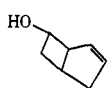
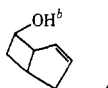
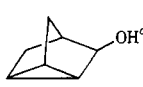
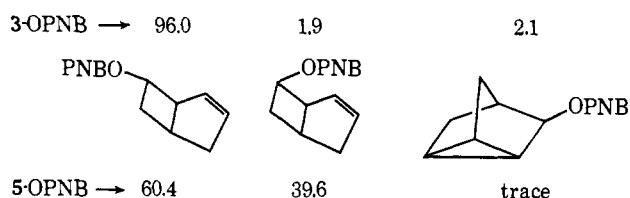


Table III. Hydrolysis Products from 3-OPNB and 5-OPNB in 70% Aqueous Acetone<sup>a</sup>

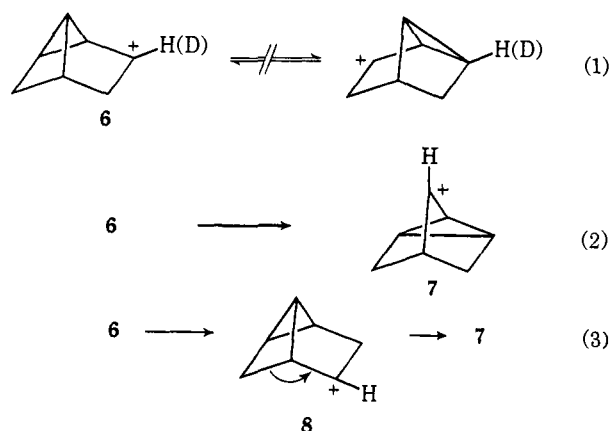
Ester	5-OH	3-OH				Unknown <sup>d</sup>
3-OPNB	61.5	4.5	22.5	2.3	2.8	6.4
5-OPNB	62.1	5.3	22.8	1.7	2.1	6.0

<sup>a</sup> Relative per cent yields; absolute yields of alcohols were *ca.* 100% based on unreturned ester. Solutions were 0.02 M in ester and 0.08 M in 2,6-lutidine, under which conditions all products were stable. <sup>b</sup> Identified only by gc peak enhancement with authentic material. <sup>c</sup> A trace of 5-norbornenol would not have been detected. <sup>d</sup> One peak on gc.

suggests a common product-determining intermediate(s) in the solvolyses. However, 3-OPNB and 5-OPNB apparently ionize, at least partially, to separate ion pairs, as the ion-pair return product distributions are different.



Degenerate cyclopropylcarbinyl-cyclopropylcarbinyl isomerization has been noted in several instances during solvolysis of some systems,<sup>13a-c</sup> but occurs to a very small extent, or not at all, in others.<sup>13d,14</sup> The isomerization proceeds by inversion of configuration at the  $\beta$ -cyclopropyl carbon.<sup>13b</sup> The 3-psinortricyclyl cation appears well suited stereochemically for the isomerization (eq 1). However, when 3-OPNB- $\alpha$ -d or 5-OPNB- $\alpha$ -d was hydrolyzed under kinetic control, no protium incorporation (<3%) could be detected by nmr at the  $\alpha$  position of recovered 5-OH.<sup>15</sup> Formation of a small amount of product derived from the nortricyclyl ion 7 may result from nondegenerate cyclopropylcarbinyl-cyclopropylcarbinyl isomerization (eq 2). An alternative, though unlikely, mechanism involves vicinal hydride transfer to give the 4-psinortricyclyl cation 8 which rearranges to 7<sup>3</sup> (eq 3). Appropriate labeling should discern the correct pathway.



(12) F. F. Nelson, Ph.D. Dissertation, University of Wisconsin, 1960.

(13) (a) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **81**, 4390 (1959); (b) K. B. Wiberg and G. Szeimies, *ibid.*, **90**, 4195 (1968); **92**, 571 (1970); (c) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303 (1968); (d) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

(14) See K. Rubenstein, Table I, footnote b.

(15) Recovered *exo*-bicyclo[3.2.0]hept-2-en-7-ol integrated for 1.0 vinyl hydrogen.

