sition state. There are insufficient data from this work to evaluate whether or not destabilizing electrostatic interactions contribute to the low reactivity of $XArCH(CF_3)^+$.

The results of theoretical calculations show no stabilization of $CF_3CH_2^+$ by fluorine bridging but some stabilization by homoconjugation of the fluorine lone pair electrons with the cationic center.[27c] The latter effect may contribute to the low reactivity of $XArCH(CF_3)^+$.

Bimolecular Substitution Reactions. No S_N2 reactions between $XArCH(CF_3)Y$ and the potent nucleophiles N_3^-, I^-, and Br^- were observed in these studies of reactants with electron-donating ring substituents. This is a further example of the extreme resistance of α-CF_3-substituted substrates to bimolecular substitution reactions.[13-15] The results reported here support the relationship proposed to exist between the mechanism for nucleophilic substitution at saturated carbon and the lifetimes for the real or hypothetical carbocation intermediates of these reactions.[8,10,11,51] It was previously shown that the addition of electron-withdrawing ring substituents at $XArCH(CH_3)Y$ leads to a change from an S_N1 to an S_N2 substitution reaction mechanism for the addition of methanol, acetate, and azide at roughly the point where the ion-sandwich "intermediate" $[Nu^-\cdot XArCH(CH_3)^+\cdot X^-]$ ceases to exist for the lifetime of even one bond vibration and is transformed from an intermediate to a transition state.[11] It has been established in the present work that this simple relationship holds for the reactions of $XArCH(CF_3)Y$, since $XArCH(CH_3)Y$ and $XArCH(CF_3)Y$ with the same ring substituent ($\sigma_x^+ \leq -0.32$) react by the same S_N1 mechanism through intermediates $ArCH(CH_3)^+$ and $ArCH(CF_3)^+$, respectively, with nearly the same lifetimes. It remains to be determined if there is an enforced change to a coupled-concerted mechanism for bimolecular substitution reactions at $XArCH(CF_3)Y$ as the intermediate $XArCH(CF_3)^+$ is destabilized by electron-withdrawing ring substituents ($\sigma^+ \gg -0.32$).

Acknowledgment. This research was supported by a Type G grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and a Bristol Meyers Co. grant of Research Corp. I gratefully acknowledge their support.

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Intramolecular Generation of Oxonium Ylides from Functionalized Arylcarbenes

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Abstract: Arylcarbenes carrying alkoxyalkyl groups in the ortho position have been generated by flash pyrolysis and photolysis of appropriate tosylhydrazone sodium salts. In the gas phase and in aprotic solvents, interaction of the carbenes with the lone electron pairs of oxygen competes efficiently with insertion into C-H bonds. Both five- and six-membered cyclic oxonium ylides have been generated. The ylides **23**, **37**, **61b**, and **74** undergo 1,2 shifts of benzyl groups with ease, even if ring contraction to highly strained benzocyclobutenes is involved (**23**, **74**). The oxonium ylides **37** and **61b** strongly prefer the nonconcerted Stevens rearrangement to the [2.3] sigmatropic Sommelet rearrangement, in contrast to analogous ammonium ylides. Alkyl shifts occur to a very minor extent, if at all. Evidence is presented that alcohols intercept both the carbenes and the oxonium ylides. Protonation of the ylides leads to cyclic oxonium ions, which undergo nucleophilic cleavage of the C-O bonds. Acid-catalyzed decomposition of the appropriate diazo compounds gives rise to six-membered, but not to five-membered, cyclic oxonium ions, thus confirming the different intramolecular reactivities of arylcarbenes and benzyl cations. The efficiency of carbene interception increases with increasing acidity of the medium, suggesting nucleophilic behavior (protonation) of the arylcarbenes.

Ylides may be defined as molecules in which a positively charged heteroatom is connected to a carbon atom carrying an unshared pair of electrons. Two fundamentally different approaches to the generation of ylides exist. The ubiquitous and synthetically useful ylides of phosphorus, sulfur, and nitrogen are commonly prepared by deprotonation of the analogous onium salts. This methodology is less well applicable to oxonium salts, which strongly prefer nucleophilic displacement to deprotonation.[1] Nevertheless, Olah recently generated dimethyloxonium methylide by deprotonation and desilylation of appropriate oxonium ions.[2] The deprotonation route to oxonium ylides is believed to play an important role in the zeolite-catalyzed conversion of methanol to ethylene.[3-5]

The alternative approach to ylides involves the interaction of carbenes with the unshared electron pairs of heteroatoms.[6] The oxygen compounds that have been utilized for the intermolecular trapping of carbenes include 2-phenyl-1,3-dioxolane,[7] styrene

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(4) (a) Rimmelin, P.; Taghavi, H.; Sommer, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1210. (b) Rimmelin, P.; Brenner, A.; Fischer, K.; Sommer, J. *Ibid.* **1986**, 1497.

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Scheme I

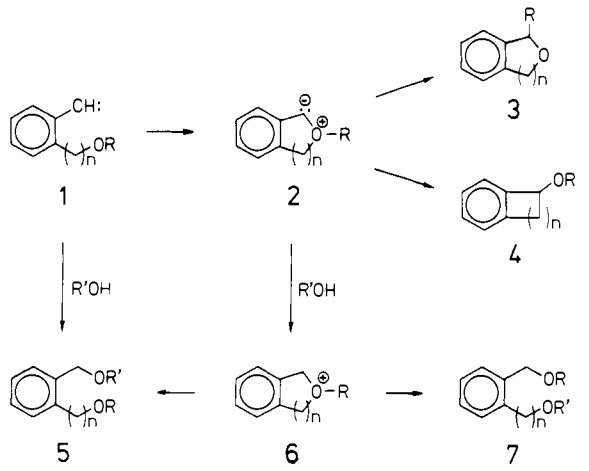


Table I. Product Distributions Obtained from **14** and **15**

conditions	product distributions, %						
	9	**12**	**16**	**17**	**18**	**19**	**20**
15, 285 °C (10^{-3} mmHg)		22.1	63.5			8.9	5.5
15, *hν*, diglyme		21.0	52.4	10.2	16.4		
14, *hν*, MeOH[a]	2.3	1.0	2.4	15.7	78.6		
14, *hν*, EtOH[a]	2.5	1.8	3.1	28.5	64.2		
14, *hν*, *t*-BuOH[b]	0.3	4.0	5.8	42.5	47.3		

[a] 0.2 M RONa. [b] 0.2 M *t*-BuOK.

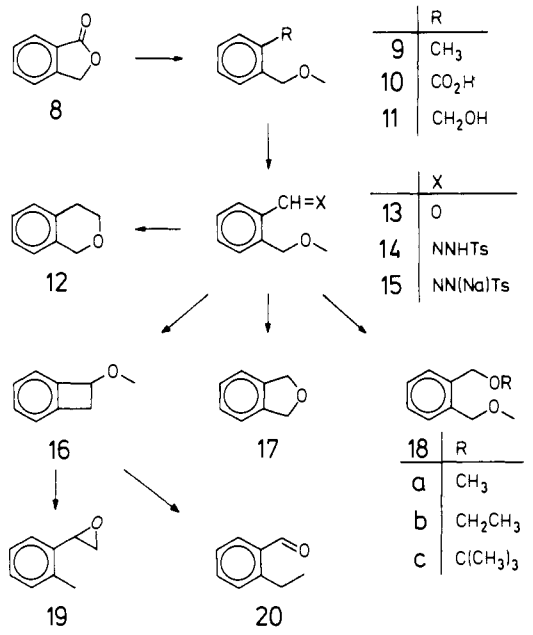
oxide,[8] allylic ethers,[9,10] aliphatic ethers,[11,12] allylic acetals,[13] and oxetanes.[14] Most recently the intramolecular generation of oxonium ylides by rhodium(II)-catalyzed decomposition of appropriate diazoketones has been reported.[15,16] For the majority of these reactions, direct C–O insertion is not readily distinguished from the formation and subsequent rearrangement of oxonium ylides. Conclusive evidence for a two-step mechanism comes from the [2.3] sigmatropic rearrangements observed with allylic substrates.[9,10,13,15,16]

In the present work we attached alkoxyalkyl groups to the ortho position of phenylcarbene (**1**). Obvious variables are the length *n* of the "spacer", determining the ring size of an eventual oxonium ylide **2**, and the nature of the alkoxy substituent. Our major goal was to compare the Stevens rearrangement, **2** → **3** + **4**, with the analogous reactions of ammonium and sulfonium ylides. The carbenes **1**, generated by thermolysis and photolysis of diazo compounds, undergo the well-known insertions into C—H and C=C bonds (if present) competitively with electrophilic attack at oxygen. In addition to studies under gas-phase and aprotic conditions, protic solvents were also employed. Hydroxyl groups intervene at two stages of the overall reaction, intercepting the carbene **1** as well as the ylide **2**. Protic solvents thus provide additional insights into reactivity and mechanisms (Scheme I).

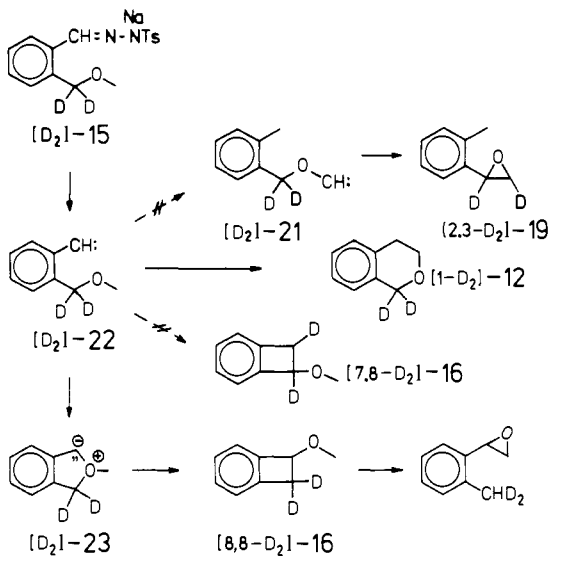
Results and Discussion

[2-(Methoxymethyl)phenyl]carbene (22). The reported route to 2-(methoxymethyl)benzaldehyde (**13**) is anodic oxidation of

Scheme II



Scheme III



18a.[17] We prepared **13** by oxidation (Jones, 61%; PCC, 74%) of the analogous benzyl alcohol **11**,[18] which was obtained from phthalide (**8**) by way of **10**.[18] Conventional procedures afforded the tosylhydrazone **14** and its sodium salt **15**.

