March, 1986] © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *59*, *929—930 (1986)* 929

Generation of the Selenonium Ylide by the Carbenic Reaction. Formation of Cyclopropane Derivatives via Selenonium Ylide

Toshikazu Ibata* and Makoto Kashiuchi
Institute of Chemistry, College of General Education, Osaka University,
Toyonaka, Osaka 560

(Received October 28, 1985)

Synopsis. The Cu(acac)2-catalyzed decomposition of α-diazoacetophenones in the presence of bis(*p*-methoxyphenyl) selenide (**3**) did not give the corresponding selenonium ylide but gave *r*-1,*c*-2,*t*-3-tribenzoylcyclopropanes through the successive reaction of the intermediary selenonium ylide. On the other hand, the reaction of diazodimedone with **3** gave bis(*p*-methoxyphenyl)selenonium 4,4-dimethyl-2,6-dioxocyclohexylide.

The chemistry of the sulfonium ylide has extensively been studied in last two decades from the structural and synthetic interests.[1] Since the early work of Diekmann,[2] thermal and photolytic decomposition of diazo compounds in the presence of sulfides has been recognized as one of the general synthetic method of stable sulfonium ylide.[3] On the other hand, synthesis of the selenonium ylides have not so widely been studied.[4] As a continuation of our work on sulfonium ylide,[5] formation of selenonium ylide by the carbenic reaction was studied.

Results and Discussion

For the stabilization of selenonium ylide, decrease of positive charge induced on selenium atom seems to be effective. Therefore, diphenyl selenide attached by electron-releasing methoxyl groups on the para positions was used as a substrate of the reaction. The Cu(acac)2-catalyzed decomposition of *p*-methoxy-α-diazoacetophenone (**1a**) in benzene solution at 80 °C in the presence of 3 molar amount of bis(*p*-methoxyphenyl) selenide (**3**) gave colorless crystals, mp 161 °C, besides the recovered selenide (**3**). The results of elemental analysis indicated that the product did not contain selenide moiety. The analytical values agreed with the calculated ones for the dimer or trimer of the corresponding carbene (**2**) generated from the diazoacetophenone (**1a**). The spectroscopic data showed that the product is *r*-1,*c*-2,*t*-3-tris(*p*-methoxybenzoyl)cyclopropane (**7a**). In its NMR spectrum the coupling pattern of methine proton signals, δ=3.62 (d, 2H) and 4.14 (t, 1H), revealed that the cyclopropane had trans configuration. Other substituted diazoacetophenones gave the corresponding cyclopropane derivatives in similar reactions in reasonable yields as is shown in Table 1.[6] In order to confirm the catalytic action of the selenide (**3**), the reactions were carried out using different amounts of **3**. When the amount of **3** was reduced to 1/3 of the amount to **1**, the yield of **7** decreased a little. However, 1/20 amount of **1** was still shown to be effective for promotion of the reaction (Table 2). Detailed inspection of these reaction mixtures by column chromatography indicated that neither *r*-1,*c*-2,*c*-3-triaroylcyclopropane nor 1,2-diaroylethylene (**8**) was detected, despite the 1,2-diaroylethylenes were obtained by the copper-catalyzed decomposition of **1** in the absence of sulfide or selenide (**3**).[7]

The reaction seems to be explained in the following Scheme. At the first stage of the reaction, the ketocarbene[8] generated by the Cu(acac)2-catalyzed decomposition of diazoacetophenone reacts with selenide (**3**) to give bis(*p*-methoxyphenyl)selenonium aroylmethylide (**4**). Failure of the isolation of selenonium ylide (**4**) may be attributed to the high reactivity of **4** to give 1:2-betaine (**5**) by the further reaction with **1**. The betaine **5** reacts with another molecule of diazoacetophenone under the liberation of nitrogen affording 1:3-betaine (**6**) which gave the cyclopropane **7** by the cyclization via elimination of selenide (**3**). The elimination process of **3** from the betaine (**5**) to give 1,2-diaroylethylene (**8**) could be neglected because of absence even a trace amount of **8** in the reaction mixture. If the dimer (**8**) was formed,

