Electroorganic Chemistry. 124. Electroreductive Intramolecular Coupling of α-(ω-Bromoalkyl) β-Keto Esters

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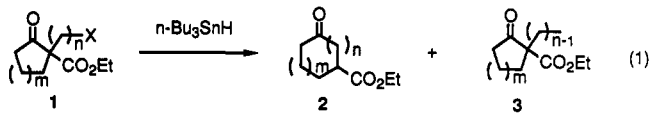
Intramolecular coupling occurs when cyclic α-(bromomethyl) β-keto esters are electrochemically reduced in the presence of trimethylsilyl chloride and one-carbon ring-enlarged products are obtained in reasonable yields. Electroreduction of α-(γ-bromopropyl) β-keto esters also affords the corresponding five-membered cyclized products and/or the corresponding ring-opened compounds. The ease of ring opening of the cyclized products is highly influenced by their stereoconfiguration. Electroreduction of α-(β-bromoethyl) β-keto ester gives the product formed by the reductive elimination of the bromoethyl group whereas α-(δ-bromobutyl) β-keto ester yields the product of the reductive elimination of bromine. This electroreductive intramolecular coupling is initiated by the reduction of the carbon–bromine bond and proceeds through a carbanion intermediate.

Introduction

The reductive intramolecular coupling of a haloalkyl group with a carbonyl group is a desirable reactions for organic synthesis. It is applicable to the synthesis of bicyclic compounds, and subsequent ring enlargement of these compounds provides large rings. Although the selective reduction of the haloalkyl moiety or carbonyl group is requisite for the intramolecular coupling, this is often difficult. Recently, it was reported that the selective reduction of the haloalkyl group of cyclic α-(ω-haloalkyl) β-keto esters **1** (X = I, Br; n = 1, 3, 4) with n-Bu_3SnH resulted in the ring enlargement of **1**, yielding **2** (eq 1).[1]



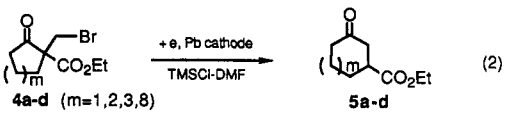
1 **2** **3** (1)

There are, however, some disadvantages to this reaction. Namely, n-Bu_3SnH is an expensive and toxic reagent, elevated temperature is required, and high dilution of n-Bu_3SnH is needed to suppress the formation of the directly reduced products **3**. These results prompted us to investigate the application of the electroreductive method to the selective reduction of the haloalkyl group since this reaction can be carried out under mild conditions.

In this paper, we report that the intramolecular coupling of α-(bromomethyl) and α-(γ-bromopropyl) β-keto esters (n = 1, 3) occurs electrochemically, and ring-enlarged products are formed from cyclic starting compounds in reasonable yields. The intramolecular Barbier type reaction of ω-halo ketones resulting from electrochemical reduction has previously been unknown. The reaction mechanism is also discussed.

Results and Discussion

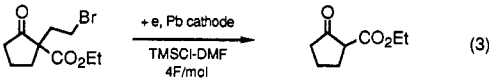
Electroreduction of α-(Bromomethyl) β-Keto Esters 4 (n = 1). The influence of the reaction conditions was studied by using ethyl 1-(bromomethyl)-2-oxocyclopentane-1-carboxylate (**4a**, m = 1) as a typical substrate (eq 2). Consequently, it was found that a one-carbon ring-enlarged product, ethyl 3-oxocyclohexane-1-carboxylate (**5a**, m = 1), was obtained in satisfactory yield (76%) when the electroreduction was carried out in DMF containing trimethylsilyl chloride (TMSCl) with lead as cathode. The reaction performed in acetonitrile also gave a similar result (74%). Using THF as the solvent (32%) or other materials as the cathode (Sn, 67%; Pt, 64%; Cu, 56%; C, 57%) resulted in a decrease in the yields.



