacuum. The resulting liquid was used directly in determination of enantiomeric excess.

Acknowledgment. We thank Dr. Stephen Moore for obtaining the 250-MHz ^1H NMR spectra.

Registry No. (*p*-Chlorophenyl)glyoxal, 4998-15-6; phenylglyoxal, 1074-12-0; (*p*-methoxyphenyl)glyoxal, 1076-95-5; methylglyoxal, 78-98-8; propylglyoxal, 7332-93-6; (*R*)-4-chloro-α-hydroxybenzeneacetic acid 1/2 Ca, 79083-97-9; (*R*)-α-hydroxybenzeneacetic acid, 611-71-2; (*R*)-4-methoxy-α-hydroxybenzeneacetic acid 1/2 Ca, 79083-98-0; (*R*)-α-hydroxypropanoic acid 1/2 Zn, 18975-98-9; (*R*)-α-hydroxypentanoic acid 1/2 Ba, 79083-99-1.

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(27) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.

(28) The method of Reuben for determining enantiomeric purity of unmodified α-hydroxy carboxylic acids led to formation of gels (Reuben, J. *J. Am. Chem. Soc.* **1980**, *102*, 2232–2237). The resolution of the method is such that it is only useful for mixtures containing significant quantities of both enantiomers. Mixtures of $Eu(dcm)_3$ (McCreary, M. D.; Lewis, D. W.; Wernick, D. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 1038–1054) and compounds of the structure $RCHOHCO_2CH_3$ gave shifted spectra but no usable splitting of enantiomeric signals.

Isolation of a Diazoalkane Intermediate in the Photic Bamford–Stevens Reaction

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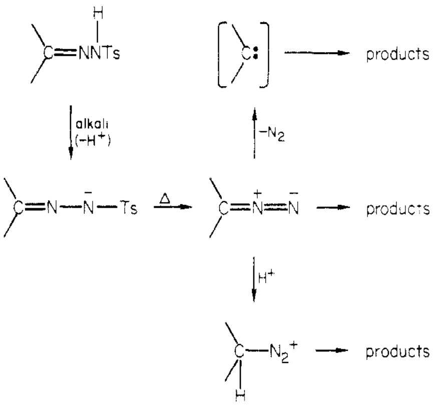
Received June 1, 1981

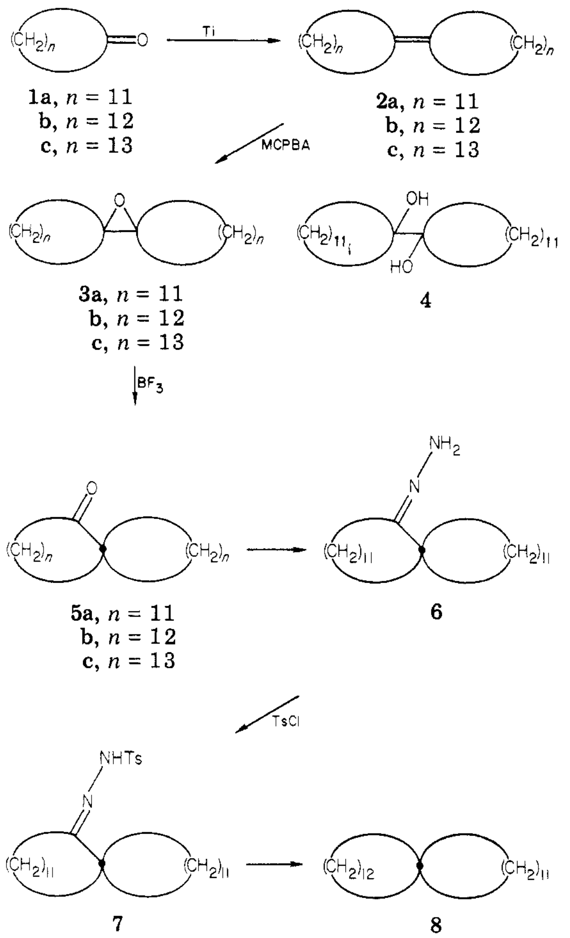
Arylsulfonylhydrazones decompose in alkaline media on thermolysis (Bamford–Stevens reaction) or on UV irradiation. The *thermal* method is known to produce a diazo hydrocarbon, which gives products by carbenic and/or cationic routes according to the reaction conditions. In contrast, mechanistic information on the *photic* decomposition is lacking. We now report a successful isolation of a diazo hydrocarbon from direct photolysis of a tosylhydrazone sodium salt and present evidence that the diazo compound is an intermediate in the overall *photic* Bamford–Stevens reaction. Our key substrate was spiro[12.11]tetracosan-13-one (**5a**), synthesized from cyclododecanone by a three-step sequence involving reductive coupling, epoxidation of the derived olefin, and rearrangement of the oxirane. Photic Bamford–Stevens reaction of the tosylhydrazone sodium salt of **5a** under different alkaline conditions was brought about by UV irradiation through a Vycor filter (i.e., $\lambda >$ ca. 220 nm). The products were (*E*)-spiroalkene **11** (75–80%), (*Z*)-spiroalkene **12** (10–14%), and saturated hydrocarbons (10–11%). The alkanes were not individually identified but are expected products of intramolecular C–H insertions by a carbene. By using lower energy light (i.e., Pyrex filter; $\lambda >$ ca. 270 nm), we isolated instead 13-diazospiro[12.11]tetracosane (**14**) in 95% yield. This diazo hydrocarbon was characterized spectroscopically, by elemental analysis, and by an independent synthesis. Then, on separate irradiation with Vycor-filtered light, **14** gave a product mixture, which, after correction for a small contribution from cationic pathways, contained *E* olefin **11**, *Z* olefin **12**, and saturated hydrocarbons in a ratio of 78:12:11, the same as that from the uninterrupted photic Bamford–Stevens reactions. We also found that *thermal* Bamford–Stevens conditions give markedly different product ratios, viz., 90% **11**, ca. 0% **12**, and 10% alkanes. These differences suggest that the "carbene" (or diazo hydrocarbon) derived thermally and the one derived photically behave differently with respect to the stereoselectivity of the 1,2 H shift that produces olefin.

Thermal decomposition of arylsulfonylhydrazones in alkaline media (the Bamford–Stevens reaction) provides an important synthetic route to olefins and cyclopropanes.[1,2] At elevated temperatures the anions of the

Scheme I



Scheme II



p-toluenesulfonylhydrazone salts first lose *p*-toluenesulfinate anion to produce a diazo intermediate,[3,4] which can sometimes be isolated but whose fate in general depends upon reaction conditions. Many external factors can influence the ultimate course of the reaction including solvent (e.g., protic vs. aprotic),[3-8] metal cations that can act as Lewis acids,[5-9] and the type and concentration of alkali.[5,7,9b,10] For example, under aprotic conditions the diazo intermediate typically expels nitrogen and generates a carbene,[3-5] whereas in the presence of a proton source (intentional or adventitious), the diazo compound can convert to a diazonium ion and thereby launch competing cationic reactions (Scheme I).[2,6-10]

As an alternative to thermal treatment, arylsulfonylhydrazone salts can also be decomposed by ultraviolet irradiation.[11-17] The mechanistic aspects of these "photic"[18] Bamford–Stevens reactions have not been elucidated, although many chemists presume (often tacitly) they involve diazoalkane and carbene intermediates analogous to those in the thermal pathway.[11-17] One basis for these presumptions was the initial observation by Dauben and Willey of a transient red color during Pyrex-filtered irradiation of camphor *p*-toluenesulfonylhydrazone sodium salt in diglyme.[11] They attributed the red to an intermediate diazoalkane but did not establish whether the color arose from the principal path or from a side reaction. Also, Moser and co-workers demonstrated through electron-spin resonance that triplet carbenes were produced at -196 °C upon irradiation of tosylhydrazone lithium salts of some aromatic ketones.[13]

The effects of irradiation wavelength in photic Bamford–Stevens reactions have been only sparsely noted and documented. Some differences in rates of substrate decomposition and in ratios of products have been found with unfiltered vs. Pyrex-filtered light.[11,13] But in most cases the effect of wavelength was not studied,[14,15] and in some instances the wavelength used is not clearly specified.[17,19]

Along with our dearth of knowledge about wavelength dependence is the added question of whether thermal and photic Bamford–Stevens reactions involve identical intermediates. Some workers have reported different product ratios[12,14,20] and speculatively attributed these to energy differences in the (putative) carbenes derived thermally and photically.[12,14] A further complication emerged in recent years from the realization that carbenes

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(1) Bamford, W. R.; Stevens, T. S. *J. Chem. Soc.* **1952**, 4735–4740.

(2) For reviews, see: (a) Shapiro, R. H. *Org. React.* **1976**, *23*, 405–507. (b) Barom, W. J.; Decamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In "Carbenes"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. I, Chapter 1. (c) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; pp 18–33.

(3) Powell, J. W.; Whiting, M. C. *Tetrahedron* **1959**, *7*, 305–310.

(4) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512–5513.

(5) Shapiro, R. H.; Duncan, J. H.; Clopton, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 471–472.

(6) (a) Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1966**, *88*, 4543–4544. (b) Nickon, A.; Werstiuk, N. H. *Ibid.* **1972**, *94*, 7081–7086.

(7) Smith, J. A.; Shechter, H.; Bayless, J.; Friedman, L. *J. Am. Chem. Soc.* **1965**, *87*, 661–663.

(8) Clarke, P.; Whiting, M. C.; Papenmaier, G.; Reusch, W. *J. Org. Chem.* **1962**, *27*, 3356–3357.

(9) (a) Shapiro, R. H. *Tetrahedron Lett.* **1966**, 3401–3407. (b) Shapiro, R. H.; Duncan, J. H.; Clopton, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 1442–1446.

(10) Kirmse, W.; von Bulöw, B-G.; Schepp, H. *Justus Liebigs Ann. Chem.* **1966**, *691*, 41–49.

(11) Dauben, W. G.; Willey, F. G. *J. Am. Chem. Soc.* **1962**, *84*, 1497–1498.

