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INTRAMOLECULAR REACTIVITY OF FUNCTIONALIZED ARYLCARBENES: 7-ALKENYLOXY-1-INDANYLIDENES

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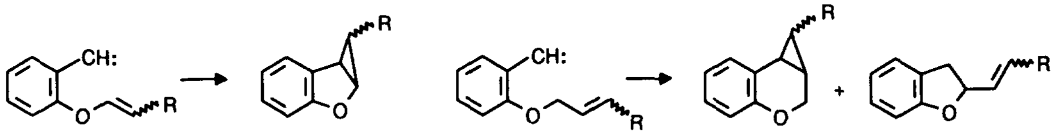
Abstract: 1,2-H shift is the only intramolecular reaction of 7-(1-propenyloxy)-1-indanylidenes (**8**) whereas 7-(2-propenyloxy)-1-indanylidene (**13**) and 7-(2-butenyloxy)-1-indanylidenes (**19**) undergo addition to the side-chain C=C bond and 1,2-H shifts competitively. Owing to the small RCR bond angle of 1-indanylidenes, the intramolecular chemistry is dominated by the singlet state even if the carbenes are generated by triplet-sensitized photolysis ($k_{TS} > k_T$). © 1997 Elsevier Science Ltd. All rights reserved.

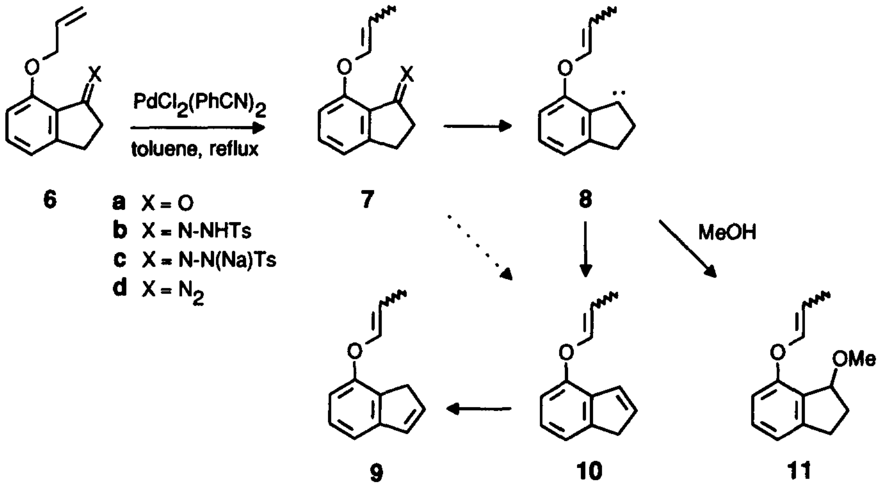
The singlet-triplet dichotomy of arylcarbenes continues to fascinate organic chemists.[1] The ground state of phenylcarbene is known to be the triplet but the chemistry observed in solution is frequently that of the more reactive singlet. Thus the reaction of phenylcarbene with alkenes gives cyclopropanes with >95% stereospecificity, regardless of the spin state in which the carbene is formed ($k_{TS} > k_T$).[2] In contrast, the intramolecular reactions of 2-alkenyloxyphenylcarbenes (**1**, **3**) proceed predominantly (**1** → **2**,[3] **3** → **4**)[4] or exclusively (**3** → **5**)[4] from the triplet state. Scavenging of the singlet carbenes by methanol indicates that $k_{TS} < k_T$ for **1** and $k_{TS} \sim k_T$ for **3**.



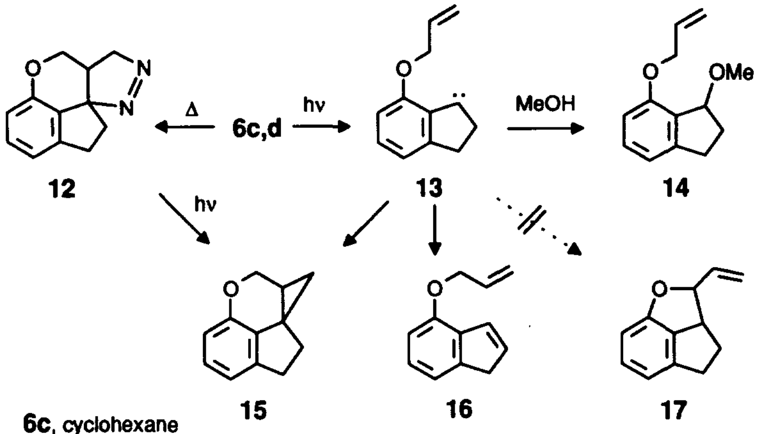
1 **2** R = H, Me **3** **4** **5**

Although geometric constraints are relieved, lengthening of the side-chain (**1** → **3**) does not promote the intramolecular *reactivity* of the singlet state. Alternatively, we aimed at enhancing the *concentration* of the singlet carbene. The singlet-triplet energy gap of carbenes is known to decrease as the RCR bond angle is contracted. The bending potential curves of $^1CH_2$ and $^3CH_2$ intersect at ∠HCH ~ 105°,[5] and ΔG_{ST} is smaller for 9-fluorenylidene (~1 kcal/mol) than for diphenylcarbene (~5 kcal/mol).[1] Replacement of R = H with R = alkyl tends to stabilize the singlet more than the triplet state.[5b, 6] Both effects will cooperate to make the singlet a readily accessible state, if not the ground state, of 1-indanylidene. Therefore, 7-alkenyloxy-1-indanylidenes (**8**, **13**, **19**) should be good candidates for intramolecular addition reactions of singlet arylcarbenes.