4a-d (m=1,2,3,8) **5a-d** (2)

TMSCl was essential to promote this reaction since rather poor results (yield <20%) were obtained in the absence of TMSCl. Protic acids such as acetic acid and methanesulfonic acid were also effective as the promoter (~50%) of the reaction though they were not always as effective as TMSCl. The results obtained with several α-(bromomethyl) β-keto esters are shown in Table I. The cyclic α-(bromomethyl) β-keto esters **4a–e** give the corresponding one-carbon ring enlarged products **5a–e** (runs 1–5). Similarly, 2-(bromomethyl)-2-phenylcyclohexanone (**4f**) affords 3-phenylcycloheptanone (**5f**) (run 6). Acyclic α-(bromomethyl) β-keto esters **4g** and **4h** yields one carbon inserted products which correspond to the ring-enlarged products (runs 7, 8). On the other hand, 2-(bromomethyl)-2-methylcyclohexanone (**4i**) gives no ring-enlarged product (run 9).

Electroreduction of α-(β-Bromoethyl) β-Keto Ester 7 (n = 2). The reaction promoted by the electroreduction of α-(β-bromoethyl) β-keto ester **7** was reductive elimination of β-bromoethyl group, and no intramolecular coupling was observed (eq 3).



7 **8** 70% (3)

Electroreduction of α-(γ-Bromopropyl) β-Keto Ester 9 (n = 3). The five- and six-membered cyclic α-(γ-bromopropyl) β-keto esters **9a** and **9b** give cis coupling products **10a** and **10b**,[2] together with small amounts of reduced products **11a** and **11b** (eq 4).[3] Since the bromo group of **9a** and **9b** is rapidly substituted by a chloro group

(1) (a) Dowd, P.; Choi, S. *J. Am. Chem. Soc.* **1987**, *109*, 3493. (b) *Ibid.* **1987**, *109*, 6548. (c) *Tetrahedron* **1989**, *45*, 77. (d) Beckwith, A. L. J.; O'Shea, M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565.

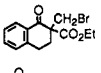
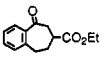
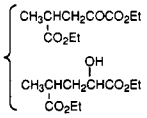
(2) Each of the products **10a** and **10b** was obtained as a single stereoisomer and the stereoconfiguration was assigned to be cis by ^{13}C NMR analysis.[4a]

(3) Similar reductive intramolecular coupling with using SmI_2 as the reducing agent has been reported.[4]

(4) (a) Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1986**, *51*, 1778. (b) Molander, G. A.; Etter, J. B.; Zinke, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 453.

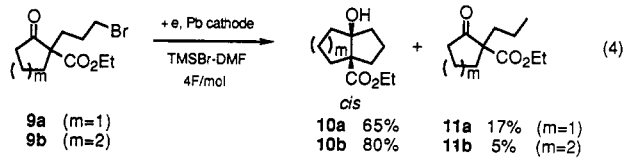
0022-3263/90/1955-5037$02.50/0

Table I. Electroreduction of 4

run	substrates		F/mol	products		% yield[a]
1		**4a**	4		**5a**	76
2		**4b**	4		**5b**	74
3		**4c**	4		**5c**	70
4		**4d**	8		**5d**	62
5		**4e**	4		**5e**	70
6		**4f**	4		**5f**	74
7		**4g**	5		**5g**	71
8		**4h**	5		**5h** **6**	52 13
9		**4i**	4			50

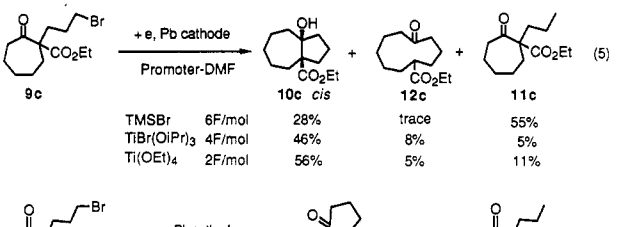
[a] Isolated yield.

in the presence of TMSCl and it brought about the decrease in the yield and current efficiency, TMSBr was used instead of TMSCl.