(12) Nickon, A.; Huang, F.-C.; Weglein, R.; Matsuo, K.; Yagi, H. *J. Am. Chem. Soc.* **1974**, *96*, 5264–5265.

(13) Moser, R. E.; Fritsch, J. M.; Matthews, C. N. *Chem. Commun.* **1967**, 770–771.

(14) Ojima, I.; Kondo, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1539–1545.

(15) (a) Lemal, D. M.; Fry, A. J. *J. Org. Chem.* **1964**, *29*, 1673–1676. (b) Masamune, S.; Fukumoto, K.; Yasunari, Y.; Darwish, D. *Tetrahedron Lett.* **1966**, 193–200. (c) Kondo, K.; Ojima, I. *Chem. Commun.* **1972**, 62–63, 63–64, 860–861. (d) Closs, G. L.; Closs, L. E.; Boll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796–3800. (e) Masamune, S.; Chin, C. G.; Hojo, K.; Seidner, R. T. *Ibid.* **1967**, *89*, 4804–4805. (f) Moser, R. E.; Fritsch, J. M.; Westman, T. L.; Kliss, R. M.; Matthews, C. N. *Ibid.* **1967**, *89*, 5673–5676. (h) Buchi, G.; White, J. D. *Ibid.* **1964**, *86*, 2884–2887. (i) Jones, W. M.; Ennis, C. L. *Ibid.* **1969**, *91*, 6391–6397.

(16) (a) Chapman, J. R. *Tetrahedron Lett.* **1966**, 113–119. (b) Cristol, S. J.; Harrington, J. K. *J. Org. Chem.* **1963**, *28*, 1413–1415.

(17) Freeman, P. K.; Hardy, T. A.; Balyeat, J. R.; Wescott, L. D., Jr. *J. Org. Chem.* **1977**, *42*, 3356–3359.

(18) The adjective "photic" may be preferable to "photochemical" in this case, because the phrase "Bamford–Stevens *reaction*" already connotes a *chemical* change.

(19) (a) Krapcho, A. P.; Donn, R. *J. Org. Chem.* **1965**, *30*, 641–644. (b) Kirmse, W.; Pook, K. H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 594. (c) Wiberg, K. B.; Burgmaier, J.; Warner, P. *J. Am. Chem. Soc.* **1971**, *93*, 246–247.

(20) O'Leary, M. A.; Wege, D. *Tetrahedron* **1981**, *37*, 801–811.

can be generated photically from alkenes.[21-23] Therefore, without careful attention to irradiation conditions and without appropriate controls, olefinic products might revert to carbenes. This reversibility could lead to secondary products and complicate interpretation.

We now report the first isolation of a diazo hydrocarbon from the direct photolysis of a tosylhydrazone sodium salt and present evidence that this diazo compound is, indeed, a discrete intermediate in the overall photic Bamford–Stevens reaction. We also show that the "carbene" ultimately produced in the photic route is less stereoselective in its intramolecular rearrangement to cis-trans olefins than is the "carbene" generated in the thermal Bamford–Stevens process.

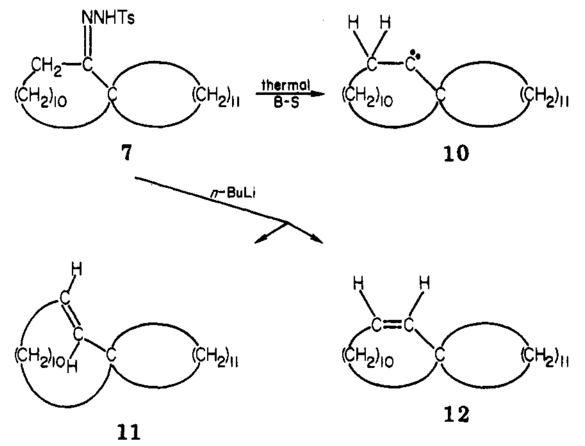
Results and Discussion

Our substrates consisted of large-ring spirocyclics, which are also of interest in connection with other syntheses in our laboratory.[24] Scheme II outlines the synthetic route to the specific compounds in our study.

Cyclododecanone (**1a**) was dimerized reductively with titanium to the known cyclododecylidenecyclododecane (**2a**).[25,26] In efforts to maximize the yield of this dumbbell-shaped olefin **2a**, we explored some of the reported experimental procedures for treatment of aldehydes and ketones with low-valent titanium reagents[25-31] as well as several variations of our own.

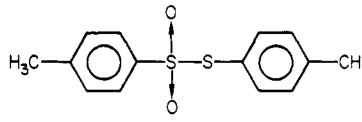
We were not able to reproduce the high yield (up to 90%) of **2a** reported by McMurry and Kees,[26b] but we obtained a 55% yield with Lenoir's method[29] involving $TiCl_4$, zinc, and pyridine in refluxing dioxane. Interestingly, when dioxane was replaced by (lower boiling) tetrahydrofuran, the amount of olefin **2a** diminished to 31% and was accompanied by significant amount of the related diol **4** (16% isolated). Although Corey et al.[27] reported that such pinacols are produced from $TiCl_4$ and magnesium, in our hands that particular combination gave only olefin **2a** (37%). The results from several different sets of reductive coupling conditions are described in the Experimental Section and illustrate the sensitivity of this reaction.

Scheme III



In the next synthetic step, we converted olefin **2a** to oxirane **3a** (63%) with *m*-chloroperoxybenzoic acid. This new oxide was characterized conventionally and was rearranged with boron trifluoride etherate–CH_2Cl_2[32] to the expected spiro ketone **5a** (80%). To confirm the general utility of this route to large-ring spiro ketones of different sizes, we carried out analogous sequences (reductive coupling, epoxidation, and rearrangement) on cyclotridecanone (**1b**) and on cyclotetradecanone (**1c**), and we obtained their corresponding coupled olefins (**2b** and **2c**), oxides (**3b** and **3c**), and spiro ketones (**5b** and **5c**) in yields comparable to those from **1a**. For our studies of the Bamford–Stevens reaction, we focused only on the C_{24} spiro ketone **5a**.

Our attempts to convert **5a** to the *p*-tosylhydrazone **7** with *p*-tosylhydrazine[2a] under a variety of conditions were unsuccessful. In every case we recovered spiro ketone **5a**, and in some runs we also isolated unsymmetrical di-*p*-tolyldisulfide dioxide **9**. In view of the finding by Hertz et al.[33] that **9** is one product from melt pyrolysis of *p*-tosylhydrazine, we presume that reluctance of spiro ketone **5a** to react allows thermal decomposition of the reagent to compete successfully with the desired process. Evidently the hydrocarbon chains on the quaternary "spiro" atom hinder attack on the carbonyl group. This recalcitrance was further demonstrated by our finding that ketone **5a** was also inert to conventional treatment with hydroxylamine or with 95% hydrazine.[34] However, a potential two-step sequence to tosylhydrazone **7** was revealed indirectly by our parallel studies of Wolff–Kishner reduction of **5a** to spiroalkane **8**. After unsuccessfully trying Nagata's modification of the Wolff–Kishner method (reported to proceed efficiently even with hindered carbonyl groups[35]), we tried Barton's forcing conditions (anhydrous hydrazine, temperature >200 °C, and prolonged reaction with sodium dissolved in diethylene glycol).[36] Barton's method produced the desired alkane **8**. Since hydrazones are intermediates in Wolff–Kishner reductions, we then separately converted ketone **5a** to its hydrazone **6** (68% yield) by omitting the sodium alkoxide in the Barton method. Without purification of **6**, its treatment with TsCl/Py under conventional conditions gave us the target *p*-tosylhydrazone **7** in 58% yield.



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To establish a basis for mechanistic comparison, we first studied the *thermal* Bamford–Stevens reaction of tosylhydrazone **7** under aprotic conditions ($NaOCH_3$ in refluxing diglyme). The product mixture (91% yield) consisted of one major component (90% relative yield) and several minor components (10%). The major product,

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[21] Kropp, P. J. In "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Vol. IV, pp 1–142.

[22] Fields, T. R.; Kropp, P. *J. Am. Chem. Soc.* **1974**, *96*, 7559–7560.

[23] (a) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1635–1642. (b) Inoue, Y.; Takamuku, S.; Sakurai, H. *Chem. Commun.* **1975**, 577–578.

[24] Nickon, A.; Zurer, P. St. J. *Tetrahedron Lett.* **1980**, 3527–3530.

[25] McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1976**, *41*, 896–897.

[26] (a) McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708–4709. (b) McMurry, J. E.; Kees, K. L. *J. Org. Chem.* **1977**, *42*, 2655–2656.

[27] Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. *J. Org. Chem.* **1976**, *41*, 260–265.

[28] McMurry, J. E.; Krepski, L. R. *J. Org. Chem.* **1976**, *41*, 3929–3930.

[29] Lenoir, D. *Synthesis* **1977**, 553–554.

[30] Mukaiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041–1044.

[31] Tyrlik, S.; Wolochowiez, I. *Bull. Soc. Chim. Fr.* **1973**, 2147–2148.

[32] See: Ryerson, G. D.; Wasson, R. L.; House, H. O. In "Organic Syntheses"; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect Vol. IV, pp 957–959.

[33] Hertz, H. S.; Coxon, B.; Siedle, A. R. *J. Org. Chem.* **1977**, *42*, 2508–2509.

[34] Iwadare, T.; Nickon, A., unpublished work.

[35] Nagata, W.; Itazaki, H. *Chem. Ind. (London)* **1964**, 1194–1195.

[36] Barton, D. H. R.; Ives, D. A. J.; Thomas, B. R. *J. Chem. Soc.* **1955**, 2056.

isolated by crystallization, showed a strong IR band at 980 cm^{-1} typical of a trans-disubstituted alkene. Catalytic hydrogenation (Pt) converted this olefin to the same spiroalkane **8** obtained earlier by Wolff–Kishner reduction of spiro ketone **5a**. These facts suggest our major product from thermal Bamford–Stevens is the (*E*)-spiroalkene **11**, presumably derived from a vicinal-hydrogen shift in the intermediate carbene **10** (Scheme III).

