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THERMAL REACTIONS OF PHENYL DERIVATIVES OF DIMETHYLSULFONIUM 1-AROYL-6-OXO-2,4-HEXADIENYLIDE. A REMARKABLE EXAMPLE OF REACTIONS CONTROLLED BY INTRAMOLECULAR STERIC INTERFERENCES 1)

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Thermal reactions of the titled compounds showed multiple mode of reactivities and gave variety of products by difference of the number and positions of phenyl groups. Those facts were interpreted in terms of the reaction paths controlled by degree of intramolecular steric interferences of phenyl groups in the dimethylsulfonium 1-aroyl-6-oxo-2,4-hexadienylide system.

In the previous paper,2) we reported a novel [1,3] ylide group rearrangement to form phenyl derivatives of dimethylsulfonium 1-benzoyl-6-oxo-2,4-hexadienylide by thermal reactions of dimethylsulfonium (phenyl-4H-pyran-4-yl)-2-oxo-2-phenylethylides. Here, we would like to report a remarkable example of the reaction paths controlled by degree of intramolecular steric interferences in dimethylsulfonium 1-aroyl-6-oxo-2,4-hexadienylide system by thermal reactions.

The compounds used in this report are dimethylsulfonium 1-benzoyl-6-oxo-[(2,4,6-triphenyl-) (1a),3) (2,4,5,6-tetraphenyl-) (1b), and (2,3,4,5,6-pentaphenyl-)(1c)]-2,4-hexadienylides and their 1-(p-chlorobenzoyl) derivatives (1a', 1b', and 1c').4) Those compounds were prepared from the corresponding pyrylium fluoroborates and 2-dimethylsulfonium phenacylide and its p-(chlorophenyl) derivatives by the analogous method reported previously.3)

Upon heating in acetonitrile,4) 1a produced 2,4,6-triphenylthioanisole (2a, mp 81°, $>$ 80%)3) and methyl benzoate (3) as sole products in 1:1 ratio.4) Heating of 1b afforded 2,3,4,6-tetraphenylthioanisole (2b, mp 159°, 73%), 3 (75%), and 2-(1,3-diphenylprop-2-en-1-on-3-yl)-3,4,5-triphenylfuran (4, mp 177°, ca. 2%). Furthermore, pentaphenyl derivative 1c upon heating gave pentaphenylthioanisole (2c, mp 329°, 21%), 6-benzoyloxypentaphenylfulvene (5, mp 201°, 24%), 1-benzoyl-2,3,4,5-tetraphenylcyclopentadiene (6, mp 215°, 7%), 1,5-dibenzoyltetraphenylcyclopentadiene (7, mp 153°, 4%), and tetraphenylfuran (8, mp 171°, 2%).5) Fulvene 5 was also formed in a good yield by thermolysis of 1,5-dibenzoylcyclopentadiene 7 at 160°.

The structure of 2b was proven by treatment with Raney Ni to give 1,2,3,5-tetraphenylbenzene,6) and that of 4 was deduced by its spectroscopic properties7) compared with those of Katritzky's

2-(1,3-diphenylprop-2-en-1-on-3-yl)-3,5-diphenylfuran derivatives.[8] Spectroscopic data[7] of 6 and 7 are consistent with the assigned structures. 6-Benzoyloxypentaphenylfulvene was synthesized from 1,2,3,4-tetraphenylcyclopentadiene[9] by an analogous method for the synthesis of 6-acetoxy-6-methylfulvene[10] and it was found to be identical with 5.

For elucidation of the mechanisms of the above reactions, 1-(p-chlorophenyl) derivatives (1a', 1b', and 1c') were treated under the same conditions. Reactions of 1a' in acetonitrile gave 2-(p-chlorophenyl)-4,6-diphenylthioanisole (2a', mp 75-78°, >80%) and 3 in 1:1 ratio, but no trace of methyl p-chlorobenzoate was detected. The formation of equal amounts of 2a' and 3 from 1a' indicates that 3 resulted from C_5 position of 1a'(and 1a). In the case of 1b', the results were similar to those of 1b, where methyl p-chlorobenzoate 3'and 2,3,4,6-tetraphenylthioanisole 2b were obtained in 1:1 ratio. This result suggests that the main reaction pathway of 1b'(and 1b) is the elimination of the benzoyl group at C_1 position. Reactions of 1c' in boiling diglyme[11] gave pentaphenylthioanisole 2c (28%) and a mixture of 6-benzoyloxy-6-(p-chlorophenyl)- and 6-(p-chlorobenzoyloxy)-6-phenyl-1,2,3,4-tetraphenylfulvenes (5', mp 166-177°, 20%) which afforded nearly 1:1 ratio of benzoic acid and p-chlorobenzoic acid on alkaline hydrolysis together with the formation of almost equal amounts of 1-benzoyl- and 1-(p-chlorobenzoyl)-tetraphenylcyclopentadienes.