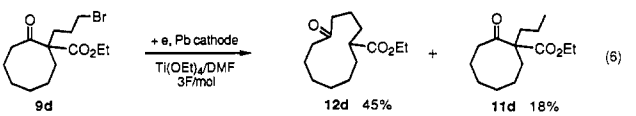


(4)

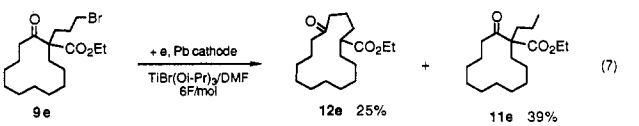
It was also found that some titanium compounds such as $TiBr(Oi\text{-}Pr)_3$ and $Ti(OEt)_4$ were more effective than trimethylsilyl halides in the promotion of the electroreductive intramolecular coupling of the large-membered cyclic α-(γ-bromopropyl) β-keto esters **9c–e** (eqs 5–7) and an acyclic starting material **9f** (eq 8). These Ti compounds



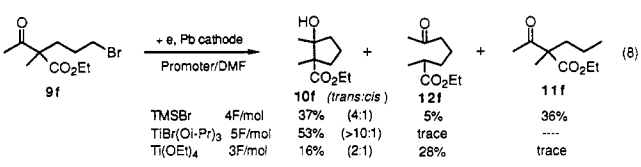
(5)



(6)



(7)



(8)

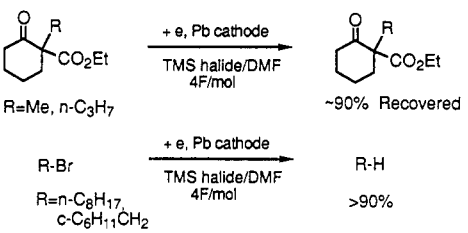
were also effective for the promotion of the electroreductive intramolecular coupling of α-(γ-bromopropyl) ketones **13** (eq 9, Table II).

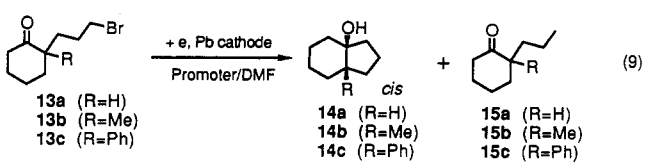
Table II. Electroreduction of 13

			% yield[a]	
13	promoter	F/mol	**14**	**15**
13a	TMSBr	5	13	23
	$TiBr(Oi\text{-}Pr)_3$	5	41	3
	$Ti(OEt)_4$	3	44	5
13b	TMSBr	4	30	31
	$TiBr(Oi\text{-}Pr)_3$	5	62	trace
	$Ti(OEt)_4$	3	54	trace
13c	TMSBr	5	42	31
	$TiBr(Oi\text{-}Pr)_3$	5	68	5
	$Ti(OEt)_4$	3	65	5

[a] Isolated yield.

Scheme I

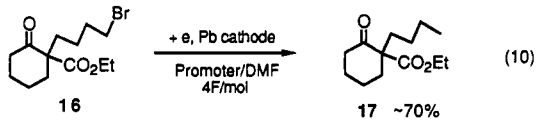




(9)

Electroreduction of α-(δ-Bromobutyl) β-Keto Ester 16 (n = 4). The electroreduction of α-(δ-bromobutyl) β-keto ester **16** gave only the reduction product **17** even though the electroreduction was carried out in the presence of Ti compounds (eq 10).

Reaction Mechanism. The electroreductive intramolecular coupling of α-(ω-bromoalkyl) β-keto esters is considered to be initiated by the reduction of the bromine–



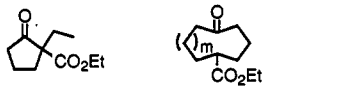
16 17 ~70% (10)

carbon bond, since the carbonyl group of α-alkyl β-keto esters are almost inert toward the electroreduction under the present reaction conditions whereas alkyl bromides are easily reduced to the corresponding hydrocarbons under these conditions (Scheme I).

The electroreduction of bromomethyl-substituted thiomalonate **18**, malonate **22**, and phenyl acetate **25** was investigated to elucidate the character of the active intermediate (Scheme II).[5] The reduction of these compounds with n-Bu_3SnH and sodium naphthalenide has already been studied.[9] The reduction with n-Bu_3SnH has been shown to proceed through radical intermediates and gives nonmigrated products **21**, **24**, and **28** and a product **27** in which the phenyl group has migrated (method A). On the other hand, the reduction with sodium naphthalenide proceeds via anion intermediates and gives an ethylthiocarbonyl group migrated product **19** and ester group migrated products **20**, **23**, and **26** (method B).

The electroreduction of these starting materials gives almost the same results as the reduction with sodium naphthalenide (method C). These results suggest that the electroreductive coupling proceeds via anion intermediates.