The present results show that neither mode of the cyclopropylcarbinyl-cyclopropylcarbinyl isomerization prevails over kinetically controlled solvent capture of 6, even though there is probably a large driving force for formation of 7.<sup>16</sup> This is perhaps surprising in light of the nearly total (degenerate) scrambling during hydrolysis of dehydroadamantyl dinitrobenzoate.<sup>13c</sup> However, it is not yet clear whether cyclobutyl carbonium ions are requisite intermediates.<sup>13c,17</sup> Such intermediates in the present case should be highly strained.

**Acknowledgments.** The author is grateful to Professor W. L. Mock for the use of his equipment, to Professor D. Schuster for unpublished spectral data, and to Professors H. G. Richey, Jr. and P. von R. Schleyer for helpful discussions.

(16) The psinortricyclene ring system may be estimated to have a free energy greater than that of nortricyclene by at least 13.6 kcal/mol [cf. P. von R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958); A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966)]. Using carbonyl stretching frequencies to account for the strain incurred by introduction of trigonal centers, one may estimate that 7 has 5.5 kcal/mol more angle strain than 6. On this basis, 7 is still favored over 6 by better than 8 kcal/mol.

(17) (a) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4311 (1968); (b) C. Trindle and O. Sinanoglu, *ibid.*, **91**, 4054 (1970).

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## On the Mechanism of Paterno-Büchi Reaction of Alkanals

Sir:

The Paterno-Büchi reaction, the photocycloaddition of carbonyl compounds to olefins, has been applied to a variety of substrates,<sup>1</sup> and contributions have been made by several groups in elucidating its mechanism.<sup>2,3</sup> However, few attempts have been made to analyze the stereochemistry and mechanism of photochemical addition of alkanals to simple olefins. Evidence is now presented that indicates the intermediacy of an exciplex between the  $1n-\pi^*$  of the aldehyde and

(1) For a review on the photocycloaddition of carbonyl compounds to unsaturated systems, see D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(2) For more recent work on the photochemical addition of alkanones to olefins, see (a) N. J. Turro, P. Wriede, J. C. Dalton, D. R. Arnold, and A. Glick, *J. Amer. Chem. Soc.*, **89**, 3950 (1967); (b) N. J. Turro, P. Wriede, and J. C. Dalton, *ibid.*, **90**, 3274 (1968); (c) N. J. Turro and P. Wriede, *ibid.*, **90**, 6863 (1968); **92**, 320 (1970); (d) J. A. Barltrop and H. A. Carless, *Tetrahedron Lett.*, 3901 (1968).

(3) For the mechanism of Paterno-Büchi reaction of aromatic carbonyl compounds see: (a) R. A. Caldwell and S. P. Jones, *J. Amer. Chem. Soc.*, **91**, 5184 (1969); (b) I. H. Kochevar and P. J. Wagner, *ibid.*, **92**, 5742 (1970); (c) N. C. Yang, R. L. Loeschen, and D. Mitchell, *ibid.*, **89**, 5465 (1967).

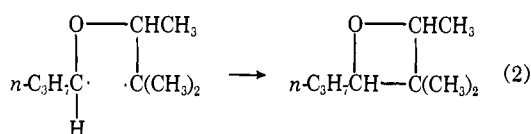
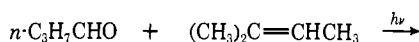
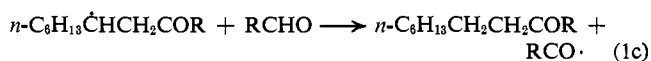
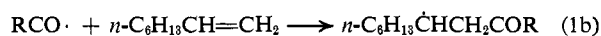
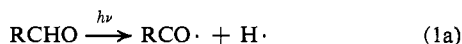
Table I

Olefin (concn) <sup>a,b</sup>	Concn of CH <sub>3</sub> CHO, M	Quantum yield, ε <sup>-e</sup>			Isomer ratio	
		Oxetane 1	Oxetane 2	Oxetane 3	(1 + 2):3	(1 + 3):2
<i>trans</i> -Butene (5 M) <sup>f</sup>	0.58	0.055 ± 0.003	0.070 ± 0.004	0.006 ± 0.001	27:1	
<i>trans</i> -Butene (neat) <sup>g</sup>	1.25				25:1	
<i>cis</i> -Butene (5 M) <sup>f</sup>	0.55	0.065 ± 0.001	0.018 ± 0.003	0.077 ± 0.001		8:1
<i>cis</i> -Butene (neat) <sup>g</sup>	1.25					10:1