Flash pyrolysis of **15** produced 3,4-dihydro-1*H*-2-benzopyran (**12**),[19] 7-methoxybicyclo[4.2.0]octa-1,3,5-triene (**16**),[20] 2-(2-methylphenyl)oxirane (**19**),[21] and 2-ethylbenzaldehyde (**20**)[22] (Scheme II and Table I). All compounds were identified by comparison of their spectra with those of authentic samples. Insertion of the carbene **22** into the C–H bonds of the methoxy group is the only reasonable route to **12**. The four-membered ring of **16**, however, may arise by insertion into the benzylic C–H bonds as well as by Stevens rearrangement of the oxonium ylide **23** (Scheme III). In order to distinguish between these alternatives, the labeled tosylhydrazone sodium salt [$^2H_2$]-**15** was prepared from deuteriated phthalide[23] and pyrolyzed. Within the limits of ^2H

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(9) Kirmse, W.; Kapps, M. *Chem. Ber.* **1968**, *101*, 994.
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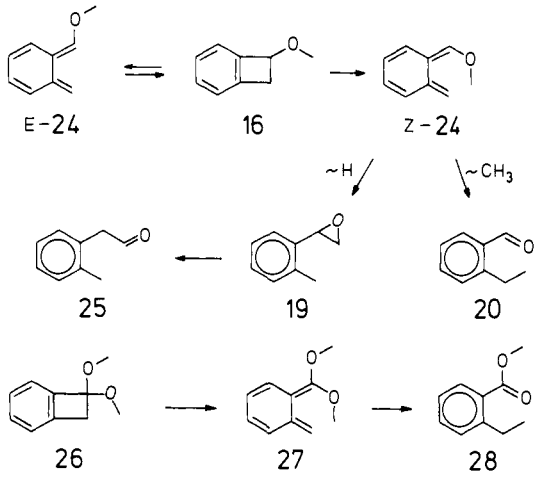
(22) Crow, W. D.; McNab, H. *Aust. J. Chem.* **1979**, *32*, 123.

Scheme IV



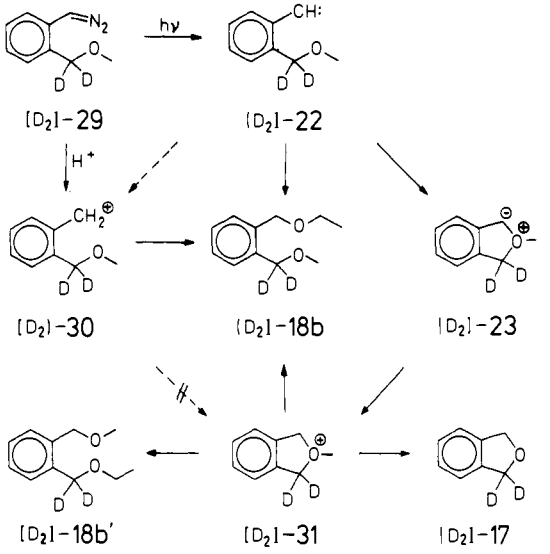
NMR detection, no deuterium was found α to the methoxy group of **16** (δ 5.0) while the methylene group was fully deuteriated (δ 3.4 and 3.1). The virtually exclusive route to **16** is C–O insertion, presumably via ylide **23**. C–H insertion occurs only into the OCH_3 group, as confirmed by the formation of [1-$^2H_2$]-**12**.

Precedent with (2-methoxyphenyl)carbenes[22,24] suggested that hydrogen transfer to give alkoxycarbene **21** might ultimately lead to **19**. According to this mechanism, [$^2H_2$]-**15** should give rise to [2,3-$^2H_2$]-**19**. In contrast to these expectations, the deuterium was located in the methyl group of **19**, pointing to **16** as the precursor of **19**. In fact, thermolysis of **16** at 275 °C afforded **19** and **20** (ca. 6:1). Subsequent conversion of **19** into the aldehyde **25** appeared to be acid-catalyzed and was suppressed in the presence of triethylamine. Above 80 °C, **16** is known to equilibrate with (*E*)-α-methoxy-*o*-xylylene [(*E*)-**24**], which may be scavenged by dienophiles.[20] A strong preference for outward rotation of alkoxy groups has also been noted in the cyclobutene–butadiene rearrangement.[25] However, at the much higher temperatures employed here, inward rotation of OMe is likely to compete. The methoxy group of (*Z*)-**24** is suitably disposed for shifts of hydrogen and methyl, leading to **19** and **20**, respectively. The pyrolysis of 7,7-dimethoxybicyclo[4.2.0]octa-1,3,5-triene (**26**) to give methyl 2-ethylbenzoate (**28**) involves an analogous methyl shift of α,α-dimethoxy-*o*-xylylene (**27**)[26] (Scheme IV).

In summary, we may safely conclude that **19** and **20** are secondary products arising from the thermolysis of **16** rather than from the carbene **22**. The only reactions of **22** observed in flash pyrolyses are C–O insertion (→**16**) and C–H insertion (→**12**) in a 3.5:1 ratio. C–O insertion occurs selectively into the benzyl–oxygen bond, despite the ring strain of **16**. A strong preference for benzyl over alkyl migration is characteristic of Stevens rearrangements.[27] Thus, our results are fully consistent with intervention of the ylide **23**.

The photolysis of **15** in diglyme afforded **16** and **12** in a slightly lower ratio (2.5:1), as compared with flash pyrolysis (Table I). The formation of two additional products, 1,3-dihydroisobenzofuran (**17**)[28] and 1,2-bis(methoxymethyl)benzene (**18a**),[17] is probably due to protic contaminants of the solvent or to intermolecular oxonium ylide formation with diglyme. In methanol, **17** and **18a** predominated while very minor amounts of **12** and **16** were obtained. The series of alcohols, methanol, ethanol, and *tert*-butyl alcohol, led to a gradual increase of **17** at the expense of **18** (Table I). A small fraction of 1-(methoxymethyl)-2-methylbenzene (**9**) was also observed. The origin of **9** is unclear since tosylhydrazones as well as diazo compounds and carbenes are amenable to reduction in basic media.

Scheme V



As was pointed out above, 1,2-bis(alkoxymethyl)benzenes **18** may arise by O–H insertion of the carbenes **22** as well as by nucleophilic cleavage of the oxonium ions **31**. In order to assess the contributions of these intermediates, [$^2H_2$]-**15** was photolyzed in ethanol. 1-(Ethoxymethyl)-2-(methoxymethyl)benzene (**18b**) derived immediately from the carbene [$^2H_2$]-**22** would retain the deuterium in the methoxymethyl group whereas intervention of the oxonium ion [$^2H_2$]-**31** would distribute the deuterium equally between the benzylic positions (ignoring secondary isotope effects). The ^1H NMR signals of **18b** were assigned by comparison with the symmetrical ethers. The fractions of [$^2H_2$]-**18b** (82%) and [$^2H_2$]-**18b′** (18%) obtained from [$^2H_2$]-**15** were estimated from the residual signal intensities of the benzylic protons. We conclude that 36% of **18b** originates from the oxonium ion **31** while 64% arises directly from the carbene **22**. In ethanol the oxonium ion **31** partitions to give **17** and **18b** in a 1.2:1 ratio (Scheme V).

Two routes to the oxonium ion **31** are conceivable: protonation of the ylide **23** and protonation of the carbene **22**, followed by intramolecular nucleophilic substitution (**22** → **30** → **31**). As a test for the latter alternative, the diazo compound [$^2H_2$]-**29** was prepared by mild thermolysis of [$^2H_2$]-**15** and subjected to acid-catalyzed decomposition in ethanol. This procedure, designed to generate the benzyl cation [$^2H_2$]-**30** via dediazoniation, afforded [$^2H_2$]-**18b** only; within the limits of NMR detection, no [$^2H_2$]-**18′** was formed. Obviously, the intramolecular substitution, **30** → **31**, cannot compete with intermolecular trapping of **30** to give **18b**. In contrast, the carbene **22** partitions between intramolecular and intermolecular processes in a 1.3:1 ratio (**16** + **17** + 0.36·**18b**:0.64·**18b**). The dramatic differences in intramolecular reactivities of benzyl cations and singlet phenylcarbenes have been rationalized in terms of much higher rotational barriers of the cations.[29] Rotation about the bond connecting the sp^2 carbon of the carbene or cation with the ring must occur in order for intramolecular substitution to take place. Our results with **22** and **30** confirm these ideas.