The reduction of **7** with n-Bu_3SnH gives the corresponding α-ethyl β-keto ester **29**, and **9a–c** afford the ring-opened products **30a–c** together with **11a–c** by the same reduction.[1b] These differences between reduction with n-Bu_3SnH and electroreduction also suggest that the radical intermediate is not involved in the product-determining step of the electroreduction.

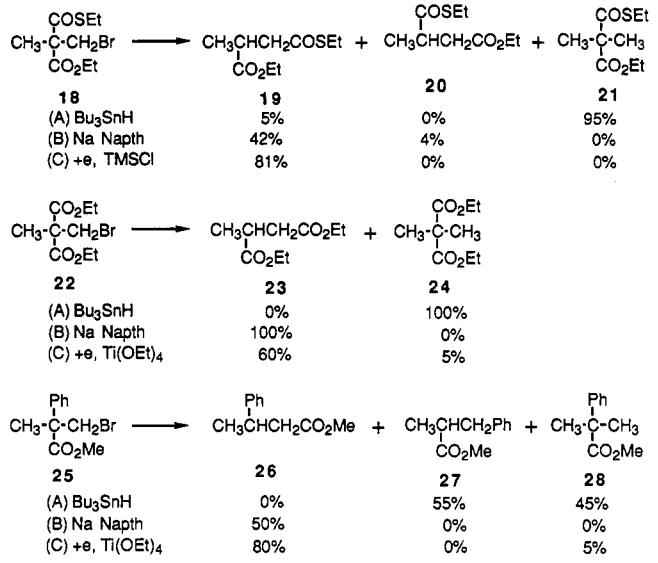


29 **30a,b,c** (m=1,2,3)

Hence, the mechanism of electroreduction of α-(ω-bromoalkyl) β-keto esters can be represented as Scheme III. Thus, two-electron transfer to the carbon–bromine bond forms the corresponding anions **31**, **34**, and **35**. In the case of n = 1, the anion **31** adds to the carbonyl group and the resulting alkoxy anion **32** gives ring opening, yielding the enolate anion of ester **33**. The ring strain of a three-membered ring and the stabilization of the intermediate anion by the ester seem to be the driving force for the ring opening, since the presence of an ester group is requisite for the ring opening (Table I, run 9). The anion **34** (n = 2) results in **8** through β-elimination. In the case of n = 3, the anion **35** attacks the carbonyl group and the alkoxy anion **36** forms the cyclized product **10** or its ring-opened product **12**.

Although the roles of trimethylsilyl halides and Ti compounds are not always clear at present, they may assist the addition of the anion intermediate to the carbonyl group.

Scheme II



Stereochemistry of the Ring Opening of Cyclized Products 10. In the electroreduction of **9c–f**, the ring-opened products **12c–f** seem to be formed from the corresponding trans isomers of the ring-closed primary products **10c–f** since the treatment of an independently prepared trans isomer of **10f** with base easily affords the ring-opened product **12f**, whereas cis isomers of **10a–c** and **10f** are perfectly inert under the same conditions (Scheme IV).[10]

Five- and six-membered substrates **9a,b**, and **13a–c** give the cis-ring-closed products predominantly, since the formation of the corresponding trans isomers is sterically impossible. The primary ring-closed products formed from the large-ring starting materials **9d,e** seem to be trans isomers, and they are immediately converted to ring-opened products **12d,e**. The open-chain starting material **9f** also mainly gives trans ring-closed product *trans*-**10f** although the reaction medium is not always sufficiently basic to promote completely the ring opening of *trans*-**10f** yielding **12f**.

Experimental Section

IR spectra were recorded on a Hitachi 260-10 spectrometer. ^1H NMR spectra were measured on a Varian EM-390 spectrometer with TMS as an internal standard. ^{13}C NMR spectra were measured on a Varian Gemini-200 or a JEOL JNM-GX400 spectrometer. Mass spectra were obtained on a JEOL IMS-DX 300 instrument. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University.

(5) As to the coenzyme-B_{12}-catalyzed rearrangement of methylmalonyl-CoA to succinyl-CoA, the acyl rearrangement induced by reduction with zinc or $NaBH_4$,[6] photolysis,[7] and electrolysis[8] has potentially been studied.

