the endo transition structure. This exo preference is similar to the exo preference for the Diels–Alder reaction of butadiene with formaldehyde imine.[1] In the endo transition structure, the nitrogen lone pair interacts with the internal carbon of the diene which is adjacent to the terminus that forms the CN bond. CHELPG charges indicate that a partial negative charge (–0.28 eu) develops on the internal carbon in the endo transition structure,[1b] making the interaction with the nitrogen lone pair repulsive. In the Diels–Alder reaction of butadiene with formaldehyde imine and in the ene reaction of propene with formaldehyde imine where CN bond formation occurs, stereoselectivity is determined by a repulsive electrostatic interaction, while in the ene reaction of propene with formaldehyde imine where CC bond formation occurs, stereoselectivity is determined by a stabilizing electrostatic interaction.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of the research. This work was supported in part by a grant of computer time on the IBM ES/9000 M900 Supercomputer at the UCLA Office of Academic Computing.

Stereoselective Cyclization of Carbene-Derived 1,5-Biradicals

Wolfgang Kirmse,* Ismail S. Özkir, and Dirk Schnitzler

Fakultät für Chemie, Ruhr-Universität Bochum
D-W-4630 Bochum, Federal Republic of Germany

Received October 26, 1992

The stereoselectivity of free radicals has been a subject of considerable interest.[1] With regard to ring closure, attention has traditionally been focused on 1,3- and 1,4-biradicals.[2] Over the past few years, high diastereoselectivities have been observed in photocyclizations of α-arylacetophenones (**1**) and *o*-alkoxybenzophenones (**2**).[3] These reactions involve δ-hydrogen abstraction by the ketone triplets, followed by cyclization of the 1,5-biradical intermediates (Scheme I). The interactions that cause diastereoselectivity can either pre-exist in the biradicals or be created as the substituents on the radical ends approach each other.[3,4] Very recently, we showed that triplet arylcarbenes (**3**) also abstract hydrogen from ortho side chains, generating 1,5-biradicals (**4**).[5] It occurred to us that the hydrogen transfer in **3** could be utilized to deuterate the benzylic site of **4** stereoselectively, depending on the location of deuterium in the carbene precursor (**3a** → (*E*)-**4**; **3b** → (*Z*)-**4**). Steric discrimination caused by the approach of terminal substituents is virtually eliminated in the cyclization of **4** to give **5**, yet we observe substantial diastereoselectivity that can be traced to conformational preferences of **4**.

The α-deuterated diazo compounds **6a** were obtained by H–D exchange, using NaOD–D_2O–dioxane in the cleavage of tosylhydrazone precursors. Side-chain deuterium (**6b**) was introduced in the course of aldehyde synthesis, proceeding from salicylaldehyde (X = O), 2-bromobenzyl bromide (X = CH_2, R = Ph), and (2-bromophenyl)ethyne (X = CH_2, R = $SiMe_3$). Photolyses of **6a,b** (Pyrex, pentane, 20 °C) afforded various derivatives of 2,3-dihydrobenzofuran (X = O) and indan (X = CH_2), which were analyzed by ^2H NMR (Table I). The assignments were confirmed, whenever possible, by cis addition of D_2 to the appropriate benzofurans and indenes. The choice of X and R was limited by our ability to resolve the signals of cis and trans deuterons; insufficient $\Delta\delta$ frustrated our work with X = O, R = *t*-Bu and X = CH_2, R = alkyl.