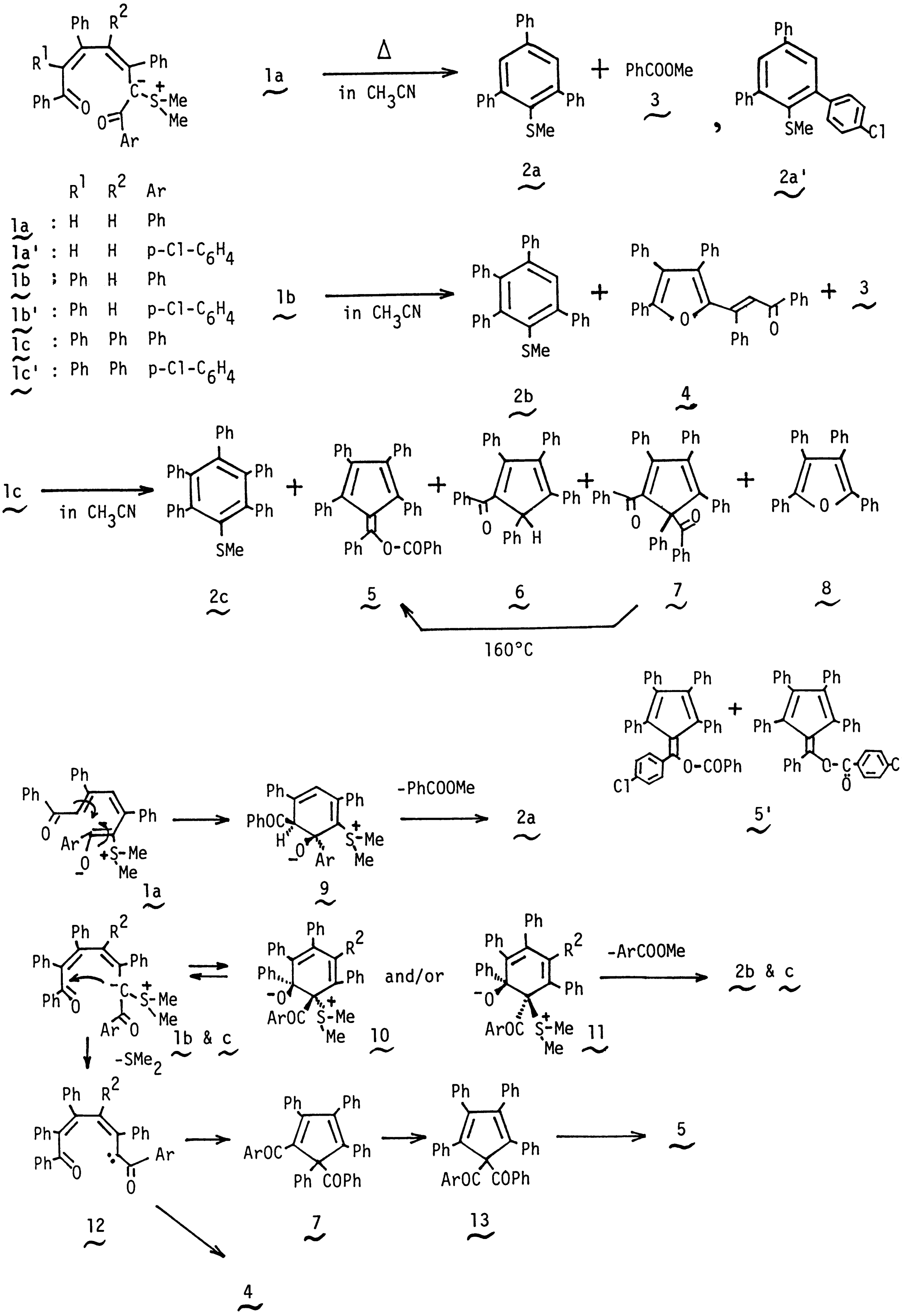
Plausible mechanisms for the above reactions can be depicted as shown in the scheme. In the thermolyses of 1a and 1a', orbital symmetry allowed 6π electronic ring closure occurs giving an intermediate (9), since the phenyl groups in the system do not interfere each other. The cis-configration of the benzoyl and alkoxy (O^-) groups in the intermediate 9 would be favored.
So that elimination of methyl benzoate 3 takes place readily to give the thioanisoles, 2a and 2a'.