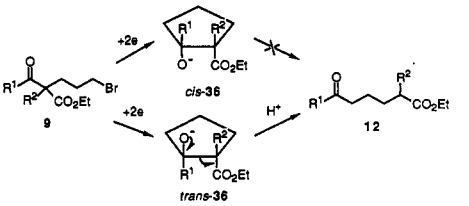
(6) For example: Grate, J. H.; J. W.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1982**, *104*, 1588.

(7) For example: Tada, M.; Nakamura, T.; Matsumoto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4647 and references cited therein.

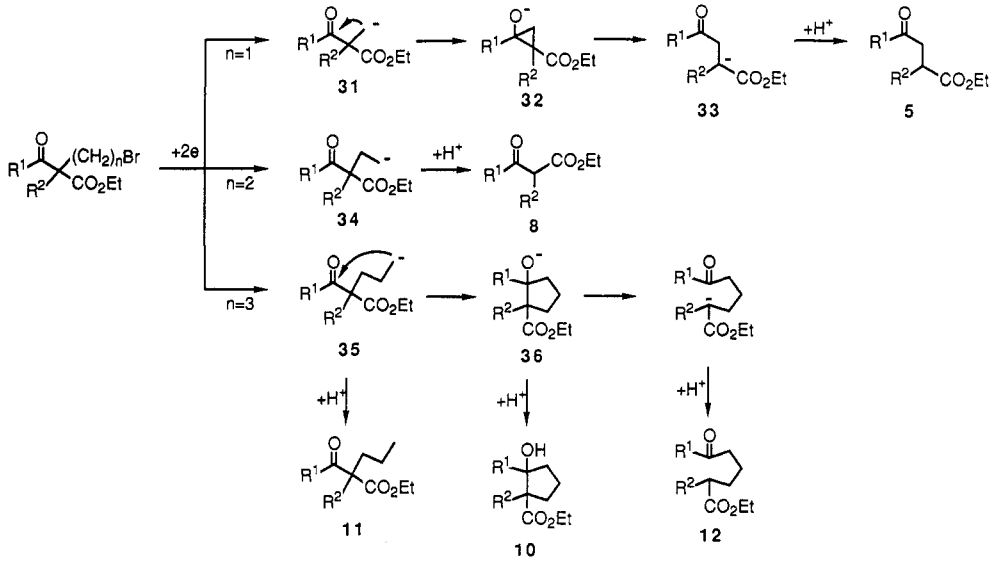
(8) Murakami, Y.; Hisaeda, Y.; Ozaki, T.; Tashiro, T.; Ohno, T.; Tani, Y.; Matsuda, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 311.

(9) Wollowitz, S.; Halpern, J. *J. Am. Chem. Soc.* **1988**, *110*, 3112.

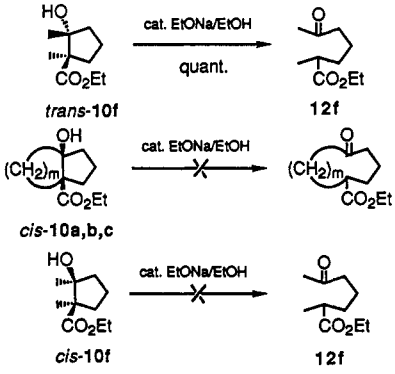
(10) Molander et al., have reported easy ring opening of *trans*-**10f** by the treatment with NaOH in $MeOH/H_2O$.[4b] Although they have also observed cis–trans equilibration of some metal (Li, Na, or K) aldolates of **10f** under strongly basic conditions, no evidence for such equilibration was detected when cis isomers of **10a–c,f** were treated under weakly basic conditions (base, EtONa or t-BuOK; solvent, EtOH, THF, or DMF). These compounds also did not show any cis–trans equilibration under conditions of the present electroreduction. Although the rather easy ring opening of the trans product is not always clearly explained, it may be assisted by the anti-parallel ring opening of the intermediate trans anion



Scheme III



Scheme IV



Starting Materials. α-(ω-Bromoalkyl) β-keto esters **4**, **7**, **9**, and **16** were prepared from the corresponding β-keto esters by usual methods of alkylation with 1,ω-dibromoalkanes.[1c,4] Other materials, **13c**, **18**, **22**, and **25**, were synthesized by similar methods. Compound **13a** was obtained by decarbethoxylation of **9b**. The material **13b** was prepared according to the reported method.[4a]