Scheme I

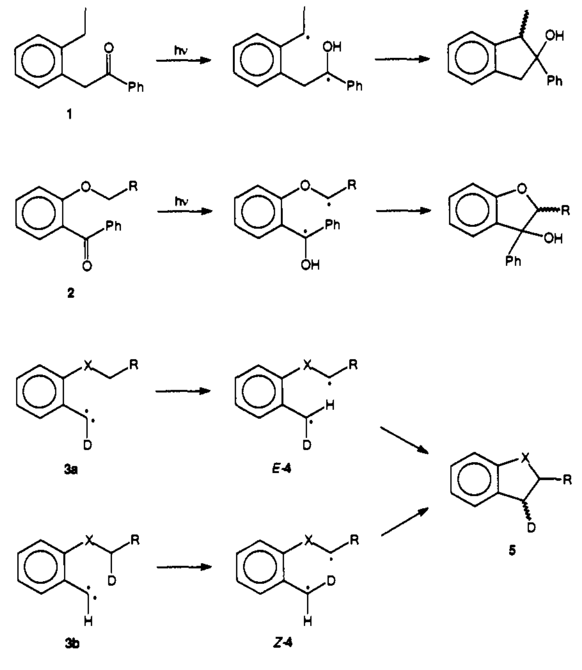
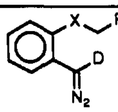
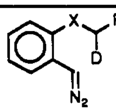


Table I. Deuterium Distributions Obtained from C–H Insertion Reactions of Arylcarbenes with Ortho Side Chains

		 **6a**		 **6b**		
X	R	*trans*-**5**	*cis*-**5**	*trans*-**5**	*cis*-**5**	k_H/k_D
O	Me	79	21			
	Et	75	25	20	80	6.7
	i-Pr	81	19			
	Ph	66	34	33	67	4.0
CH_2	Ph	85	15	10	90	4.6
	$SiMe_3$	58	42	31	69	4.4
	CH_2SiMe_3	65	35			

The data in Table I reveal that the α-deuterium of **6a** prefers the trans position in **5**. Most of the δ-deuterium in **6b** is recovered at C-2 of **5**; large deuterium isotope effects support the abstraction–recombination route to **5**. The (minor) transfer of deuterium, **3b** → (*Z*)-**4**, leads to an excess of *cis*-D in **5**, the distribution being inverse to that observed with **3a**. Our findings are clearly incompatible with an intermediate biradical **4** that rotates freely on both ends. The interconversion of (*E*)-**4** and (*Z*)-**4** is thought to be slow relative to ring closure,[6] given the large rotational barriers of benzyl radicals.[7] On the other hand, rotational equilibration of the side chain will be fast, as indicated by racemization in the case of chiral δ-carbons.[5,8] Two major

---

[1] (a) The stereoselectivity of intermolecular reactions has been reviewed: Giese, B. *Angew. Chem.* **1989**, *101*, 993; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 609. (b) For the stereoselectivity of alkenyl radical ring closure, see: Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

[2] Dervan, P. B.; Dougherty, D. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 3.

[3] (a) Wagner, P. J.; Zhou, B.; Hasegawa, T.; Ward, D. L. *J. Am. Chem. Soc.* **1991**, *113*, 9640. (b) Wagner, P. J.; Meador, M. A.; Zhou, B.; Park, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 9630. (c) Wagner, P. J.; Park, B. S. *Tetrahedron Lett.* **1991**, *32*, 165. (d) Wagner, P. J.; Meador, M. A.; Park, S. R. *J. Am. Chem. Soc.* **1990**, *112*, 5199. (e) For a review of earlier work, see: Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83.

[4] Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1972**, *94*, 3852.

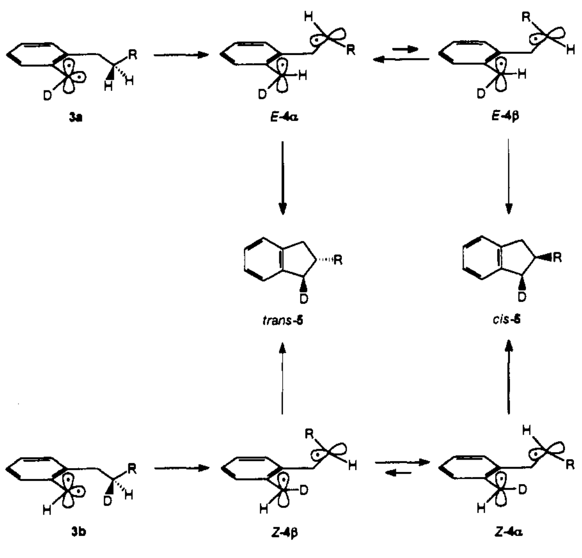
[5] (a) Kirmse, W.; Özkir, I. S. *J. Am. Chem. Soc.* **1992**, *114*, 7590. (b) Stereorandom "insertion" of **3b** (X = CH_2, R = Ph) has been demonstrated, employing (R^*,R^*)-2-Ph-CHD-CHD-C_6H_4-CHN_2 as the precursor. Thus, the abstraction–recombination mechanism holds for X = CH_2 as well as for X = O.[5a]

