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DECOMPOSITION REACTIONS OF UNSATURATED α-PHENYLSULFONYL-α-DIAZO KETONES

Isao KUWAJIMA, Yasushi HIGUCHI, Hiroyuki IWASAWA, and Toshio SATO
Department of Chemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152

Thermal decomposition of unsaturated α-phenylsulfonyl-α-diazo ketones afforded various types of cyclization products derived from the phenylsulfonylketene intermediates, along with ones from the usual ketocarbene intermediates, which are dependent closely on the position and alkyl substitution of the olefinic parts.

Unsaturated α-diazo ketones are widely employed for the preparation of fused cyclopropane ring systems.[1,2] We wish to report herein thermal decomposition reactions of unsaturated α-phenylsulfonyl-α-diazo ketones which leads to the formation of unusual cyclization products.

Several types of unsaturated α-phenylsulfonyl-α-diazo ketones, 1a-1d, were prepared and their decomposition reactions were examined by heating them at 174°C in n-decane. The results are shown in the Table.

$C_6H_5SO_2C(N_2)CO(CH_2)_nCH{=}CR^1R^2$ 1

a) $n = 2$, $R^1 = R^2 = H$
b) $n = 2$, $R^1 = R^2 = CH_3$
c) $n = 3$, $R^1 = H$, $R^2 = CH_3$
d) $n = 3$, $R^1 = R^2 = CH_3$

As shown in the Table, two types of the cyclization products were obtained, one of which is derived from the phenylsulfonylketene intermediates and the other is formed from the C-H insertion of the corresponding ketocarbenes, along with the normal cyclopropane derivatives.

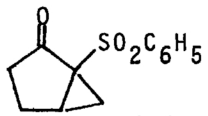
Decomposition of 1d under various conditions were also examined. From these results, the yield of 9 derived from the ketene appears to be decreased at lower temperature and C-H insertion product 10 is formed increasingly. At higher temperature, copper powder does not show any catalytic effects, but a homogeneous catalyst such as copper(II) acetylacetonate effects to suppress the formation of 9.

The mechanism of the decomposition reactions of 1 can be explained by Scheme 1.

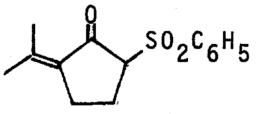
Table. Decomposition Reactions of Diazo Ketones (1a-1d).

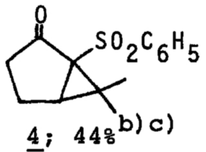
Diazo Ketone Product[3,4] and Yield

1a

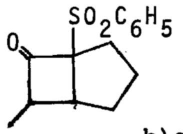

2; 34%a)c)

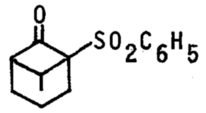
1b

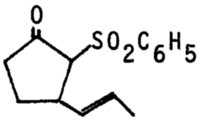

3; 37%b)c)

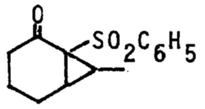

4; 44%b)c)

1c

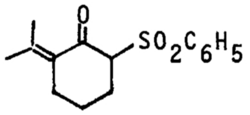

5; 31%b)c)


6; 12%b)c)


7; 12%b)c)


8; 10%a)c)