General Procedure of Electroreduction. A solution of Et_4NOTs (5 g) in DMF (40 mL) was put into a divided cell (50-mL beaker) equipped with a lead cathode (5 × 10 cm^2), a carbon rod anode (diameter 8 mm), and a ceramic diaphragm. To the catholyte were added an α-(ω-bromoalkyl) β-keto ester (5 mmol) and TMSCl (15 mmol). Electricity was passed at a constant current of 0.2 A until almost all of the substrate was consumed (4–5 F/mol). The catholyte was poured into water (200 mL) and extracted with ether. After evaporation of ether, the product was isolated by distillation or column chromatography on silica gel.

Identification of Products. Direct reduction products such as **11**, **15**, and **17** were identified by comparison of them with authentic samples prepared by usual alkylation of β-keto esters with 1-bromoalkanes. Ethyl 3-oxocyclohexane-1-carboxylate (**5a**),[1c] ethyl 3-oxocycloheptane-1-carboxylate (**5b**),[1c] ethyl 3-oxocyclooctane-1-carboxylate (**5c**),[1c] ethyl 2-methyl-4-oxopentanoate (**5g**),[1c] diethyl 2-methyl-4-oxoglutarate (**5h**),[1c] ethyl *cis*-5-hydroxybicyclo[4.3.0]nonane-1-carboxylate (*cis*-**10b**),[4a] ethyl *cis*-5-hydroxybicyclo[5.3.0]decane-1-carboxylate (*cis*-**10c**),[4a] ethyl 5-oxocyclodecane-1-carboxylate (**12c**),[1c] ethyl 1,2-dimethyl-2-hydroxypentane-1-carboxylate (**10f**),[4b] *cis*-1-hydroxybicyclo[4.3.0]nonane (*cis*-**14a**),[4a] *cis*-1-hydroxy-5-methylbicyclo[4.3.0]nonane (*cis*-**14b**),[4a] *O*-ethyl *S*-ethyl 2-methylmonothiosuccinate (**19**),[11] diethyl 2-methylsuccinate (**23**),[12] and methyl 3-phenylbutanoate (**26**)[13] were identified by comparison of their spectroscopic behaviors with those described in the references or with authentic samples. The other products were confirmed by spectroscopic and elemental analyses as shown below.

Ethyl 3-oxocyclotridecane-1-carboxylate (5d) was isolated by column chromatography on silica gel as a colorless oil: R_f 0.50 (AcOEt–hexane, 1:5); IR (neat) 1730, 1710 cm^{-1}; ^1H NMR (CCl_4) δ 0.94–3.14 (m, 23 H), 1.25 (t, 3 H, J = 7 Hz), 4.00 (q, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) 13.99 (q), 23.35 (t), 23.43 (t), 24.00 (t), 24.30 (t), 25.20 (t), 25.76 (t, 2 C), 25.90 (t), 29.24 (t), 39.43 (d), 42.20 (t), 43.37 (t), 60.45 (t), 175.44 (t), 210.56 (t) ppm; exact mass calcd for $C_{16}H_{28}O_3$ 268.2031, found 268.1997. Anal. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.52. Found: C, 71.52; H, 10.49.

Ethyl 9-oxo-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-7-carboxylate (5e) was isolated by Kugelrohr distillation as a colorless oil: bp 170–180 °C (1 mmHg); IR (neat) 1730, 1680, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 1.17 (t, 3 H, J = 7 Hz), 1.53–3.54 (m, 7 H), 3.96 (q, 2 H, J = 7 Hz), 6.64–7.75 (m, 4 H); ^{13}C NMR ($CDCl_3$) 13.65 (q), 28.05 (t), 30.67 (t), 37.79 (d), 42.39 (t), 60.55 (t), 126.79 (d), 128.54 (d), 129.63 (d), 132.40 (d), 138.04 (s), 140.66 (s), 174.22 (s), 202.79 (s) ppm; exact mass calcd for $C_{14}H_{16}O_3$ 232.1100, found 232.1103. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.09; H, 7.17.