[6] The necessary biradical triplet → singlet intersystem crossing has been proposed to occur along the cyclization reaction coordinate.[3c]

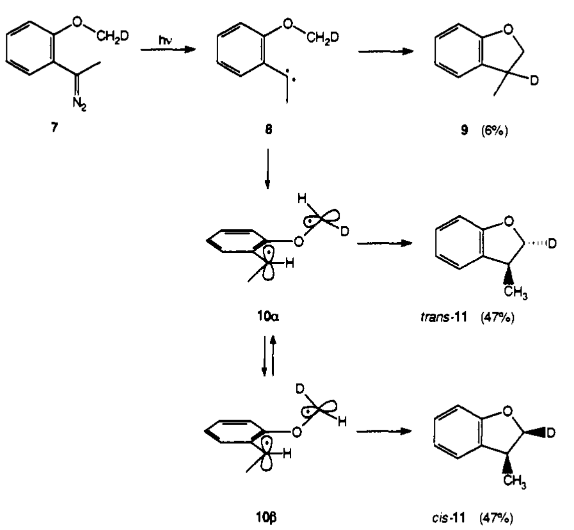
[7] Dorigo, A. E.; Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 6942 and references therein.

0002-7863/93/1515-792$04.00/0

Scheme II



Scheme III



conformers, **4α** and **4β**, must then be considered for product formation. We suggest that the sterically less congested anti conformer **4α**, leading to pseudoequatorial orientation of R in the incipient indan, will be favored over the more congested syn (axial) conformer **4β** (Scheme II).

If these views are correct, the stereoselection should disappear in the case of R = D. The experiment was not practical with **4** (R = D) due to problems with product analysis. Therefore, we resorted to the deuterated (2-methoxyphenyl)methylcarbene **8** (Scheme III). The large isotope effect ($k_H/k_D = 7.8$) supports the abstraction–recombination mechanism for **8**. In contrast to **4**, the negligible energy difference between the biradical conformers **10α** and **10β** leads to a stereorandom distribution of deuterium in **11**.

In summary, an unprecedented steric discrimination between hydrogen and deuterium has been observed in the cyclization of carbene-derived 1,5-biradicals. In view of their magnitude and direction, the stereoselectivities cannot be correlated with the "effective size" of the hydrogen isotopes.[9] Our data demonstrate that pre-existing energy differences between conformers of the biradicals control the preferred mode of cyclization.[3a-c]

---

(8) ESR detection and ab initio computation of the rotational barriers in (aryloxy)methyl radicals support this notion: Casarini, D.; Lunazzi, L.; Placucci, G.; Venturini, A. *J. Org. Chem.* **1991**, *56*, 414.

(9) For definitions and examples of "steric isotope effects", see: Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 189-197.

Novel Structure of Langmuir–Blodgett Films of Chloroplatinic Acid Using *n*-Octadecylamine: Evidence for Interdigitation of Hydrocarbon Chains[†]

P. Ganguly,* D. V. Paranjape, and Murali Sastry

Materials Chemistry Division
National Chemical Laboratory
Pune 411008, India

Received August 25, 1992

We report for the first time the deposition of crystalline Langmuir–Blodgett (LB) films[1] with a novel X-ray diffraction pattern using *n*-octadecylamine monolayers at the air–water interface and chloroplatinic acid in the aqueous subphase. Evidence is given for an interdigitation of hydrocarbon chains in the new structure.

