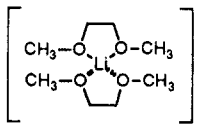
to THF appears to have the same effect as a decrease in temperature, which causes a decrease in the E/Z ratio due to increased solvation of alkoxide intermediate **3** at lower temperatures. However, an increase in the E/Z ratio would be expected when the solvent was changed from DME to THF because of the greater ability of DME to solvate cations by the formation of a bidentate chelate (structure **7**). In some cases, the larger dielectric constant and dipole moment[8,9] of THF allow it to be superior to DME in cation solvating ability due to the formation of a stable THF solvate, as is the case for Grignard reagents.[10] Alternatively, the change in E/Z ratio could be a result of a change in the kinetic ratio of alkoxides **3E**/**3Z** by the change of solvent. But since the intermediate alkoxide **3** cannot be isolated or observed, the occurrence of such phenomena cannot be rigorously corroborated. To lend some support, the reaction was carried out in two other nonchelating solvents, ether and benzene, under conditions that produced a large solvent effect (aldehyde **2a**, lithium cation, room temperature). The E/Z ratio for these reactions was 20/1, the same ratio observed when DME was used as the solvent.



7

In summary, we have described the effects of metal cation, reaction temperature, and solvent on the E/Z ratio of unsaturated esters resulting from the Horner–Emmons reaction of trimethyl phosphonoacetate with three aldehyde of varying degrees of alkyl substitution. Although none of these effects alone are very large, the combination of the effects allows for a rather large effect on the stereoselectivity of the reaction. Hence, it is possible to obtain either the E or Z unsaturated ester as the major product in the reaction without changing the nature of the phosphonate reagent,[11] but by judicious choice of metal cation, reaction temperature and solvent, providing that the inherent E/Z selectivity of the aldehyde in the reaction permits (e.g., aldehyde **2b**).

Experimental Section

General. Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. Ether, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone ketyl immediately prior to use. Benzene and pentane were distilled from CaH_2 prior to use. All reactions were conducted under an atmosphere of dry argon in oven-dried glassware. NaH and KH were rinsed free of mineral oil with pentane under an atmosphere of dry argon and then dried in vacuo and stored in a glovebox under a nitrogen atmosphere. IR spectra were measured as films on NaCl plates. ^1H and ^{13}C NMR spectra were measured as solutions in $CDCl_3$ at 250 MHz and 125 MHz, respectively. J values are in hertz.

General Procedure for Horner–Emmons Reactions. Lithium Cation. To a stirring solution of 275 mg (1.50 mmol, 245 μL) of trimethyl phosphonoacetate in 2.5 mL of dry solvent, cooled to 0 °C, was added dropwise 650 μL (1.38 mmol) of a 2.11 M solution of *n*-butyllithium in hexanes. After 10 min, the reaction mixture was brought to the desired temperature and 1.25 mmol of aldehyde was added dropwise. After being stirred for 1.5 h, the mixture was quenched by the addition of 3 mL of water. The mixture was diluted with 5 mL of ether, the organic layer was washed with saturated brine, dried ($MgSO_4$), and filtered, and the solvents were removed with a rotary evaporator to give the product as a colorless liquid.

Sodium and Potassium Cation. To a stirring suspension of 1.38 mmol of NaH or KH in 2.5 mL of dry solvent was added dropwise 275 mg (1.50 mmol, 245 μL) of trimethyl phosphonoacetate. The mixture (a slurry in the case of sodium anion) was brought to the desired temperature and 1.25 mmol of aldehyde was added dropwise. After being stirred for 1.5 h, the mixture was worked up as above.

Spectral Data for New Compounds (5a and 6a). (*E*)-Methyl 5,5,8-trimethylnona-2,7-dienoate (5a): bp 55–56 °C, 0.01 mm (with *Z* isomer). IR: 1735 cm^{-1}. ^1H NMR: δ 0.89 (s, 6), 1.59 (s, 3), 1.72 (s, 3), 1.90 (d, 2, J = 7.6), 2.09 (dd, 2, J = 1.3, 7.9), 3.73 (s, 3), 5.17 (m, 1), 5.81 (dt, 1, J = 1.3, 15.5), 6.99 (dt, 1, J = 7.9, 15.5). ^{13}C NMR: δ 17.904, 26.054, 26.867 (2 C), 35.054, 40.227, 44.488, 51.341, 120.491, 122.787, 133.434, 147.201, 166.931. Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.43; H, 10.69.