Our identification is supported by ^1H and ^{13}C NMR data. The ^1H spectrum showed vinylic, allylic, and aliphatic protons in the ratio 1:1:20 in accord with structure **11**. The ^{13}C NMR (broad-band proton decoupled) showed 18 distinct resonance peaks. Two signals had chemical shifts typical of olefinic carbons (δ 126.67 and 141.42).[37] With off-resonance decoupling, each olefinic signal appeared as a doublet, indicating attachment of a single H to each olefinic carbon. Further, two carbons absorbed at δ 39.48 and 42.01, i.e., in the region expected for allylic carbons.[37] One of these allylic centers (δ 39.48) carried two H's, and the other (δ 42.01) is quaternary as evidenced by the splitting patterns (triplet and singlet, respectively) in a single-frequency, off-resonance decoupling experiment.

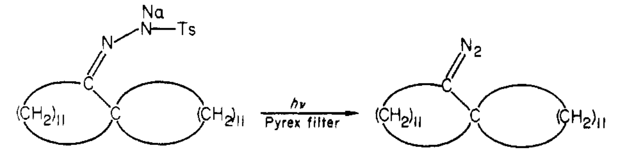
To get some notion of the minor hydrocarbons from the thermal Bamford–Stevens reaction, in a second run we oxidized the crude product mixture with *m*-chloroperoxybenzoic acid, which epoxidized spiroalkene **11** but not the other components. These minor products were then readily separated from the oxide by column and thin-layer chromatography. On GLC, the mixture of minor hydrocarbons showed three peaks (one of which was broad and probably itself a composite peak). Interestingly, however, the ^{13}C NMR of this mixture showed no olefinic carbons and so, within the limit of NMR detectability, ruled out the possibility that these side products were unsaturated. This aspect is noteworthy for two reasons. First, one of the competing fates for carbene **10** might have been a 1,2 alkyl shift to produce tetrasubstituted olefins (three possible isomers). Evidently, therefore, even in this spirocyclic system, hydrogen shift wins handily over alkyl shift.[2b,c,19] Second, the H shift in **10** produced only the (*E*)-alkene and not the (*Z*)-alkene. Ordinarily, open-chain[38] and large-ring (e.g., C_{13})[39] aliphatic ketones give mixtures of (*Z*)- and (*E*)-alkenes in thermal Bamford–Stevens reactions. The high stereoselectivity in our spiro substrate may indicate that nonbonded interactions prevent the molecule from adopting the proper transition-state geometry[12] for *Z* olefin formation. The ^{13}C NMR of the minor product mixture did show a signal at unusually high field (δ 6.78), indicating that at least one byproduct contains a cyclopropyl ring.[37] Very likely the minor components are alkanes from various hominal,[40] and perhaps transannular, C–H insertions by spirocarbene **10**.

To confirm our structural assignment for spiroalkene **11**, we applied the Shapiro reaction[2a] to tosylhydrazone **7**. In this reaction tosylhydrazones of appropriate structure, when treated with an excess of an alkyllithium, produce terminal or disubstituted alkenes without skeletal or double-bond rearrangements. In our case a hexane suspension of tosylhydrazone **7** with *n*-butyllithium gave us a 2:1 mixture (50% yield) of two hydrocarbons. The predominant component, isolated by preparative $AgNO_3$ TLC, was identical with (*E*)-spiroalkene **11** from the earlier aprotic thermal Bamford–Stevens reaction. Although we were not able to separate the minor component, a chromatographic fraction enriched in this component (i.e., 1:1 mixture) was examined spectroscopically. The ^1H NMR spectrum was similar to that of pure (*E*)-alkene **11**, with vinylic, allylic, and aliphatic protons in the expected ratio of 1:1:20. The IR spectrum showed a peak at 980 cm^{-1} (trans CH=CH) that was less intense relative to CH absorption at 2920 cm^{-1} than in the spectrum of pure **11**. We hydrogenated this 1:1 mixture and obtained an 87% yield of spiroalkane **8**. This high yield indicates the unidentified component in the 1:1 mixture has the same spirocyclic skeleton as **11**. The combined evidence, along with the known reliability of the Shapiro reaction to produce only unrearranged alkenes,[2a] leads us to assign to the minor "Shapiro" product the (*Z*)-spiroalkene structure **12**. Interestingly, when we used diethyl ether as the solvent in place of hexane, the Shapiro reaction gave the same two olefins, **11** and **12**, but the *E*/*Z* ratio was markedly higher (viz., 92:8 compared to 2:1). This behavior has precedent because Waegell and Casanova found that the cis/trans olefin ratio from "Shapiro" treatment of a series of cycloalkanone tosylhydrazones varied with solvent.[39]

In our study of the photic Bamford–Stevens reaction, we irradiated a heptane suspension of the sodium salt **13** (prepared in situ from **7** and sodium methoxide). The results differed according to the light filter used. With Vycor-filtered UV irradiation ($\lambda > 220$ nm), we obtained a hydrocarbon mixture (90% yield) comprised of one major component and several minor ones, in the ratio of 80:20 (GLC). Column chromatography on $AgNO_3$-impregnated silica gel first gave an oil (10% relative yield) identified as alkanes, likely resulting from hominal and/or transannular insertions by carbene **10**.

Next we eluted a liquid mixture (90% relative yield) of (*E*)-spiroalkene **11** and (*Z*)-spiroalkene **12** in the ratio 89:11, respectively. We identified these olefins by GLC and $AgNO_3$ TLC comparisons with samples obtained earlier in the Shapiro reaction. Control experiments established that these two olefins were stable to our irradiation conditions. When we used sodium hydride in place of sodium methoxide to generate the salt **13**, our yield of hydrocarbon mixture after Vycor-filtered irradiation was quantitative, and the ratios of the components were alkanes (11%), (*E*)-spiroalkene **11** (73%), (*Z*)-spiroalkene **12** (14%), and three unidentified products (total 2%).

In contrast to the Vycor-filtered irradiations, when we used Pyrex-filtered UV light ($\lambda >$ ca. 270 nm), we did not obtain hydrocarbon products. Instead, we isolated in virtually quantitative yield a pink liquid, identified as diazoalkane **14** spectroscopically and by C and H analyses.



13 **14**

The strongest band in its IR spectrum is at 2015 cm^{-1}, characteristic of the C=N=N unit in diazohydrocarbons.[41]

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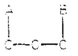
[37] (a) Stothers, J. B. In "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. (b) Johnson, L. F. In "Topics in Carbon-13 NMR Spectroscopy"; Levy, G. C., Ed.; Wiley: New York, 1969; pp 2–16.

[38] Yamamoto, Y.; Moritani, I. *Tetrahedron* **1970**, *26*, 1235–1242.

[39] Casanova, J.; Waegell, B. *Tetrahedron* **1975**, *31*, 1035–1045.

[40] Hominal is a term used to indicate a 1,3-relationship between groups. See: Nickon, A.; Weglein, R. C.; Mathew, C. T. *Can. J. Chem.* **1981**, *59*, 302–313.



hominal

vicinal

geminal

[41] Ben-Efraim, D. A. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: New York, 1978; Part 1, pp 149–178.

Table I. Product Ratios from Photic and Thermal Bamford–Stevens Reactions and from Diazoalkane Irradiation

reaction	base (temp, °C)	$h\nu$ filter	rel % (normalized) 11	12	alkanes	other
photic B-S on 13	$NaOCH_3$ (20)	Vycor[a]	80	10	10	
photic B-S on 13	NaH (20)	Vycor[a]	75	14	11	b
photolysis of 14[c]	$NaOCH_3$ (20)	Vycor[a]	78	12	10	d
thermal B-S on 13	$NaOCH_3$ (140)		90		10	

[a] Transmits $\lambda >$ ca. 220 nm. [b] Unidentified products amounted to ca. 2% of the total hydrocarbon product. [c] Prepared in situ from 13 and $NaOCH_3$ by prior irradiation through a Pyrex filter (transmits $\lambda >$ ca. 270 nm). [d] Of the total hydrocarbon product, 7% were olefins 2a, 16, 17, and 18 from cationic paths, and 4% were unidentified.

In heptane it showed UV maxima at 231 (ϵ 5000) and at 490 nm (ϵ 3). We confirmed the structure of 14 by preparing it (83% yield) independently through manganese dioxide oxidation of hydrazone **6**.

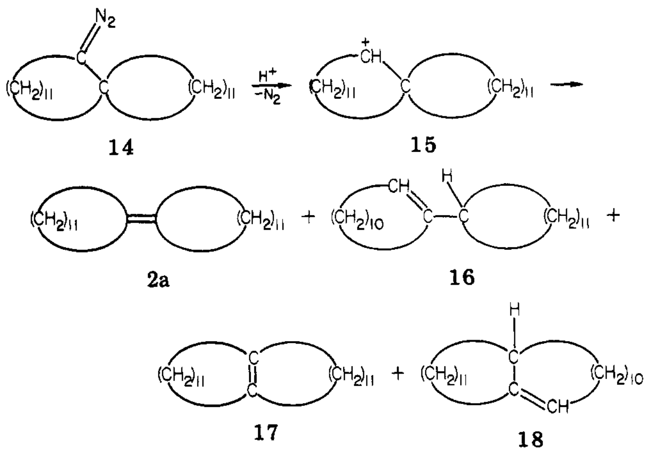
Our isolation of diazoalkane 14 suggests that diazo compounds are, indeed, initial intermediates in photic Bamford–Stevens reactions. Diazoalkane 14 appears unusual in its stability to Pyrex-filtered UV light.[39] Its pink color and its UV absorption spectrum leave no doubt that it does absorb, albeit weakly [λ 490 (ϵ 3)] above the Pyrex cutoff. Evidently, however, photoreaction from the resulting excited state of the diazo compound is slow enough to permit its accumulation and isolation.