7-(2-Propenyloxy)-1-indanone (**6a**)[7] was isomerized with $PdCl_2$ to give a mixture of *E*- and *Z*-7-(1-propenyloxy)-1-indanone (**7a**, 36:64)[8] which was separated by LPLC; each isomer was converted into the corresponding tosylhydrazone **7b**.[9] Photolyses of the tosylhydrazone sodium salts **7c** in cyclohexane gave the alkenes **10** exclusively whereas mixtures of **9** and **10** were obtained on thermolysis. Photolyses of **7c** in methanol afforded the methyl ethers **11** (82-84%) along with minor amounts of **9** and **10**. The indene **10** arises by 1,2-H shift from the carbene **8** or from a carbene precursor (e.g., the excited diazo compound).[10] Scavenging of **8** by methanol proceeds faster than rearrangement by 1,2-H shift, a feature that distinguishes 1-indanylidenes from cyclopentylidenes.[11] The formation of **9** is attributed to base-induced and/or thermal isomerization of **10**. In contrast to **1**, no intramolecular addition of **8** was observed. Aside from spin state effects, this result may be due to substantial ring strain of the hypothetical adduct.[12]

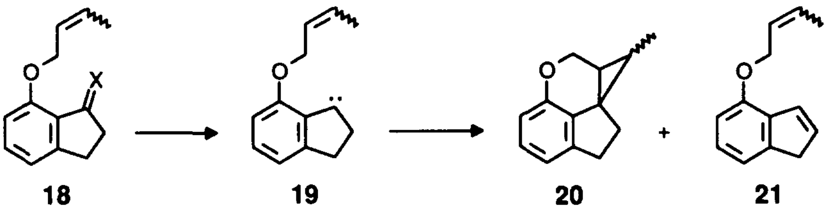


The geometric constraints inherent to **8** are minimized in 7-(2-propenyloxy)-1-indanylidene (**13**). In fact, the adduct **15** was obtained from **13** as well as from the pyrazoline **12**. In order to eliminate the **6d** → **12** → **15** route, the carbene was generated by photolysis of the tosylhydrazone sodium salt **6c**, and product distributions were extrapolated to $t = 0$. The intramolecular addition of **13** competes favorably with the 1,2-H shift leading to **16**, regardless how the carbene is generated. The small effect of triplet sensitization on the **15** : **16** ratio argues against a carbene precursor as a significant source of **16**.[10c] Moreover, **13** is scavenged by methanol to give the ether **17** (90-95%) in strong preference to intramolecular products (0.5-1% of **15**, 1-2% of **16**). No reaction of **13** with the allylic C-H bonds, leading to **17**, was observed. Since **5** arises from the triplet state of **3**,[4] the absence of **17** points to singlet reactivity of **13**. The ring strain of **17** may be an additional factor (the strain energy of **17** exceeds that of **5** by ~17 kcal/mol while the strain energies of **15** and **4** differ by only ~6 kcal/mol).[12]



	15	16	17
6c, cyclohexane			
hv, $t \to 0$	79.6	20.4	
hv, 0.25 M Ph_2CO $t \to 0$	78.9	21.1	

The stereochemistry of the intramolecular addition was probed with the 7-(2-butenyloxy)-1-indanylidenes **19**. Photolysis of the tosylhydrazone sodium salts *E*-**18c** and *Z*-**18c** afforded **20** and **21** in a ratio similar to that of **15** to **16**.[13] The formation of **20** was fully stereoselective in direct photolyses and ≥95% stereoselective in sensitized photolyses. Singlet reactivity predominates regardless how **19** is generated, i.e., $k_T < k_{TS}$. The behavior of **19** contrasts strongly with that of **3**.



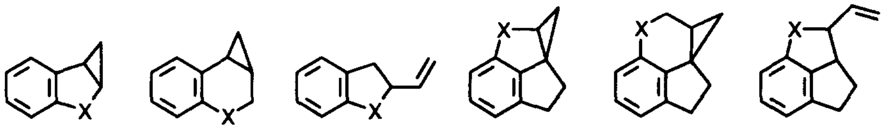
a X = O
b X = N-NHTs
c X = N-N(Na)Ts

	20 *cis*	20 *trans*	21
E-**18c**, cyclohexane			
hv, $t \to 0$	-	62.6	37.4
hv, 0.25 M Ph_2CO, $t \to 0$	2.5	68.9	28.6
Z-**18c**, cyclohexane			
hv, $t \to 0$	59.6	-	40.4
hv, 0.25 M Ph_2CO, $t \to 0$	70.1	3.6	26.3

To summarize, we have shown that the intramolecular reaction mode of aryl carbenes with neighboring alkenyloxy groups switches from triplet to singlet as the RCR bond angle is contracted. However, in all cases studied, the intramolecular addition of singlet carbenes is barely competitive with quenching by methanol, i.e. k_S is but slightly affected. We conclude that k_T/k_{TS} is most sensitive to structural variations. Examples for $k_T > k_{TS}$ (**1**),[3] $k_T \sim k_{TS}$ (**3**),[4] and $k_T < k_{TS}$ (**19**, this work) have now been reported.