<sup>a</sup> Olefin purity, 99.5%. <sup>b</sup> There was no detectable isomerization of starting olefin in all cases studied. <sup>c</sup> Irradiation carried out at 22 ± 1° and at 313 nm using an apparatus previously described: D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966). <sup>d</sup> 2-Hexanone was used as the secondary actinometer. <sup>e</sup> Starting with either olefin, oxetanes accounted for 93.5% of all products formed. <sup>f</sup> *n*-Hexane was used as the solvent, and the samples were not degassed. <sup>g</sup> Irradiation carried out at -60° with a Hanovia 450-W lamp with a Correx filter.

the ground state of the olefin in the Paterno-Büchi reaction of alkanals.

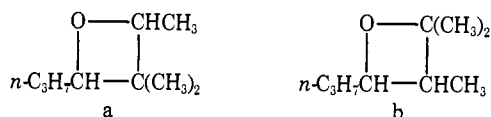
Kharasch, Kuderna, and Urry reported that irradiation of mixtures of alkanals and 1-octene at a high aldehyde to 1-octene ratio gave ketones as the only identified adduct and proposed a radical-chain mechanism for the ketone formation (eq 1a-c),<sup>4</sup> while Büchi and his coworkers reported that irradiation of *n*-butanal in 2-methyl-2-butene gave an oxetane as the major product and proposed a biradical intermediate for the oxetane formation (eq 2).<sup>5</sup> Propanal was irradiated with various olefins at a 6:1 olefin-aldehyde ratio in order to study the structure-reactivity relationship in the photochemical addition of alkanals to olefins. The olefins used include: 1-hexene, *cis*-3-hexene, *trans*-3-hexene, isobutene, *cis*-3-methyl-2-pentene, and 2,3-dimethyl-2-butene. We found that 3-nonanone was the major product in the propanal-1-hexene reaction,<sup>6</sup> while oxetanes were the major products in all of the other reactions with little or no detectable ketone formation. In all cases for olefins which may exist in geometrical isomers, there was no detectable isomerization during the reactions. Due to the complexity of the nmr spectra of oxetanes formed from propanal, these systems were not chosen to study the stereochemistry of oxetane formation and the simpler ethanal-2-butene system was used instead.



The cycloaddition of ethanal to 2-butene yields all three possible oxetanes (**1**, **2**, and **3**) which are readily separable by vpc, and whose structures may be assigned

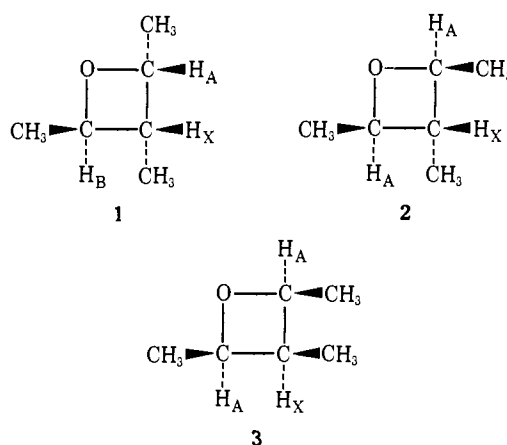
(4) M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

(5) (a) G. H. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **78**, 876 (1956); (b) P. de Mayo, *Advan. Org. Chem.*, **2**, 379 (1960); (c) unpublished results by A. Shani in this laboratory showed that oxetanes a and b were formed in a 4:1 ratio.



(6) Oxetane-like products were also detected as minor products.

unambiguously by high-resolution 100-MHz nmr spectrometry.<sup>7</sup> We found that oxetanes **1** and **2** were formed predominantly in the reaction from *trans*-2-butene while oxetanes **1** and **3** were formed predominantly from *cis*-2-butene. The results are summarized in Table I. The assignment of structures is consistent



