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Tetramethylcyclopropanone. II. Mechanism of the Favorskii Rearrangement

Sir:

The Favorskii rearrangement of α -halo ketones to carboxylic esters is believed to involve a symmetrical intermediate which may be formulated as a cyclopropanone¹ or as a mesomeric zwitterion.^{1,2} The possible intermediacy of a cyclopropanone hemiketal (as its anion) has also been suggested.³ The Favorskii rearrangement is complicated by the fact that reaction conditions may control the stereochemistry and nature of the products formed.^{1,3,4} Thus, the detailed mechanism of a Favorskii rearrangement and the involvement of the postulated intermediates is expected to vary with reaction conditions.^{3,4} Available evidence suggests that the intermediacy of the cyclopropanone and the stereospecific Favorskii rearrangement^{3,4} are favored by (heterogeneous) nonpolar media (e.g., ether, dimethoxyethane (DME), etc.) and that the mesomeric zwitterion are favored by polar media³ (e.g., methanol). It appears that α -alkoxy ketone formation becomes a significant path and sometimes even the dominant path of reaction in polar solvents as a result of stabilization of the proposed mesomeric zwitterion.^{2c,3} It has not been possible to establish conclusively the intermediacy of a mesomeric zwitterion in α -alkoxy ketone formation, since it is formally a substitution reaction.

We wish to report the first direct experimental tests of the relationship of some of the proposed intermediates to the Favorskii rearrangement of 2-bromo-2,4-dimethyl-3-hexanone (1). Tetramethylcyclopropanone (2) and its methyl hemiketal⁵⁻⁷ are now available from the photolysis of tetramethyl-1,3-cyclobutanedione^{5,8-10} under appropriate conditions. The results of our studies¹¹ are summarized by eq. 1-4.

(1) (a) A. S. Kende, *Org. Reactions*, **11**, 261 (1960); (b) R. B. Loftfield, *J. Am. Chem. Soc.*, **72**, 632 (1950); **73**, 4707 (1951); **76**, 35 (1954).

(2) (a) W. D. McPhee and E. Klingberg, *ibid.*, **66**, 1132 (1944); (b) J. G. Aston and J. D. Newkirk, *ibid.*, **73**, 3900 (1951); (c) A. W. Fort, *ibid.*, **84**, 2620, 2625, 4979 (1962); (d) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954); (e) R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.*, 123 (1963); *J. Chem. Soc.*, 2009 (1965).

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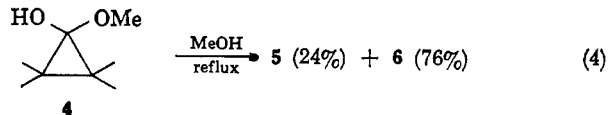
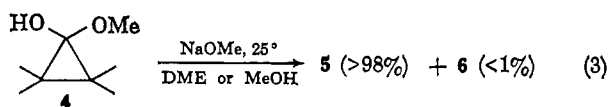
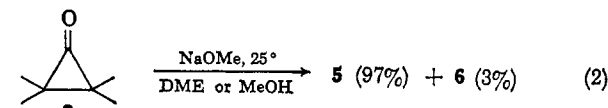
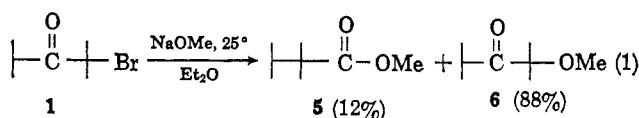
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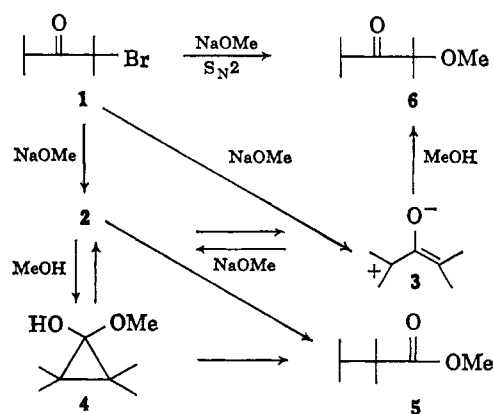
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(11) The treatment of 1 with sodium methoxide in dry ether (conditions which usually result in good yield of rearranged ester) has been reported^{2a} to yield only 2-methoxy-2,4-dimethyl-3-pentanone (6). We have found that the Favorskii product is actually formed in low (12%) yield. (House and Frank^{3b} have found that the Favorskii rearrangement (sodium methoxide as base) of 1 is only a minor course of reaction in both methanol and DME). The yields are determined by vapor phase chromatography on 1,2,3-triscyanoethoxypropane (8 ft. \times 0.25 in.) at 150°. In each case (except eq. 4) reported⁷ only minor amounts of other products besides 5 and 6 could be detected. There is a slightly greater amount of 6 produced in methanol (3%) than in DME (<1%).



We have also been able to detect the adduct^{6b,c} of 2 and furan when a furan solution of 4 is allowed to reflux (36°) for 10 days. This result, together with those reported earlier,⁸ provides strong evidence for an equilibrium between 2 and 4. Furthermore, the fact that 6 becomes the predominant product when 4 is heated in methanol indicates that the mesomeric dipolar ion 3 (*vide infra*) is in equilibrium with 2 and 4.

The results presented above allow us to conclude that base attack on 1 probably does not lead to 2 or 4, since these compounds smoothly rearrange to the Favorskii product 5 under the same reaction conditions that yield mainly the substitution product 6 from 1. This provides the first direct evidence for the long-standing hypothesis that cyclopropanones are readily cleaved to Favorskii products by strong base. The following scheme is proposed to explain these results.



