[Chem. Pharm. Bull. 30(1) 119—124 (1982)]

New Methods and Reagents in Organic Synthesis. 18.[1] Homologation of Ketones with Trimethylsilyldiazomethane ($TMSCHN_2$)[2]

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(Received June 5, 1981)

Trimethylsilyldiazomethane ($TMSCHN_2$) easily reacts with various ketones in the presence of boron trifluoride etherate in methylene chloride solution to give chain- or ring-homologated ketones, and can be used as a stable and safe substitute for hazardous diazomethane. The reaction proceeds below 0°C during 1—4 h, and permits much more efficient homologation than can be achieved with diazomethane.

Keywords——trimethylsilyldiazomethane; homologation; boron trifluoride; ketone; ring enlargement; diazomethane

In our previous paper[1] of this series, we proposed the use of trimethylsilyldiazomethane ($TMSCHN_2$, $(CH_3)_3SiCHN_2$) as a stable and safe substitute for hazardous diazomethane, and we reported that the homologation of carboxylic acids can be conveniently carried out by the use of $TMSCHN_2$ as the Arndt-Eistert synthesis with diazomethane. We now wish to report that the chain or ring homologation of ketones[3] can be efficiently achieved with $TMSCHN_2$ in the presence of boron trifluoride etherate. The overall process is depicted in Chart 1.

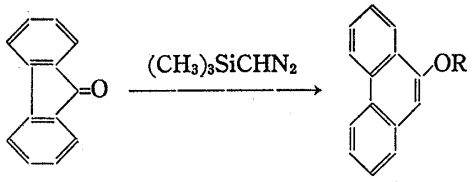
$$RCOR' \xrightarrow[BF_3\cdot(C_2H_5)_2O]{(CH_3)_3SiCHN_2} [RCOCHR' \longrightarrow RC{=}CHR'] \longrightarrow RCOCH_2R'$$

Chart 1

We first investigated the ring enlargement of 9-fluorenone (**1**)[4] with $TMSCHN_2$. Reaction of **1** with diazomethane was reported[5] to give a mixture of 9-phenanthrol (**2a**, 5%) and 9-methoxyphenanthrene (**2b**, 30%), the latter of which was produced from **2a** with an excess of diazomethane. Later, Eistert and El-Chahawi[6] modified the reaction conditions and increased the yield of **2b** to 90%. Since **2a**, the primary ring-enlarged product, was not the major product in either case, we thought it was worth trying to improve the yield of **2a**. As shown in Table I, however, simple mixing of **1** with $TMSCHN_2$ in diethyl ether did not give any products, even after a week. Addition of methanol, known as an accelerator of the homologation with diazomethane,[3] to the above mixture resulted in slight reaction to give **2a** and **2b**, though in low yields. Boron trifluoride etherate[7] was much more effective, furnishing **2a** in 44% yield accompanied with 9-trimethylsilyloxyphenanthrene (**2c**) in 7% yield. Increase of the amount of boron trifluoride etherate accelerated the reaction to give **2a** in 83% yield together with small amounts of **2b** and 9-ethoxyphenanthrene (**2d**). A small amount of the silyl ether **2c** is presumably formed in this case, but it would undergo hydrolysis to give **2a** during column chromatography on silica gel. Changing the reaction solvent from diethyl ether to methylene chloride resulted in easier ring-enlargement with $TMSCHN_2$. In this case, water was added to the reaction mixture after the homologation reaction and the mixture was refluxed for 1 h to hydrolyze a presumed intermediate **2c** and to permit the easy isolation of **2a**, as described in "Experimental."

