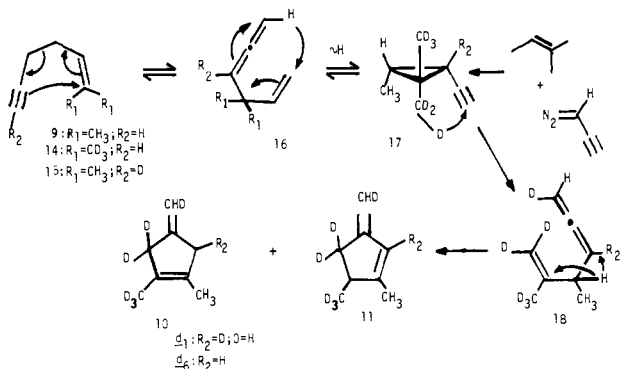Scheme II

the methylenecyclopentenes found and plausibly rationalized by Huntsman[5] in the pyrolyses of certain 1-en-5-ynes or their valency tautomeric eneallenes (1,2,5-trienes), in fact are structurally different in a crucial sense. They are formed by a novel multistep mechanism (Scheme II), involving Cope rearrangement, two successive hydrogen shifts, and ring closure by either of two formal intramolecular ene reactions.

Two separate isotope-position-labeling experiments were carried out. Pyrolysis at 700 °C of —C≡C—D labeled enyne 15 gave product 10-d_1 with the label exclusively at the ring methylene position (^{2}H NMR absorption at δ 3.02). The same treatment of $(CD_3)_2C$=C < labeled enyne 14 gave 10 with one exocyclic methylene deuteron (δ 4.91), two ring methylene deuterons, and three methyl deuterons (δ 1.63). Evidently, one of the two methyl groups of the reactant 14 does not survive intact in the product 10-d_6. In addition to a rationalization of the labeling patterns, the mechanism[6,7] of Scheme II predicts that pyrolysis of the proposed cyclopropane intermediate 17 should give 10. This prediction was confirmed by the independent synthesis of a mixture of 17 and its trans stereoisomer (from 3-diazopropyne and 2-methyl-2-butene), which upon pyrolysis gave >95% of an approximately equimolar mixture of 10 and 11, each identified by isolation and independent synthesis.

Scheme I and Table I show that the dominant thermal reaction of the TMM 1 is cleavage of the C_4–C_5 bond, but cyclization to 12 is competitive. The enyne 9 derived from 12 thus represents the interface of two connected energy surfaces (Schemes I and II).

Supplementary Material Available: Descriptions of isolation, characterization, and independent syntheses of products (2 pages). Ordering information is given on any current masthead page.

(5) (a) For an excellent review, see: Huntsman, W. D. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; Vol. 2, p 522. (b) Huntsman, W. D.; De Boer, J. A.; Woosley, M. H. *J. Am. Chem. Soc.* **1966**, *88*, 5846. (c) Huntsman, W. D.; Dykstra, K. A., unpublished work as cited in ref 5a. (d) Huntsman, W. D.; Dykstra, K. A.; Giannamore, V. P.; Weaver, K. C.; Yin, T. K. 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981; American Chemical Society: Washington, D. C., 1981; PETR 14.

(6) Although the labeling in 10-d_6 was apparently the same as that which would result from a statistical distribution of *all* the deuteriums, the specificity of the labeling in 10-d_1 (from pyrolysis of 15) showed that such randomization did not occur.

(7) (a) Precedent exists for the *reverse* of 16 → 17: Dalacker, V.; Hopf, H. *Tetrahedron Lett.* **1974**, 15. (b) Pyrolysis of the proposed eneallenic intermediate 16 gave 9, in accord with a previous observation.[5c]

Surface Photochemistry: Deviation of the Course of Reaction in Benzoin Ether Photolysis by Adsorption on Silica Gel[1]

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Recently, we have been concerned to show the occurrence of, and constraints on, movement of closed-shell molecules[2] and radical pairs[3] when adsorbed on silica gel. From these studies it seemed to us that the constraints imposed were such that the reaction course of a photochemical process in solution having important steric demands ought to be capable of profound change when the reactant was adsorbed on a silica gel surface. We report the first clear example of such a major deviation in reaction pathway.