A conceivable alternative mechanism which our results do not rule out is the direct formation of the zwitterion 3 from 1. This may be followed by rapid attack of nucleophile on 3 to yield 6, in competition with a slower formation of 2 (which in turn is rapidly attacked by nucleophile to yield 4 or 5). However, the fact that 6 is the major product (eq. 1) in nonpolar media leads us to suggest that a substitution reaction, unrelated to the normal Favorskii rearrangement, may be occurring. If this is correct then the direct displacement of bromide from 1 represents a departure from previous results from the studies of symmetrical^{1b} and unsymmetrical^{2b,3} systems. Appropriate labeling experiments to test these possibilities are in progress.

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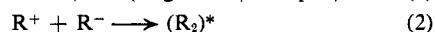
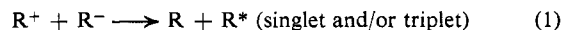
(12) National Science Foundation Predoctoral Fellow, 1964-present.

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Excimer Formation and Emission via the Annihilation of Electrogenerated Aromatic Hydrocarbon Radical Cations and Anions

Sir:

The formation of singlet excited hydrocarbon molecules (R^*) via the reaction of aromatic hydrocarbon radical cations (R^+) with the corresponding radical anions (R^-) has been reported.¹ The results obtained from a detailed study of 9,10-diphenylanthracene and qualitative studies of other hydrocarbons led to the inference of the generality of this reaction which is related to the chemiluminescent oxidations of various radical anions.² *A priori*, two related pathways can be envisioned for the R^+-R^- reaction.



We have studied the course of this reaction for several flat aromatic hydrocarbons unencumbered by bulky substituents and found that path 2, leading to the formation of an excimer,³ is a common process. These observations have interesting mechanistic implications and we have been able to demonstrate the existence of some previously unknown excimers. Our results and known fluorescent properties of these hydrocarbons are summarized in Table I.

Table I^a

	Excimer Soln.	Excimer Exptl.	Self-quenching	Triplet monomer	Annihilation Excimer	Electroluminescence Monomer	Electroluminescence Excimer
Anthracene	—	—	+	+	—	+	+
9,10-Dimethylantracene	—	—	—	0	0	+	+
9,10-Diphenylantracene	—	—	—	—	—	+	—
Phenanthrene	—	—	+	+	—	+	+
Pyrene	+	+	+	+	+	0	0
Naphthacene	—	—	+	—	—	+	—
Rubrene	—	—	—	0	0	+	—
Perylene	+	+	+	+	—	—	+
3,4-Benzpyrene	+	+	+	+	+	—	+

^a Symbols: + indicates that it has been observed; — that it has been found not to be present; and 0 that no results are available.

The chemiluminescent reaction of R^+ and R^- was achieved by alternating-current electrolysis of a solution of the hydrocarbon in acetonitrile or dimethylformamide.^{1,4} The emission spectra commonly contained a broad structureless band shifted toward the

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(3) T. Forster and K. Kasper, *Z. Elektrochem.*, **59**, 977 (1955).

(4) The chemiluminescence, which is modulated at the same or twice the frequency (15–400 c.p.s.) of the voltage imposed on the cell, was measured by modulation spectrometry⁵ which employed phase sensitive detection synchronized to the input frequency. The spectra were easily reproducible.

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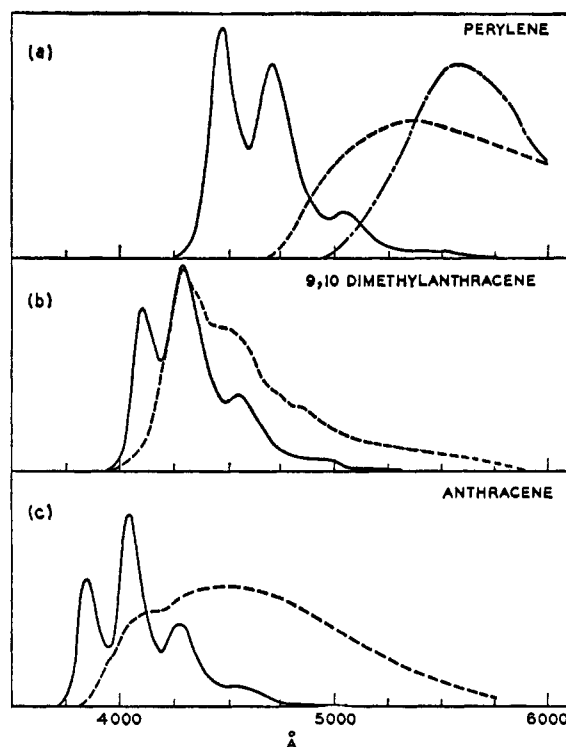


Figure 1. Fluorescence (—) and electrochemiluminescence (---) spectra; perylene crystalline excimer (---) shown in 1a.

red from the normal fluorescence of the same solution. This is a characteristic feature of excimer fluorescence and is a compelling reason for the choice of path 2 for the mechanism of the reaction. The only unsubstituted hydrocarbon which failed to yield excimer emission was naphthacene. It has never been observed to form an excimer and this may be a consequence of its marked tendency to undergo self-quenching.

The chemiluminescence and normal fluorescence spectra of these solutions (0.001–0.01 *M*) are presented in Figure 1 which also includes the known crystalline state excimer emission of perylene.⁶

The emission from perylene (Figure 1a) resembles that of the known excimer and contrasts sharply with the fluorescence of the same solution which has no excimer component. Other hydrocarbons exhibit both monomer and excimer fluorescence. 9,10-Dimethylantracene, 9,10-diphenylantracene, and rubrene were electrolyzed under potentiostatic conditions which restricted the electrode potential to the range between the first oxidative and reductive potentials of the hy-

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