In contrast with the result using diazomethane, in which the major product was 9-methoxyphenanthrene (**2b**),[5,6] the major product was 9-phenanthrol (**2a**) when $TMSCHN_2$

Table I. Reaction of 9-Fluorenone with $TMSCHN_2$



2a: R=H
2b: R=CH_3
2c: R=$(CH_3)_3Si$
2d: R=CH_3CH_2

Run	$(CH_3)_3SiCHN_2$ (eq)	$BF_3\cdot(C_2H_5)_2O$ (eq)	Reaction			Yield (%)			
			Solvent	Temp. (°C)	Time (h)	2a	2b	2c	2d
1	1.2	—	$(C_2H_5)_2O$	2	8 d	—	—	—	—
2	2.0	—	$(C_2H_5)_2O$ -CH_3OH	2	47	10	11	—	—
3	1.2	0.1	$(C_2H_5)_2O$	Room temp.	20	44	—	7	—
4	1.5	1.5	$(C_2H_5)_2O$	−10 Room temp.	0.4 3.5	83	4	—	4
5	1.5	1.5	CH_2Cl_2	−15——10	3	80	4	—	—

was used. The initial product of the ring enlargement with $TMSCHN_2$ might be the β-ketosilane **3**, which would undergo rearrangement[8] to give the silyl ether **2c**, shown in Chart 2. Hydrolysis of **2c** would finally afford **2a**. Alternatively, **2c** might be attacked by boron trifluoride during the reaction to give the boranate **2e**, which would furnish **2a** after aqueous treatment.[9] The intermediate formation of **3**, **2c**, and/or **2e** would ultimately lead to **2a** as the major product instead of **2b**.

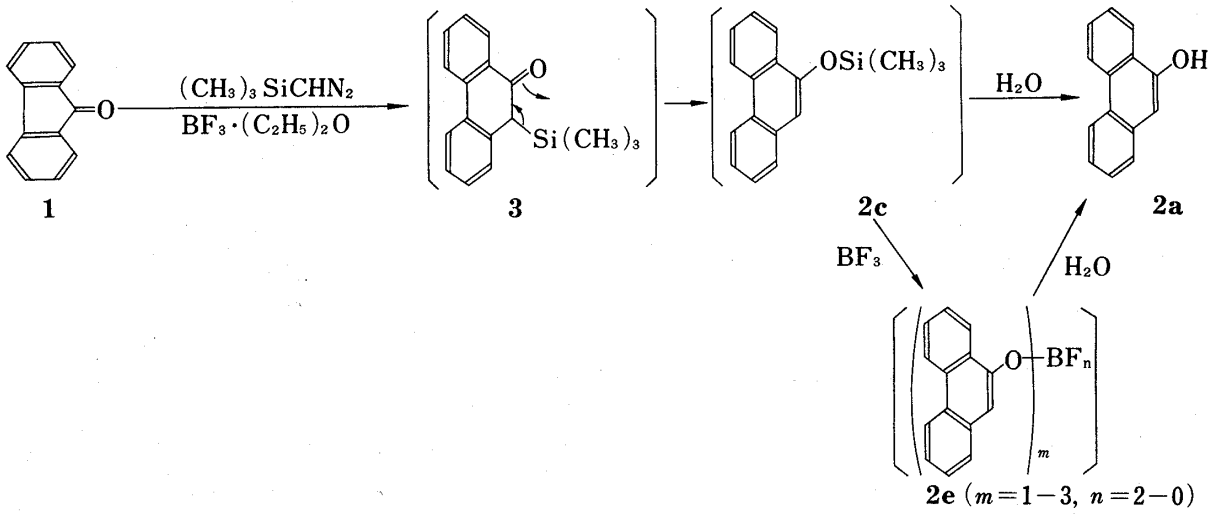
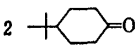
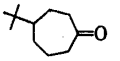
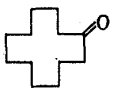
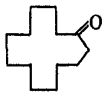
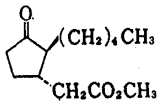
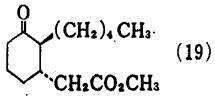
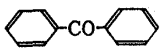
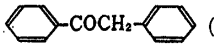
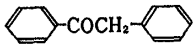
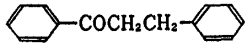