The photolysis of benzoin derivatives in solution has been studied extensively, and the main details of the reaction have been elucidated.[4,5] In the case of benzoin ethers (1a,b; Scheme I) the reaction proceeds via the triplet and the radical pair (2; type I cleavage) to give, as main products, the pinacol ethers (4) and benzil (5), derived from both geminate pair escape and combination, together with minor amounts of benzaldehyde and benzyl methyl ether. It appeared possible that a silica gel surface might function in two senses: (a) restrict the translational movement in the radical pairs and permit other forms of recombination, for which there is some analogy;[6,7] (b) if the absence of the potentially possible type II hydrogen abstraction (to give 3) were to be attributed, in part, to the low occupancy by 1 of the necessary cisoid conformation in solution, then hydrogen bonding with the silica gel could produce the required conformation.[9]

Our results in methanolic solution, obtained as controls, and on a silica gel surface are summarized in Table I.[14] In the solution photolysis the previously unreported type II contributes in a minor way and decreases further at lower temperatures. Photolysis on a silica gel surface[15] provided a dramatic difference in behavior.

(1) Publication No. 285 from the Photochemistry Unit, University of Western Ontario.

(2) Bauer, R. K.; Borenstein, R.; Mayo, P. de; Okada, K.; Rafalska, M.; Ware, W. R.; Wu, K. C. *J. Am. Chem. Soc.* **1982**, *104*, 4635. Mayo, P. de; Okada, K.; Rafalska, M.; Weedon, A. C.; Wong, G. S. K. *J. Chem. Soc., Chem. Commun.* **1981**, 820.

(3) (a) Avnir, D.; Mayo, P. de; Ono, I. *J. Chem. Soc., Chem. Commun.* **1978**, 1109. (b) Avnir, D.; Johnston, L. J.; Mayo, P. de; Wong, S. K. *Ibid*, **1981**, 958. See also: Leffler, J. E.; Zupancic, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 259. Leffler, J. E.; Barbas, J. T. *Ibid.* **1981**, *103*, 7768.

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(5) Sondner, M. R.; Osborn, C. L. *Tetrahedron Lett.* **1974**, 415.

(6) Turro[8] has reported the formation of minor amounts of *p*-methylphenylacetophenone from the photolysis of dibenzyl ketone in micelles.

(7) We have observed *p*-methylphenylacetophenone formation from the photolysis of dibenzyl ketone on a silica gel surface. (L. J. Johnston, unpublished results from these laboratories).

(8) Turro, N. J.; Chow, M. F.; Chung, C. J.; Kraeutler, B. *J. Am. Chem. Soc.* **1981**, *103*, 3886.

(9) The factors affecting the ratio of type I/type II for phenyl ketones have been discussed from the points of view of rigidity of the structure,[10] stereochemistry,[11a,12] and electronic effects.[11b,13]

(10) Padwa, A. *Acc. Chem. Res.* **1971**, *4*, 48. Padwa, A.; Alexander, E.; Niemcyzk, M. *J. Am. Chem. Soc.* **1969**, *91*, 456.

(11) (a) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5896. (b) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

(12) Yang, N. C.; Dominh, T. *Tetrahedron Lett.* **1966**, 3671. Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 6672.

(13) Turro, N. J.; Lewis, F. D. *J. Am. Chem. Soc.* **1970**, *92*, 311.

(14) Benzaldehyde and benzyl methyl ether were produced in trace amounts.

Scheme I[a]

4 (*dl-* and *meso-*)
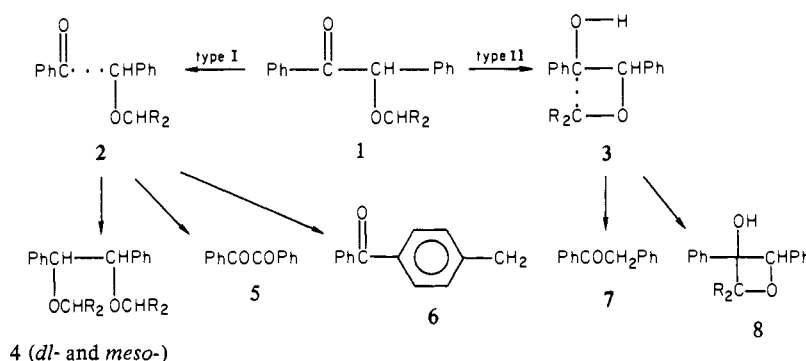
[a] a, R = H; b, R = Me.