To establish that diazoalkane 14 is a true intermediate in the photic Bamford–Stevens process and not produced in an unrelated side reaction, we generated 14 in situ by Pyrex-filtered irradiation for 40 min. We then replaced the Pyrex filter with a Vycor filter and continued irradiation another 40 min. Workup gave a hydrocarbon mixture (80% yield). Column chromatography on $AgNO_3$-impregnated silica gel gave an alkane fraction (9% relative yield); presumably these are products of hominal and/or transannular C–H insertions by carbene 10. Gas chromatography revealed that later fractions contained two major olefins, (*E*)-spiroalkene 11 (69%) and (*Z*)-spiroalkene 12 (11%) as well as four minor alkenes (total 7%) and three unidentified components (total 4%). The four minor alkenes were identified as **2a** (1%), 16 (1%), 17 (trace) and 18 (5%) (Scheme IV).[42] The following three lines of evidence suggest they arise from competitive cationic decomposition of diazo hydrocarbon 14 brought about by traces of adventitious protons: (a) olefins 16 and 18 cannot be primary products of rearrangement of a carbene from 14; (b) although tetrasubstituted olefins **2a** and 17 could conceivably arise by a 1,2 alkyl shift in carbene 10, we did not encounter either of these two isomers when we generated this carbene thermally (Scheme III); (c) a separate study has shown that cation 15, generated solvolytically, gives olefins **2a** and 16–18.[24]

Table I summarizes the relative proportions of hydrocarbon products from two *photic* Bamford–Stevens reactions of 7 (Vycor; sodium salt generated in situ with sodium methoxide and with sodium hydride), from Vycor-filtered irradiation or diazoalkane 14, and from *thermal* Bamford–Stevens reaction of 7.

For the three photic reactions, the normalized product ratios of 11:12:alkanes are very similar if we ignore the 2–4% of unidentified hydrocarbons and also subtract the small proportions (7%) of olefins attributable to competitive cationic paths. Given the slightly different experimental conditions necessary in each case and the known difficulty in excluding cationic paths completely, our results indicate that diazoalkane 14 is a discrete intermediate in the photic decomposition of sodium salt 13 with Vycor-filtered light.

Scheme IV



When we compare the ratio of *E* olefin 11 to *Z* olefin 12 from the thermal and photic Bamford–Stevens reactions, we note lower stereoselectivity in the latter case. We established that the photoproducts are stable to our reactions' conditions, and so the difference is real. Several interpretations may be offered, including the possibility that a carbene from a photic path can rearrange from a different singlet state than does the carbene generated from the thermal Bamford–Stevens route.[12] This possibility is strengthened by recent work by Chang and Shechter.[43] They found experimental evidence that intramolecular rearrangements and hominal C–H insertions can occur from two different *singlet* states of carbenes. Also, Chambers and Jones have shown that products can arise from different singlet carbenes even in intermolecular reactions.[44] We wish to stress, as we and others have done before,[2,12,45] that products of "carbene" reactions (e.g., rearrangements) might sometimes arise from excited diazo compounds[46] or from species in which the departing nitrogens play some role.[47] The essential features of our present paper are not altered whether we invoke true carbenes or diazo compounds as the rearranging species.

Experimental Section

General Methods. Melting points are uncorrected and were obtained in Pyrex capillaries on a Thomas-Hoover Unimelt apparatus.

Infrared (IR) spectra were obtained with a Perkin-Elmer Model

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[42] Olefins 16–18 were isolated and characterized in connection with another project.[24]

[43] Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082–5084.

[44] Chambers, G. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4516–4518.

[45] Wulfman, D. S.; Poling, B.; McDaniels, R. S., Jr. *Tetrahedron Lett.* **1975**, 4519–4522.

[46] Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072–3075.

[47] Tomioka, H.; Ueda, H.; Kondo, S.; Izawa, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7817–7818.

457A grating spectrophotometer as solutions in $CHCl_3$ or CCl_4 (0.5-mm Irtran cells), or neat films, or as Nujol mulls (sodium chloride cells). The 1602-cm^{-1} band of polystyrene film was used as an external calibration standard.

Proton magnetic resonance (^1H NMR) spectra were obtained at 100 MHz on a JEOL MH-100 spectrometer. Chemical shifts are reported in δ units downfield from the internal standard tetramethylsilane.

Carbon-13 magnetic resonance spectra (^{13}C NMR) were obtained on a Varian Model CFT-20 spectrometer (20 MHz) with Fourier transform and with full proton broad-band noise decoupling. Carbon shifts are reported in δ units downfield from the internal standard Me_4Si. When given, carbon multiplicities were obtained from separate single-frequency, off-resonance decoupling experiments. These spectra were obtained in $CDCl_3$ solution except as noted, and the internal deuterium lock was maintained on the solvent.

Elemental microanalyses were performed by Galbraith Laboratories.

Tetrahydrofuran (THF), dioxane, and diethyl ether (ether) were distilled from sodium benzophenone ketyl under nitrogen.[48] Boron trifluoride etherate and pyridine were distilled from calcium hydride. Titanium tetrachloride ($TiCl_4$) was distilled under argon. Methylene chloride (CH_2Cl_2) and hexane were commercial "reagent grade". Heptane was "distilled in glass" spectrophotometric grade.

The term molecular sieves refers to Davison molecular sieves, Type 4A, Grade 514, 8–12 mesh.

Brine refers to saturated aqueous sodium chloride solution.

The notation TLC refers to analytical thin-layer chromatography on 7.5 × 1.5 cm microscope slides coated with Merck silica gel GF-254. The plates were developed with ethyl acetate/cyclohexane (4/1).

The designation $AgNO_3$ TLC refers to analytical thin-layer chromatography on 20 × 5 cm silica gel GF-254 plates with 15% $AgNO_3$, 250 μm thick, purchased from Analtech. The plates were developed with hexane. Preparative $AgNO_3$ TLC refers to chromatography on 20 × 20 cm plates with the same adsorbant, 1500 μm thick, also purchased from Analtech and developed with hexane.

The term GLC refers to analytical studies with a Perkin-Elmer Model 900 gas chromatograph equipped with a flame-ionization detector and a Honeywell Model 16 recorder. Integrations were obtained from triangulation, from a disk integrator, or from the digital readout of a Perkin-Elmer Sigma 10 chromatography data station. Helium carrier gas was used. The columns used were 9 ft × $^1/_8$ in. o.d. stainless steel (1.5% SE-30 on Chromosorb W-HMDS, 50/100-mesh) and 4 ft × $^1/_8$ in. o.d. stainless steel (2.5% BBBT[49] on Chromosorb W-HP, 100/200-mesh). The analyses were performed at a 40-psi inlet pressure and at a temperature of 200 or 210 °C (SE-30) or at a 30-psi inlet pressure at a temperature of 190 °C (BBBT). In describing GLC analyses, we list the peaks in order of elution.

The designation $AgNO_3$ silica gel refers to Merck silica gel 60 impregnated as follows with $AgNO_3$ so that the adsorbent was 20% $AgNO_3$ by weight. A solution of $AgNO_3$ (6 g) in distilled water (15 mL) was added to a slurry of silica gel (24 g) in distilled water in a round-bottomed flask. Most of the water was evaporated in vacuo, and the flask containing the moist silica was kept in an oven (140 °C) overnight. The resulting free-flowing silica gel was stored in a brown bottle.

Cyclododecylidenecyclododecane (2a) from Cyclododecanone (1a). The known[25,26] olefin **2a** was prepared by a modification of pinacolic coupling described by Corey.[27] The reaction as described by Corey produces pinacols. In our hands the reaction required higher temperatures and afforded the corresponding olefins rather than pinacols.

Magnesium (0.730 g, 30 mmol; 70–80 mesh, Alfa) was added to a solution of mercuric chloride (0.220 g, 0.8 mmol) in distilled THF (15 mL) under an N_2 atmosphere. The mixture was stirred at room temperature for 30 min, and then the turbid supernatant liquid was removed by syringe. The residue was triturated with three 10-mL portions of THF, and then was covered with 24 mL of THF. The mixture was cooled to −10 °C in a dry ice/acetone bath and treated dropwise with 1.65 mL (2.85 g, 15 mmol) of titanium tetrachloride (Alfa). (A yellowish green precipitate formed, which may be a complex between THF and $TiCl_4$.) A solution of cyclododecanone (1.82 g, 10 mmol; Aldrich) in THF (25 mL) was added all at once. The mixture was allowed to warm gradually. At 10 °C the mixture gradually turned purplish black. It was held between 5 and 15 °C and stirred for 1.5 h. The dark black mixture was cooled to 0 °C, and saturated aqueous NaCl (6 mL) was added cautiously. After 15 min at room temperature, the stirred mixture was diluted with ether and was passed through Celite filter aid, which was washed well with ether. The filtrate was dried over $MgSO_4$ and evaporated in vacuo. The crude product was chromatographed on Merck silica gel 60 (hexane elution) and then was recrystallized from hexane: mp 154.5–155.5 °C (lit.[26b] mp 150–152 °C); 37% yield; IR ($CHCl_3$) 2920, 2850, 1470 (CH_2 scissor) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–1.70 (br envelope, 36 H, ring methylenes), 1.90–2.18 (br m, 8 H, allylic methylenes); ^{13}C NMR ($CDCl_3$) δ 22.06, 23.04, 24.47, 26.01, 26.16, 27.44, 133.69.

Anal. Calcd for $C_{24}H_{44}$ (mol wt. 332.60): C, 86.66; H, 13.34. Found: C, 86.47; H, 13.50.

Cyclotridecylidenecyclotridecane (2b) from Cyclotridecanone (1b). New olefin **2b** was prepared from cyclotridecanone (Aldrich) according to the procedure described for olefin **2a**. The crude product was chromatographed on Merck silica gel 60 (hexane elution) and then was recrystallized from ethanol as a white solid (**2b**): mp 101.5–102.5 °C; 20% yield; IR ($CHCl_3$) 2920, 2850, 1455 (CH_2 scissor) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–1.58 (br envelope, 40 H, ring methylenes), 1.85–2.15 (br m, 8 H, allylic methylenes); ^{13}C NMR ($CDCl_3$) δ 24.50, 25.49, 25.78, 26.53, 27.36, 31.96, 133.89.

Anal. Calcd for $C_{26}H_{48}$ (mol wt. 360.64): C, 86.58; H, 13.42. Found: C, 86.54; H, 13.22.