Chart 2

The other cyclic ketones, except methyl dihydrojasmonate, smoothly underwent ring enlargement with $TMSCHN_2$–boron trifluoride etherate in methylene chloride, giving the homologous ketones in good yields. The homologation yields with $TMSCHN_2$–boron trifluoride etherate are compared with those with diazomethane in Table II. In the homologation of 2-methylcyclohexanone with $TMSCHN_2$, the insertion of a methylene group occurred predominantly from the less hindered side to give mainly 2-methylcyclohexanone, whereas the homologation with diazomethane[10] showed no regioselectivity and a mixture of 2-methylcycloheptanone, 3-methylcycloheptanone, and 1,1-epoxymethylene-2-methylcyclohexane was obtained in 10, 7, and 26% yields, respectively. Methyl dihydrojasmonate also gave a ring-enlarged product in which a methylene group derived from $TMSCHN_2$ was inserted from the less

TABLE II. Homologation of Ketones with $TMSCHN_2$–BF_3·$(C_2H_5)_2O$ in Methylene Chloride

Run	Ketone	Product (Yield, %)
1		 (57) [33–36][a,b]  (5)
2		 (70) [55][a,c]
3		 (69) [10][a,d]
4		 (72)
5		 (19)
6	$CH_3CO(CH_2)_8CH_3$[e]	$CH_3CO(CH_2)_9CH_3$ (25) $CH_3CH_2CO(CH_2)_8CH_3$ (24)
7		 (27)
8		 (74)

a) Yield with the use of diazomethane.
b) Th. J. de Boer and H.J. Backer, "Org. Syntheses," Col. Vol. 4, 1963, p. 225.
c) T. Nozoe, H. Kishi, and A. Yoshikoshi, *Proc. Japan Acad.*, **27**, 149 (1951) [*C.A.*, **46**, 4523 (1952)].
d) D.W. Adamson and J. Kenner, *J. Chem. Soc.*, 1939, 181.
e) The reaction was carried out in diethyl ether.

hindered side. The high regioselectivity of the methylene insertion with $TMSCHN_2$ is presumably due to the bulky trimethylsilyl group of $TMSCHN_2$. Reaction of 2-undecanone with $TMSCHN_2$ was carried out in diethyl ether to furnish a mixture of 2- and 3-dodecanone in almost equal amounts, while the reaction with diazomethane gave 1,2-epoxy-2-methylundecane as the sole product.[11] Even if the epoxide is once formed with $TMSCHN_2$, boron trifluoride etherate would transform it to the homologated ketones.[7] Benzophenone has been described[12] as "unreactive toward diazomethane," but $TMSCHN_2$ reacted with benzophenone in the presence of boron trifluoride etherate to give deoxybenzoin, though in low yield. Deoxybenzoin predominantly afforded dihydrochalcone. A methylene group was again inserted from the less hindered side in this case.

Homologation of ketones with $TMSCHN_2$ proceeds smoothly with much higher efficiency and regioselectivity than that with diazomethane and can be conducted without risk of explosion. Thus, stable and safe $TMSCHN_2$ can replace hazardous diazomethane and should find wide use in organic synthesis.[1,13]

Experimental

^{1}H-NMR spectra were recorded on a JEOL JNM-MH-100 spectrometer with tetramethylsilane as an internal standard. IR spectra were obtained using a JASCO IRA-2 spectrometer. Mass spectra were measured with a Hitachi M-52 mass spectrometer. GLC analyses were performed on a JEOL JGC-750 chromatograph. All melting points and boiling points are uncorrected. Silica gel (70—230 mesh ASTM, Merck Art. 7734) was used for column chromatography. Preparative layer chromatography (PLC) was carried out on plates (20 cm × 20 cm, 2 mm thick) precoated with silica gel $60F_{254}$ (Merck). $TMSCHN_2$

used for the homologation was a mixture of trimethylsilyldiazomethane (61 w/w%) and hexamethyldisiloxane (39 w/w%).[1] Methylene chloride was dried by distillation over phosphorus pentoxide.