Table I. Product Distribution in the Photolysis of 1a,b in MeOH and on Silica Gel with Temperature (mol % of Product Based on Starting Material Consumed)[a–c]

system	T, °C	type I			type II	
		4	5	6	7	8
1a–MeOH[d]	+56	43.7	8.6	5.7	3.3	2.4
	+4	39.6	16.7	3.9	1.0	1.8
	−51	38.1	20.3	3.6	0.4	0.7
	−78	29.9	14.2	3.6	0	0.3
1a–silica gel[e]	+56	43.8	3.0	6.7	13.0	3.1
	+4	30.0	3.8	7.1	4.6	3.3
	−55	25.7	7.2	38.3	9.8	8.9
	−78	10.8	2.5	39.6	6.2	6.0
1b–MeOH[d]	+56	40.7	5.0	12.8	2.9	1.4
	+11	44.9	13.9	8.7	1.2	0
	−44	47.1	23.6	9.1	0	0
	−80	44.7	25.2	18.3	0	0
1b–silica gel[e]	+56	39.4	1.6	10.2	10.2	3.9
	+12	38.2	10.6	16.5	10.6	6.8
	−40	18.1	8.2	35.8	11.5	14.7
	−78	6.8	6.4	58.3	13.4	20.2

[a] New compounds were characterized spectroscopically and mass spectroscopically. Compound 8a was synthesised. [b] Analysis by GC with docosane as an internal standard. [c] Silica gel irradiations were performed on degassed samples in horizontal rotating cylinders in front of a 500-W medium-pressure mercury arc, λ >300 nm. Conversion: 14–36%. [d] 0.18 mmol in 10 mL of MeOH. [e] Ca. 0.18 mmol on 3.0 g of silica gel (Merck 60, 35–70 mesh); approximately 5–10% coverage.

With 1a, at room temperature, the amount of type II reaction (7a + 8a) is considerably increased over that found in methanolic solution. On lowering the temperature the pinacol ethers (4a) become minor products, and the rearranged radical pair combination product 6a becomes major, the proportions being essentially reversed. This is interpreted as an indication of the suppression of translational motion in the radical pairs 2a[3b] but not of their rotational motion.

In addition to the increase in the type II process over that found in solution, the proportion of cyclization (of 3a) to cleavage (8a:7a) is higher than that expected for a conformationally mobile system[16] that can assume either of the planar conformations necessary for cleavage.[10,11] This argues for a cisoid, but nonplanar, stereochemistry for 3a when hydrogen bonded to the silica gel surface.

With 1b the contrast between solution reaction and that on the silica gel surface is deepened. At 56 °C in both systems the results are comparable except for an increased amount, on silica gel, of type II reaction, mainly cleavage. At −78 °C the nongeminate pair combination 4b has decreased to a sixth, whereas the rearranged geminate pair combination has increased 6-fold, to 58%. Again, translational, but not rotational, movement has been suppressed. The type II biradical is also being formed in increasing amount (33% of 7b + 8b) with cyclization dominating its subsequent behavior.

The results here reported are a consequence of two separate functions of the silica gel on the reacting species: conformational control and restricted movement. These are expected to be found acting independently and to have generality.

Stable Gold Hydride Complexes

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No solid gold hydride species appear to be known,[1] although a monomeric gold hydride AuH has been detected in the gas phase.[2] Our previous studies on bridging hydride complexes[3] have shown that unstable mononuclear hydrides can be stabilized by complex formation to a second transition-metal center, e.g., [(PEt₃)₂Pt(μ-H)₂PtR(PEt₃)₂]BPh₄ (R = H and Ph)[4] and [(diphos)Rh(μ-H)₂IrH₂(P-*i*-Pr₃)₂].[5] We have, therefore, attempted the preparation of stable complexes containing Au–H bonds by formation of species of the type LAuHML′$_n$ by the reaction of an (AuL)+ cation with a neutral metal hydride (MH$_m$L′$_n$).

The compounds [AuCl(PR₃)] (1, a, R = Ph; b, R = Et) react with AgBF₄ in THF to give the solvated cations [Au(THF)-

(15) The ketones were deposited on the silica gel by removing the solvent from a dry methylene chloride slurry under 10⁻⁵ mmHg.

(16) Evidence was found, from variable-temperature ¹H NMR studies of 1b, to be reported elsewhere, of slow (on the NMR time scale) rotation about the central bond, which cannot compete with the fast α cleavage.[5] The ether 1a can do so more effectively.

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(2) Ringström, U. *Nature (London)* **1963**, *198*, 918.

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(4) Bracher, G.; Grove, D. M.; Pregosin, P. S.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 155.

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(6) This reaction also gives an iridium hydride complex whose structure is, as yet, unknown.