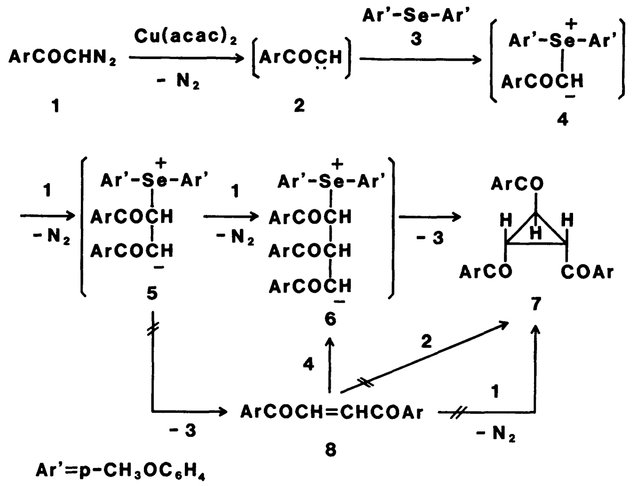
Table 1. Yields and NMR Chemical Shift of *r*-1, *c*-2, *t*-3-Tribenzoylcyclopropanes

Run	Ar	Yield/%	Chemical shift of methine/δ	
a	p-$CH_3OC_6H_4$	55	3.63(d)	4.14(t)
b	p-$CH_3C_6H_4$	68	3.71(d)	4.20(t)
c	m-$CH_3C_6H_4$	54	3.74(d)	4.24(t)
d	C_6H_5	59	3.74(d)	4.19(t)
e	p-ClC_6H_4	54	3.67(d)	4.13(t)
f	m-ClC_6H_4	49	3.70(d)	4.14(t)
g	p-BrC_6H_4	48	3.67(d)	4.08(t)
h	p-NCC_6H_4	41	3.76(d)	4.16(t)

Table 2. The Effect of the Amount of **3** on the Yield of *r*-1, *c*-2, *t*-3-Tritoluoylcyclopropane (**7b**)[a]

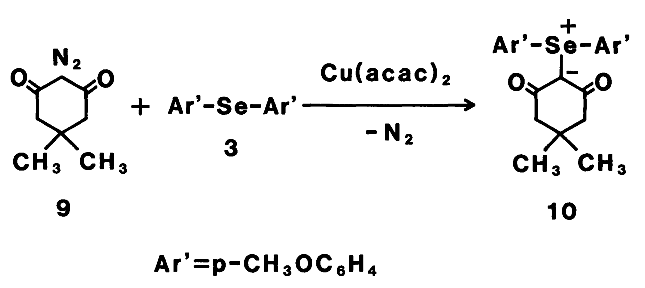
Amount of **3**/g	Yield of **7b**/%
1.00	68
0.50	69
0.30 (1 mmol)	61
0.15	54
0.05	44

a) The reaction was carried out in benzene solution using 3 mmol of *p*-methyldiazoacetophenone and 0.050 g of $Cu(acac)_2$ at 80 °C.



Scheme

the next steps to give cyclopropane (**7**) are: (a) reaction with **1** affording **7** and N_2 directly; (b) reaction with **1** to give **7** and N_2 via corresponding 1,3-dipolar cycloadduct; (c) reaction with the carbene (**2**) to give **7**; (d) reaction with **4** to give the 1:3-betaine (**6**).[10] The processes (a) and (b) are shown not to occur under the reaction conditions (1 atm., 70 °C), and the process (c) can be neglected from the previous observation.[7] The process (d) is possible deducing from the case of sulfonium ylide.[10] The preferential formation of the *trans*-isomer may be explained by the steric factor on the cyclization process.[6]