By excluding alternative routes to the oxonium ion **31**, we have demonstrated that alcohols protonate the oxonium ylide **23** efficiently and fast enough to quench the Stevens rearrangement,

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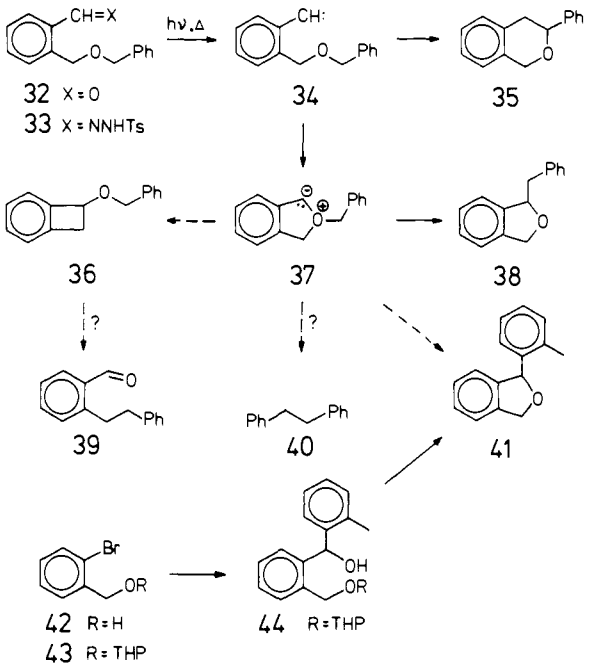
Table II. Product Distributions Obtained from 33

conditions	product distributions, % 35	36	38	39	40	41
Li salt, $h\nu$, diglyme[a]	22.2		75.9			
Li salt, $h\nu$, DMF[b]	17.2		80.2			
Na salt, Δ, 280 °C[c]	42.0	0.3	21.0	10.8	17.9	1.4

conditions	product distributions, % 35	36	38	49	17	51	52
$h\nu$, MeOH, 0.2 M NaOMe[d]	4.1	0.9	8.0	60.4	22.5	(19.5)	(3.0)

[a] 1.9% of **49**. [b] 2.6% of 2-[(benzyloxy)methyl]toluene. [c] Two unidentified compounds, 5.1 and 1.5%. [d] 2.4% of 2-[(benzyloxy)methyl]-toluene and one unidentified product (1.7%). Products **51** and **52** have been disregarded in the normalization to 100% since **17**, **51**, and **52** arise from the same precursor.

Scheme VI



23 → **16**. Methanol, ethanol, and *tert*-butyl alcohol do not differ much in that regard (a slight increase of the Stevens product **16** is seen with decreasing acidity of ROH; Table I). The next step, nucleophilic attack at the oxonium ion **31**, is more profoundly affected by the nature of the alcohol. The sterically less hindered methyl site is preferred over the benzylic sites with increasing bulk of the nucleophile, thus lowering the **18**:**17** ratio (Table I).

[2-((Benzyloxy)methyl)phenyl]carbene (34). In the preceding section, the ring contraction of the oxonium ylide **23** was attributed to the preferential migration of benzyl groups in the Stevens rearrangement. For further support of this interpretation, we extended our studies to the carbene **34**, in order to generate an oxonium ylide with endocyclic and exocyclic benzyl groups. The tosylhydrazone **33** was prepared from phthalide (**8**) by an adaption of the methods outlined for **14** in Scheme II. Photolyses of the lithium salt of **33** (preferred to the sodium salt because of its enhanced solubility) in aprotic solvents proceeded cleanly, albeit with poor yields (20–25%). The major products were readily identified as 3,4-dihydro-3-phenyl-1*H*-2-benzopyran (**35**)[30] and 1-benzyl-1,3-dihydroisobenzofuran (**38**). The structure of **38** was confirmed by an unequivocal synthesis, starting from benzylidenephthalide. Although the C–H bonds available for carbene insertion are now benzylic, ylide formation remains predominant. The rearrangement of the oxonium ylide **37** proceeds exclusively

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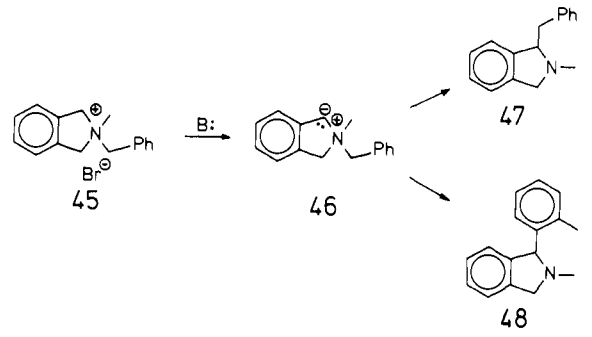
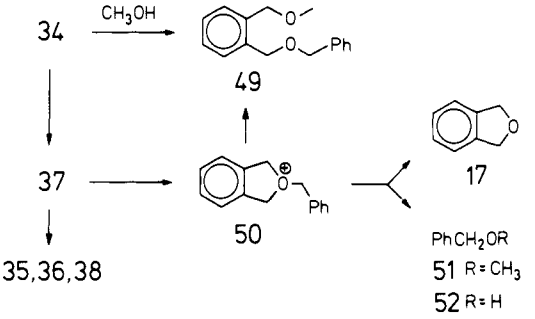
Scheme VII



Scheme VIII



with migration of the exocyclic benzyl group (Table II).

Flash pyrolysis of the sodium salt of **33** afforded a more complex product mixture. In addition to **35** and **38**, substantial amounts of 2-(2-phenylethyl)benzaldehyde (**39**)[31] and 1,2-diphenylethane (**40**) as well as several minor components were detected. Comparison (GC) with authentic samples indicated 7-(benzyloxy)-bicyclo[4.2.0]octa-1,3,5-triene (**36**)[20] and 1,3-dihydro-1-(2-methylphenyl)isobenzofuran (**41**) as minor products. Compound **41** was prepared from 2-bromobenzyl alcohol (**42**) as outlined in Scheme VI. It should be emphasized that **36** and **41** have been identified only by their GC retention times and that the figures in Table II constitute upper limits of their relative yields.

The results of the pyrolysis suggest that the ring-contracting Stevens rearrangement of the oxonium ylide **37** may compete with migration of the exocyclic benzyl group at elevated temperatures. We note that **39** could arise by thermolysis of **36** (cf. **16** → **20**; Scheme IV). The formation of **40** may be due to the escape of benzyl radicals from the radical pair presumably[27] intervening in the Stevens rearrangement, **37** → **38** (however, we did not observe a complementary product, e.g. **17**). Such side reactions would explain the low relative yield of **38** in thermal, gas-phase reactions as compared with photolytic, condensed-phase experiments (Table II).

The small to negligible yields of **41** indicate that the Sommelet rearrangement is at best a minor reaction path of the oxonium ylide **37**. In contrast, base-induced formation of the analogous ammonium ylide **46** from the ammonium salt **45** afforded the Sommelet product **48** at low to ambient temperature and the Stevens product **47** at 80–180 °C[32] (Scheme VII). A strong preference for the Sommelet rearrangement was also observed with benzyldialkylammonium methylides at 25 °C.[33] The temperature dependence has been interpreted in terms of a higher enthalpy of activation for the dissociative, two-step Stevens rearrangement as compared with the concerted, [2.3] sigmatropic Sommelet process. Against this background, our experience with **37** suggests more facile homolysis of oxonium than of ammonium ylides (although, in general, C–O bonds are stronger than C–N bonds).

The reactions of the carbene **34** with methanol conform to those of the methyl analogue **22**, 1-[(benzyloxy)methyl]-2-(methoxy-

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Table III. Product Distributions Obtained from **55**

precursor conditions	product distributions,[a] %						
	56	**58**	**59**	**60**	**62**	**65**	**12**
a, Na salt, Δ, 320 °C	81.3	0.2	5.0		8.3	1.3	0.7
b, Na salt, Δ, 320 °C	34.8		5.0			16.8	
a, Na salt, *hν*, diglyme	36.0	2.4	0.8	1.4	0.7		54.7
b, Na salt, *hν*, diglyme	35.5	1.6	5.0	3.7		33.1	
a, 0.2 M NaOMe, *hν*	5.7	1.2		71.5			16.1
b, 0.2 M NaOMe, *hν*	5.7	1.2	0.7	78.3		5.7	8.9

[a] Unidentified and trivial products (e.g., aldehydes, azines, nitriles) have been omitted; they account for the difference to 100%.

methyl)benzene (**49**) being the major product. Quenching of the Stevens rearrangement of the oxonium ylide is less efficient for **38** than for **23**, as the exocyclic benzyl group of **38** migrates more readily. The intermediacy of the oxonium ion **50** is indicated by nucleophilic displacement to give 1,3-dihydroisobenzofuran (**17**) as well as an equimolar amount of benzylic products **51** and **52** (Table II and Scheme VIII).

[2-(2-Methoxyethyl)phenyl]carbene (57a) and [2-(2-(Benzyloxy)ethyl)phenyl]carbene (57b). The procedures outlined above for phthalide were applied analogously to 3,4-dihydro-1*H*-2-benzopyran-1-one (**53**) in the preparation of the tosylhydrazones **55**. Extending the side chain by an additional CH_2 group places C–H bonds in the most favorable position for intramolecular insertion.[22,24,34] Not surprisingly, the carbenes **57** afforded the 2-indanyl ethers **56** as major products while C–H insertion to give four- and seven-membered rings (**58** and **59**, respectively) occurred to a minor extent (Table III). The Stevens rearrangement of the oxonium ylide **61a** requires alkyl migrations, known to proceed reluctantly.[27] In fact, only flash pyrolysis of the **55a** sodium salt produced **62a** and **65a** in small amounts. On the other hand, the facile migration of the exocyclic benzyl group in **61b** afforded **65b** as a major product. On photolytic generation of the carbene **57a**, the oxonium ylide **61a** appears to terminate as 3,4-dihydro-1*H*-2-benzopyran (**12**), but the course of this transformation remains unclear. Protic impurities (i.e., formation of the oxonium ion **64**) cannot be responsible as photolysis of the diazo compound **66a** in hexafluorobenzene gave similar results. No **12** was obtained from the readily rearranging ylide **61b**, which is exclusively diverted to **65b** in aprotic solvents. The product expected from the Sommelet rearrangment of **61b** was searched for with the aid of an authentic sample (see the Experimental Section) but was not detected (Scheme IX).

In methanolic solution, partial quenching of both the carbenes **57** and the oxonium ylides **61** is observed. The diethers **60** are formed at the expense of C–H insertion (**56**, **59**) and Stevens rearrangement (**65b**). The intervention of oxonium ions (**64**) is supported by nucleophilic displacement of the exocyclic substituent to give **12** (Table III). Acid-catalyzed decomposition of the diazo compound **66a** in ethanol also afforded **60a** (R′ = Et, 91%) and **12** (9%). Thus, in contrast to the lower homologue **30** (Scheme V), the benzylic cation **63a** does undergo intramolecular nucleophilic substitution with formation of **64a**. As a consequence of the extended chain, the oxygen of **63a** can approach the vacant p orbital without concomitant rotation about the Ar–CH_2^+ bond.