Reaction of 9-Fluorenone (1) with $TMSCHN_2$——(a) To a stirred mixture of 9-fluorenone (**1**) (900 mg, 5 mmol) in diethyl ether–methanol (1: 2, 15 ml) was added $TMSCHN_2$ (1872 mg, 10 mmol) at 2°C. The whole was stirred at the same temperature for 47 h, then evaporated to dryness. Diethyl ether was added to the residue, and the mixture was extracted with 10% aqueous sodium hydroxide. The alkaline extract was made acidic with 10% aqueous hydrochloric acid and extracted with diethyl ether. The ethereal extracts were washed with saturated aqueous sodium chloride, dried over sodium sulfate, and concentrated to give 9-phenanthrol (**2a**) (101 mg, 10%), mp 153—155°C (brown needles from benzene) (lit.,[5] mp 153—155°C). IR ν_{max}^{Nujol} cm^{-1}: 3250 (OH). NMR (δ in $CDCl_3$): 5.30 (1H, s, OH), 7.02—8.80 (9H, m, aromatic H).

The first ether layer was washed with saturated aqueous sodium chloride, and dried over sodium sulfate. Removal of the solvent by evaporation gave a yellow oil, which was purified by silica gel column chromatography (benzene–hexane=1: 10) to give 9-methoxyphenanthrene (**2b**) (116 mg, 11%), mp 93—94.5°C (colorless needles from methanol), (lit.,[5] mp 95—96°C). NMR (δ in $CDCl_3$): 4.07 (3H, s, OCH_3), 6.95—8.70 (9H, m, aromatic H).

(b) To a stirred mixture of **1** (540 mg, 3 mmol) and boron trifluoride etherate (0.038 ml, 0.3 mmol) in diethyl ether (10 ml) was added dropwise a solution of $TMSCHN_2$ (674 mg, 3.6 mmol) in diethyl ether (10 ml) at 0°C. The mixture was stirred at room temperature for 20 h, and then treated with 10% aqueous sodium hydroxide (10 ml). After the separation of the alkaline layer, the ether layer was extracted with 10% aqueous sodium hydroxide. The combined alkaline layer was worked up as described above for (a) to give **2a** (100 mg, 17%).

The ether layer was washed with saturated aqueous sodium chloride and dried over sodium sulfate. Removal of the solvent by evaporation gave a yellow oil, which was purified by silica gel column chromatography (hexane–benzene=10: 1).

The first eluate fraction afforded 9-trimethylsilyloxyphenanthrene (**2c**) (57 mg, 7%), mp 80—83°C (colorless needles from methanol). IR ν_{max}^{Nujol} cm^{-1}: 1250, 850 (Si–CH_3). NMR (δ in $CDCl_3$): 0.40 (9H, s, $Si(CH_3)_3$), 7.10—8.80 (9H, m, aromatic H). MS *m/e*: 266 (M^+). *Anal.* Calcd for $C_{17}H_{18}OSi$: C, 76.64; H, 6.81. Found: C, 76.00; H, 6.73.

The second eluate fraction afforded the starting ketone (**1**) (202 mg, 37%).

The third eluate fraction afforded **2a** (160 mg, 27%). Total yield of **2a** was 260 mg (44%).

(c) To a stirred mixture of **1** (540 mg, 3 mmol) and boron trifluoride etherate (0.57 ml, 4.5 mmol) in diethyl ether (10 ml) was added dropwise a solution of $TMSCHN_2$ (842 mg, 4.5 mmol) in diethyl ether (10 ml) at −10°C during 25 min. The mixture was stirred at room temperature for 3.5 h, and then treated with 5% aqueous sodium hydroxide. After the separation of the alkaline layer, the ether layer was extracted with 5% aqueous sodium hydroxide. The combined alkaline layer was worked up as described above for (a) to give **2a** (428 mg, 73.5%).

The ether layer was washed with saturated aqueous sodium chloride and dried over sodium sulfate. Removal of the solvent by evaporation gave a yellow oil, which was purified by silica gel column chromatography (hexane–benzene=10: 1).