Since steric interferences due to the C_5 phenyl group of 1b become an important factor, the ring closure of 1b occurs by non-concerted process to give intermediates (10 and/or 11), but not by the 6π electronic ring closure process.[12] Elimination of methyl benzoate (or p-chlorobenzoate) from 10 and/or 11 yields tetraphenylthioanisole 2b.

In the case of the pentaphenyl derivatives 1c and 1c', non-concerted process which is operative for the tetraphenyl compounds takes place to give pentaphenylthioanisole 2c. However, increased steric interferences of the phenyl groups in 1c may not allow non-concerted process to proceed readily.[12] Instead, elimination of dimethylsulfide occurs in parallel with non-concerted process to form a keto carbene type intermediate such as (12) which leads to the products (6, 7, and 8).

This type of carbene formation was also observed in the reactions of 1b to give small amounts of furan 4. Formation of the fulvene 5 by thermolysis of 1,5-dibenzoyltetraphenylcyclopentadiene 7 and formation of the 1:1 mixture of 6-benzoyloxy-6-(p-chlorophenyl)- and 6-(p-chlorobenzoyloxy)-

THE REACTION SCHEME



	R^1	R^2	Ar
1a	H	H	Ph
1a'	H	H	p-Cl-C_6H_4
1b	Ph	H	Ph
1b'	Ph	H	p-Cl-C_6H_4
1c	Ph	Ph	Ph
1c'	Ph	Ph	p-Cl-C_6H_4

6-phenyl-1,2,3,4-tetraphenylfulvenes 5'from 1c' indicates the intermediacy of 5,5-dibenzoylcyclopentadiene (13). Intermediate 13 might result from intermediate 10 and/or 11 by non-concerted process, but none of the cyclopentadiene or fulvene derivatives could be detected in the reactions of tetraphenyl compounds 1b and 1b'. Therefore, the formation of 13 from 10 or 11 is not likely. Although carbene formation from sulfonium ylides by thermal process has not been proved yet,13) we prefer the carbene formation in the reactions of the pentaphenyl derivatives 1c and 1c', especially for the furan and fulvene derivatives formation.14)

References

1) Presented at the 11th Symposium on Structural Organic Chemistry in Oct., 1978 at Osaka, and at the 8th International Congress of Heterocyclic Chemistry in Aug., 1981 at Graz, Austria.

2) T. Toda, A. Tokida, T. Mukai, and Y. Suzuki, Chem. Lett., 1981, 1535.

3) Y. Suzuki, T. Toda, and T. Mukai, Heterocycles, 4, 739 (1976).

4) All new compounds reported in this paper gave satisfactory elemental analyses, and the yields were isolated ones. All thermal reactions were carried out in ca. 10% solution and at boiling point of acetonitrile.

5) M. Libert and C. Caullet, Bull. Soc. Chim. Fr., 1974, 805.

6) K. Dimroth and G. Neubauer, Chem. Ber., 92, 2042 (1959).

7) Spectral data of 4, 6, and 7. 4 [$\nu_{C=O}^{KBr}$; 1655 cm^{-1}: λ_{max}^{EtOH}, nm (log ε); 245 (sh), 272 (4.38), 390 (4.11)]. 6 [$\nu_{C=O}^{KBr}$; 1620 cm^{-1}: δ (ppm in C_6D_6); 5.62 (s, 1H), 6.6-7.8 (m, 25H): λ_{max}^{MeCN}, nm (log ε); 246 (4.52), 342 (3.95)]. 7 [$\nu_{C=O}^{KBr}$; 1690, 1630 cm^{-1}: λ_{max}^{MeCN}, nm (log ε); 246 (4.52), 358 (3.83)].

8) A. R. Katritzky, S. Q. Abbas Rizvi, and J. W. Suwinski, J. Chem. Soc., Perkin Trans. 1, 1975, 2489.

9) K. Hafner, Angew. Chem., 69, 393 (1957).

10) K. Hafner, G. Schluz, and K. Wagner, Justus Liebigs Ann. Chem., 678, 39 (1964).

11) The resutls in acetonitrile were identical with those in diglyme, but prolonged heating was necessary for completion of reactions in acetonitrile.

12) Increased steric interferences of the reactants appeared in their reaction rates. It took 2-3 hrs for 1a, ca. two days for 1b, and several days for 1c for completion of the reactions.

13) B. M. Trost and L. S. Melvin, Jr., "Sulfur Ylides," p 48 , Academic Press, New York, 1975.

14) By the thermolyses of 1c in ethanol, 2-(1,3-diphenylprop-2-en-1-on-3-yl)-5-ethoxy-2,3,4,5-tetraphenyl-2,5-dihydrofuran was obtained. This also supports the carbene intermediate formation.

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