Another method to attain the stability of ylides is to attach electron-attracting groups on anionic carbon of the ylide. Therefore, the diazodimedone (**9**) was used as an example of diazodiacyl compound instead of diazoacetophenones. Decomposition of **9** in a similar manner in the presence of selenide (**3**) gave 40% yield of expected selenonium ylide (**10**), which was confirmed by the spectroscopic data showing singlet ^{1}H NMR signals of two methoxyl, two methyl, and two methylene groups at δ 1.10, 3.82, and 2.37 ppm, respectively together with those of aromatic protons. This indicates that the product includes both selenide and carbene components. The C=O absorption of the selenonium ylide (**10**) at 1580 cm^{-1} also supported the ylide structure **10** in comparison to that of dimethylsulfonium diacetylide at 1565 and 1595 cm^{-1}.[9]

Experimental

The IR spectra were recorded on Perkin-Elmer model 983 and the ^{1}H NMR spectra were measured in $CDCl_3$ solution at 90 MHz on a Varian Spectrometer model EM390 using TMS as an internal standard.

Materials. Substituted α-diazoacetophenones were synthesized by the reaction of corresponding acid chlorides with excess diazomethane according to the method of Newman.[11] Diazodimedone was prepared from dimedone via diazo group transfer reaction using tosyl azide and triethylamine.[12] Bis(*p*-methoxyphenyl) selenide was prepared by the reaction of *p*-methoxyphenyldiazonium chloride with potassium selenide.[13]

General Procedure of the Cu(acac)$_2$-Catalyzed Decomposition of α-Diazoacetophenones in the Presence of 3. A benzene solution of α-diazoacetophenone (3 mmol) and **3** (1.00 g, 3.4 mmol) was heated at 70 °C in the presence of 10 mg (0.04 mmol) of Cu(acac)$_2$ until the evolution of N_2 ceased. The reaction mixture was separated by silica-gel column chromatography.[14]

Decomposition of Diazodimedone in the Presence of 3. A benzene solution of diazodimedone (0.50 g, 3 mmol) and **3** (1.00 g, 3.4 mmol) was refluxed for 10 h in the presence of catalytic amount of Cu(acac)$_2$. Separation of the reaction mixture through silica-gel column chromatography gave white crystals; mp 194-6 °C, 0.52 g (40%). Found: C, 61.04; H, 5.72%. Calcd for $C_{22}H_{24}O_4Se$: C, 61.25; H, 5.61%.

References

1) B. M. Trost and L. S. Melvin, Jr. "Sulfur Ylides," Academic Press, New York (1975).

2) J. Diekmann, *J. Org. Chem.*, **30**, 2272 (1965).

3) W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Am. Chem. Soc.*, **91**, 2786 (1969): W. Illger, A. Liedhegener, and M. Regitz, *Ann. Chem.*, **760**, 1 (1972).

4) D. Lloyd and M. I. C. Singer, *Chem. Commun.*, **1967** 390; S. Tamagaki and K. Sakai, *Chem. Lett.*, **1976**, 503.

5) M. Takebayashi, T. Kashiwada, M. Hamaguchi, and T. Ibata, *Chem. Lett.*, **1972**, 809.

6) Although Lotz and Gosselck reported the formation of *r*-1,*c*-2,*t*-3-tribenzoylcyclopropane in the decomposition of α-diazoacetophenone in the presence of dimethyl selenide, no experimental details were described; W. W. Lotz and J. Gosselck, *Tetrahedron*, **1973**, 917.

7) C. Grundmann, *Ann.*, **536**, 29 (1938): M. Takebayashi, T. Ibata, and K. Ueda, *Bull. Chem. Soc. Jpn.*, **43**, 1500 (1970).

8) The ketocarbene may probably react as a corresponding copper-carbenoid.

9) W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, **37**, 1721 (1972).

10) A. W. Johnson and R. T. Amel, *Tetrahedron Lett.*, **1966**, 819; F. Serratosa and J. Quintana, *Tetrahedron Lett.*, **1967**, 2245.

11) M. S. Newmann and P. F. Beal, *J. Am. Chem. Soc.*, **72**, 1506 (1949).

12) M. Regitz and D. Stadler, *Ann.*, **687**, 2314 (1965).

13) *Org. Synth.*, Coll. Vol 2, 238 (1948).

14) Cyclopropanes obtained were characterized by the spectroscopic and analytical data.