(*Z*)-Methyl 5,5,8-trimethylnona-2,7-dienoate (6a): bp 55–56 °C, 0.01 mm (with *E* isomer). IR: 1735 cm^{-1}. ^1H NMR: δ 0.90 (s, 6), 1.59 (s, 3), 1.72 (s, 3), 1.93, (d, 2, J = 7.6), 2.60 (dd, 2, J = 1.7, 7.7), 3.71 (s, 3), 5.18 (m, 1), 5.90 (dt, 1, J = 1.7, 11.7), 6.32 (dt, 1, J = 7.7, 11.7). ^{13}C NMR: δ 17.881, 26.054, 26.652 (2 C), 34.975, 40.163, 40.270, 50.910, 120.383, 120.800, 133.193, 147.964, 166.887. Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.63; H, 10.76.

(*E*)-Methyl 4-methyl-2-pentenoate (**5b**), (*Z*)-methyl 4-methyl-2-pentenoate (**6b**), and (*E*)-methyl 4,4-dimethyl-2-pentenoate (**5c**) exhibited spectral data identical with those previously reported.[12,13]

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-8418427).

(8) Agami, C. *Bull. Soc. Chim. Fr.* **1968**, 1205.
(9) Coetzee, J. F.; Chang, T. H. *Pure Appl. Chem.* **1985**, *57*, 633.
(10) House, H. O.; Latham, R. A.; Whitesides, G. *J. Org. Chem.* **1967**, *32*, 24.
(11) Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405.
(12) McGreer, D. E.; Chiu, N. W. K. *Can. J. Chem.* **1968**, *46*, 2225.
(13) Wilson, J. W.; Stubblefield, V. S. *J. Am. Chem. Soc.* **1968**, *90*, 3423.

Palladium(0)-Catalyzed Reaction of (*Z*)-2-Butene-1,4-diyl Bis(methyl carbonate) and (*Z*)-2-Butene-1,4-diyl Diacetate with Bifunctional Nitrogen Nucleophiles

Tetsuo Tsuda,* Takao Kiyoi, and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

Received October 25, 1989

Allylic monoacetates and monocarbonates are extensively used in palladium(0)-catalyzed allylation of nucleophiles, which provides a useful method in organic synthesis.[1] On the other hand, there are few reports on palladium(0)-catalyzed reaction of bifunctional allylic diacetates and dicarbonates with nucleophiles featuring their bifunctionality.[2] We now report that the palladium(0)-catalyzed reaction of (*Z*)-2-butene-1,4-diyl bis(methyl carbonate) (**1**) and (*Z*)-2-butene-1,4-diyl diacetate

(1) See, for example: (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980. (b) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Ed.; Pergamon: New York, 1982; Vol. 8, p 799. (c) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140.
(2) (a) Genêt, J. P.; Balabane, M.; Bäckvall, J. E.; Nyström, J. E. *Tetrahedron Lett.* **1983**, *24*, 2745. (b) Keinan, E.; Sahai, M.; Roth, Z. *J. Org. Chem.* **1985**, *50*, 3558. (c) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1985**, *26*, 3825. (d) Tsuda, T.; Okada, M.; Nishi, S.; Saegusa, T. *J. Org. Chem.* **1986**, *51*, 421. (e) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1987**, *28*, 4837.

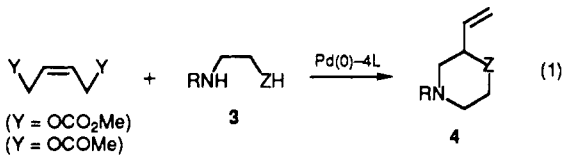
0022-3263/90/1955-3388$02.50/0 © 1990 American Chemical Society

Table I. Palladium(0)-Catalyzed Reaction of (*Z*)-2-Butene-1,4-diyl Bis(methyl carbonate) (1) and (*Z*)-2-Butene-1,4-diyl Diacetate 2 with Bifunctional Nitrogen Nucleophiles 3, 5 (eqs 1, 2)[a]