[2-(1,3-Dioxolan-2-yl)phenyl]carbene (71). The carbene **71** was included in our study in order to explore the intramolecular generation and reactions of a bicyclic oxonium ylide. A published route, starting from 2-bromobenzaldehyde (**67**), served to prepare **68**[35] and its tosylhydrazone **69**. In contrast to previous examples, C–H insertion was not a prominent reaction in the flash pyrolysis of the sodium salt of **69**. A trace of the spirocyclic acetal **70** was detected by GC with the aid of an authentic sample[20] (Table IV). 1,4-Epoxy-1,3,4,5-tetrahydro-2-benzoxepin (**72**) was isolated from the product mixture and identified by ^1H NMR and COSY

Scheme IX

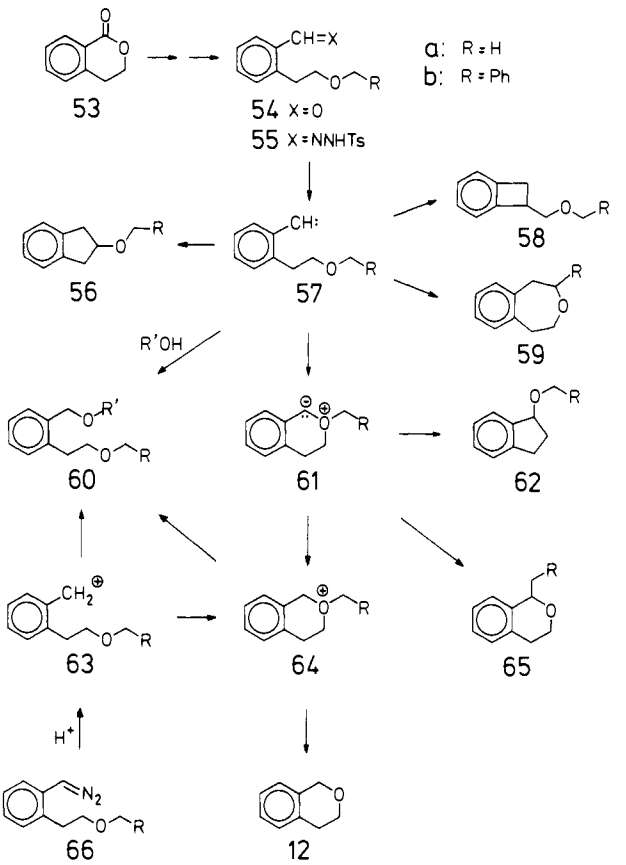

Table IV. Product Distributions Obtained from **69**

conditions	product distributions, %					
	70	**72**	**75**	**78**	**73**	**76**
Na salt, Δ, 320 °C	0.3	9.5	38.7	28.7		
Na salt, Δ, 300 °C	0.5	6.7	57.7	28.3		
Na salt, Δ, 280 °C	0.5	9.7	68.2	6.9		
Na salt, *hν*, diglyme		6.6	66.1			
hν, MeOH, 0.4 M NaOMe	0.7	0.7	7.0		47.6	42.6
hν, MeOH, 0.2 M NaOMe	0.6	0.8	6.4		48.0	42.1
hν, MeOH, 0.1 M NaOMe	0.2	0.1	2.1		77.8	17.0
hν, MeOH, 0.05 M NaOMe	0.2	0.1	1.8		83.0	12.4
hν, CF_3CH_2OH, 0.2 M NaOR			1.8		98.2	

[a] Unidentified and trivial products (e.g., aldehydes, nitriles) have been omitted; they account for the difference to 100%.

spectra. Insertion into the methylene groups of the acetal accounts for ca. 10% of **71**. The major product was tetrahydrobenzo-[3.4]cyclobuta[1,2-*b*]dioxin (**75**), accompanied by phthalaldehyde (**78**). With increasing temperature, **78** increased at the expense of **75**. Pyrolysis of **75** afforded **78** as the only product in an apparent [2 + 2 + 2]cycloreversion. Photolysis of the sodium salt of **69** in diglyme afforded **75** and **72** in a 10:1 ratio; **78** was not observed. The Stevens rearrangement of the oxonium ylide **74**, proceeding with migration of the endocyclic benzyl group, is analogous to that of **23**. The high ratio of ylide formation to C–H insertion of the carbene **71** may be attributed to the availability of two equivalent oxygen atoms as well as to the rather strained transition state leading to **72** (Scheme X).

Photolyses of **69** in ROH–RONa afforded the ether **73**, retaining the original acetal structure, and the tetrahydro-2,5-benzodioxocin **76**. Hydrolysis of **76** occurred with extreme ease, yielding 2-[(2-hydroxyethoxy)methyl]benzaldehyde. Most likely, **73** originates from the carbene **71**. Nucleophilic cleavage of the oxonium ion **77** is an eventual route to **73** and the only route to **76**. The **73**:**76** ratio was found to depend on the nature of the alcohol and on the concentration of the base (Table IV). With decreasing concentration of methoxide, **73** increased at the expense of **76**. In trifluoroethanol, **73** was obtained exclusively. The more

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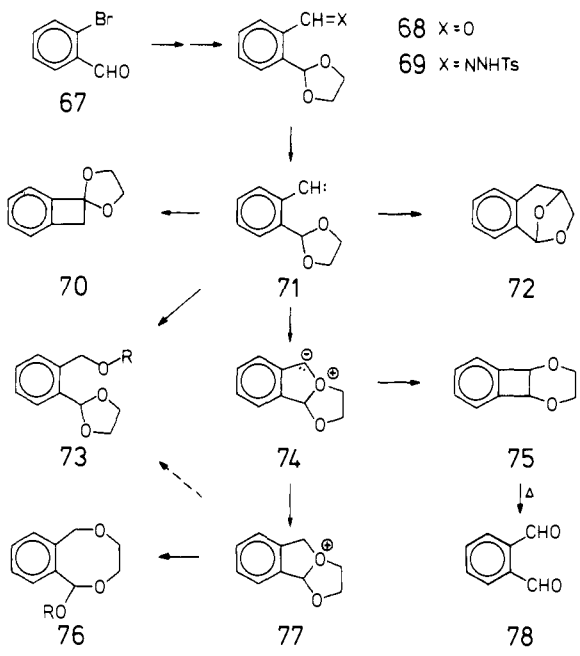
Scheme X



acidic media lead to more efficient quenching of the carbene **71**. These observations support the notion that arylcarbenes behave as nucleophiles toward alcohols.[6c,25,36]

Conclusion

Cyclic oxonium ylides are readily generated from arylcarbenes carrying alkoxalkyl groups in the ortho position. Interaction of the carbenes with the lone electron pairs of oxygen competes efficiently with insertion into C–H bonds. While intramolecular C–H insertions of arylcarbenes lead preferentially to five-membered rings,[22,24,34] the generation of oxonium ylides appears to be less sensitive to ring size. Some of our examples (**22**, **34**, **71**) compare C–H insertions to give six-membered rings with the formation of five-membered oxonium ylides, others (**57a,b**) afford five-membered carbocycles and six-membered oxonium ylides. The latter case is clearly less favorable for ylide formation. The differences (factors of 2–4 may be estimated from the product distributions) are not dramatic in terms of $\Delta G^{\ddagger}$ but sufficient to discourage the application of six-membered ylides in synthesis.

The oxonium ylides **23**, **37**, **61b**, and **74** undergo 1,2 shifts of benzyl groups with ease, even if ring contraction to highly strained benzocyclobutenes is involved (**23**, **74**). However, when both exocyclic and endocyclic benzyl groups are available (**37**), the exocyclic group migrates almost exclusively. The oxonium ylides **37** and **61b** strongly prefer the Stevens rearrangement to the [2.3] sigmatropic Sommelet rearrangement, in contrast to analogous ammonium ylides.[32,33] In terms of the radical-pair mechanism of the Stevens rearrangement,[27,37] these observations suggest more facile homolysis of oxonium ylides as compared with ammonium ylides. Accordingly, alkyl shifts occur to a very minor extent if no benzyl groups are available.

We have presented evidence that alcohols intercept both the carbenes and the oxonium ylides. Protonation of the ylides leads to oxonium ions, which undergo nucleophilic cleavage of both exocyclic and endocyclic C–O bonds. Six-membered cyclic oxonium ions (**64**) are also accessible from the appropriate benzyl cations (**63**), but five-membered cyclic oxonium ions (**31**) are not. The different intramolecular reactivities of arylcarbenes and benzyl cations have been rationalized in terms of the higher rotational barriers of the cations.[29] The efficiency of arylcarbene interception increases with increasing acidity of the medium, suggesting protonation of the carbenes, although direct (concerted) O–H insertion is not excluded. All carbene reactions reported here are tentatively assigned to the singlet state. Photosensitization affected the product distributions but slightly. The singlet and triplet states of arylcarbenes are thought to equilibrate rapidly.[38] As a rule, both direct and sensitized photolyses of diazo precursors are dominated by the higher reactivity of the singlet. Exceptions are known,[39] and work aimed at exploring the potential role of triplet arylcarbenes is continuing.

Experimental Section

General Methods. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were obtained at 80 (Bruker WP 80) and 400 MHz (Bruker AM 400). Chemical shifts in $CDCl_3$ are reported in δ relative to tetramethylsilane as an internal standard, unless otherwise indicated. Gas chromatography (GC) was performed by the use of a Siemens Sichromat equipped with glass capillary columns. Varian Aerograph 920 instruments equipped with packed glass columns were used for preparative gas chromatography (PGC). High-pressure liquid chromatography (HPLC) was carried out with LDC (Milton Roy) chromatographs and refractometric detection.

