2.10–2.45 (m, methylene), 1.61 (br s, methylene); IR (neat) 1699, 1668, 1587 $cm^{-1}$; MS, $m/z$ 310 ($M^+$). Anal. Calcd for $C_{20}H_{19}ClO$: C, 77.28; H, 6.16. Found: C, 77.10; H, 6.05.

**α-Cyclohexylidenebenzyl 3-methylphenyl ketone (8j)**: colorless crystal; mp 72.0–72.5 °C; $^{13}C$ NMR ($CDCl_3$) δ 198.6 (s), 141.9 (s), 138.1 (s), 136.9 (s), 136.5 (s), 133.7 (d), 133.4 (s), 129.6 (d), 129.0 (d), 128.2 (d), 128.0 (d), 127.0 (d), 126.8 (d), 32.9 (t), 30.7 (t), 28.1 (t), 27.8 (t), 26.2 (t), 21.1 (q); $^1H$ NMR (100 MHz, $CDCl_3$) δ 7.12–7.85 (m, Ar, 9 H), 2.33 (s, $CH_3$, 3 H), 2.14–2.25 (m, methylene, 4 H), 1.57 (br s, methylene, 6 H); IR (KBr) 1658, 1597 $cm^{-1}$; MS, $m/z$ 290 ($M^+$). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.69; H, 7.75.

**α-Cyclohexylidenebenzyl 3-chlorophenyl ketone (8k)**: colorless crystal; mp 60–61 °C; $^{13}C$ NMR ($CDCl_3$) δ 197.1 (s), 143.5 (s), 138.7 (s), 136.2 (s), 134.8 (s), 133.0 (s), 132.9 (d), 129.8 (d), 129.2 (d), 128.3 (d), 127.7 (d), 127.2 (d), 33.1 (t), 30.9 (t), 28.2 (t), 27.9 (t), 26.2 (t); $^1H$ NMR (100 MHz, $CDCl_3$) δ 7.27–7.96 (m, Ar, 9 H), 2.02–2.30 (m, methylene, 4 H), 1.60 (br s, methylene, 6 H); IR (KBr) 1657, 1635, 1587, 1570 $cm^{-1}$; MS, $m/z$ 310 ($M^+$). Anal. Calcd for $C_{20}H_{19}ClO$: C, 77.28; H, 6.16. Found: C, 77.12; H, 6.12.

**Reaction of 2-Phenylbutyryl Chloride (6) with Aryl Halide.** A mixture of 2-phenylbutyryl chloride (1 mmol, 0.17 mL), aryl halide (1 mmol), triethylamine (3 mmol, 0.42 mL), and $Pd(PPh_3)_4$ (0.05 mmol, 0.058 g) in 5 mL of THF was placed in a 50-mL stainless steel autoclave under an argon atmosphere and stirred at 120 °C for 5 h. The product (**4a**) was identified by comparing GLC and FT-IR with those of the authentic sample.

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# 2-(Chloromethyl)-3,5-dioxahex-1-ene. An Effective Acetonylating Reagent

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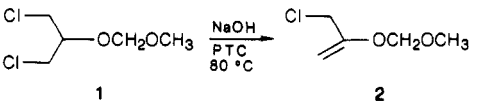
By β-elimination of 2-chloro-1-(chloromethyl)ethyl methoxymethyl ether (1) under solid–liquid phase-transfer catalytic conditions, 2-(chloromethyl)-3,5-dioxahex-1-ene (2) of high purity was readily obtained in 85%. Allyl chloride **2** is found to be stable at ambient conditions and to be a superior reagent as $CH_3COCH_2^+$ synthon for converting active proton-containing compounds such as carboxylic acids, amines, phenols, alcohols, thiols, malonate, β-diketones, β-keto esters, phenylacetonitrile, fluorene, and indene to the corresponding acetonyl derivatives in good to excellent yields (61–93%), usually under phase-transfer catalytic conditions or in a *t*-BuONa–*t*-BuOH system.

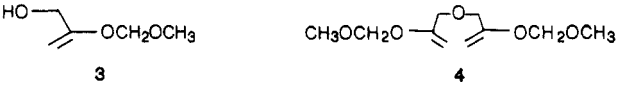
The acetonyl unit is one of the most basic functional groups due to its high and versatile reactivity, and introduction of this group has become a very important operation in organic synthesis. Until now, several kinds of reagents for introduction of acetonyl groups have been described. One of the most useful compounds among them, methoxyallyl bromide, developed by Horning[1] and Jacobson,[2] has attracted attention as a masked electrophilic acetonylation reagent. This reagent, however, requires some care in its preparation and preservation, for example, as they mentioned, high pyrolytic temperatures, inevitable side reactions, difficult isolation, and instability to polymerization.[1-3] Since the review concerning acetonylating reagents was published in 1978,[4] several new methods have been developed. A free-radical acetonylation has been applied successfully,[5] although the vigorous conditions that were necessary for the free-radical reaction led inevitably to isomerization. Kjonaas used dilithio acetoacetate as an acetone enolate equivalent for substitution of halogen by an acetonyl group.[6] Alkylation of