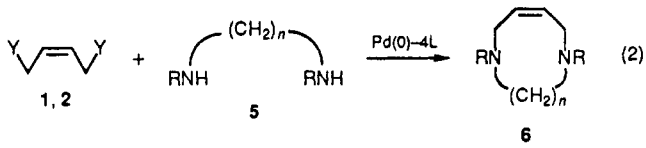
1, 2	3, 5	product 4, 6, %[b]
1	3a	4a [33][c]
	3b	4b 74
	3c	4c 51 [62],[c] 40[e]
	3d	4d 61, 76[e,f]
	3e	4e 69
2	3f	4f 62[d]
1	5a	6a 50, 47[g]
	5b	6b 45[h]

[a] 1, 2, 0.10–0.20 mmol; $Pd_2(dba)_3{\cdot}CHCl_3$/1, 2 = 0.025; $P(OPr^i)_3$/$Pd_2(dba)_3{\cdot}CHCl_3$ = 8; solvent, THF, 2 mL; temperature, room temperature; time, 4 h. [b] Isolated yield by PLC. [c] The value in brackets is the GC yield. [d] NEt_3/2 = 2.1; time, 22 h. [e] Catalyst, $Pd(PPh_3)_4$/1 = 0.05. [f] Time, 96 h. [g] Solvent, benzene, 2.0 mL. [h] Solvent, toluene, 5.0 mL.

(2) with bifunctional nucleophiles 3 and 5 affords 2-vinylpiperazines 4 and 1,5- and 1,6-diazacycles 6 (eqs 1 and 2).

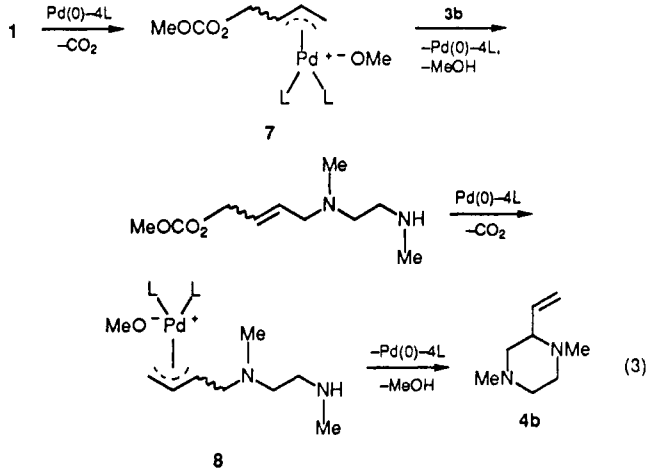


a, R = $PhCH_2$(Bz), Z = NH; **b**, R = Me, Z = NMe; **c**, R = Bz, Z = NBz; **d**, R = Me, Z = 4-Me-$C_6H_4SO_2N$(TsN); **e**, R = Ts, Z = NTs; **f**, R = Bz, Z = O



a, R = Ts, *n* = 3; **b**, R = Ts, *n* = 4

Our palladium(0) catalyst was generated from $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone) and 8 equiv of triisopropyl phosphite as we have previously described for the Pd(0)-catalyzed reaction of methyl γ,δ-epoxysorbate with nitrogen nucleophiles.[3] When *N*,*N*′-dimethylethylenediamine (**3b**) was reacted with 1 in THF at room temperature in the presence of the palladium(0) catalyst (5 mol %), 2-vinyl-*N*,*N*′-dimethylpiperazine (**4b**) was obtained in a good yield (eq 1, Table I). *N*-Benzylethylenediamine (**3a**) and *N*,*N*′-dibenzylethylenediamine (**3c**) similarly gave the corresponding 2-vinylpiperazines **4a** and **4c**. It is noteworthy that the piperazine ring was regioselectively formed without competing eight-membered ring formation or intermolecular polymerization.[4] The presumed mechanism of the reaction of **3b** with 1 is depicted in eq 3.[5] Intermolecular nucleophilic attack of **3b** on a π-allylpalladium intermediate **7** occurs at the less substituted terminus, and concomitant intramolecular nucleophilic attack on the second π-allylpalladium intermediate **8** at the more substituted internal allylic carbon atom then leads to the formation of the six-membered piperazine ring.