The first eluate fraction afforded a colorless solid (53 mg). NMR analysis of the solid showed the presence of **2b** (25 mg, 4%) and 9-ethoxyphenanthrene (**2d**) (27 mg, 4%). NMR (δ in $CDCl_3$): 1.60 (3H, t, J=7 Hz, CH_3CH_2O), 4.06 (3H, s, OCH_3), 4.28 (2H, q, J=7 Hz, CH_3CH_2O), 6.96—8.80 (18H, m, aromatic H). MS *m/e*: 222 (M^+ for **2d**), 208 (M^+ for **2b**).

The second eluate fraction afforded a brown solid, which was recrystallized from benzene–hexane to give **2a** (56 mg, 9.7%). Total yield of **2a** was 484 mg (83%).

(d) To a stirred mixture of **1** (450 mg, 2.5 mmol) and boron trifluoride etherate (0.48 ml, 3.75 mmol) in methylene chloride (10 ml) was added dropwise a solution of $TMSCHN_2$ (702 mg, 3.75 mmol) in methylene chloride (10 ml) at −15°C during 30 min, and then the whole was stirred at −15——10°C for 2.5 h. Water (10 ml) was added, and the whole was stirred under reflux for 1 h. After the separation of the organic layer, the aqueous layer was extracted with chloroform. The combined organic layer was washed with saturated aqueous sodium chloride, and dried over sodium sulfate. Removal of the solvent by evaporation gave a brown solid, which was purified by silica gel column chromatography (hexane–benzene=10: 1) to give **2b** (20 mg, 4%) and **2a** (388 mg, 80%).

Reaction of Cyclohexanone with $TMSCHN_2$——To a stirred mixture of cyclohexanone (249 mg, 3 mmol) and boron trifluoride etherate (0.57 ml, 4.5 mmol) in methylene chloride (10 ml) was added dropwise a solution of $TMSCHN_2$ (842 mg, 4.5 mmol) in methylene chloride (10 ml) at −45°C during 20 min. The whole was stirred at −45——40°C for 1.2 h, and then treated with ice-water. After separation of the organic layer, the aqueous layer was extracted with methylene chloride. The combined organic layer was washed with saturated aqueous sodium chloride, and dried over sodium sulfate. Removal of the solvent by evaporation gave a yellow oil, which was purified by PLC (benzene–ethyl acetate=10: 1) to give a colorless oil (220 mg). GLC analysis (20% Tergitol NP 35; 4-*tert*-butylcyclohexanone as an internal standard) of the oil showed the presence of cycloheptanone (192 mg, 57%) and cyclooctanone (19 mg, 5%).

Reaction of 4-*tert*-Butylcyclohexanone with $TMSCHN_2$——As described above for the homologation of cyclohexanone, 4-*tert*-butylcyclohexanone (162 mg (95% purity), 1 mmol), $TMSCHN_2$ (281 mg, 1.5 mmol), and boron trifluoride etherate (0.19 ml, 1.5 mmol) were allowed to react in methylene chloride (20 ml) at −13——10°C for 2.3 h, and then the mixture was treated with ice-water. The resulting mixture was worked up as usual to afford a yellow oil, which was purified by silica gel column chromatography (hexane–ethyl acetate=20: 1) to give 4-*tert*-butylcycloheptanone (117 mg, 70%) as a colorless oil. IR ν_{max}^{Film} cm^{-1}: 1700 (C=O). NMR (δ in $CDCl_3$): 0.90 (9H, s, $C(CH_3)_3$), 1.00—2.30 (7H, m, $-CH_2CH_2CHCH_2-$), 2.30—2.50 (4H, m, CH_2COCH_2). MS *m/e*: 168 (M^+). *Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.36; H, 12.21.

Reaction of 2-Methylcyclohexanone with $TMSCHN_2$——As described above for the homologation of cyclohexanone, 2-methylcyclohexanone (112 mg, 1 mmol), $TMSCHN_2$ (281 mg, 1.5 mmol), and boron trifluoride etherate (0.19 ml, 1.5 mmol) were allowed to react in methylene chloride (20 ml) at −15°C for 4 h, and then the mixture was treated with saturated aqueous sodium carbonate. The resulting mixture was worked up as usual to afford a yellow oil, which was purified by distillation to give 2-methylcycloheptanone (87 mg, 69%) as a colorless oil, bp 100—103°C (45 mmHg). IR ν_{max}^{Film} cm^{-1}: 1700 (C=O). NMR (δ in $CDCl_3$): 1.06 (3H, d, J=6 Hz, CH_3), 1.20—2.00 (8H, m, $-(CH_2)_4-$), 2.30—2.78 (3H, m, $CHCOCH_2$).