Cyclotetradecylidenecyclotetradecane (2c) from Cyclotetradecanone (1c). This new olefin was synthesized from cyclotetradecanone (mp 54–55 °C) by the procedure described for olefin **2a**. The crude product was chromatographed on 30 g of Merck silica gel 60 and eluted with a hexane–ether gradient. Hexane eluted 0.45 g of white solid, and hexane–ether (1:1) eluted 0.400 g of starting ketone. Recrystallization from hexane gave white **1c**: mp 122–123 °C (31% yield); IR ($CHCl_3$) 2920, 2850, 1460 (CH_2 scissor); ^1H NMR (CCl_4) δ 1.10–1.60 (br envelope, 44 H, ring methylenes), 1.80–2.15 (br shapeless t, 8 H, allylic methylenes); ^{13}C NMR ($CDCl_3$) δ 24.26, 25.74, 25.82, 26.23, 26.50, 26.95, 30.66, 133.40.

Anal. Calcd for $C_{28}H_{52}$ (mol wt 388.73): C, 86.52; H, 13.48. Found: C, 86.67; H, 13.55.

Reductive Coupling with $TiCl_3$ and Potassium. Cyclododecanone was coupled with Ti° produced from $TiCl_3$ and K in refluxing THF according to the procedure described by McMurry.[25] The yield of olefin **2a** isolated by column chromatography, as described earlier, was 24% (mp 153–155 °C). Cyclotetradecanone coupled in the same manner gave 34–40% of olefin **2c** (mp 122.5–123.5 °C).

Reductive Coupling with $TiCl_3$ and Lithium. Cyclododecanone was coupled with Ti° produced from $TiCl_3$ and Li in refluxing dimethoxyethane according to McMurry and Krepski.[28] Olefin **2a** was isolated by column chromatography in 26% yield (mp 154–155 °C).

Reductive Coupling with $TiCl_4$ and Lithium. A piece (14.75 cm) of $^1/_8$-in. diameter lithium wire (0.6 g, 90 mmol) was cut into small chunks under an argon atmosphere. The metal was washed with hexane (2 × 4 mL) and ether (2 × 4 mL) and then was covered with distilled dimethoxyethane (30 mL) under argon. The mixture was stirred at room temperature while $TiCl_4$ (2.2 mL, 3.8 g, 20 mmol) was added slowly by syringe. During addition the solvent turned red, a yellow-green suspension developed, and then the solvent turned black as the yellow-green solid dissolved. The mixture was refluxed for 1.5 h and gave a black solution with pieces of undissolved lithium visible. Cyclododecanone (0.910 g, 5.0 mmol) was added all at once, and the mixture was refluxed overnight. It was cooled, hexane (50 mL) was added, and the mixture was stirred 2 h at room temperature. The solution was separated from a black, gummy residue by decantation and by

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[48] Finke, R. G.; Sorrell, T. N. *Org. Synth.* **1979**, *59*, 102–112. See Note 4.

[49] Janini, G. M.; Muschik, G. M.; Zielinski, W. L., Jr. *Anal. Chem.* **1976**, *48*, 809–813.

filtration through Celite filter aid, which was washed well with hexane. The filtrate was evaporated in vacuo, and the crude product was chromatographed on silica gel. Hexane eluted 0.037 g (4% yield) of olefin **2a** (melting point not recorded). Starting ketone (0.520 g) was eluted with 5% ether/hexane.

Reductive Coupling with $TiCl_4$ and Potassium. Potassium (1.8 g, 46 mmol) was covered with distilled THF (50 mL) under argon and was chilled to 0 °C. Titanium tetrachloride (1.25 mL, 2.16 g, 11.4 mmol) was added dropwise by syringe. A yellow-green precipitate formed. The mixture was heated to reflux. As the potassium melted, the yellow solid dissolved, and a black precipitate formed (Ti° metal?). The mixture was refluxed 1 h. A solution of cyclododecanone (0.520 g, 2.9 mmol) in THF (10 mL) was added, and the mixture was refluxed overnight. It was cooled, and CH_3OH (3 mL) was added cautiously. The mixture was passed through Celite filter aid, which was washed well with ether. The filtrate was dried (molecular sieves) and was evaporated in vacuo. The crude mixture was chromatographed on silica gel. Olefin **2a** was eluted with hexane and was recrystallized from hexane: mp 154–155 °C; 25% yield.

Reductive Coupling with $TiCl_4$ and Zinc in THF and Pyridine. Preparation of 1,1′-Bicyclododecanol (4). Cyclododecanone was coupled with a titanium species prepared by treatment of zinc dust (activated by being washed with HCl[50]) with $TiCl_4$ and pyridine in THF according to the procedure described by Lenoir.[29] The reaction mixture was refluxed before workup. The crude product was purified by column chromatography on Merck silica gel 60. Hexane eluted olefin **2a** as a white solid: 31% yield; mp 154–155 °C (after recrystallization from hexane). Ether eluted white, solid 1,1′-bicyclododecanol (**4**): 16% yield; mp 156.5–157.5 °C (after recrystallization from hexane); IR ($CHCl_3$) 3620–3450 cm^{-1} (complex bands due to free, intramolecularly, and intermolecularly bonded OH); ^1H NMR ($CDCl_3$) δ 1.0–2.0; ^{13}C NMR ($CDCl_3$) δ 20.81, 22.83, 23.08, 26.20, 27.30, 31.83, 79.97.

Anal. Calcd for $C_{24}H_{46}O_2$ (mol wt 364.58): C, 78.62; H, 12.52. Found: C, 78.45; H, 12.52.

Reductive Coupling with $TiCl_4$ and Zinc in Dioxane and Pyridine. Cyclododecanone was coupled with a titanium species prepared from activated Zn dust[50] and $TiCl_4$ in pyridine and dioxane according to the procedure of Lenoir.[29] The reaction mixture was refluxed for 20 h and then was worked up. Cyclododecylcyclododecylidene **2a** (mp 154–155 °C) was isolated in 55% yield after column chromatography and recrystallization from hexane.

Cyclotetradecylidenecyclotetradecane Oxide (3c) from Olefin 2c. A suspension of alkene **2c** (0.230 g, 0.59 mmol) in methylene chloride (10 mL) was stirred at room temperature while commercial 85% *m*-chloroperoxybenzoic acid (0.240 g, 1.18 mmol, 2 equiv) was added all at once. Complete solution occurred. The solution was stirred 1 h at room temperature, and then 10% aqueous Na_2SO_3 (10 mL) was added. After 10 min the stirred solution gave a negative starch–iodide test. The organic layer was separated, washed with saturated $NaHCO_3$ and with brine, and was dried (molecular sieves). Evaporation in vacuo left the oxide **3c** as a white solid, which was crystallized from hexane: 0.140 g (59%); mp 126–127 °C; IR ($CHCl_3$) 2920, 2855, 1470 (CH_2 scissor) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55–1.75 (br envelope); ^{13}C NMR ($CDCl_3$) δ 21.66, 23.92, 25.00, 25.94, 26.37, 26.82, 29.75, 67.76.

Anal. Calcd for $C_{28}H_{52}O$ (mol wt 404.70) C, 83.09; H, 12.95. Found: C, 83.17; H, 12.80.

Cyclododecylidenecyclododecane Oxide 3a from Olefin 2a. The epoxidation was carried out as described for **3c**. Recrystallization of the crude **3a** from hexane gave white crystals: mp 153–154 °C; 63% yield; IR ($CHCl_3$) 2920, 2850, 1460 (CH_2 scissor) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.85 (br envelope); ^{13}C NMR ($CDCl_3$) δ 20.25, 22.00, 22.28, 26.09, 26.46, 26.79, 68.29.

Anal. Calcd for $C_{24}H_{44}O$ (mol wt 348.59): C, 82.69; H, 12.72. Found: C, 82.45; H, 12.81.

Cyclotridecylidenecyclotridecane Oxide 3b from Olefin 2b. This oxide was prepared as described for **3c**. The crude **3b** was recrystallized from hexane: mp 99–100 °C; 90% yield; IR ($CHCl_3$) 2920, 2850, 1460 (CH_2 scissor) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15–1.80 (br envelope); ^{13}C NMR ($CDCl_3$) δ 22.31, 25.13, 25.58, 26.32, 27.30, 30.39, 67.73.

Anal. Calcd for $C_{26}H_{48}O$ (mol wt 376.64): C, 82.91; H, 12.85. Found: C, 83.07; H, 12.98.

Spiro[14.12]octacosan-15-one (5c) from Oxide 3c. A solution of oxide **3c** (0.116 g) in methylene chloride (10 mL) was treated with distilled $BF_3 \cdot Et_2O$, (20 mL) and was stirred at room temperature for 2 h. Aqueous $NaHCO_3$ (1 mL) was added, and stirring was continued 15 min. The organic layer was dried (molecular sieves). Evaporation in vacuo left **5c** as a white solid, which was recrystallized from hexane: 0.085 g (73%); mp 97.5–98.5 °C; IR ($CHCl_3$) 2920, 2850 (CH), 1691 (C=O), 1460 (CH_2 scissor) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80–1.85 (br m, 50 H, ring methylenes), 2.40 (t, J = 7 Hz, 2 H, methylene α to C=O); ^{13}C NMR ($CDCl_3$) δ 19.96, 22.45, 23.10, 23.56, 24.08, 25.87, 26.09, 26.54, 26.91, 27.34, 27.64, 27.75, 31.36, 36.18, 37.06, 54.28, 216.17.

Anal. Calcd for $C_{28}H_{52}O$ (mol wt 404.70): C, 83.09; H, 12.95. Found: C, 83.25; H, 13.08.

Spiro[12.11]tetracosan-13-one (5a). Ketone **5a** was prepared from oxide **3a** by the procedure described for ketone **5c**. The crude product after recrystallization from hexane had the following: mp 106–107 °C (80% yield); IR ($CHCl_3$) 2920, 2850 (CH), 1691 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90–1.85 (br m, 42 H, ring methylenes), 2.50 (t, J = 6 Hz, 2 H, methylene α to C=O); ^{13}C NMR ($CDCl_3$) δ 18.98, 21.96, 22.51, 24.54, 25.44, 25.61, 26.17, 26.38, 26.70, 27.18, 29.09, 36.08, 36.96, 54.29, 216.32.