Noteworthy is the unreactivity of the parent ethylenediamine, which even under forcing conditions (THF/reflux) did not react with 1. These findings indicate that the present palladium(0)-catalyzed 2-vinylpiperazine formation requires the presence of at least one secondary amino group in the 1,2-diaminoethane nucleophile. The *p*-toluenesulfonamides of *N*-methylethylenediamine **3d** and ethylenediamine **3e** could also be used as bifunctional nitrogen nucleophiles to afford the corresponding 2-vinylpiperazines **4d** and **4e** in good yields.[6] *N*-Benzylethanolamine (**3f**) reacted with allylic diacetate **2** in the presence of triethylamine to give *N*-benzyl-2-vinylmorpholine (**4f**). On the other hand, ethylene glycol and 1,2-ethanedithiol did not serve as suitable nucleophiles in this regard. It is noteworthy that the cyclization of the unsymmetrical bifunctional nucleophiles **3a**, **3d**, and **3f** with 1 proceeded chemoselectively to give **4a**, **4d**, and **4f**, respectively. No other isomers were detected in these reactions.

The number (*n*) of the methylene groups connecting two nitrogen atoms of the nitrogen nucleophile was found to be an important factor in the palladium(0)-catalyzed reaction of 1 with bifunctional nitrogen nucleophiles. The nitrogen nucleophile **5a** with *n* = 3 did not produce the corresponding 2-vinyl-1,4-diazacycloheptane, but instead afforded 1,5-diaza-7-cyclononene (**6a**) having an internal olefinic moiety (eq 2, Table I). Similarly the nitrogen nucleophile **5b** with *n* = 4 gave 1,6-diaza-8-cyclodecene (**6b**).

In conclusion, the palladium(0)-catalyzed reaction of the bifunctional allylic dicarbonate 1 and diacetate **2** with bifunctional nitrogen nucleophiles was found to effect a characteristic chemo- and regioselective cyclization to afford 2-vinylpiperazines[7] and medium-sized diazacycles having an internal olefinic moiety depending upon the structure of the nitrogen nucleophiles.

Experimental Section

IR spectra were determined on a Hitachi 260-50 grating spectrophotometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were taken on a JEOL JNM-JX-400 instrument. ^1H NMR (200 MHz) spectra were taken on a Varian GEMINI-200 instrument. The NMR measurement was carried out in $CDCl_3$. All chemical shifts are reported in δ downfield from internal tetramethylsilane. Coupling constants (*J*) are reported in hertz. Mass spectra were obtained on a JEOL DX-300 instrument. Gas

(3) Tsuda, T.; Horii, Y.; Nakagawa, Y.; Ishida, T.; Saegusa, T. *J. Org. Chem.* **1989**, *54*, 977.

(4) Suzuki, M.; Lim, J.-C.; Oguni, M.; Eberhardt, A.; Inoue, K.; Saegusa, T. Manuscript in preparation, where the palladium-catalyzed diazacycle formation from 1,3-diacetoxy-2-methylenepropane and *N*,*N*′-dimethylethylenediamine is reported.

(5) $Pd(PPh)_4$-catalyzed equimolar reaction of 2 with diethylamine has been reported to produce (*E*)-4-(*N*,*N*′-diethylamino)-2-butenyl acetate: see ref 2a.

(6) Bystöm, S. E.; Aslanian, R.; Bäckvall, J.-E. *Tetrahedron Lett.* **1985**, *26*, 1749.

(7) Porter, A. E. A. In *Comprehensive Heterocyclic Chemistry*; Boulton, A. J., McKillop, A., Ed.; Pergamon: Oxford, England, 1984; Vol. 3, p 178.

chromatographic analyses (GC) were made on a Shimadzu 4CPT instrument. GC quantitative analyses of reaction products were made with internal standards with calibration based upon authentic samples employing a 20% silicone DC 550 on Celite 545 column. Preparative-layer chromatography (PLC) was carried out by using 20 × 20 × 0.2 cm plates prepared with Merck aluminum oxide 60 PF-254. Preparative medium-pressure liquid chromatography (MPLC) was carried out by using a prepacked silica gel column (CPS-223L-1) supplied by Kusano Kagaku Co. Melting points were determined on a Yanaco MP melting point measurement apparatus and are uncorrected.

Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under nitrogen. Benzene and toluene were distilled from CaH_2 under nitrogen. (*Z*)-2-Butene-1,4-diyl diacetate (**2**) was distilled under nitrogen after drying over $CaSO_4$. (*Z*)-2-Butene-1,4-diyl bis(methyl carbonate) (**1**) was prepared by the reaction of (*Z*)-2-butene-1,4-diol with methyl chloroformate in THF in the presence of pyridine. *N*- and *N,N'*-substituted ethylenediamines **3a–c** and *N*-benzylethanolamine (**3f**) were commercially available and were distilled under nitrogen after drying over anhydrous KOH. *N,N'*-Bis(*p*-tolylsulfonyl)diamines **3e**, **5a**, and **5b** were prepared by tosylation of the corresponded unsubstituted diamines according to the published method.[8] *N*-Methyl-*N'*-(*p*-tolylsulfonyl)ethylenediamine (**3d**) was prepared according to the published method.[8] $Pd_2(dba)_3{\cdot}CHCl_3$[9] and $Pd(PPh_3)_4$[10] were prepared by the reported procedures. $P(OPr^i)_3$ was a commercial reagent, which was distilled under nitrogen after drying over $CaSO_4$.

Palladium(0)-Catalyzed Reaction of (*Z*)-2-Butene-1,4-diyl Bis(methyl carbonate) (1) with *N,N'*-Bis(*p*-tolylsulfonyl)-ethylenediamine (3e). To a stirred THF (1.6 mL) solution containing $Pd_2(dba)_2{\cdot}CHCl_3$ (0.0046 g, 0.0050 mmol), $P(OPr^i)_3$ (0.010 ml, 0.040 mmol), and **3e** (0.0733 g, 0.200 mmol) was added under N_2 a THF (0.4 mL) solution of **1** (0.0408 g, 0.20 mmol) at room temperature. GC analysis of the mixture after 4 h showed disappearance of **1**. The reaction mixture was concentrated under vacuum to give a residue. Purification by PLC (hexane–ethyl acetate = 3:2 (v/v)) gave *N,N'*-bis(*p*-tolylsulfonyl)-2-vinylpiperazine (**4e**) (0.058 g, 69%), which was further purified by MPLC (chloroform–ethyl acetate = 1:1 (v/v)) to give a white solid: mp 181.5–182.7 °C; IR (KBr, cm^{-1}) 1630, 1455, 1345, 1155, 920, 815; ^1H NMR (200 MHz) 2.35–2.55 (m, 1 H), 2.40 (s, 3 H), 2.45 (s, 3 H), 2.57 (dd, *J* = 11.6, 3.6, 1 H), 3.15–3.30 (m, 1 H), 3.50–3.70 (m, 3 H), 4.45 (br s, 1 H), 5.19 (d, *J* = 9.2, 1 H), 5.26 (d, *J* = 16.0, 1 H), 5.73 (ddd, *J* = 17.2, 10.7, 6.4, 1 H), 7.24 (d, *J* = 9.0, 2 H), 7.33 (d, *J* = 7.9, 2 H), 7.56 (d, *J* = 8.3, 2 H), 7.60 (d, *J* = 8.3, 2 H); MS *m/e* (relative intensity) 420 (M^+, 0.7), 328 (13), 265 (100), 110 (24), 109 (18). Anal. Calcd for $C_{20}H_{24}N_2O_4S_2$: C, 57.12; H, 5.75; N, 6.66; S, 15.25. Found: C, 57.03; H, 5.80; N, 6.70; S, 15.09.