2-(Methoxymethyl)benzaldehyde Tosylhydrazone (14). To a solution of sodium dichromate (13.8 g, 53 mmol) in water (160 mL) and concentrated sulfuric acid (5.2 g, 53 mmol) was added a solution of 2-(methoxymethyl)benzyl alcohol (**11**)[18] (8.0 g, 53 mmol) in ether (160 mL). The mixture was stirred at room temperature for 3 h. The organic phase was separated, washed with water, and dried over $MgSO_4$. Distillation in vacuo afforded 4.8 g (61%) of the aldehyde **13**,[17] bp 60 °C (0.05 mmHg). Alternatively, **11** (7.6 g, 50 mmol) was oxidized with PCC[40] (16.15 g, 75 mmol) in dichloromethane (110 mL) for 1.5 h at room temperature to give 5.53 g (74%) of **13**.

Aldehyde **13** (2.53 g, 16.9 mmol), *p*-toluenesulfonylhydrazine (3.14 g, 16.9 mmol), and anhydrous ethanol (20 mL) were heated for 3 h at 60 °C. The mixture was stirred for an additional 3 h at room temperature and kept overnight at −20 °C. The tosylhydrazone **14** (4.88 g, 91%) was filtered with suction and recrystallized from methanol; mp 108–110 °C. ^{1}H NMR: δ 2.40 (s, 3 H), 3.33 (s, 3 H), 4.52 (s, 2 H), 7.2–8.1 (m, 10 H). Anal. Calcd for $C_{16}H_{18}N_2O_3S$: C, 60.36; H, 5.70; N, 8.80. Found: C, 60.47; H, 5.66; N, 8.80.

Flash Pyrolysis of 15. To a solution of **14** (3.18 g, 10 mmol) in anhydrous THF (40 mL) was added sodium hydride (60% dispersion in mineral oil, 0.40 g, 10 mmol) in small portions. The mixture was stirred for 2 h, pentane (80 mL) was added, and stirring was continued for 2 h. The sodium salt (3.36 g, 99%) was filtered with suction and stored in the dark in vacuo.

The sodium salt **15** (0.34 g, 1 mmol) was added slowly in vacuo (10^{-4} mmHg) to a flask preheated to 285 °C (metal bath). The volatile products (90 mg, 67%) were collected in a trap cooled with liquid nitrogen. The products **12**,[19] **16**,[20] **19**,[21] and **20**[22] were analyzed by GC and isolated by successive HPLC (Lichrosorb-Merck Si 60, hexane–ether, 20:1) and PGC (carbowax + KOH). The deuteriated tosylhydrazone [$^2H_2$]-**14** and sodium salt [$^2H_2$]-**15** was processed analogously. Relevant NMR data of the parent and deuteriated products follow. **12**: ^{1}H NMR δ 2.88 (t, J = 5.6 Hz, 2 H), 4.00 (t, J = 5.6 Hz, 2 H), 4.79 (s, 2 H), 6.9–7.5 (m, 4 H). [$^2H_2$]-**12**: ^{2}H NMR (CCl_4, 61.42 MHz) δ 4.70. **16**: ^{1}H NMR δ 3.12 (dd, J = 14 and 2 Hz, 1 H), 3.48 (dd, J = 14 and 4 Hz, 1 H), 3.50 (s, 3 H), 5.00 (dd, J = 4 and 2 Hz, 1 H), 7.0–7.5 (m, 4 H). [$^2H_2$]-**16**: ^{2}H NMR (CCl_4) δ 3.1 and 3.4 (1:1). **19**: ^{1}H NMR δ 2.43 (s, 3 H), 2.71 (dd, J = 5.6 and 2.6 Hz, 1 H), 3.16 (dd, J = 5.6 and 4 Hz, 1 H), 4.01 (dd, J = 4 and 2.6 Hz, 1 H), 7.2 (br s, 4 H). [$^2H_2$]-**19**: ^{2}H NMR (CCl_4) δ 2.38.

Photolyses of 14 and 15. A solution of **15** (0.34 g, 1 mmol) in anhydrous diglyme (30 mL) was irradiated (medium-pressure mercury arc, Pyrex vessel) for 2 h at room temperature. The mixture was diluted with pentane–ether (1:1) and washed with water in order to remove the diglyme. The organic layer was dried over $MgSO_4$, concentrated, and analyzed by GC. Solutions of **14** (318 mg, 1 mmol) in 0.2 M NaOMe–MeOH, 0.2 M NaOEt–EtOH, and 0.2 M KO*t*-Bu–*t*-BuOH (30 mL) were treated analogously. The products **17**[28] and **18** were

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(37) Partial racemization has been demonstrated for the Stevens rearrangement of oxonium ylides.[14b]

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isolated by PGC. **18a**:[17] ^{1}H NMR δ 3.37 (s, 6 H), 4.50 (s, 4 H), 7.15–7.45 (m, 4 H). **18b**: ^{1}H NMR δ 1.23 (t, J = 6.8 Hz, 3 H), 3.37 (s, 3 H), 3.53 (q, J = 6.8 Hz, 2 H), 4.52 (s, 2 H), 4.55 (s, 2 H), 7.2–7.4 (m, 4 H). **18c**: ^{1}H NMR δ 1.30 (s, 9 H), 3.39 (s, 3 H), 4.49 (s, 2 H), 4.54 (s, 2 H), 7.2–7.5 (m, 4 H).

In order to assign the benzylic methylene groups of **18b** unequivocally, a sample of [$^2H_2$]-**18b** was prepared by ethylation (NaH, EtI, THF, 1-h reflux) of [$^2H_2$]-**11**. The ^{1}H NMR spectrum of this sample displayed a signal at δ 4.55 (s, 2 H) while the signal of **18b** at δ 4.52 was missing. The photolysis of [$^2H_2$]-**14** in 0.2 M NaOEt–EtOH afforded a mixture of [$^2H_2$]-**18b** and [$^2H_2$]-**18b′**, displaying signals at δ 4.52 (s, 0.36 H) and δ 4.55 (s, 1.64 H). Thus 82% of the label is located in the methoxymethyl group and 18% in the ethoxymethyl group.

Acid-Catalyzed Decomposition of [$^2H_2$]-29. The sodium salt [$^2H_2$]-**15** (342 mg, 1 mmol) was flash-pyrolyzed at 210 °C. The products collected in the cold trap were dissolved in ethanol (2 mL), and *p*-toluenesulfonic acid (10 mg) was added. The mixture was stirred for 30 min at room temperature and then neutralized with solid sodium carbonate. The product distribution (**9**, 3.1%; **12**, 24.4%; **16**, 41.8%; **18b**, 28.3%; **20**, 2.4%) indicated that the preparation of [$^2H_2$]-**29** was accompanied by substantial thermal decomposition (leading to **12**, **16**, and **20**). The ether [$^2H_2$]-**18b** from this experiment was isolated by PGC. The ^{1}H NMR spectrum proved to be identical with that of the sample prepared above from [$^2H_2$]-**11**; i.e., no signal at δ 4.52 was observed. In accordance with this result, **17** was not detected among the products.

2-[(Benzyloxy)methyl]benzaldehyde Tosylhydrazone (33). A solution of phthalide (**8**) (26.8 g, 0.2 mol) and potassium hydroxide (11.2 g, 0.2 mol) in methanol–water (85:15, 100 mL) was heated at reflux for 1 h. The solvents were evaporated, and the residue was dried in vacuo at 110 °C. The potassium 2-(hydroxymethyl)benzoate (38.0 g, 0.2 mol) thus obtained was dissolved in anhydrous DMF (200 mL). Sodium hydride (4.8 g, 0.2 mol) was added in small portions with stirring. When the evolution of hydrogen was complete, benzyl bromide (68.4 g, 0.4 mol) was added dropwise. The mixture was heated for 10 h at 80 °C, cooled to room temperature, and partitioned between water and ether. The organic phase was dried over $MgSO_4$ and evaporated to give 48.0 g (72%) of benzyl 2-[(benzyloxy)methyl]benzoate. ^{1}H NMR: δ 4.61 (s, 2 H), 4.97 (s, 2 H), 5.32 (s, 2 H), 7.1–8.05 (m, 14 H). Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C, 79.43; H, 6.04.

A solution of benzyl 2-[(benzyloxy)methyl]benzoate (33.2 g, 0.1 mol) and sodium hydroxide (8.0 g, 0.2 mol) in ethanol–water (8:2, 125 mL) was heated at reflux for 10 h. The solvent was evaporated to dryness, and the residue was dissolved in water. The aqueous solution was extracted repeatedly with ether and then acidified with hydrochloric acid. The precipitate was purified by partitioning between aqueous $NaHCO_3$ and ether to give 16.5 g (68%) of 2-[(benzyloxy)methyl]benzoic acid; mp 99–101 °C. ^{1}H NMR: δ 4.65 (s, 2 H), 4.97 (s, 2 H), 7.1–8.1 (m, 9 H), 9.9 (br s, 1 H). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.28; H, 5.73.

To lithium aluminum hydride (2.85 g, 75 mmol) in ether (300 mL) was added dropwise with stirring a solution of 2-[(benzyloxy)methyl]-benzoic acid (12.1 g, 50 mmol) in ether (100 mL). Upon completion of the addition, the mixture was refluxed for 1 h. It was then cooled to 0 °C, and sufficient water was added to give a flaky precipitate of aluminum hydroxide. The precipitate was filtered and washed with ether. The combined ether solution was dried ($MgSO_4$) and concentrated in vacuo to give 9.1 g (80%) of 2-[(benzyloxy)methyl]benzyl alcohol. ^{1}H NMR: δ 2.95 (br s, 1 H), 4.57 (s, 2 H), 4.64 (s, 2 H), 4.66 (s, 2 H), 7.3 (br s, 9 H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.95; H, 7.03.