Anal. Calcd for $C_{24}H_{44}O$ (mol wt 348.59): C, 82.69; H, 12.72. Found: C, 82.54; H, 12.58.

In other runs, spiro ketone **5a** was obtained as a white solid with a melting point of 94–96 °C when recrystallized from ethanol. When a melted sample solidified, it remelted at 105–107 °C. Analysis of a sample with a melting point of 94–96 °C gave C (82.53) and H (13.02) analyses as expected for $C_{24}H_{44}O$.

Spiro[13.12]tetracosan-14-one (5b). Ketone **5b** was prepared from oxide **3b** as described for ketone **5c**. The product was recrystallized from absolute ethanol: mp 89–91 °C; 65% yield; IR ($CHCl_3$) 2920, 2840 (CH), 1690 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85–1.85 (br m, 46 H, ring methylenes), 2.43 (t, J = 7 Hz, 2 H, methylene α to C=O); ^{13}C NMR ($CDCl_3$) δ 20.55, 20.66, 21.63, 23.68, 24.00, 24.22, 24.34, 25.61, 25.76, 26.12, 26.38, 26.99, 27.12, 28.15, 31.54, 33.97, 37.24, 54.32, 215.82.

Anal. Calcd for $C_{26}H_{48}O$ (mol wt 376.64): C, 82.91; H, 12.85. Found: C, 83.03; H, 13.13.

Attempted Preparation of Tosylhydrazones from Ketones 5a–c. Various reaction conditions were examined in attempts to prepared tosylhydrazones from these three ketones. In every experiment, the starting ketone was recovered unchanged. In some cases known,[33] unsymmetrical di-*p*-tolyldisulfide dioxide **9** was isolated. The reaction conditions we tried with **5c** included tosylhydrazine (1.2 equiv) in refluxing methanol (with and without catalytic hydrochloric acid), tosylhydrazine (2 equiv) in refluxing xylene with azeotropic water separation, tosylhydrazine (10 equiv) in refluxing absolute ethanol, tosylhydrazine (5 equiv) in refluxing ethylene dichloride; tosylhydrazine (1.2 equiv) in refluxing ethanol with $BF_3 \cdot Et_2O$ (1 equiv) as catalyst, and tosylhydrazine (3 equiv) in refluxing toluene with $TiCl_4$ (0.5 equiv) as a catalyst. Trials with **5a** included tosylhydrazine (1.2 equiv) in refluxing ethanol and tosylhydrazine (1.1 equiv) in refluxing acetonitrile with catalytic hydrochloric acid. One attempt with **5b** involved ketone and tosylhydrazine (1.1 equiv) in refluxing ethanol.

Attempted Preparation of the Oxime of Ketone 5a. A solution of ketone **5a** and hydroxylamine hydrochloride (5 equiv) in ethanol and pyridine was refluxed 3 h and then stirred 72 h at room temperature. A normal workup resulted in recovery of starting ketone, with no evidence for formation of an oxime.

Attempted Preparation of Hydrazones of Ketones 5c and 5a at Atmospheric Pressure. Ketone **5c** was refluxed overnight with an excess of 95% hydrazine in n-butyl alcohol (the method of Iwadare[34]). The ketone was recovered unchanged. (Ketone **5a** also gave no reaction under the same conditions.) Similarly, ketone **5c** did not react with hydrazine after refluxing 18 h in ethanol with catalytic hydrochloric acid.

Attempted Wolff–Kishner Reduction of Ketone 5a according to the Procedure of Nagata.[35] Ketone **5a** (0.10 g, 0.29 mmol), *p*-toluenesulfonic acid (1.77 g, 9.3 mmol), distilled triethylene glycol (5.75 mL), and hydrazine (Eastman, 95+%, 3.9

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[50] Frank, R. L.; Smith, P. V. In "Organic Syntheses"; Horning, E. C., Ed.; Wiley: New York, 1955; Collect. Vol. III, pp 410–412.

mL, 120 mmol) were combined, and the heterogeneous mixture was stirred magnetically. The reaction mixture was then refluxed (internal temperature 135 °C, complete solution) for 3 h. Potassium hydroxide pellets (95%, 1.32 g, 20 mmol) were added, and the mixture was distilled slowly until the internal temperature reached 210 °C, where it was held for 3 h, during which time a white solid precipitated. After being allowed to stand at room temperature overnight, the semisolid mixture was partitioned between water and ether (4 × 10 mL). The workup left a white solid (0.10 g) identical with starting ketone by IR, TLC, and GLC.

Wolff-Kishner Reduction of Ketone 5a via the Barton Modification.[36] In oven-dried glassware under nitrogen was dissolved sodium (~0.09 g, ~4 mmol) in freshly distilled diethylene glycol (5 mL). Ketone **5a** (0.035, 0.1 mmol) and anhydrous hydrazine (1.5 mL) were added. [We prepared the anhydrous hydrazine by refluxing 95+% hydrazine (10 mL) over NaOH pellets (10 g) and then distilling it under nitrogen.] The heterogeneous mixture was heated (internal temperature 185 °C, complete solution) and refluxed overnight. (**Caution**: When we attempted to repeat this reaction under seemingly identical conditions, the reaction mixture caught fire while being heated to reflux.) During the night the reaction temperature rose to 202 °C. The reaction mixture was distilled until the internal "pot" temperature reached 210 °C. A reflux condenser was attached, and the mixture was heated at an internal temperature of 210–220 °C overnight. The cooled mixture was partitioned between water and ether (4 × 10 mL). Some white solid was not soluble in either phase. The combined ether was washed with 3 N HCl and brine, was dried (molecular sieves), and was evaporated in vacuo. The viscous oil (0.027 g) was a mixture of starting ketone **5a** (15%) and hydrocarbon **8** (85%) by GLC (SE-30). The crude product was chromatographed on Merck silica gel 60 (1.5 g). Alkane **8** (0.012 g) was eluted with hexane. It crystallized on trituration with hexane. Recrystallization from pentane gave a white solid: mp 84–86 °C; IR ($CHCl_3$) 2920, 2860, 1470 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05–1.60; ^{13}C NMR δ 18.72, 20.28, 22.20, 22.77, 25.73, 25.94, 26.29, 27.02, 28.60, 33.02, 35.53, 37.71.

Anal. Calcd for $C_{24}H_{46}$ (mol wt 334.61): C, 86.14; H, 13.86. Found: C, 86.03; H, 13.91.

Spiro[12.11]tetracosan-13-one Tosylhydrazone (7) from Ketone 5a via Hydrazone 6. A heterogeneous mixture of ketone **5a** (0.50 g, 1.4 mmol), distilled diethylene glycol (10 mL), anhydrous hydrazine (2.5 mL, prepared by the method of Kusama[51]), and 10 drops of concentrated H_2SO_4 in a thick-walled Pyrex tube was flushed with nitrogen and sealed at atmospheric pressure. The tube was heated in a Carius oven for 87 h at 170–180 °C and then cooled to 0 °C. [**Caution**: When this sealed-tube reaction was attempted on a larger scale (1.2 g of ketone), one tube exploded in the Carius oven.] The tube was opened cautiously (some pressure), and the content was partitioned between water and ether (4 × 25 mL). The ether was washed exhaustively with water (until the washings were neutral) and then with brine, was dried (molecular sieves), and was evaporated in vacuo. The viscous oil (0.48 g) was combined with crude product from another run (0.125 g from 0.5 mmol of ketone) and chromatographed on Merck silica gel 60 by elution with a hexane–ether gradient. Hydrazone **6** was eluted with 20% ether/hexane: viscous oil; 0.46 g (68%); IR ($CHCl_3$) 3400, (NH), 2920, 2855, 1640 (C=N), 1460, 1440 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–1.7 (br enveloped, methylene), 2.00–2.15 (distorted t, CH_2 α to C=N), 4.70–5.30 (br, NH_2). Without further purification, the hydrazone was used directly in the next step.

A solution of hydrazone **6** (0.46 g, 1.3 mmol) in pyridine (20 mL) was stirred in an ice bath while tosyl chloride (0.28 g, 1.5 mmol; Aldrich; mp 66–68 °C) was added. The resulting yellow solution was stored in the freezer overnight. Water (20 mL) was added, and the mixture was stirred at room temperature 0.5 h. It was partitioned between water and CH_2Cl_2 (4 × 20 mL). The CH_2Cl_2 was washed successively with water, aqueous 3 N HCl (twice), aqueous $NaHCO_3$, and brine, was dried (molecular sieves), and was evaporated in vacuo. The yellow solid (0.54 g) was recrystallized from 2-propanol/hexane (1/1): off-white solid; mp 230–232 °C dec; 0.38 g (58%). An analytical sample of the tosylhydrazone was crystallized from ethyl acetate: mp 233–234 °C dec; IR ($CHCl_3$) 3280, 3220, 2920, 2860, 1620 (sh, C=N), 1600 (aromatic C–C), 1330 (SO_2), 1165 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70–1.80 (br envelope, 42 H, methylenes), 1.90–2.15 (br, 2 H, CH_2 α to C=N), 2.45 (s, 3 H, $ArCH_3$), 7.70 (br 1 H, NH, exchanges with D_2O), 7.42 and 8.02 (4 H, 2 quasi-doublets, J = 8 Hz, aromatic AA′BB′). A complete ^{13}C spectrum could not be obtained because of the limited solubility of this tosylhydrazone in the usual NMR solvents. A partial spectrum was obtained in THF-d_8: δ 164.06, 143.41, 129.67, 129.21. The remaining peaks were obscured by solvent.

Anal. Calcd for $C_{31}H_{52}N_2O_2S$ (mol wt 516.82): C, 72.04; H, 10.14. Found: C, 72.31; H, 10.32.