3-Phenylcycloheptanone (5f) was isolated by column chromatography on silica gel as a colorless oil: R_f 0.30 (AcOEt–hexane, 1:10); IR (neat) 1705, 1605, 1500 cm^{-1}; ^1H NMR (CCl_4) δ 1.20–2.20 (m, 6 H), 2.37–2.93 (m, 5 H), 7.17 (s, 5 H); ^{13}C NMR ($CDCl_3$) 23.80 (t), 28.92 (t), 38.92 (t), 42.42 (t), 43.65 (t), 50.97 (t), 126.31 (d), 126.39 (d, 2 C), 128.61 (d, 2 C), 146.95 (s), 213.67 (s) ppm; exact mass calcd for $C_{13}H_{16}O$ 188.1202, found 188.1185. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.92; H, 8.67.

Diethyl 2-methyl-4-hydroxyglutarate (6) was isolated by column chromatography on silica gel as a colorless oil (ca. 1:1 mixture of two diastereoisomers): R_f 0.50 (AcOEt–hexane, 1:2); IR (neat) 3500, 1730 cm^{-1}; ^1H NMR (CCl_4) δ 1.24 (t, 3 H, J = 7 Hz), 1.29, (t, 3 H, J = 7 Hz), 1.31 (d, 3 H, J = 7 Hz), 1.60–3.00 (m, 4 H), 4.00 (q, 2 H, J = 7 Hz), 4.15 (q, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) 13.83 (q), 16.36 (q), 17.57 (q), 35.51 (d), 35.69 (d), 37.48 (t), 37.77 (t), 60.32 (t), 61.59 (t), 68.45 (d), 68.67 (d), 175.09 (s), 176.40 (s), 176.62 (s) ppm; exact mass calcd for $C_{10}H_{18}O_5$ 218.1149, found 218.1122. Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.84; H, 8.32.

Ethyl *cis*-5-hydroxybicyclo[3.3.0]octane-1-carboxylate (*cis*-10a) was isolated by column chromatography on silica gel as a colorless oil: R_f 0.50 (AcOEt–hexane, 1:2); IR (neat) 3490, 1720 cm^{-1}; ^1H NMR (CCl_4) δ 1.26 (t, 3 H, J = 7 Hz), 1.47–2.84 (m, 12 H), 4.08 (q, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) 14.13 (q), 23.72 (t), 37.26 (t), 41.43 (t), 60.59 (t), 61.63 (s), 92.43 (s), 176.62 (s) ppm; exact mass calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1266.

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Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.61; H, 9.08.

Ethyl 5-oxocycloundecane-1-carboxylate (12d) was isolated by column chromatography on silica gel as a colorless oil: R_f 0.33 (AcOEt-hexane, 1:5); IR (neat) 1735, 1700 cm^{-1}; ^1H NMR (CCl_4) δ 1.22 (t, 3 H, J = 7 Hz), 1.36-2.69 (m, 19 H), 3.96 (q, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) 13.80 (q), 22.44 (t), 24.33 (t), 25.01 (t), 25.22 (t), 26.96 (t), 31.43 (t), 32.32 (t), 33.83 (t), 41.79 (t), 49.94 (d), 60.00 (t), 173.49 (s), 220.36 (s) ppm; exact mass calcd for $C_{14}H_{24}O_3$ 240.1726, found 240.1697. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.68; H, 10.36.

Ethyl 5-oxocyclotetradecane-1-carboxylate (12e) was isolated by column chromatography on silica gel as a colorless oil: R_f 0.55 (AcOEt-hexane, 1:5); IR (neat) 1730, 1700 cm^{-1}; ^1H NMR (CCl_4) δ 1.22 (t, 3 H, J = 7 Hz), 1.25-2.88 (m, 27 H), 3.96 (q, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) 13.92 (q), 21.53 (t), 21.87 (t), 22.15 (t), 22.68 (t), 22.98 (t), 23.34 (t), 23.72 (t), 25.50 (t), 25.85 (t), 29.21 (t), 30.19 (t), 33.94 (t), 36.67 (t), 51.77 (t), 60.15 (t), 176.60 (s), 214.91 (s) ppm; exact mass calcd for $C_{18}H_{32}O_3$ 296.2353, found 296.2335. Anal. Calcd for $C_{18}H_{32}O_3$: C, 72.93; H, 10.88. Found: C, 72.93; H, 10.97.