The π–A isotherms of *n*-octadecylamine spread at the air–water interface at pH = 4.0 and 9.0 in the presence and absence of H_2PtCl_6 (10^{-4} M solution) in the aqueous subphase are shown in Figure 1. It is well-known[2,3] that in acidic medium the π–A isotherms of *n*-octadecylamine are governed by the nature of the complex formed with the acid. In the presence of H_2PtCl_6 at pH = 4.0, the π–A isotherms show a large liquid expanded phase extending up to an area of ~34 Å^2/molecule compared to that at pH = 9.0 (~30 Å^2/molecule). The extrapolated area of ~34 Å^2/molecule in Figure 1a in the presence of H_2PtCl_6 is close to the basal plane area per Cl_6 octahedral unit reported for the layered perovskite structure of $(R\text{-}NH_3)_2MCl_4$ compounds.[4] It is likely that at low pressures the $(R\text{-}NH_3)Pt_{0.5}Cl_3$ monolayer is derived from the $(R\text{-}NH_3)_2MCl_4$ monolayer with vacancies at $R\text{-}NH_3$, M, and axial Cl sites. In the initial stages of compression the close-packed chloride ions of the layered perovskite imparts rigidity to a single monolayer. The area per mole of amine in the solid condensed phase at pH = 4.0 (~15–17 Å^2/molecule) is nearly half that at pH = 9.0 (~28 Å^2/molecule). The formation of a bilayer of the amine at the air–water interface is indicated at high pressures.

The octadecylamine–H_2PtCl_6 surface layers are easily deposited at pH = 4.0 onto a substrate (HF-treated Si(111) in this study; chromic acid treated quartz or glass plates gave the same results) at 30 dyn/cm using an oleic acid piston and a homemade apparatus.[5] The unusual feature is that *the oleic acid piston is displaced by an area equal to the area of the substrate only during the upward movement and not during the downward movement* (see insert of Figure 1a). This fact and the low area per mole at the deposition pressure shows clearly that a *bilayer* is deposited during the upward movement. Interferometric studies as well as ellipsometric studies (assuming a refractive index of 1.5) of the deposited (31 dips, 1 dip = upward + downward movement) multilayers gave a thickness of 28 ± 3 Å/dip. The infrared spectrum shows prominent CH_2 bands at ~2919 and 2850 cm^{-1}. The frequencies and relative intensities of these bands correspond well with those reported for crystalline LB films.[2]

The X-ray diffraction pattern (Figure 2) is novel for an LB film. It may be indexed on the basis of a repeat unit along the *c* axis with a separation of 27.05 ± 0.02 Å. We propose the body-centered unit cell (*c* parameter = 54.02 Å) of Figure 1b for the $(R\text{-}NH_3)_2MCl_6$ formula unit. The calculated intensities of

---

[†] Communication No. 5430 from National Chemical Laboratory, Pune, India.

(1) Blodgett, B. *J. Am. Chem. Soc.* **1935**, *57*, 1007. See also: *Langmuir Blodgett Films*; Roberts, G. G., Ed.; Plenum Press: New York, 1990.

(2) Gaines, L. M. *Nature* **1982**, *298*, 544. Petrov, J. G.; Kuhn, H.; Mobius, D. *J. Colloid Interface Sci.* **1980**, *73*, 66.

(3) Loyons, C. G.; Rideal, E. K. *Proc. R. Soc. London* **1929**, *A124*, 333.

(4) Peterson, R.; Willett, R. D. *J. Chem. Phys.* **1972**, *56*, 1879. Steadman, J. P.; Willett, R. D. *Inorg. Chim. Acta* **1970**, *4*, 367.

(5) Sastry, M.; Ganguly, P.; Badrinarayanan, S.; Mandale, A. B.; Sainkar, S. R.; Paranjape, D. V.; Patil, K. R.; Chaudhary, S. K. *J. Chem. Phys.* **1991**, *95*, 8631 and references therein.

0002-7863/93/1515-793$04.00/0