Aprotic Bamford–Stevens Reaction[2a] **of Tosylhydrazone 7. Isolation of (*E*)-Spiro[12.11]tetracos-13-ene (11).** A suspension of tosylhydrazone **7** (0.275, 0.53 mmol; mp 232–234 °C) in distilled diglyme (8 mL) was stirred in oven-dried glassware under N_2. Sodium methoxide (0.110 g, 2 mmol, 4 equiv) was added, and the solids slowly dissolved. The reaction mixture was refluxed 1 h during which time a white solid precipitated and the liquid turned pink and then clear. The mixture was cooled to room temperature and then was partitioned between water and ether (5 × 20 mL). The combined ether layers were washed with water (3 × 50 mL) and brine, were dried (molecular sieves), and were evaporated in vacuo. Thin-layer chromatography revealed that all the tosylhydrazone had been consumed. The oily product (0.160 g, 91% yield) showed one major peak (90%) in the GLC (BBBT) and several minor peaks (10%). On $AgNO_3$ TLC the product mixture produced two spots. The smaller spot had the same R_f as did a reference sample of tetracosane and other saturated hydrocarbons, whereas the major spot moved more slowly. The crude product was repeatedly recrystallized from pentane (freezer) to a constant melting point of 64–66 °C. The recrystallized material had one component by GLC and $AgNO_3$ TLC. The strong IR band at 980 cm^{-1} suggested that this major product is the (*E*)-spiroalkene **11**: IR (CCl_4) 2920, 2850, 1440, 980 (trans HC=CH); ^{1}H NMR ($CDCl_3$) δ 0.9–1.6 (40 H, br), 1.8–2.0 (2 H, allylic CH_2), 4.95–5.10 (2 H, m, vinylic H's); ^{13}C NMR ($CDCl_3$) δ 19.31, 20.84, 22.28, 22.77, 24.63, 24.72, 24.94, 26.25, 26.34, 26.98, 27.62, 27.77, 31.13, 31.73, 39.48 (t), 42.01 (s), 126.67 (d), 141.24 (d).

Anal. Calcd for $C_{24}H_{44}$ (mol wt 332.60): C, 86.66; H, 13.34. Found: C, 86.78; H, 13.04.

Isolation of Minor Products from the Aprotic Bamford–Stevens Reaction. In another run, we oxidized the original oily product with *m*-chloroperoxybenzoic acid. The major olefin **11** was converted to its oxide, from which we separated the original (unreactive) minor products of the Bamford–Stevens reaction as follows. Commercial *m*-chloroperoxybenzoic acid (0.33 g, 1.6 mmol) was added to a solution of the product mixture (0.23 g, from 0.41 g of starting tosylhydrazone) in CH_2Cl_2 (25 mL). The solution was stirred at room temperature 3 h, and then 10% aqueous Na_2SO_3 (50 mL) was added. The heterogeneous mixture gave a negative starch–iodide test. The organic layer was separated, was washed with aqueous $NaHCO_3$ and brine, and was dried (molecular sieves). Evaporation in vacuo left a viscous oil (0.22 g) which was chromatographed on Merck silica gel 60 (6 g). The unchanged "minor" hydrocarbons were eluted with hexane as a clear oil (0.026 g) and the crude oxide of **11** was eluted with 5% ether/hexane as a white semisolid: 0.160 g; IR ($CHCl_3$) 2920, 2850, 900, 880 cm^{-1}; ^{1}H NMR δ 0.75–2.25, 2.42 (d, J = 2 Hz), 2.97 (m). The oxide was not purified for analysis.

The oil eluted with hexane contained a trace of alkene **11** ($AgNO_3$ TLC), which was removed by preparative $AgNO_3$ TLC. The remaining saturated "minor" components were eluted together as an oil (0.020 g) and on GLC (BBBT) showed three peaks, one of which was unusually broad (probably due to overlap of two or more peaks): ^{13}C NMR ($CDCl_3$) 6.78, 19.72, 20.74, 21.22, 22.22, 22.47, 22.87, 23.31, 23.96, 24.06, 25.25, 25.53, 26.03, 26.32, 26.49, 26.75, 26.93, 27.04, 27.16, 27.59, 28.05, 28.70, 29.30, 29.64, 36.16, no signals at lower field; ^{1}H NMR ($CDCl_3$) δ 0.15–0.40, 0.75–2.00.

Anal. Calcd for $C_{24}H_{44}$ (mol wt 332.60): C, 86.66; H, 13.34. Found: C, 86.80; H, 13.06.

Spiro[12.11]tetracosane (8) from Hydrogenation of (*E*)-Spiroalkene 11. A solution of alkene **11** (0.095 g) in hexane (20 mL), absolute ethanol (20 mL), and glacial acetic acid (5 mL)

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(51) Kusama, K. *J. Biochem. (Tokyo)* **1957**, *44*, 375–381.

was shaken for 18 h with platinum oxide (0.175 g) in a hydrogen atmosphere (initial pressure 41 psi) in a Parr hydrogenator. The catalyst was removed by filtration through filter aid and was washed with absolute ethanol. The filtrate was partitioned between 10% aqueous NaOH and ether (2 × 25 mL). The combined ether layers were washed with brine, were dried (molecular sieves), and were evaporated in vacuo. The viscous oily residue (0.090 g) crystallized when scratched. Recrystallization from pentane gave **8** as a white solid, mp 83–85 °C. It was identical with **8** (obtained from Wolff–Kishner reduction of spiro ketone **5a**) by mixture melting point and GLC (BBBT, confirmed by peak enhancement).

Shapiro Reaction[2a] of Tosylhydrazone 7. A suspension of tosylhydrazone **7** (0.35 g, 0.68 mmol; mp 232–234 °C) in hexane (10 mL) was stirred at room temperature under N_2. A solution of *n*-butyllithium in hexane (6.25 mL of a 1.6 M solution, 10 mmol; Aldrich) was added by syringe over 5 min. The solid dissolved and gave a yellow solution. After 40 h at room temperature, water (1 mL) was added cautiously. A white precipitate formed as the yellow color disappeared. The reaction mixture was partitioned between water and ether (3 × 50 mL). The combined organic layers were washed with aqueous 3 N HCl and brine, were dried (molecular sieves), and were evaporated in vacuo. The yellow viscous oil (0.35 g) contained some starting tosylhydrazone as evidenced by TLC. The mixture was chromatographed on Merck silica gel 60 (10 g). A clear viscous oil (0.11 g, 49% yield) was eluted with hexane and contained two components as revealed by GLC (BBBT) and $AgNO_3$ TLC. The major component (67%) had a GLC retention time and $AgNO_3$ TLC R_f identical with those of (*E*)-spiroalkene **11**. The minor component (33%) had a longer retention time on GLC (BBBT or SE 30) and a smaller R_f on $AgNO_3$ TLC. We attempted to separate the components of the mixture by preparative $AgNO_3$ TLC. The fractions enriched with the major product were combined and recrystallized from pentane to give a white solid (mp 64.5–66.5 °C) which had one peak (corresponding to alkene **11**) on GLC (BBBT). The remaining fractions were rechromatographed by preparative $AgNO_3$ TLC. A clear oil was collected that contained a 1:1 mixture of the original two components according to GLC (BBBT). We believe the minor product is (*Z*)-spiroalkene **12** on the basis of the following arguments. The ^1H NMR spectrum ($CDCl_3$) of the 1:1 mixture was similar to the ^1H NMR spectrum of pure **11**: δ 0.9–1.6 (40 H, br), 1.8–2.0 (2 H, allylic CH_2), 5.0–5.2 (2 H, m, vinylic H). The IR spectrum ($CHCl_3$) of the 1:1 mixture showed a peak at 980 cm^{-1} (trans HC=CH) which was less intense relative to the CH absorption at 2920 cm^{-1} than the corresponding absorption in the spectrum of pure **11**. We hydrogenated the 1:1 mixture (H_2, Pt, EtOH, 3 atm) and obtained a single alkane (87% yield) identical with spiroalkane **8** by mixture melting point and by GLC (BBBT, confirmed by peak enhancement).

In another run of the Shapiro reaction on **7**, we used ether as the solvent in place of hexane. Otherwise, the procedure and workup were as before. A mixture of two olefins (66% yield) was obtained with a higher ratio of (*E*)-spiroalkene **11** (92%) to (*Z*)-spiroalkene **12** (8%) than was obtained in the first run (viz., 67:33).

Photochemical Bamford–Stevens Reaction of Tosylhydrazone 7 with $NaOCH_3$ as Base. A suspension of tosylhydrazone **7** (0.097 g, 0.19 mmol) in heptane (180 mL) was stirred at room temperature as oxygen-free N_2 was bubbled through. Sodium methoxide (0.11 g, 2.0 mmol, 10 equiv) was added, and the mixture was stirred for 2 h with a continued N_2 flow. The suspension was then irradiated for 0.9 h with a Vycor-filtered 450-W Hanovia medium-pressure mercury lamp through a water-cooled quartz immersion well. The temperature of the reaction mixture was 20 °C immediately after radiation was stopped. The resulting yellow suspension was washed with water and brine, and was dried (molecular sieves). Evaporation in vacuo left a brown oil. According to TLC all the tosylhydrazone had been consumed. Chromatography on Merck silica gel 60 (2.5 g) and elution with hexane gave a colorless viscous oil (0.059 g, 93% yield of hydrocarbons). Analysis by GLC showed one major component (~80%) with the same retention time as (*E*)-spiroalkene **11** (confirmed by peak enhancement). Another sizable component (>10%) had the same retention time as (*Z*)-spiroalkene **12**. Several minor peaks were also present but were not completely resolved from those of the spiroalkenes. The product mixture showed three spots on $AgNO_3$ TLC. The largest spot corresponded to (*E*)-alkene **11**. Another spot had the same R_f as that for (*Z*)-alkene **12**. The third spot was not retarded on $AgNO_3$ TLC and had the same R_f as tetracosane and other saturated hydrocarbons. We chromatographed the product mixture on a column of $AgNO_3$ silica gel (3 g) to isolate and identify the minor products and to quantify the product yields. The first hexane fractions (30 mL) contained a clear viscous oil (0.005 g), which showed one spot on $AgNO_3$ TLC with an R_f corresponding to that of a saturated alkane, tetracosane. On GLC (BBBT) the oil showed two major peaks and one small peak. The ^1H NMR ($CDCl_3$) showed a δ 0.8–1.8 signal. These alkanes are probably transannular or hominal[40] insertion products.