1d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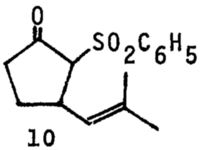
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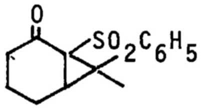
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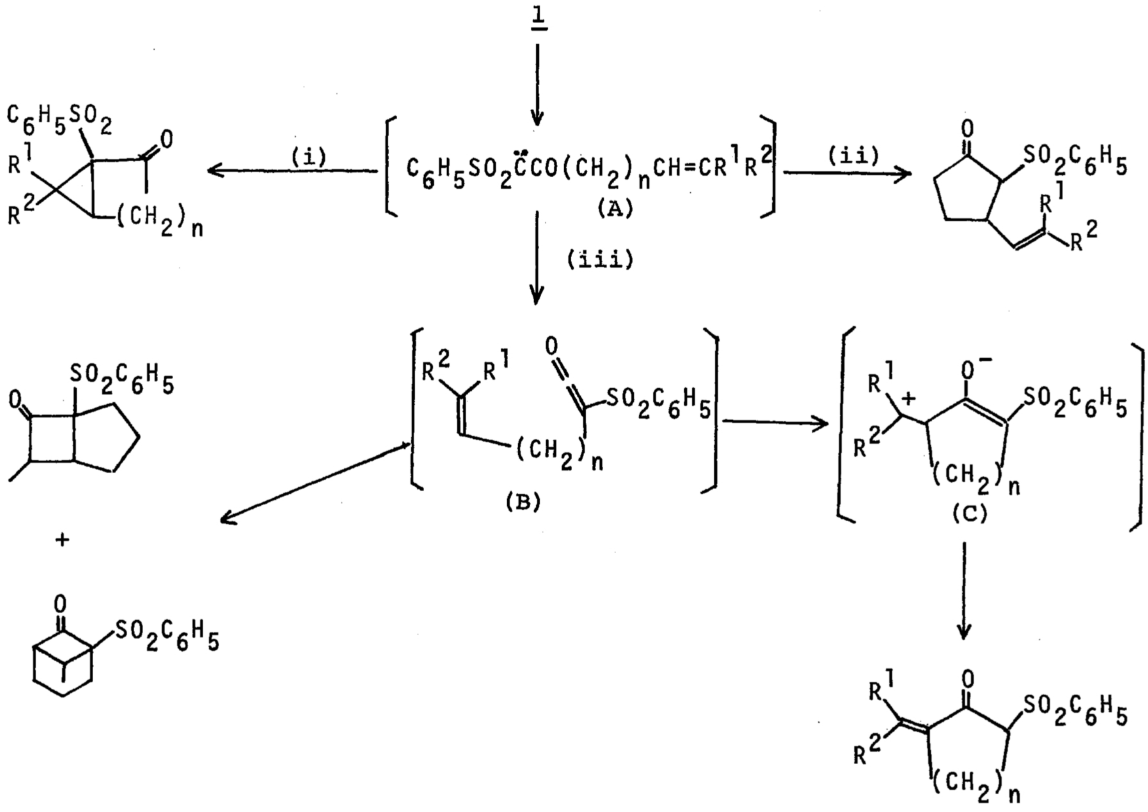
Solvent	Temp.(°C)	Time	Catalyst	Yield[b] (%)		
				9	10	11
n-Heptane	80	10 hr	Cu	13	26	14
n-Decane	174	10 min	Cu	43	12	19
n-Decane	174	10 min	None	42	13	21
n-Decane	174	10 min	$Cu(AcAc)_2$[d]	0	23	22

a) Isolated yield. b) Yield determined by GLPC analysis. c) Decomposed in n-decane at 174°C for 10 min. d) Copper(II) acetylacetonate.

Thus, ketocarbene intermediate (A) initially formed seems to react through the following three paths. (i) Usual addition of (A) to the carbon-carbon double bond leads to the formation of cyclopropane derivatives. (ii) In the cases of δ,ε-unsaturated diazo ketones (1c and 1d), insertion of the ketocarbene (A) into the allylic C-H bond[5] also takes place effectively to yield the cyclopentanone derivatives 7 and 10. (iii) Further, ketocarbene (A) undergoes Wolff rearrangement competitively to form phenylsulfonylketene intermediate (B). Since the ketene (B) is considered to be highly electrophilic because of activation by sulfonyl group, it can react predominantly with the intramolecular olefinic part. Usual [2 + 2] cycloaddition of a ketene to an olefin occurs in the case of δ,ε-disubstituted olefin to afford cyclobutanone derivatives 5 and 6. The ketene (B) possessing intramolecular trisubstituted olefin, however, undergoes electrophilic cyclization

Scheme 1.



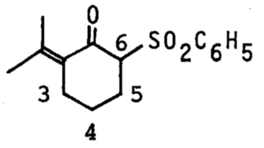
to yield exo-enone derivatives 3 and 9. This unusual behavior suggests that the reaction proceeds through stepwise ionic cyclization mechanism. The higher cation stability of the intermediate (C) might favor this process.

As described above, position and alkyl substitution of olefinic part have an important effect on decomposition products.[6] 1a with monosubstituted olefin at γ,δ-position gives 1-phenylsulfonylbicyclo[3.1.0]hexan-2-one as only detectable product. 1b and 1d with trisubstituted olefin afford exo-enone derivatives. Cyclobutanone derivatives are obtained from 1c with trans-disubstituted olefin. Further, δ,ε-unsaturated ones, 1c and 1d, yield cyclopentanone derivatives via allylic C-H insertion, while such kind of products are little formed from the γ,δ-unsaturated diazo ketones, because of unfavorable process for formation of cyclobutanone system.

References and Notes

1. W. Kirmse, "Carbene Chemistry," 2nd ed., Academic Press, New York, 1971, p. 338; "Carbenes," ed. by R. A. Moss and M. Jones, Jr., John Wiley & Sons, New York, 1973, vol. 1, p. 107.
2. On application to the synthesis of sesquicarene and sirenin, see:"The Total Synthesis of Natural Products," ed. by J. ApSimon, John Wiley & Sons, New York, 1973, vol. 2, p. 428.
3. Each decomposition product (2-11) exhibited the following spectral data.