Ethyl 2-methyl-6-oxoheptanoate (12f) was isolated by column chromatography on silica gel as a colorless oil: R_f 0.33 (AcOEt-hexane, 1:5); IR (neat) 1720 cm^{-1}; ^1H NMR (CCl_4) δ 1.15 (d, 3 H, J = 7 Hz), 1.24 (t, 3 H, J = 7 Hz), 1.38-2.70 (m, 7 H), 2.05 (s, 3 H), 4.04 (q, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) 14.00 (q), 16.86 (q), 21.19 (t), 29.71 (q), 32.88 (t), 39.21 (d), 43.29 (t), 60.14 (t), 176.80 (s), 209.07 (s) ppm; exact mass calcd for $C_{10}H_{18}O_3$ 186.1256, found 186.1242. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49, H, 9.74. Found: C, 64.53; H, 9.81.

***cis*-1-Hydroxy-5-phenylbicyclo[4.3.0]nonane (*cis*-14c)** was isolated by column chromatography on silica gel as a colorless oil: R_f 0.50 (AcOEt-hexane, 1:5); IR (neat) 3580, 3460, 1600, 1500 cm^{-1}; ^1H NMR (CCl_4) δ 1.00-2.35 (m, 14 H), 6.74-7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$) 18.45 (t), 21.41 (t), 23.30 (t), 34.84 (t), 36.15 (t), 36.89 (t), 38.06 (t), 52.30 (s), 81.10 (s), 125.76 (d), 127.97 (d, 2C), 128.33 (d, 2C), 145.78 (s) ppm; exact mass calcd for $C_{15}H_{20}O$ 216.1515, found 216.1508. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.15; H, 9.26.

Conversion of *trans*-10f to 12. To a solution of sodium ethoxide (0.2 mmol) in ethanol (5 mL) was added *trans*-**10f** (2 mmol) at room temperature, and the mixture was stirred for 3 h. After usual workup, the product **12** was isolated by column chromatography on silica gel.

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Photochemical Reaction of Phenyliodonium Ylides of β-Dicarbonyl Compounds with Terminal Alkynes

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The photochemical reaction of phenyliodonium ylides of acyclic β-dicarbonyl compounds bearing at least one benzoyl group with terminal alkynes leads to the formation of 4-substituted-2-acyl-1-naphthol derivatives, probably through iodanes and ethynylated derivatives **6**. A hydroxy benzothiophene derivative, **15**, was also isolated from the reaction of ylide **14** with (trimethylsilyl)acetylene.

Introduction

Phenyliodonium ylides constitute an interesting class of hypervalent iodine compounds, for which the chemistry up to 1982 has been reviewed.[1] There are various types of these ylides, depending on the ylidic carbon moiety, but the best known are those derived from β-dicarbonyl compounds. Among the reactions of these species, perhaps the most interesting are those leading to C-C bond formation: phenyliodonium dimedonide undergoes cycloaddition reactions with unsaturated compounds (dipolarophiles) such as diphenylketene,[2] carbon disulfide,[3] and alkenes,[4] whereas phenyliodonio 1,2,4-trioxo-1,2,3,4-tetrahydronaphthalenide reacts with both alkenes and alkynes.[5] Some reactions of iodonium ylides of acyclic β-dicarbonyl compounds leading to C-C bond formation have also been reported: phenyliodonium dibenzoylmethylide gives 1,3-oxathiole-2-thione[3] with carbon disulfide and gives dihydrofurans[6] with alkenes, while phenyliodonium dimethylmalonate reacts with various olefins in the presence of Lewis acids and lithium perchlorate[7] to afford 3-carbomethoxy δ-lactones. Recently, Moriarty reported the intramolecular cyclopropanation of iodonium ylides of β-dicarbonyl compounds in the presence of CuCl as catalyst.[8]

Results and Discussion

In our continuing exploration of the reactions of iodonium ylides and iodonium zwitterions with various dipolarophiles,[3,5,6,9] we have studied the reactivity of phenyliodonium dibenzoylmethylide (**1**), a typical iodonium ylide derived from an acyclic β-diketone, with alkynes.

No reaction between the ylide and alkynes (terminal or internal) was observed in acetonitrile at room temperature

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