with the observation that the *trans* vicinal H-H coupling constant in oxetanes is smaller than the corresponding *cis* coupling constant.<sup>2c,8</sup> Oxetane **1** displays: nmr (CDCl<sub>3</sub>) δ 4.79 (doublet of quartets, 1,  $J_{A-X} = 7.0$  Hz,  $J_{A-CH_3} = 6.5$  Hz, H<sub>A</sub>), 4.30 (quintet, 1,  $J_{B-X} \sim J_{B-CH_3} = 6.0$  Hz, H<sub>B</sub>), 2.55 (sextet, broad, 1,  $J_{X-CH_3} = 7.0$  Hz, H<sub>X</sub>), 1.33 (d, 3,  $J = 6.0$  Hz, CH<sub>3</sub>CH<sub>B</sub>), 1.24 (d, 3,  $J = 6.5$  Hz, CH<sub>3</sub>CH<sub>A</sub>), and 1.05 ppm (d, 3,  $J = 7.0$  Hz, CH<sub>3</sub>CH<sub>X</sub>). Oxetane **2** displays: nmr (CDCl<sub>3</sub>) δ 4.26 (quintet, 2,  $J_{A-X} \sim J_{A-CH_3} = 6.1$  Hz, H<sub>A</sub>), 2.06 (sextet, 1,  $J_{X-CH_3} = 6.7$  Hz, H<sub>X</sub>), 1.29 (d, 6,  $J = 6.1$  Hz, CH<sub>3</sub>CH<sub>A</sub>), and 1.08 ppm (d, 3,  $J = 6.7$  Hz, CH<sub>3</sub>H<sub>X</sub>). Oxetane **3** displays: nmr (CDCl<sub>3</sub>) δ 4.86 (quintet, 2,  $J_{A-X} \sim J_{A-CH_3} = 6.7$  Hz, H<sub>A</sub>), 2.88 (sextet, 1,  $J_{X-CH_3} = 7.5$  Hz, H<sub>X</sub>), 1.18 (d, 6,  $J = 6.7$  Hz, CH<sub>3</sub>CH<sub>A</sub>), and 1.01 ppm (d, 3,  $J = 7.5$  Hz, CH<sub>3</sub>CH<sub>X</sub>). The signal for the H<sub>X</sub> proton would have been a triplet of quartets in oxetanes **2** and **3** and an even more complex pattern in oxetane **1**. Due to the similarity of  $J_{CH_3-HX}$  to other coupling constants, accidental degeneracy of the signals occurs and they were not completely resolved. Furthermore we found, in the range of temperature and olefin concentration studied, the stereoselectivity of addition does not seem

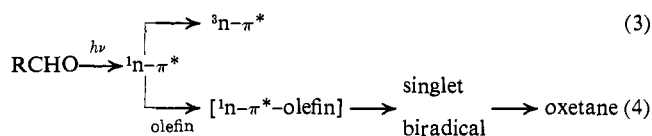
(7) Satisfactory elemental analyses and ir and mass spectra compatible with the assigned structures were obtained. It is interesting to note that oxetanes 1-3 do not give parent molecular ions in their mass spectra but rather give strong peaks corresponding to fragmentation to olefin and aldehyde. This behavior has been observed previously.<sup>5,8</sup>

(8) J. J. Beereboom and M. S. von Wittenau, *J. Org. Chem.*, **30**, 1231 (1965).

to vary for either isomeric 2-butene. The quantum yield is of the order of 0.13–0.15 in 5 M 2-butene indicating that there is an efficient mode of radiationless deactivation of the excited state. There is no detectable isomerization of starting 2-butenes. In view of the known photoreactivity of alkanals toward 1,3-dienes,<sup>9</sup> attempted quenching of oxetane formation by 1,3-dienes was not undertaken.