2,4-Dinitrophenylhydrazone, mp 117.5—119°C (orange needles from ethanol) (lit.,[14] mp 121—122°C).

Reaction of Cyclododecanone with $TMSCHN_2$——As described above for the homologation of cyclohexanone, cyclododecanone (182 mg, 1 mmol), $TMSCHN_2$ (281 mg, 1.5 mmol), and boron trifluoride etherate (0.19 ml, 1.5 mmol) were allowed to react in methylene chloride (20 ml) at −13——10°C for 2 h. Methanol (10 ml) was added to the mixture, and the whole was stirred under reflux for 30 min, and then concentrated. The residual oil was purified by silica gel column chromatography (hexane–ethyl acetate=20: 1) to give crude cyclotridecanone (175 mg) as a colorless oil. A solution of crude cyclotridecanone (175 mg) in methanol (5 ml) was added to a mixture of 2,4-dinitrophenylhydrazine (200 mg) and concentrated hydrochloric acid (10 drops) in methanol (20 ml), and the mixture was stirred at 50°C for 3 min, then at room temperature for 10 min. After addition of water, the resulting precipitate was collected by filtration, washed with water and dried to give the 2,4-dinitrophenylhydrazone of cyclotridecanone (270 mg, 72%) as orange needles, mp 112—113°C. *Anal.* Calcd for $C_{19}H_{28}N_4O_4$: C, 60.62; H, 7.54; N, 14.88. Found: C, 60.29; H, 7.45; N, 14.62.

Semicarbazone, mp 204.5—209°C (colorless needles from ethanol) (lit.,[15] mp 206—207°C).

Reaction of Methyl Dihydrojasmonate with $TMSCHN_2$——As described above for the homologation of cyclohexanone, methyl dihydrojasmonate (452 mg, 2 mmol), $TMSCHN_2$ (562 mg, 3 mmol), and boron trifluoride etherate (0.38 ml, 3 mmol) were allowed to react in methylene chloride (20 ml) at −13—0°C for 2.3 h, and then the mixture was treated with saturated aqueous sodium carbonate. The resulting mixture was worked up as usual to afford a yellow oil, which was purified by silica gel column chromatography (hexane–diethyl ether=10: 1) to give 3-methoxycarbonylmethyl-2-pentylcyclohexanone (91 mg, 19%) as a colorless oil, bp 106°C (0.22 mmHg). IR ν_{max}^{Film} cm^{-1}: 1733 (C=O), 1709 (C=O). NMR (δ in $CDCl_3$): 0.88 (3H, t, J= 5 Hz, $CH_3(CH_2)_4-$), 1.26 (6H, broad s, $CH_3(CH_2)_3CH_2-$), 1.44—1.96 (7H, m, H–C(3), H_2–C(4), H_2–C(5), $CH_3(CH_2)_3CH_2-$), 2.00—2.60 (5H, m, H–C(2), H_2–C(6), CH_2CO), 3.64 (3H, s, $COOCH_3$). MS *m/e*: 240 (M^+).

2,4-Dinitrophenylhydrazone, mp 112—114°C (yellow powder from ethyl acetate). *Anal.* Calcd for $C_{20}H_{28}N_4O_6$: C, 57.13; H, 6.71; N, 13.32. Found: C, 56.53; H, 6.36; N, 13.27.

