CHEMISTRY LETTERS, pp.113-116, 1974. Published by the Chemical Society of Japan

NEW CYCLIC α-KETOSULFENES

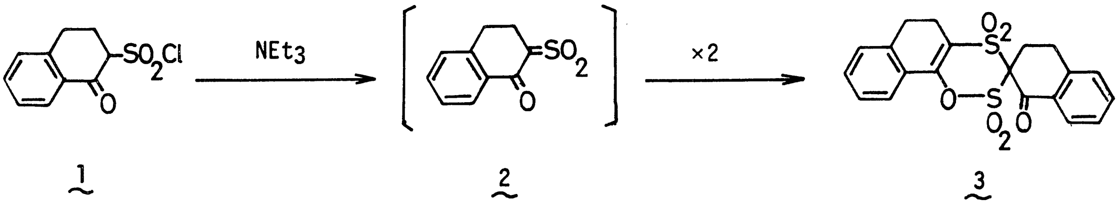
Otohiko TSUGE* and Michihiko NOGUCHI

Research Institute of Industrial Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

New cyclic α-ketosulfenes 2 and 8 were generated in situ from the treatment of 2-chlorosulfonyl-1-tetralone (1) and -1-indanone (7) with NEt_3. It was found that these two α-ketosulfenes show different characteristics in their dimerization and cycloaddition reactions.

The existence of sulfenes as reactive intermediates has been conclusively demonstrated,1) and the chemistry of sulfenes has received considerable attention. Up to the present, benzoyl-,2) phenylbenzoyl-,3) and ethoxycarbonylsulfene4) as sulfenes conjugated with carbonyl group have been appeared in literatures. Recently, we reported that benzoylsulfene generated in situ from benzoylmethanesulfonyl chloride and triethylamine (NEt_3) reacts with the C=N bonds of anils,5) carbodiimides,6) and keteneimines7) to give the corresponding [4+2] and/or [2+2] cycloadducts, while ordinary sulfenes ($RCH=SO_2$, R=alkyl or aryl) do not react with the C=N bond.8) This indicates that the electron-attracting benzoyl group makes benzoylsulfene more reactive than ordinary sulfenes, and that benzoylsulfene behaves as a 1,4- and/or 1,2-dipole. In this communication, we like to report the generation and reaction of new cyclic α-ketosulfenes possessing a cisoidal arrangement.

When 2-chlorosulfonyl-1-tetralone (1)9) was treated with one equivalent of NEt_3 in THF at room temperature for 20 hr, 1,2,4-oxadithiin tetraoxide 3 whose structure corresponds to a [4+2] cycloadduct of two molecules of α-ketosulfene 2, was obtained in a 73.5% yield. A similar dimerization of benzoylsulfene was reported previously.10) We believe that this reaction indicates the generation of 2 in the reaction system. The structure of the dimer 3 was confirmed on the basis of its spectral data.

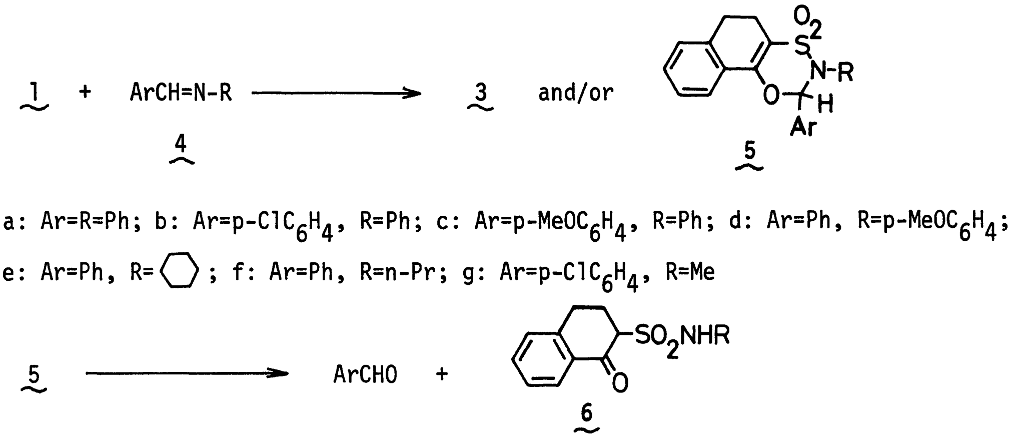


3: mp 174-175°C; IR (KBr) 1680 (νC=O), 1390, 1300, 1220, 1180 cm^{-1} (νSO_2); NMR ($CDCl_3$) δ 3.0, 3.3

(each 4H, m,-CH_2), 7.2-8.25 (8H, m, aromatic protons); mass spectrum m/e 352 [M^+- SO_2], 288 [352^+-SO_2, base peak].