Oxidation of 2-[(benzyloxy)methyl]benzyl alcohol (6.4 g, 35 mmol) with PCC (11.3 g, 52.5 mmol), following the literature procedure,[40] afforded 5.0 g (63%) of 2-[(benzyloxy)methyl]benzaldehyde (**32**). ^{1}H NMR: δ 4.65 (s, 2 H), 4.96 (s, 2 H), 7.3–8.0 (m, 9 H), 10.2 (s, 1 H). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.59; H, 6.31.

The tosylhydrazone **33**, mp 123–124 °C, was prepared in 79% yield as described previously in the preparation of **14**. ^{1}H NMR: δ 2.36 (s, 3 H), 4.49 (s, 2 H), 4.61 (s, 2 H), 7.1–7.9 (m, 14 H), 7.93 (s, 1 H). Anal. Calcd for $C_{22}H_{22}N_2O_3S$: C, 66.98; H, 5.62; N, 7.10. Found: C, 66.92; H, 5.61; N, 7.21.

Reactions of 33. To a solution of **33** (495 mg, 1.25 mmol) in anhydrous THF (5 mL) was added lithium hydride (10 mg, 1.25 mmol). The mixture was stirred at 0 °C for 2 h. Pentane (200 mL) was then added, and stirring at 0 °C was continued for 2 h. The lithium salt (0.52 g, 100%) was filtered with suction and dried in vacuo. Dilute solutions (0.025 M) of the lithium salt in diglyme and DMF were photolyzed as described previously in the photolysis of **15**. Product distribution (Table II) and yields (diglyme, 24%; DMF, 22%) were estimated by GC with dibenzyl ether as an internal standard. The major products, **35**[30] and **38** (see below), were isolated by HPLC (silica gel, *n*-hexane-ether, 19:1). ^{1}H NMR: (**35**) δ 3.03 (d, J = 5.8 Hz, 1 H), 3.06 (d, J = 8.6 Hz, 1 H), 4.75 (dd, J = 8.6 and 5.6 Hz, 1 H), 5.02 (s, 2 H), 7.0–7.6 (m, 9 H); (**38**) δ 3.10 (d, J = 6.4 Hz, 2 H), 5.05 d (J = 2.0 Hz, 2 H), 5.52 (tt, J = 6.4 and 2.0 Hz, 1 H), 7.0–7.4 (m, 9 H).

The sodium salt of **33** (0.50 g, 1.2 mmol) was prepared and flash-pyrolyzed, as described previously for **15**, to give 0.10 g (40%) of volatile products. In addition to **35** and **38**, 2-(2-phenylethyl)benzaldehyde (**39**)[31] [^{1}H NMR: δ 2.8–3.5 (m, 4 H), 7.1–7.9 (m, 9 H), 10.18 (s, 1 H)] and 1,2-diphenylethane (**40**) were isolated by HPLC; small amounts of 7-(benzyloxy)bicyclo[4.2.0]octa-1,3,5-triene (**36**)[20] and 1,3-dihydro-1-(2-methylphenyl)isobenzofuran (**41**, see below) were detected by GC on two different columns.

The photolysis of **33** in 0.2 M NaOMe–MeOH was carried out as described for **14**. GC indicated 1-[(benzyloxy)methyl]-2-(methoxymethyl)benzene (**49**, see below), 1,3-dihydroisobenzofuran (**17**),[28] and benzyl methyl ether (**51**) as major products. Small amounts of **35**, **36**, **38**, and benzyl alcohol were also detected (Table II); the combined yield (internal standard) was 74%.

1-Benzyl-1,3-dihydroisobenzofuran (38). Reduction of benzylidenephthalide with zinc and aqueous potassium hydroxide (92% yield), followed by reduction of benzylphthalide with lithium aluminum hydride (61% yield) afforded 1-[2-(hydroxymethyl)phenyl]-2-phenylethanol,[41] mp 99–101 °C. To a solution of triphenylphosphine (1.31 g, 5 mmol) and diethyl azodicarboxylate (1.13 g, 6.5 mmol) in chloroform (50 mL) was added at 0 °C with stirring a solution of the diol (1.14 g, 5 mmol) in chloroform (100 mL). The mixture was stirred for 2 h at 0 °C and then concentrated in vacuo. Flash chromatography on silica gel (*n*-pentane–ether, 3:1) was followed by HPLC (silica gel, *n*-hexane–ether, 19:1) to give 0.75 g (71%) of **38**. ^{1}H NMR: δ 3.10 (d, J = 6.4 Hz, 2 H), 5.05 (d, J = 2.0 Hz, 2 H), 5.52 (tt, J = 6.4 and 2.0 Hz, 1 H), 7.0–7.4 (m, 9 H).

1,3-Dihydro-1-(2-methylphenyl)isobenzofuran (41). To a stirred mixture of 2-bromobenzyl alcohol (9.35 g, 50 mmol) and 3,4-dihydro-2*H*-pyran (10.1 g, 0.12 mol) was added concentrated hydrochloric acid (5 drops). When the exothermic reaction had subsided, more 2-bromobenzyl alcohol (9.35 g, 50 mmol) was added. The mixture was stirred for 10 h at room temperature, diluted with ether, and neutralized with solid $NaHCO_3$. The solution was filtered, dried over $MgSO_4$, and concentrated. Distillation in vacuo gave 25.4 g (94%) of the tetrahydropyranyl ether **43**, bp 92–94 °C (10^{-3} mmHg). ^{1}H NMR: δ 1.4–2.0 (m, 6 H), 3.4–4.1 (m, 2 H), 4.5–4.9 (m, 1 H), 4.75 (s, 2 H), 7.0–7.9 (m, 4 H).

To the Grignard reagent prepared from 2-(2-bromobenzyloxy)tetrahydropyran (1.0 g, 3.7 mmol) and magnesium turnings (0.1 g, 4.1 mmol) in 5 mL of THF (2-h reflux) was added a solution of 2-methylbenzaldehyde (0.45 g, 3.7 mmol) in THF (2 mL). After 10 h at room temperature, ether (100 mL) and saturated aqueous NH_4Cl (20 mL) were added. The organic phase was separated, dried ($MgSO_4$), and concentrated to give 0.87 g (75%) of **44**. ^{1}H NMR: δ 1.45–1.95 (m, 6 H), 2.07 (s, 3 H), 3.55 (br s, 1 H), 3.5–4.1 (m, 2 H), 4.45–5.25 (m, 1 H), 4.84 (s, 2 H), 6.27 (br s, 1 H), 6.95–7.75 (m, 8 H).

A solution of **44** (0.78 g, 2.5 mmol) in ether (10 mL) and concentrated hydrochloric acid (10 mL) was stirred for 10 h at room temperature. The mixture was partitioned between water and ether. The organic phase was repeatedly extracted with aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo. The product was purified by HPLC (silica gel, *n*-pentane–ether 95:5) to give 0.35 g (67%) of **41**. ^{1}H NMR: δ 2.40 (s, 3 H), 5.23 (br s, 2 H), 6.42 (br s, 1 H), 6.95–7.35 (m, 8 H). Anal. Calcd for $C_{15}H_{14}O$: C, 85.86; H, 6.71. Found: C, 85.80; H, 6.72.

1-[(Benzyloxy)methyl]-2-(methoxymethyl)benzene (49). To a solution of 2-[(benzyloxy)methyl]benzyl alcohol (0.9 g, 4 mmol) in anhydrous THF (10 mL) was added sodium hydride (0.15 g, 6 mmol) in small portions. The mixture was refluxed for 30 min. Methyl iodide (1.1 g, 8 mmol) was added, heating at reflux was continued for 10 h, and the mixture was then partitioned between water and ether. The organic phase was dried ($MgSO_4$) and concentrated in vacuo. The product was purified by HPLC (silica gel, *n*-pentane–ether, 9:1) to give 0.82 g (86%) of **49**. ^{1}H NMR: δ 3.37 (s, 3 H), 4.54 (s, 2 H), 4.57 (s, 2 H), 4.63 (s, 2 H), 7.25–7.45 (m, 9 H). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.24; H, 7.48.

2-(2-Methoxyethyl)benzaldehyde Tosylhydrazone (55a). 3,4-Dihydro-1*H*-2-benzopyran-1-one (**53**)[42] was converted to 2-(2-methoxyethyl)benzyl alcohol[18] by way of methyl 2-(2-methoxyethyl)benzoate. The procedure was identical with that used in the preparation of **32**. Oxidation of the benzyl alcohol with PCC[40] gave 2-(2-methoxyethyl)-benzaldehyde (**54a**) in 92% yield. ^{1}H NMR: δ 3.27 (t, J = 6.2 Hz, 2 H), 3.30 (s, 3 H), 3.63 (t, J = 6.2 Hz, 2 H), 7.25–7.65 (m, 3 H), 7.75–7.9

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(m, 1 H), 10.25 (s, 1 H). The tosylhydrazone **55a** was prepared in 61% yield as described previously in the preparation of **14**; mp 83–85 °C (recrystallized from ether–*n*-pentane). ^{1}H NMR: δ 2.40 (s, 3 H), 2.96 (t, *J* = 6.6 Hz, 2 H), 3.27 (s, 3 H), 3.50 (t, *J* = 6.6 Hz, 2 H), 7.15–7.95 (m, 9 H), 8.07 (s, 1 H). Anal. Calcd for $C_{17}H_{20}N_2O_3S$: C, 61.42; H, 6.06; N, 8.43. Found: C, 61.40; H, 6.06; N, 8.49.