2-Vinylpiperazine derivatives **4a–d**, *N*-benzyl-2-vinylmorpholine (**4f**), and diazacycles **6a** and **6b** were similarly obtained as described above and were identified as follows. The regiochemistries of the products **4a**, **4d**, and **4f** produced from unsymmetrically substituted ethylenediamines were determined by ^1H NMR NOE measurements. The product purity was judged to be ≥95% for the products **4c**, **4f**, and **6b** and ≥90% for the products **4a** and **4b** by ^1H NMR spectral determinations. The product **4a** was isolated by preparative GC: IR (neat, cm^{-1}) 1640, 1490, 1060, 1020, 740, 680; ^1H NMR (400 MHz) 1.70 (s, 1 H), 1.84 (t, *J* = 10.5, 1 H), 2.06 (td, *J* = 10.9, 3.6, 1 H), 2.70–2.80 (m, 1 H), 2.81 (ddd, *J* = 10.8, 2.8, 1.8, 1 H), 2.90–3.00 (m, 2 H), 3.30–3.40 (m, 1 H), 3.51 (s, 2 H), 5.07 (dt, *J* = 10.5, 1.4, 1 H), 5.20 (dt, *J* = 17.3, 1.5, 1 H), 5.78 (ddd, *J* = 17.2, 10.7, 6.4, 1 H), 7.20–7.35 (m, 5 H); MS *m/e* (relative intensity) 202 (M^+, 7), 134 (83), 111 (37), 91 (100), 49 (35); HRMS (*m/e*) 202.1468, calcd for $C_{13}H_{18}N_2$ 202.1470. **4b** (column chromatography on alumina, pentane–ether = 1:1 (v/v)): IR (neat, cm^{-1}) 1635, 1435, 1085, 790; ^1H NMR (200 MHz) 1.95–2.10 (m, 1 H), 2.24 (s, 3 H), 2.28 (s, 3 H), 2.15–2.35 (m, 2 H), 2.55–2.90 (m, 4 H), 5.15 (dd, *J* = 10.2, 2.0, 1 H), 5.25 (dd, *J* = 17.0, 2.0, 1 H), 5.69 (ddd, *J* = 18.0, 10.0, 8.4, 1 H); MS *m/e* (relative intensity) 140 (M^+, 40), 96 (61), 91 (24), 84 (41), 83 (100), 82 (45), 43 (71); HRMS (*m/e*) 140.1314, calcd for $C_8H_{16}N_2$ 140.1314. **4c** (PLC, THF–triethylamine = 10:1 (v/v)): IR (neat, cm^{-1}) 1635, 1120, 1070, 1045, 915, 735, 700, 680; ^1H NMR (200 MHz) 2.05–2.25 (m, 3 H), 2.60–2.75 (m, 3 H), 2.93 (td, *J* = 9.1, 2.9, 1 H), 3.07 (d, *J* = 13.5, 1 H), 3.48 (s, 2 H), 4.05 (d, *J* = 13.5, 1 H), 5.18 (dd, *J* = 10.2, 1.8, 1 H), 5.27 (dd, *J* = 17.4, 1.8, 1 H), 5.84 (ddd, *J* = 17.4, 10.1, 8.2, 1 H), 7.15–7.35 (m, 10 H); MS *m/e* (relative intensity) 292 (M^+, 30), 201 (72), 161 (25), 160 (77), 91 (100); HRMS (*m/e*) 292.1937, calcd for $C_{20}H_{24}N_2$ 292.1940. **4d** (PLC, hexane–ethyl acetate = 1:1 (v/v)): IR (neat, cm^{-1}) 1630, 1445, 1345, 1155, 810, 795; ^1H NMR (400 MHz) 2.07 (td, *J* = 11.2, 3.4, 1 H), 2.20 (s, 3 H), 2.25 (dd, *J* = 11.4, 3.9, 1 H), 2.42 (s, 3 H), 2.60–2.70 (m, 2 H), 3.25 (ddd, *J* = 12.7, 11.0, 3.1, 1 H), 3.51 (dtd, *J* = 12.8, 3.2, 1.0, 1 H), 4.33 (br s, 1 H), 5.13 (dt, *J* = 11.7, 1.3, 1 H), 5.18 (dt, *J* = 17.3, 1.4, 1 H), 5.86 (ddd, *J* = 17.2, 10.5, 6.6, 1 H), 7.27 (d, *J* = 7.6, 2 H), 7.67 (d, *J* = 8.4, 2 H); ^{13}C NMR 21.5, 42.0, 46.2, 54.4, 56.2, 59.8, 117.4, 127.6, 129.5, 134.9, 136.8, 143.7; MS *m/e* (relative intensity) 280 (M^+, 1.5), 216 (8), 126 (100), 125 (100), 82 (54). Anal. Calcd for $C_{14}H_{20}N_2O_2S$: C, 59.97; H, 7.19; N, 9.99; S, 11.44. Found: C, 59.70; H, 7.15; N, 9.86; S, 11.36. **4f** (PLC, ethyl acetate): IR (neat, cm^{-1}) 1640, 1105, 1075, 1020, 735, 