The reaction of 1 with benzylideneanilines (4a-4c) in the presence of NEt_3 afforded only the dimer 3, instead of an expected 1:1 adduct of 2 to 4. The reaction with other anils (4d-4g) under similar conditions, however, gave the corresponding [4+2] cycloadducts (5d-5g) of 2 to the C=N bond of 4, accompanied with only small amount of 3. The yields in these reactions and physical properties of 5 are listed in Table I. The structures of 5 were confirmed on the basis of their spectral data.

Scheme 1



a: Ar=R=Ph; b: Ar=p-ClC_6H_4, R=Ph; c: Ar=p-$MeOC_6H_4$, R=Ph; d: Ar=Ph, R=p-$MeOC_6H_4$;
e: Ar=Ph, R=⬡; f: Ar=Ph, R=n-Pr; g: Ar=p-ClC_6H_4, R=Me

As shown in Scheme 1, 5 are easily hydrolyzed under mild conditions to the corresponding benzaldehydes (ArCHO) and sulfonamides 6. The structures of 6 were identified by the comparison with authentic samples prepared from 1 and amines (RNH_2).

Table I. Reaction of 1 with 4 in the Presence of NEt_3

4	3	5				
	Yield, %	Yield, %	Mp., °C	IR (KBr), cm^{-1} a) νSO_2 (as)	 νSO_2 (s)	NMR ($CDCl_3$), δ ⩾CH
a	39	0				
b	50	0				
c	28	0				
d	14	25	198-200	1330	1160	6.98 (s)
e	9	53	167-169	1330	1170	7.05 (s)
f	6.5	67	132-134	1330	1170	6.93 (s)
g	0	67	124-125	1340	1150	6.91 (s)

a) All 5 did not show any bands ascribable to νC=O.

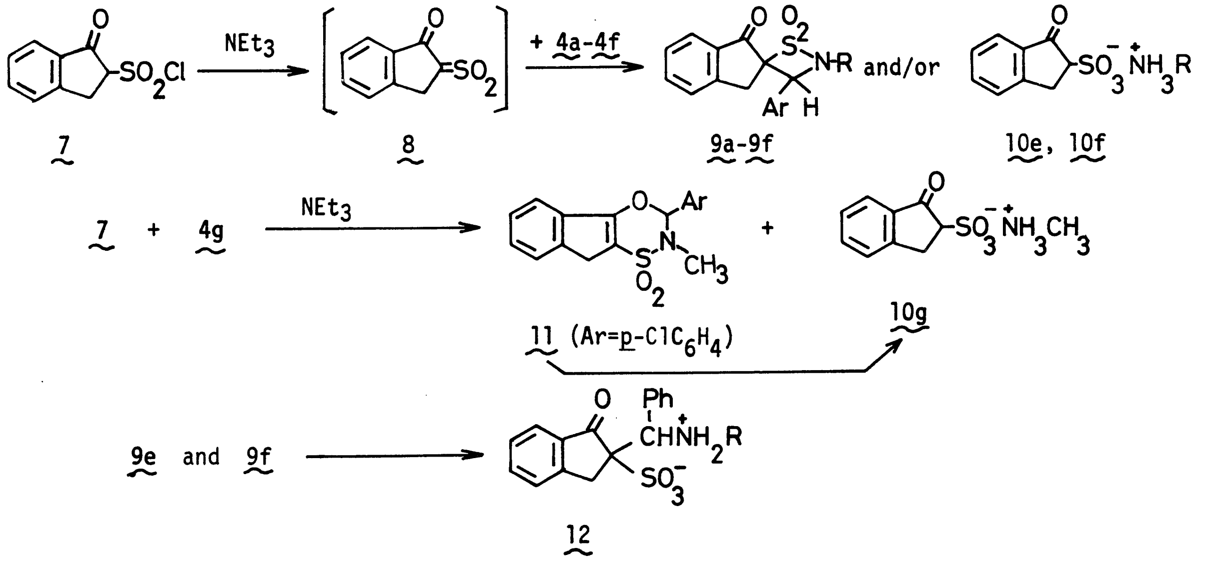
The chemical behavior of α-ketosulfene (8), generated from 2-chlorosulfonyl-1-indanone (7)[9] and NEt_3, is quite different from that of 2. The dimer of 8, corresponding to 3, could not be isolated in the reaction of 7 with one equivalent of NEt_3.[11] The reaction of 7 with benzylideneanilines (4a-4d) in the presence of NEt_3 gave the corresponding [2+2] cycloadducts (9a-9d) alone. That with benzylidenealkylamines (4e-4f), however, gave both [2+2] cycloadducts (9e-9f) and amine sulfonates (10e-10f) as shown in Table II. The [4+2] cycloadduct (11), mp 152-153.5°C, was produced in a 51.5% yield, together with a 21% yield of methylamine sulfonate (10g), mp 226-227°C (decomp.). The structures of all products were confirmed on the basis of their spectral data.