The next hexane fractions (200 mL) contained a viscous oil (0.045 g). On both $AgNO_3$ TLC and GLC (BBBT) this oil showed two components identical with (*E*)- and (*Z*)-spiroalkenes **11** and **12**. The relative amounts of the two isomers by GLC (BBBT) were 89% alkene **11** and 11% alkene **12**. When all products were considered, the relative yields of hydrocarbons were 10% alkanes, 80% (*E*)-spiroalkene **11**, and 10% (*Z*)-spiroalkene **12**.

The photochemical Bamford–Stevens reaction was repeated three times under the same conditions. The crude product mixtures appeared to be identical with that described above according to both GLC (BBBT) and $AgNO_3$ TLC.

Study of the Photic Stability of Products of the Photochemical Bamford–Stevens Reaction. Sodium *p*-toluenesulfinate dihydrate (0.049 g, 0.23 mmol; Aldrich) and sodium methoxide (0.062 g, 1.1 mmol, 5 equiv) were added to a solution in heptane (150 mL) of a mixture of products (0.075 g, 0.23 mmol) from the photochemical Bamford–Stevens reaction described above. The suspension was purged with oxygen-free N_2 for 2.5 h at room temperature and then was irradiated for 4 h with a Vycor-filtered 450-W Hanovia medium-pressure mercury lamp through a water-cooled quartz immersion well. Aliquots were removed at 1-h intervals. An internal standard (tetracosane) was added to each of the four aliquots, which were then washed with water. On GLC (BBBT) analysis the heptane solutions of all the samples showed no change in the relative proportions of the hydrocarbon components.

In another experiment, we bubbled oxygen through the mixture of products, sodium *p*-toluenesulfinate, and sodium methoxide as we irradiated it for 1 h. Analysis by GLC (BBBT) again revealed no change in relative proportions and so the products are stable to the reaction conditions even in the presence of oxygen.

Photochemical Bamford–Stevens Reaction of Tosylhydrazone 7 with NaH as Base. Sodium hydride (0.050 g of a 50% by weight dispersion in mineral oil, 0.025 g NaH, 1.10 mmol) was washed with heptane (5×) and then was covered with heptane (100 mL). Tosylhydrazone **7** (0.051 g, 0.1 mmol) was added, and the suspension was stirred at room temperature for 4 h while oxygen-free N_2 was bubbled through. (A control reaction, worked up at this point, afforded only starting tosylhydrazone.) The suspension was then irradiated for 1 h with a Vycor-filtered 450-W Hanovia medium-pressure mercury lamp contained in a quartz immersion well. Ethanol (2 mL) was added to destroy the excess of sodium hydride. The reaction mixture was then washed with water and brine and was dried (molecular sieves). Evaporation in vacuo left a yellow oil that contained no starting tosylhydrazone by TLC. Analysis of the product by GLC (BBBT) and $AgNO_3$ TLC revealed a mixture similar to that produced in the photochemical reaction with sodium methoxide described above. The product mixture was separated by chromatography on $AgNO_3$ silica gel (1.5 g). Hexane first eluted a viscous oil (0.0035 g) that showed on $AgNO_3$ TLC a single spot with the same R_f as that of a saturated hydrocarbon, tetracosane, but which was a mixture of components by GLC (BBBT). These components are presumably alkanes and probably arise from transannular or hominal insertions. Additional hexane eluted a viscous oil (0.0275 g). Analysis by GLC (BBBT) showed a mixture of (*E*)-spiroalkene **11** (82%), (*Z*)-spiroalkene **12** (16%), and three minor unidentified components with shorter retention times (2% total). The relative yields of all products eluted with hexane were 11% alkanes, 73% alkene **11**, 14% alkene **12**, and 2% unidentified products.

Preparation of 13-Diazospiro[12.11]tetracosane 14 by Photolysis of the Sodium Salt of Tosylhydrazone 7. A suspension of tosylhydrazone **7** (0.135 g, 0.26 mmol; mp 232–234 °C) in heptane (20 mL) in a Pyrex flask was stirred at room temperature while N_2 was bubbled through for 20 min. Sodium methoxide (0.07 g, 1.3 mmol, 5 equiv) was added, and the mixture was stirred for 3 h with a continued N_2 flow. The suspension was then irradiated for 1 h with an external Pyrex-filtered 450-W Hanovia medium-pressure mercury lamp. The temperature of the mixture was 16 °C immediately after the lamp was switched off, and the mixture consisted of a white solid in a pink solution. Water (20 mL) was added, and the solids dissolved. The layers were separated, and the heptane layer was washed with water and then brine and was dried (molecular sieves). Careful evaporation in vacuo at room temperature left diazoalkane **14** as a dark pink, viscous oil, 0.090 g (95% yield). The oil would not crystallize from hydrocarbon solvents even at −78 °C and decomposed during attempted chromatography over Merck silica gel 60 or Florisil: IR ($CHCl_3$) 2920, 2860, 2015 (NN stretch) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00–1.70, 2.00–2.15; UV (heptane) λ_{max} 231 nm (ϵ 5000), 490 (3).

Anal. Calcd for $C_{24}H_{44}N_2$ (mol wt 360.61): C, 79.93; H, 12.30. Found: C, 80.02; H, 12.12.

We tried to obtain a ^{13}C NMR spectrum, but the sample decomposed during the long accumulation period (>24 h) required.

Preparation of Diazoalkane 14 by Oxidation of Hydrazone 6. Manganese dioxide was prepared by a modified Attenburrow[52] procedure, was activated by the procedure of Goldman,[53] and was stored under dry benzene. Activated manganese dioxide (0.15 g) and benzene (5 mL) were stirred in a round-bottomed flask, and the benzene was distilled off to remove any traces of water. The flask was cooled under N_2, and ether (3 mL), flamed calcium oxide (0.2 g), and hydrazone **6** (0.038 g, 0.10 mmol) were added. The mixture was stirred at room temperature for 2 h (the supernatant turned pink). The ether was decanted, and the solid residue was washed with ether (4 × 5 mL). The combined ether was washed with saturated aqueous $NaHCO_3$ and then with brine and was dried (molecular sieves). Careful evaporation in vacuo at room temperature left a pink oil, 0.032 g (83%). The IR spectrum was identical with that of diazoalkane **14** produced photochemically. In other runs where water was not carefully excluded, the IR spectrum ($CHCl_3$) of the product showed a band at 1690 cm^{-1}. We think this band stems from ketone contaminant produced by manganese dioxide oxidation of an alcohol formed by reaction of diazoalkane **14** with water.

Vycor-Filtered UV Irradiation of Diazoalkane 14 (Generated in Situ by Prior Pyrex-Filtered Irradiation). A suspension of tosylhydrazone **7** (0.107 g, 0.21 mmol) in heptane (175 mL) was stirred at room temperature while oxygen-free N_2 was bubbled through. Sodium methoxide (0.042 g, 0.78 mmol, 3.7 equiv) was added, and the suspension was stirred at room temperature for 2 h and then irradiated 40 min with an internal Pyrex-filtered 450-W Hanovia medium-pressure mercury lamp housed in a water-cooled quartz immersion well. An aliquot (10 mL) was removed, washed with water and brine, dried (molecular sieves), and evaporated in vacuo. The residual pink oil showed no starting tosylhydrazone on TLC, and its IR ($CHCl_3$) showed a strong diazoalkane band at 2015 cm^{-1}. The Pyrex filter sleeve was replaced by a Vycor filter, and the original reaction mixture was again irradiated 40 min. The yellow suspension was washed with water and then with brine and was dried (molecular sieves). Evaporation in vacuo gave a yellow oil, which was chromatographed on Merck silica gel 60 (3 g). A clear viscous oil was eluted with hexane (0.056 g, 80% yield of hydrocarbons). The GLC (BBBT) showed one large peak with the same retention time as (*E*)-spiroalkene **11**, a smaller peak with the retention time of (*Z*)-spiroalkene **12**, and at least six ill-resolved minor peaks. The mixture was chromatographed on $AgNO_3$ silica gel (3 g). The first hexane fractions contained an oil (0.005 g) which on $AgNO_3$ TLC showed a single spot with the same R_f as that of a saturated hydrocarbon, tetracosane. GLC (BBBT) showed two major peaks and a minor peak. These alkanes are probably a mixture of transannular or hominal insertion products. The fractions eluted later with hexane contained an oily mixture of alkenes (0.050 g). The major components of the mixture were (*E*)-spiroalkene **11** (76%) and (*Z*)-spiroalkane **12** (12%). Seven other components (12% total) comprised the rest of the mixture. Four of the minor products, listed in the order of elution, were identified as follows and are those expected[24] from partial cationic decomposition of the diazoalkane: alkene **16** (1%), alkene **18** (5%), dumbbellene **2a** (1%), alkene **17** (trace). The other three minor components were not identified. Of the total hydrocarbon products, the relative yields were 9% alkanes, 69% (*E*)-spiroalkene **11**, 11% (*Z*)-spiroalkene **12**, 7% cationic decomposition products, and 4% unidentified products.

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Registry No. **1a**, 830-13-7; **1b**, 832-10-0; **1c**, 3603-99-4; **2a**, 53416-00-5; **2b**, 79084-13-2; **2c**, 79084-14-3; **3a**, 76713-42-3; **3b**, 79084-15-4; **3c**, 79084-16-5; **4**, 79101-60-3; **5a**, 76713-43-4; **5b**, 79084-17-6; **5c**, 79084-18-7; **6**, 79084-19-8; **7**, 79084-20-1; **8**, 77173-12-7; (*E*)-**11**, 76713-47-8; (*Z*)-**12**, 76725-34-3; **13**, 79084-21-2; **14**, 79084-22-3.

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(52) Attenburrow, J.; Cameron, A. F. B.; Chapman, R. M.; Evans, R. M.; Hems, B. A.; Jansen, A. B. A.; Walker, T. *J. Chem. Soc.* **1952**, 1094–1111.

(53) Goldman, I. M. *J. Org. Chem.* **1969**, *34*, 1979–1981.