700; ^1H NMR (400 MHz) 1.94 (dd, *J* = 11.2, 10.3, 1 H), 2.18 (td, *J* = 11.4, 3.3, 1 H), 2.67 (dq, *J* = 11.5, 2.0, 1 H), 2.77 (dt, *J* = 11.3, 2.1, 1 H), 3.51 (s, 2 H), 3.71 (td, *J* = 11.4, 2.4, 1 H), 3.90 (ddd, *J* = 11.3, 3.3, 1.7, 1 H), 4.00–4.05 (m, 1 H), 5.15 (dt, *J* = 10.8, 1.5, 1 H), 5.29 (dtd, *J* = 17.4, 1.6, 0.4, 1 H), 5.79 (ddd, *J* = 17.3, 10.7, 5.6, 1 H), 7.25–7.35 (m, 5 H); MS *m/e* (relative intensity) 203 (M^+, 21), 202 (12), 146 (71), 103 (19), 91 (100); HRMS (*m/e*) 203.1297, calcd for $C_{13}H_{17}NO$ 203.1310. **6a** (PLC, hexane–ethyl acetate = 1:1 (v/v); MPLC, hexane–ethyl acetate = 3:2 (v/v)): mp 148.5–150.2 °C; IR (KBr, cm^{-1}) 1645, 1320, 1150, 820, 665; ^1H NMR (200 MHz) 1.90–2.05 (m, 2 H), 2.43 (s, 6 H) 3.29 (t, *J* = 5.7, 4 H), 3.90 (d, *J* = 5.6, 4 H), 5.72 (t, *J* = 4.2, 2 H), 7.33 (d, *J* = 8.3, 4 H), 7.68 (d, *J* = 8.2, 4 H); ^{13}C NMR 21.5, 30.5, 47.5, 47.8, 127.2, 128.8, 129.7, 135.1, 143.5; MS *m/e* (relative intensity) 434 (M^+, 2), 280 (17), 279 (100), 155 (10), 123 (14), 82 (15). Anal. Calcd for $C_{21}H_{26}N_2O_4S_2$: C, 58.04; H, 6.03; N, 6.45; S, 14.76. Found: C, 57.57; H, 5.97; N, 6.39; S, 14.64. **6b** (PLC, hexane–ethyl acetate = 1:1 (v/v); MPLC, chloroform–ethyl acetate = 1:1 (v/v)): mp 227.5–229.5 °C; IR (KBr, cm^{-1}) 1320, 1145, 805, 670; ^1H NMR (200 MHz) 1.55–1.85 (m, 4 H), 2.43 (s, 6 H), 2.93 (br s, 2 H), 3.08 (br s, 2 H), 3.47 (br s, 2 H), 3.91 (br s, 2 H), 5.77 (t, *J* = 4.0, 2 H), 7.32 (d, *J* = 8.8, 4 H), 7.68 (d, *J* = 8.3, 4 H); MS *m/e* (relative intensity) 354 (4), 207 (9), 197 (6), 44 (100). HRMS did not also produce the parent peak. Anal. Calcd for $C_{22}H_{28}N_2O_4S_2$: C, 58.90; H, 6.29; N, 6.24; S, 14.29. Found: C, 57.99; H, 6.24; N, 6.12; S, 14.04. The purity of the product **6b** judged by ^1H NMR spectral determination was ≥95%.

Supplementary Material Available: ^1H NMR spectra showing the purity of the products **4a–c**, **4f**, and **6b** (5 pages). Ordering information is given on any current masthead page.

(8) Araki, T.; Kubo, Y.; Gohbara, S.; Fujimoto, T.; Notsu, A.; Nakahara, M.; Isono, T.; Masuda, N.; Fukumoto, K. *Macromolecules* **1988**, *21*, 1995.

(9) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, T. A. *J. Organomet. Chem.* **1974**, *65*, 253.

(10) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

A Facile Synthesis of 2-Acetonylcycloalkanones by Using 2-(Halomethyl)-3,5-dioxahex-1-ene

Xue-Ping Gu, Yoichi Kirito, Isao Ikeda, and Mitsuo Okahara*

Department of Applied Chemistry Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan

Received April 7, 1989

Many biologically active natural products are characterized by a cyclopentenone moiety as a main structural feature, hence an interest exists in developing new synthetic routes to substituted cyclopentenones.[1] One important method for obtaining cyclopentenones depends on

(1) Ellison, R. A. *Synthesis* **1973**, 397.

0022-3263/90/1955-3390$02.50/0 © 1990 American Chemical Society