Table II. Reaction of 7 with 4 in the Presence of NEt_3
(Reaction time: 50 hr)

4	9								10	
	Yield,%	Mp., °C	IR (KBr), cm^{-1}			NMR ($CDCl_3$), δ			Yield,%	Mp., °C
			νC=O	νSO_2	νSO_2	$-CH_2$[a]		≥CH[b]		
a	32	229-230	1730	1320	1170	2.82	3.92	5.55	0	
b	24	192-193.5	1725	1335	1170	2.80	3.92	5.55	0	
c	31	181-182	1730	1330	1170	2.86	3.92	5.51	0	
d	39	208-209	1720	1325	1170	2.83	3.92	5.55	0	
e	43	132-133	1720	1315	1165	2.68	3.82	5.02	14	213-214
f	40[c]	84-85	1720	1330	1170	2.76	3.84	4.86	20[c]	201-203

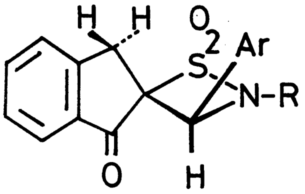
a) Doublets with coupling constant of 18 Hz. b) Singlet. c) Reaction time: 20 hr.

Scheme 2

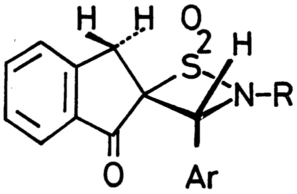


Since the [4+2] cycloadduct (11) can be hydrolyzed easily to 10g under mild conditions (Scheme 2), the formation of 10 from 4e and 4f may be deemed to pass through the corresponding [4+2] cycloadducts. On the other hand, the [2+2] cycloadducts (9a-9d) in which the substituent is aromatic show considerable resistance to hydrolysis, and were recovered quantitatively even after the treatment of hydrochloric acid at room temperature for 50 hr. The hydrolysis of 9e and 9f in which R is aliphatic gave sulfonates (12).[12]

Now, two stereoisomers A and B are possible for the structure of [2+2] cycloadduct 9. In NMR spectra of 7, 10, and 12, two methylene protons of the respective indanone ring show a singlet at about δ 3.6, while they in 9 appeared as two doublets at around δ 2.8 and 3.9 as shown in Table II. This suggests that the methylene protons in 9 are non-equivalent owing to the anisotropic effect of 3-aryl group on the thiazetidine ring. The inspection of Dreiding models indicates that the configuration B must be prohibited by steric effect. Hence, it may be concluded that the [2+2] cycloadduct 9 exists in the configuration A. Further investigations are now in progress.



A



B

REFERENCES

1) J. F. King and T. Durst, J. Amer. Chem. Soc., 86, 287 (1964); W. E. Truce, R. W. Campbell, and J. R. Norell, ibid., 86, 288 (1964).

2) R. Fusco, S. Rossi, S. Maiorana, and G. Pagani, Gazz. Chim. Ital., 95, 774 (1965).

3) T. Nagai, M. Tanaka, and N. Tokura, Tetrahedron Lett., 1968, 6293; J. B. Stothers, L. J. Danks, and J. F. King, ibid., 1971, 2551.

4) L. A. Paquette, J. P. Freeman, and R. W. Houser, J. Org. Chem., 34, 2901 (1969).

5) O. Tsuge and S. Iwanami, Bull. Chem. Soc. Jap., 43, 3543 (1970).

6) O. Tsuge and S. Iwanami, Nippon Kagaku Zasshi, 92, 448 (1971).

7) O. Tsuge and S. Iwanami, Org. Prep. & Procd. Int., 3, 283 (1971).

8) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, London (1967), p. 286.

9) 2-Chlorosulfonyl compounds, 1 (mp 87-88.5°C) and 7 (mp 95-98°C), were prepared from the sulfonation of 1-tetralone and 1-indanone with SO_3-dioxane complex, followed by the reaction with PCl_3. The structures of 1 and 7 were confirmed on the basis of their spectral data. All new compounds reported here gave satisfactory analytical values.

10) Fusco et al.[2)] reported that benzoylmethanesulfonyl chloride reacted with NEt_3 to give the dimer, but we found that excess NEt_3 is necessary for the formation of the dimer (O. Tsuge and S. Iwanami, The Reports of Research Institute of Industrial Science, Kyushu University, No. 51, 19 (1970)).

11) In this case, 2,2'-diindanylidene-1,1'-dione, mp 232-233°C, whose structure corresponds to the compound derived from a dimer of 8 with the elimination of two moles of SO_2, was isolated, together with an unidentified compound.

12) 12a (R=cyclohexyl): mp 201.5-202.5°C; IR (KBr) 3040-2800 (νNH_2^+), 1715 ($\nu C=O$), 1180, 1050 cm^{-1} (νSO_2). 12b (R=n-Pr): mp 208-209°C; IR (KBr) 3200-2800 (νNH_2^+), 1730 ($\nu C=O$), 1175, 1050 cm^{-1} (νSO_2); NMR (CF_3COOH) δ 1.0 (3H, t, CH_3), 1.5-2.2, 2.8-3.4 (each 2H, m,$-CH_2-$), 7.1-7.9 (9H, m, aromatic protons), 8.2-8.9 (2H, broad,$=NH_2$).

(Received November 26, 1973)