Reaction of 2-Undecanone with $TMSCHN_2$——As described above for the homologation of cyclohexanone, 2-undecanone (180 mg, 1.06 mmol), $TMSCHN_2$ (281 mg, 1.5 mmol), and boron trifluoride etherate (0.19 ml, 1.5 mmol) were allowed to react in diethyl ether (20 ml) at −10°C for 2.5 h, and then the mixture was treated with water. The resulting mixture was worked up as usual to afford a yellow oil, which was purified by PLC (benzene) to give a colorless oil. The oil was further purified by silica gel column chromatography (benzene–hexane=1: 5). The first eluate fraction afforded 3-dodecanone (47 mg, 24%). IR ν_{max}^{Film} cm^{-1}: 1715 (C=O). NMR (δ in $CDCl_3$): 0.76—0.96 (3H, m, $CH_3(CH_2)_6$), 1.04 (3H, t, J=8 Hz, $COCH_2CH_3$), 1.26 (12H, broad s, $(CH_2)_6CH_3$), 1.40—1.72 (2H, m, CH_2CH_2CO), 2.36 (2H, t, J=7 Hz, CH_2CH_2CO), 2.42 (2H, q, J=8 Hz, $COCH_2CH_3$). Semicarbazone, mp 84—85°C (colorless needles from methanol) (lit.,[16] mp 86°C).

The second eluate fraction afforded 2-dodecanone (49 mg, 25%). IR ν_{max}^{Film} cm^{-1}: 1720 (C=O). NMR (δ in $CDCl_3$): 0.76—1.00 (3H, m, $CH_3(CH_2)_7$), 1.26 (14H, broad s, $CH_3(CH_2)_7$), 1.48—1.80 (2H, m, CH_2CH_2CO), 2.12 (3H, s, $COCH_3$), 2.40 (2H, t, J=8 Hz, CH_2CH_2CO). 2,4-Dinitrophenylhydrazone, mp 78—79°C (yellow needles from ethanol) (lit.,[17] mp 81°C).

Reaction of Benzophenone with $TMSCHN_2$——As described above for the homologation of cyclohexanone, benzophenone (274 mg, 1.5 mmol), $TMSCHN_2$ (374 mg, 2 mmol), and boron trifluoride etherate (0.26 ml, 2 mmol) were allowed to react in methylene chloride (20 ml) at −5°C for 2.5 h, and then the mixture was treated with 2% aqueous sodium hydroxide. The resulting mixture was worked up as usual to afford a yellow oil, which was purified by PLC (hexane–ethyl acetate–diethyl ether=15: 1: 1) to give a colorless oil (150 mg). NMR analysis of the oil showed the presence of deoxybenzoin (79 mg, 27%) and the starting ketone (71 mg, 26%). Deoxybenzoin was isolated by silica gel column chromatography (hexane–diethyl ether=40: 1); mp 50—51.5°C (colorless needles from ethanol) (lit.,[18] mp 55—56°C). IR ν_{max}^{Nujol} cm^{-1}: 1675 (C=O). NMR (δ in $CDCl_3$): 4.25 (2H, s, CH_2CO), 7.20—8.00 (10H, m, aromatic H).

Reaction of Deoxybenzoin with $TMSCHN_2$——As described above for the homologation of cyclohexanone, deoxybenzoin (294 mg, 1.5 mmol), $TMSCHN_2$ (421 mg, 2.25 mmol), and boron trifluoride etherate (0.28 ml, 2.25 mmol) were allowed to react in methylene chloride (20 ml) at −17——−15°C for 1 h, and the mixture was treated with ice-water. The resulting mixture was worked up as usual to afford a yellow oil, which was purified by silica gel column chromatography (benzene–hexane=2: 1) to give dihydrochalcone (234 mg, 74%), mp 70—71.5°C (colorless scales from hexane) (lit.,[19] mp 72—73°C). IR ν_{max}^{Nujol} cm^{-1}: 1682 (C=O). NMR (δ in $CDCl_3$): 2.92—3.48 (4H, m, CH_2CH_2CO), 7.25—7.95 (10H, m, aromatic H).

Acknowledgement This work was supported in part by the Naito Foundation, to which our thanks are due. One of the authors (N. H.) is grateful to the Miyata Research Foundation for a research fellowship. We are grateful to Dr. K. Miki of Takasago Perfumery Co. Ltd. for a gift of methyl dihydrojasmonate.

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