2: ir(KBr); 1730 (C=O), 1325 (SO_2), and 1160 cm^{-1}(SO_2). nmr(CCl_4); δ 1.4-3.2 (7H, m) and 7.4-8.2 (5H, m). 3: ir(KBr); 1700 (C=O), 1625 (C=C), 1308 (SO_2), and 1155 cm^{-1}(SO_2). nmr($CDCl_3$); δ 1.83 (3H, s, $C\underline{H}_3$), 2.17 (3H, s, $C\underline{H}_3$), 2.3-2.9 (4H, m, $-C\underline{H}_2C\underline{H}_2-$), 3.93 (1H, d.d, J= 5.0 and 9.0 Hz, $-CH_2C\underline{H}(SO_2C_6H_5)C=O$), and 7.4-8.0 (5H, m). m/e; 264 (M^+) and 123 ($M^+ - C_6H_5SO_2$). 4: ir(KBr); 1730 (C=O), 1314 (SO_2), and 1150 cm^{-1}(SO_2). nmr($CDCl_3$); δ 1.07 (3H, s, $C\underline{H}_3$), 1.43 (3H, s, $C\underline{H}_3$), 2.0-3.0 (5H, m), and 7.4-8.3 (5H, m). 5: ir(KBr); 1790 (C=O), 1310 (SO_2), and 1160 cm^{-1}(SO_2). nmr($CDCl_3$); δ 1.55 (3H, d, J= 7.0 Hz, $C\underline{H}_3$), 1.4-2.9 (8H, m), and 7.5-8.3 (5H, m). m/e; 264 (M^+), 208 ($M^+ - CH_3CH=C=O$), 123 ($M^+ - C_6H_5SO_2$), 95 ($M^+ - C_6H_5SO_2 - CO$), 67 ($M^+ - C_6H_5SO_2 - CH_3CH=C=O$), and 65 ($C_3H_3O^+$). 6: ir(KBr); 1785 (C=O), 1310 (SO_2), and 1155 cm^{-1}(SO_2). nmr($CDCl_3$); δ 1.07 and 1.25 (3H, d.+d. J= 7.0 Hz, $C\underline{H}_3$ in the mixture of stereoisomers), 1.7-3.1 (8H, m), and 7.5-8.1(5H, m). Structures of 5 and 6 were also assigned by ^1H N.M.R. spectra with shift reagent Eu(fod)$_3$. A change in the chemical shift of the doublet peak of methyl groups at the same weight ratio of Eu(fod)$_3$ to the compound 5 was greater than that of the compound 6; Δδ 0.25 at the weight ratio Eu(fod)$_3$/6 = 0.746 and Δδ 0.32 at Eu(fod)$_3$/5 = 0.500. 8: ir(KBr); 1700 (C=O), 1325 (SO_2), and 1160 cm^{-1}(SO_2). nmr($CDCl_3$); δ 1.4-2.4 (11H, m) and 7.4-8.2 (5H,m). 9: ir(KBr); 1675 (C=O), 1610 (C=C), 1307 (SO_2), and 1151 cm^{-1}(SO_2). nmr($CDCl_3$); δ 1.86 (3H, s, $C\underline{H}_3$), 2.00 (3H, s, $C\underline{H}_3$), 1.6-2.1 (2H, m, H-4), 2.1- 2.9 (4H, m, H-3 and H-5), 4.04 (1H, t, J= 6.0 Hz, H-6), and 7.4-8.1 (5H, m). 10: ir(KBr); 1755 (C=O), 1315 (SO_2), and 1155 cm^{-1}(SO_2). nmr($CDCl_3$); δ 1.73 (3H, s, $C\underline{H}_3$), 1.80 (3H, s, $C\underline{H}_3$), 1.5-2.0 (2H, m, H-4), 2.0-2.6 (3H, m, H-3 and H-5), 3.23 (1H, d, J= 6.0 Hz, H-2), 5.03 (1H, d, J= 8.4 Hz, olefinic proton), and 7.4-8.0 (5H, m). m/e; 278 (M^+), 223 ($M^+ - CH=C(CH_3)_2$), and 137 ($M^+ - C_6H_5SO_2$).



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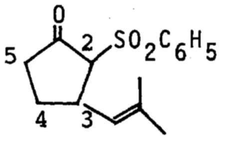

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4. Since isolation of the product 7 and 11 was unsuccessful, each in the reaction mixture was identified and analyzed by GLPC by comparison with the authentic samples prepared by standard methods.
5. Only a few examples of carbene insertion to allylic C-H bond have been reported; F. Weygand, H. Deorschuk, K. Kock, and S. Konstas, Angew. Chem., 73, 409 (1961); B. W. Peace and D. S. Wulfman, Synthesis, 137 (1973); R. H. Fischer, M. Bauman, and G. Kobrich, Tetrahedron Lett., 1207 (1974).
6. F. Leyendecker, Tetrahedron, 32, 349 (1976).

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