The Paterno–Büchi reactions of aromatic carbonyl compounds with isomeric olefins are known to give essentially the same mixture of isomeric oxetanes<sup>10</sup> and to cause extensive isomerization of the starting olefins.<sup>11</sup> The reactive intermediate in these reactions is the  $^3n-\pi^*$  of the carbonyl compounds or the  $^3n-\pi^*$ -olefin complex.<sup>3a,3b</sup> Our observations that the photocycloaddition of ethanal to 2-butenes proceeds with a high degree of stereoselectivity and that there is no detectable isomerization of starting 2-butenes during the reaction are in marked contrast to the reactions from aromatic carbonyl compounds, and suggest that the reactions from ethanal proceed *via* its  $^1n-\pi^*$ .<sup>12</sup> Since the addition is highly stereoselective but not stereospecific, a singlet biradical intermediate may be formed in the reaction. The ring closure of singlet biradicals is known to be appreciably faster than the bond rotation which will cause randomization in the product formation.<sup>13</sup> A secondary biradical intermediate will be formed from the reaction of  $^1n-\pi^*$  of an alkanal with either terminal or nonterminal *n*-alkenes. In view of the fact that ethanal reacts with 1-octene photochemically to give 2-decanone and propanal reacts with 1-hexene to give 3-nonanone as the major products, while they react with nonterminal olefins to give oxetanes, the nature of product formed in these reactions is not determined by the stability of the intermediate biradical but rather by the degree of alkylation on the olefinic double bond. Since the carbonyl oxygen is electron deficient in the  $n-\pi^*$  states of carbonyl compounds, the  $^1n-\pi^*$  of alkanals may interact with the  $\pi$  system of olefins to form an exciplex. The ionization potential of an olefin decreases with an increasing number of alkyl substituents;<sup>14</sup> the ease of exciplex formation will then depend on the degree of alkylation of the olefin. Our results imply that oxetane formation is controlled by the ease of formation of the exciplex which may collapse subsequently to give the biradical intermediate. Turro and his coworkers have suggested such an exciplex as the intermediate in the photocycloaddition of alkanones to a variety of olefins.<sup>2b-d</sup> Since there is no appreciable isomerization of the starting olefin during the reaction, the behavior of  $^1n-\pi^*$  of alkanals differs from that of alkanones such that the intersystem crossing of  $^1n-\pi^*$  of alkanals or its exciplex is not an important process in the presence of nonterminal olefins

(reaction 3). Similar exciplexes from  $^3n-\pi^*$  of aromatic carbonyl compounds have been suggested in other Paterno–Büchi reactions.<sup>3a,3b</sup> In conclusion, we propose the following sequence of steps in the Paterno–Büchi reaction of alkanals (reaction 4).



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### Nucleation Studies of Supercooled Cholesteric Liquid Crystals

Sir:

Supercooling of liquids before crystallization lends itself to thermodynamic interpretation of the processes involved in nucleation and growth.<sup>1</sup> In this regard, the high degree of supercooling in cholesteric liquid crystals is unique. Here, for example, supercooling of a liquid crystalline compound by 86°K persisted for several minutes. Nucleation proceeds from a semi-ordered<sup>2</sup> (liquid crystalline) to an ordered (crystalline) phase. We now report the first application of nucleation rate theory to this process using cholesteryl nonanoate and caproate and mixtures thereof.

Samples were placed in glass tubes, which were evacuated and sealed at  $10^{-5}$  mm. The sample was heated to the isotropic state, rotated to ensure a thin liquid coating on the tube, then plunged into a thermostated bath. The time was noted at the first visual evidence of crystallinity, which was always at the liquid crystal–vacuum interface. Nucleation times were corrected for heat transfer from sample tubes to the bath<sup>3</sup> (less than 6 sec). A Perkin-Elmer differential scanning calorimeter (DSC-1B) afforded the enthalpies of transition.

The plot of  $\ln$  (nucleation rate) (uncorrected for any crystal growth) *vs.*  $1/T$  for cholesteryl nonanoate (Figure 1) is typical of mixed and pure systems. The maximum exists because at low temperature nucleation is transport controlled while at high temperatures it is governed by the thermodynamic driving force of supercooling. Turnbull and Fisher<sup>4</sup> and Mandelkern<sup>1</sup> derived an expression for the rate of nucleation in condensed systems

$$N = N_0 T \exp(-E_d/RT) \times \exp[-\alpha \delta \pi \sigma_u^2 \sigma_e T_m^2 / R(\Delta H)^2 T(\Delta T)^2] \quad (1)$$

(1) L. Mandelkern, "Crystallization of Polymers," McGraw-Hill, New York, N. Y., 1964, p 215.

(2) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962, p 66.

(3) R. B. Bird, W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, New York, N. Y., 1960, p 356.

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(12) An earlier suggestion that propanal reacts with alkoxyolefins photochemically *via* its  $^3n-\pi^*$  (S. H. Schroeter, *Chem. Commun.*, 12 (1969)) may be reinterpreted to proceed *via* its  $^1n-\pi^*$ .

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(14) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).