Reactions of 55a. The sodium salt of **55a** was prepared and flash-pyrolyzed as described previously for **15**. The yield (GC) of volatile products was 46%. 2-Methoxyindan (**56a**)[43] [^{1}H NMR: δ 2.93 (dd, *J* = 16.4 and 5.0 Hz, 2 H), 3.20 (dd, *J* = 16.4 and 6.4 Hz, 2 H), 3.37 (s, 3 H), 4.25 (tt, *J* = 6.4 and 5.0 Hz, 1 H), 7.15 (br s, 4 H)], 7-(methoxymethyl)bicyclo[4.2.0]octa-1,3,5-triene (**58a**) (see below), 1,2,4,5-tetrahydro-3-benzoxepin (**59a**),[44] 1-methoxyindan (**62a**),[45] 3,4-dihydro-1-methyl-1*H*-2-benzopyran (**65a**)[46] [^{1}H NMR: δ 1.65 (d, *J* = 6.4 Hz, 3 H), 2.68 (ddd, *J* = 16.0, 5.6, and 3.6 Hz, 1 H), 3.07 (ddd, *J* = 16.0, 9.2, and 4.4 Hz, 1 H), 3.82 (ddd, *J* = 11.2, 9.2, and 4.4 Hz, 1 H), 4.18 (ddd, *J* = 11.2, 5.6, and 3.6 Hz, 1 H), 4.87 (q, *J* = 6.4 Hz, 1 H), 7.0–7.3 (m, 4 H)], and 3,4-dihydro-2*H*-2-benzopyran (**12**)[19] were identified by comparison with authentic samples. Photolyses of the sodium salt of **55a** in diglyme and of **55a** in 2 M NaOMe–MeOH, carried out as described previously for **15** and **14**, respectively, gave the same compounds in different ratios (Table III), with 1-(2-methoxyethyl)-2-(methoxymethyl)benzene (**60a**, *R*′ = CH_3) as an additional product.

Methylation of bicyclo[4.2.0]octa-1,3,5-triene-7-methanol,[47] as described previously in the preparation of **49**, afforded **58a** in 68% yield. ^{1}H NMR: δ 2.89 (dd, *J* = 13.1 and 2.0 Hz, 1 H), 3.40 (dd, *J* = 13.1 and 4.9 Hz, 1 H), 3.44 (s, 3 H), 3.5–3.9 (m, 3 H), 7.05–7.3 (m, 4 H). Compound **60a** (*R*′ = CH_3) was obtained analogously from 2-(2-methoxyethyl)benzyl alcohol in 84% yield. ^{1}H NMR: δ 2.95 (t, *J* = 7.2 Hz, 2 H), 3.36 (s, 3 H), 3.40 (s, 3 H), 3.60 (t, *J* = 7.2 Hz, 2 H), 4.49 (s, 2 H), 7.15–7.45 (m, 4 H).

Acid-Catalyzed Decomposition of the Diazo Compound 66a. The procedure used was identical with that used in the preparation of **29**. However, much lower temperatures were sufficient for the decomposition of the sodium salt of **55a**, e.g. 60 °C (10^{-3} mmHg). Thus, in contrast to **29**, **66a** was not contaminated with products of its thermolysis. The diazo compound **66a** was decomposed by *p*-toluenesulfonic acid in ethanol to give **12** (8.9%) and 1-(ethoxymethyl)-2-(2-methoxyethyl)benzene (**60a**, *R*′ = C_2H_5) (91.1%). For comparison, the latter compound was prepared in 84% yield by ethylation (NaH, EtI) of 2-(2-methoxyethyl)benzyl alcohol. ^{1}H NMR: δ 1.24 (t, *J* = 7.0 Hz, 3 H), 2.94 (t, *J* = 7.2 Hz, 2 H), 3.36 (s, 3 H), 3.55 (q, *J* = 7.0 Hz, 2 H), 3.60 (t, *J* = 7.2 Hz, 2 H), 4.52 (s, 2 H), 7.15–7.4 (m, 4 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.26; H, 9.29.

2-[2-(Benzyloxy)ethyl]benzaldehyde Tosylhydrazone (55b). 3,4-Dihydro-1*H*-2-benzopyran-1-one (**53**)[42] was converted to 2-[2-(benzyloxy)ethyl]benzoic acid (70%), 2-[2-(benzyloxy)ethyl]benzyl alcohol (91%), and 2-[2-(benzyloxy)ethyl]benzaldehyde (**54b**, 98%) by procedures that were identical with those used in the preparation of **32**. ^{1}H NMR: (**54b**) δ 3.32 (t, *J* = 6.2 Hz, 2 H), 3.70 (t, *J* = 6.2 Hz, 2 H), 4.47 (s, 2 H), 7.2–7.55 (m, 8 H), 7.75–7.9 (m, 1 H), 10.24 (s, 1 H). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.91; H, 6.82.

p-Toluenesulfonylhydrazine (3.8 g, 42 mmol) was dissolved in refluxing methanol. The aldehyde **54b** (10.0 g, 41.5 mmol) was added, and the mixture was refluxed for 24 h. Concentration in vacuo gave a viscous residue, which was extracted with *n*-pentane–ether (2:1). The solid obtained by evaporation of the extracts was recrystallized from methanol to give 6.4 g (38%) of **55b**, mp 93–95 °C. ^{1}H NMR: δ 2.34 (s, 3 H), 2.95 (t, *J* = 7.0 Hz, 2 H), 3.54 (t, *J* = 7.0 Hz, 2 H), 4.42 (s, 2 H), 7.2–7.85 (m, 13 H), 8.23 (s, 1 H), 11.32 (s, 1 H). Anal. Calcd for $C_{23}H_{24}N_2O_3S$: C, 67.62; H, 5.92; N, 6.86. Found: C, 67.53; H, 5.99; N, 6.96.

Reactions of 55b. The sodium salt of **55b** was prepared and photolyzed in diglyme as described for **15**. The product mixture was separated by HPLC (silica gel, *n*-hexane–ether, 9:1) to give **56b** + **59b** (see below), 1-benzyl-3,4-dihydro-1*H*-2-benzopyran (**65b**)[48] [^{1}H NMR: δ 2.7–2.9 (m, 2 H), 3.03 (dd, *J* = 14.2 and 8.0 Hz, 1 H), 3.25 (dd, *J* = 14.2 and 4.4 Hz, 1 H), 3.6–3.9 (m, 1 H), 4.0–4.25 (m, 1 H), 5.03 (dd, *J* = 8.0 and 4.4 Hz, 1 H), 7.15–7.35 (m, 9 H)], 1-[2-(benzyloxy)ethyl]-2-(methoxymethyl)benzene (**60b**, R = CH_3) (see below), 2-[2-(benzyloxy)ethyl]-benzaldehyde (**54b**) (8%), 2-[2-(benzyloxy)ethyl]benzonitrile (see below) (12%), and 2-[2-(benzyloxy)ethyl]benzaldehyde azine (see below) (25%). The fraction containing **56b** + **59b** was separated by HPLC (silica gel, *n*-pentane–ether, 95:5) to give 2-(benzyloxy)indan (**56b**)[49] [^{1}H NMR: δ 3.11 (d, *J* = 6.0 Hz, 2 H), 3.15 (d, 6.0 Hz, 2 H), 4.44 (quin, *J* = 6.0 Hz, 1 H), 4.57 (s, 2 H), 7.15–7.40 (m, 9 H)] and an impure sample of 2-phenyl-1,2,4,5-tetrahydro-3-benzoxepin (**59b**) [^{1}H NMR: δ 2.79 (ddd, *J* = 15.7, 4.9, and 0.8 Hz, 1 H), 2.91 (d, *J* = 15.7 Hz, 1 H), 3.40 (ddd, *J* = 15.7, 11.2, and 2.3 Hz, 1 H), 3.49 (dd, *J* = 15.7 and 9.7 Hz, 1 H), 3.66 (ddd, *J* = 12.3, 11.2, and 0.8 Hz), 4.30 (ddd, *J* = 12.3, 4.9, and 2.3 Hz, 1 H), 4.46 (d, *J* = 9.7 Hz, 1 H), 7.1–7.4 (m, 9 H). 7-[(Benzyloxy)methyl]bicyclo[4.2.0]octa-1,3,5-triene (**58b**) was assigned by GC comparison with an authentic sample (see below). The presence of 1-(benzyloxy)indan (**62b**) was excluded with the aid of an authentic sample.[50]

The flash pyrolysis of the sodium salt of **55b** gave 1,2-diphenylethane (**40**) (9%), 2-[2-(benzyloxy)ethyl]benzonitrile (13%), and three unidentified products (17%) in addition to **56b**, **59b**, and **65b**. The azine was not detected in the pyrolysate, due to its low volatility. The decomposition of azines is known to give rise to nitriles.[51] The photolysis of **55b** in 0.2 M NaOMe–MeOH, as described for **14**, proceeded most cleanly (67% yield) to give **60b** (*R*′ = CH_3) as the major product (Table III). The minor components were identified by GC.

Reference Samples. Benzylation of bicyclo[4.2.0]octa-1,3,5-triene-7-methanol[47] (NaH, benzyl, bromide) as described previously in the preparation of **49**, afforded **58b** in 92% yield. ^{1}H NMR: δ 2.87 (dd, *J* = 14.5 and 2.1 Hz, 1 H), 3.2–3.5 (m, 1 H), 3.73 (d, *J* = 1.5 Hz, 2 H), 3.6–3.9 (m, 1 H), 4.57 (s, 2 H), 7.05–7.35 (m, 9 H). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.66; H, 7.30.

1-[2-(Benzyloxy)ethyl]-2-(methoxymethyl)benzene (**60b**, R = CH_3) was obtained by methylation of 2-[2-(benzyloxy)ethyl]benzyl alcohol, as described previously in the preparation of **49**. ^{1}H NMR: δ 3.03 (t, *J* = 7.2 Hz, 2 H), 3.40 (s, 3 H), 3.73 (t, *J* = 7.2 Hz, 2 H), 4.50 (s, 2 H), 4.55 (s, 2 H), 7.2–7.4 (m, 9 H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.46; H, 7.72.