REFERENCES AND NOTES

1. For reviews, see: (a) Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311. (b) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; Chapter 8. (c) Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487.
2. (a) Gutsche, C. D.; Bachman, G. L.; Coffee, R. S. *Tetrahedron* **1962**, *18*, 617. (b) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042. (c) Moss, R. A.; Dolling, U.-H. *J. Am. Chem. Soc.* **1971**, *93*, 954. (d) Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611.
3. (a) Hömberger, G.; Dorigo, A. E.; Kirmse, W.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 475. (b) Kirmse, W.; Hömberger, G. *J. Am. Chem. Soc.* **1991**, *113*, 3925:
4. Gotzhein, F.; Kirmse, W. *Tetrahedron Lett.* **1997**, *38* (preceding paper).
5. (a) For a review of the older literature, see: Shavitt, I. *Tetrahedron* **1985**, *41*, 1531. (b) For a recent high-level calculation, see: Sulzbach, H. M.; Bolton, E.; Lenoir, D.; Schleyer, P. v. R.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1996**, *118*, 9908.
6. (a) Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 3685. (b) Richards, C. A., Jr.; Kim, S.-J.; Yamaguchi, Y.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 10104.
7. Moody, C. J.; Roberts, S. M.; Toczek, J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1401.
8. *E*-**7a**: 31%, mp 64 °C, ^{1}H NMR ($CDCl_3$): δ 1.68 (dd, *J* = 7 and 2 Hz, CH_3), 2.65 (m, CH_2), 3.08 (m, CH_2), 5.55 (m, =CHMe), 6.42 (dd, *J* = 12 and 2 Hz, =CH-O), 6.82, 7.04, 7.47 (Ar-H). *Z*-**7a**: 55%, mp 61°C, ^{1}H NMR ($CDCl_3$): δ 1.76 (dd, *J* = 7 and 2 Hz, CH_3), 2.65 (m, CH_2), 3.10 (m, CH_2), 5.04 (m, =CHMe), 6.42 (dd, *J* = 6 and 2 Hz, =CH-O), 6.82, 7.04, 7.47 (Ar-H).
9. Treatment of the appropriate ketones with tosylhydrazine (1.1 eq., MeOH, 30-60 min reflux) afforded the tosylhydrazones **6b**: 93%, mp 200 °C, *E*-**7b**: 59%, mp 197 °C, *Z*-**7b**: 60%, mp 164 °C, *E*-**18b**: 79%, mp 182 °C, and *Z*-**18b**: 83%, mp 174 °C.
10. For reviews, see: (a) Platz, M. S.; White, W. R.; Modarelli, D. A.; Celebi, S. *Res. Chem. Intermed.* **1994**, *20*, 175. (b) Liu, M. T. H. *Acc. Chem. Res.* **1994**, *27*, 287. Specifically for 1-diazoindan /1-indanylidene, see: (c) Reed, S. C.; Modarelli, D. A. *Tetrahedron Lett.* **1996**, *37*, 7209.
11. Photolysis of 1-indanone tosylhydrazone in 0.2 M NaOMe-MeOH gave 1-methoxyindan and indene in a 7:3 ratio. Only 38% of 1-methoxyindan was reportedly obtained from 1-diazoindan.[10c] In our hands, samples of 1-diazoindan were contaminated with indene.
12. Force field (MMX) calculations gave the following data (kcal/mol):



X =	CH_2	O	CH_2	O	CH_2	O	CH_2	O	CH_2	O	CH_2	O
ΔH_f^0	42.6	18.9	34.0	6.1	32.0	4.8	54.7	33.5	32.7	8.0	41.7	17.8
SE	43.0	46.4	39.8	39.2	16.1	17.4	59.6	65.4	43.5	45.9	30.7	35.2

13. Alkylation of 7-hydroxyindan-1-one with *E*-1-bromo-2-butene (EtOH, 1 eq. K_2CO_3) afforded *E*-**18a** (92%, mp 68-69 °C) while 7-(2-butynyloxy)indan-1-one (94%, mp 152 °C) was hydrogenated (Lindlar catalyst, EtOAc, quinoline) to obtain *Z*-**18a** (79%, mp 42 °C). The stereochemical purity of *E*-**18b** (97.4%) and *Z*-**18b** (97.6%) was assessed by cleavage [Sacks, C. E.; Fuchs, P. L. *Synthesis* **1976**, 456], followed by GC of **18a**. Product distributions are corrected to pure **18b**.

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