The aldehyde **54b** (0.24 g, 1 mmol), hydroxylamine hydrochloride (0.28 g, 4 mmol), sodium acetate (0.33 g, 4 mmol), and glacial acetic acid (20 mL) were refluxed for 10 h. The mixture was filtered, the filtrate was concentrated in vacuo, and the residue was partitioned between water and ether. The organic phase was washed with aqueous $NaHCO_3$ and with water, dried over $MgSO_4$, and concentrated in vacuo. The product was purified by HPLC (silica gel, *n*-pentane–ether, 9:1) to give 0.23 g (97%) of 2-[2-(benzyloxy)ethyl]benzonitrile. ^{1}H NMR: δ 3.17 (t, *J* = 6.6 Hz, 2 H), 3.79 (t, *J* = 6.6 Hz, 2 H), 4.53 (s, 2 H), 7.2–7.75 (m, 9 H). Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.86; H, 6.41; N, 6.03.

The aldehyde **54b** (0.24 g, 1 mmol), hydrazine hydrate (25 mg, 0.5 mmol), and ethanol (10 mL) were refluxed for 10 h. The mixture was diluted with water and extracted with ether. The extracts were dried ($MgSO_4$) and concentrated in vacuo. The product was purified by HPLC (silica gel, *n*-pentane–ether, 75:25) to give 0.20 g (84%) of 2-[2-(benzyloxy)ethyl]benzaldehyde azine, mp 53–55 °C. ^{1}H NMR: δ 3.18 (t, *J* = 7.0 Hz, 4 H), 3.72 (t, *J* = 7.0 Hz, 4 H), 4.50 (s, 4 H), 7.25–7.4 (m, 16 H), 8.0–8.15 (m, 2 H), 9.0 (s, 2 H). Anal. Calcd for $C_{32}H_{32}N_2O_2$: C, 80.64; H, 6.77; N, 5.88. Found: C, 80.79; H, 6.77; N, 5.92.

1-(2-Methylphenyl)-3,4-dihydro-1*H*-2-benzopyran. To a solution of 3,4-dihydro-1*H*-2-benzopyran (7.4 g, 55 mmol) in benzene (50 mL) was added bromine (8.9 g, 56 mmol) with irradiation (2000-W sunlamp). Upon complete decolorization, anhydrous pyridine (4.5 mL) was added. The solution of 1-bromo-3,4-dihydro-1*H*-2-benzopyran[46] thus obtained was added with stirring under nitrogen at −5 °C to the Grignard reagent prepared from 2-bromotoluene (9.44 g, 55 mmol), magnesium turnings (1.35 g, 55 mmol), and ether (25 mL). The mixture was stirred for 2 h at room temperature and then refluxed for 1 h. Saturated aqueous NH_4Cl (50 mL) was added, the organic phase was separated, and the aqueous phase was extracted with ether. The combined organic solutions were dried ($MgSO_4$) and concentrated in vacuo to give 7.4 g (60%) of crude product, part of which was purified by HPLC (silica gel, *n*-pen-

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tane-ether, 95:9). ^{1}H NMR: δ 2.37 (s, 3 H), 2.65-3.4 (m, 2 H), 3.95 (ddd, J = 11.2, 9.0, and 4.0 Hz, 1 H), 4.24 (ddd, J = 11.2, 6.0, and 4.0 Hz, 1 H), 5.95 (br s, 1 H), 6.65-7.35 (m, 8 H). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.61; H, 7.22. This compound should be formed by Sommelet rearrangement of the ylide **61b** but was not detected among the reaction products of **55b**.

2-(1,3-Dioxolan-2-yl)benzaldehyde Tosylhydrazone (69). The tosylhydrazone **69** was obtained from the analogous aldehyde **68**[35] in 94% yield as described previously in the preparation of **14**; mp 129-131 °C. ^{1}H NMR: δ 2.37 (s, 3 H), 3.8-4.2 (m, 4 H), 5.83 (s, 1 H), 7.3-7.85 (m, 8 H), 8.31 (s, 1 H), 11.45 (br s, 1 H). Anal. Calcd for $C_{17}H_{18}N_2O_4S$: C 58.94; H, 5.24; N, 8.09. Found: C, 58.88; H, 5.32; N, 8.17.

The sodium salt of **69** was prepared and flash-pyrolyzed as described previously for **15**. Pyrolysis of 1.2 g (3.25 mmol) of the sodium salt afforded 0.35 g (66%) of volatile products. Spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,2'-[1,3]dioxolane] (**70**)[20] and phthalaldehyde were identified by comparison (GC) with authentic samples. Separation by HPLC (silica gel, *n*-hexane-ether, 8:2) yielded 1,4-epoxy-1,3,4,5-tetrahydro-2-benzoxepin (**72**) [^{1}H NMR: δ 2.58 (br d, J = 17.0 Hz, 1 H), 3.37 (br dd, J = 17.0 and 4.6 Hz, 1 H), 3.66 (dd, J = 7.3 and 4.6 Hz, 1 H), 3.96 (dd, J = 7.3 and 6.1 Hz, 1 H), 4.83 (dddd, J = 6.1, 4.6, 1.9, and 0.8 Hz, 1 H), 5.97 (s, 1 H), 7.05-7.25 (m, 4 H)], 2,3,4a,8b-tetrahydrobenzo-[3,4]cyclobuta[1,2-*b*]dioxin (**75**) [^{1}H NMR: δ 3.74 (s, 4 H), 5.34 (s, 2 H), 7.35 (br s, 4 H). ^{13}C NMR: δ 61.7, 73.8, 123.7, 129.9, 145.8. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.97; H, 6.26.], and 2-(1,3-dioxolan-2-yl)benzonitrile[52] (9-10%).

Photolyses of **69** in NaOMe-MeOH were carried out as described for **14**. The major products were isolated by HPLC (silica gel, *n*-pentane-ether, 9:1). 2-[2-(Methoxymethyl)phenyl]-1,3-dioxolane (**73**, R = CH_3): ^{1}H NMR δ 3.37 (s, 3 H), 3.95-4.15 (m, 4 H), 4.60 (s, 2 H), 6.05 (s, 1 H), 7.25-7.65 (m, 4 H). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.04; H, 7.10. 1-Methoxy-1,3,4,6-tetrahydro-2,5-benzodioxocin (**76**, R = CH_3): ^{1}H NMR δ 3.32 (s, 3 H), 3.3-3.8 (m, 4 H), 4.58 (d, J = 12.4 Hz, 1 H), 5.04 (d, J = 12.4 Hz, 1 H), 5.58 (s, 1 H), 7.0-7.25 (m, 3 H), 7.7-7.85 (m, 1 H). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.16; H, 7.29. Traces of hydrochloric acid or of aluminum trichloride converted **73** (R = CH_3) to 2-(2-hydroxyethoxymethyl)benzaldehyde. ^{1}H NMR: δ 1.37 (br s, 1 H), 3.15-3.3 (m, 2 H), 3.4-3.55 (m, 2 H), 4.73 (s, 2 H), 6.95-7.25 (m, 3 H), 7.35-7.5 (m, 1 H), 9.92 (s, 1 H).

Photolysis of **69** in 0.2 M CF_3CH_2ONa-TFE afforded almost exclusively 2-[2-((2,2,2-trifluoroethoxy)methyl)phenyl]-1,3-dioxolane (**73**, R = CF_3CH_2). ^{1}H NMR: δ 3.84 (q, J = 8.6 Hz, 2 H), 3.95-4.15 (m, 4 H), 4.87 (s, 2 H), 6.00 (s, 1 H), 7.25-7.7 (m, 4 H). Anal. Calcd for $C_{12}H_{13}F_3O_3$: C, 54.96; H, 5.00. Found: C, 55.10; H, 5.06.

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The NEER Principle. Ground-State Conformational Bias in Triene Photocyclizations

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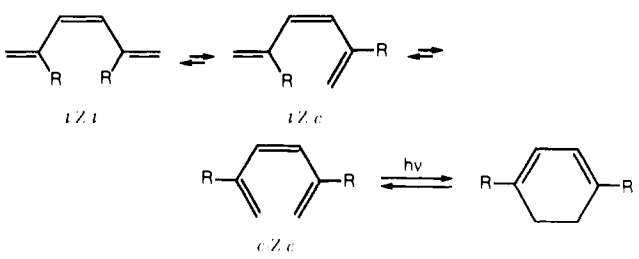
Abstract: A series of closely related trienes was transformed to cyclohexadienes by photocyclization. The diastereoselectivity observed for the series can be rationalized as the result of conformational bias in the ground states of the starting trienes. The results thereby lend experimental support to the Non-Equilibration of Excited Rotamers or NEER principle.

The fascinating subtleties involved in the photochemistry of vitamin D_3 has stimulated a high level of research in the light-induced transformations of simple, 1,3,5-hexatrienes and related systems.[1] A key concept has emerged from these combined studies that is applicable to the analysis of excited singlet states in general: the Non-Equilibration of Excited-state Rotamers, or NEER principle. First advanced by Havinga[2] to explain anomalies in vitamin D_3 photochemistry, it was latter extended to the analysis of the chemistry of simple hexatrienes[3] where it has its most fundamental application. In these systems, the yield of cyclohexadiene is increased by substituents at the 2- and 5-positions, consistent with the NEER principle that concludes that the various conformers of the excited singlet of the triene (*t-Z-t*, *c-Z-t*, *c-Z-c*) can not interconvert within the lifetime of that state (Scheme I).

Further studies by Dauben[4] confirmed the importance of the equilibrium, ground-state population of the *c-Z-c* conformer, as

Scheme I



t Z t *t Z c* *c Z c*

influenced by steric factors, on the cyclization to form cyclohexadiene products. In a related study, Baldwin[5] drew a correlation between the conformational bias in a cyclohexadiene and the stereochemistry of the triene cycloreversion product.

On the basis of these fundamental investigations, we devised a synthesis of the novel natural material ikarugamycin (**1**) in which one of the three separate, key concepts that we employed for stereochemical control is illustrated in Scheme II and involved the photoinduced closure of triene **2** to cyclohexadiene **3**. Critical to the control of stereochemistry at the new chiral centers at C-13 and C-14 was the concept inherent in the NEER principle that closure of the singlet photoexcited state of a triene would occur more rapidly than conformational changes. Indeed, it has been

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