**Scheme I**




1 2

**Scheme II**



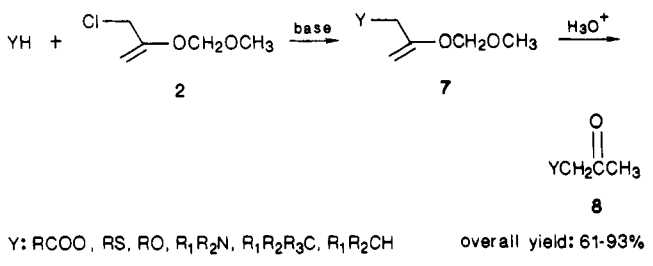

3 4

β-dicarbonyl compounds with 3-acetoxy-2-chloroprop-1-ene in the presence of palladium(II) acetate as a catalyst was also reported.[7] 3-Acetonyl-2-methyl-1,4-naphthoquinone was synthesized by photochemical reaction of 2-methyl-1,4-naphthoquinone with isopropenyl methyl ether and subsequent oxidation of the photoproduct under acidic conditions.[8] These methods have certain drawbacks either in preparation or use or in both. In our attempts to extend the utility of 2-chloro-1-(chloromethyl)ethyl methoxymethyl ether (1), we have found that **1** is a useful reagent for conversion of hydroxyl compounds to the corresponding acetonyl ethers in good yields.[9] This made us desire the development of an effective method for introducing an acetonyl unit by substituting the protons of other active

(1) Horning, D. E.; Kavadias, G.; Muchowski, M. *Can. J. Chem.* **1970**, *48*, 975.
(2) Jacobson, R. M.; Raths, R. A.; McDonald, J. H., III *J. Org. Chem.* **1977**, *42*, 2545.
(3) Greenwood, G.; Hoffmann, H. M. R. *J. Org. Chem.* **1972**, *37*, 611.
(4) Nakai, T. *J. Synth. Org. Chem. Jpn.* **1978**, *36*, 49; *Chem. Abstr.* **1978**, *89*, 41560p.
(5) Jaouhari, R.; Maillard, B.; Filliatre, C.; Villenave, J. *Synthesis* **1982**, 760.
(6) Kjonaas, R. A.; Patel, D. D. *Tetrahedron Lett.* **1984**, *25*, 5467.
(7) Schuda, P. F.; Bernstein, B. *Synth. Commun.* **1984**, *14*, 293.
(8) Maruyama, K.; Tai, S. *Chem. Lett.* **1985**, 681.
(9) Gu, X.-P.; Ikeda, I.; Komada, S.; Masuyama, A.; Okahara, M. *J. Org. Chem.* **1986**, *51*, 5425.

0022-3263/87/1952-3192$01.50/0 

**Scheme III**




proton-containing compounds.

In this paper, we report a general and effective method for synthesis of acetonyl derivatives by the reaction of a series of active proton-containing compounds with the stable electrophilic reagent 2-(chloromethyl)-3,5-dioxahex-1-ene (**2**). Compound **2** was easily prepared in high yield from compound **1**, which was readily synthesized in 93% yield.[10]

## Results and Discussion

In the acetonylation of hydroxyl compounds using **1**, we suggested that 2-(chloromethyl)-3,5-dioxahex-1-ene (**2**) was first formed from **1** by β-elimination and then was attacked by an alkoxide anion, since compound **2** was also isolated.[9]

In this study, the preparation of **2** was carried out by treating **1** with 1.5 equiv of pulverized sodium hydroxide in the presence of tetrabutylammonium bisulfate as a phase-transfer (PT) catalyst at 80 °C under reduced pressure (about 30 Torr) (Scheme I). Under these conditions, **2** was immediately distilled into a receiver flask directly from the reaction mixture as soon as it formed during the course of the elimination reaction. Since the boiling points of **1** and **2** are 94–95 °C/30 Torr and 62–63 °C/35 Torr, respectively, the conditions of 80 °C at 30 Torr were the optimum both for dehydrohalogenation and isolation by distillation. The undesirable displacement reaction leading to allylic alcohol **3**, which would further react with **2** to form **4**, are avoided (Scheme II) by the short residence time of **2** in the reaction system. The reaction was completed within 2.5 h (on the 70-g scale) and **2** was obtained in a yield of 85% as a product pure enough to employ in further reactions without redistillation. This procedure worked well on the present experimental scale, 10–270 g. These results may suggest that the scale of this reaction can be enlarged without any serious problems or decrease in the yield. Allyl chloride **2** is stable at room temperature, at least for 1 year.

Also the preparation of 2-(iodomethyl)-3,5-dioxahex-1-ene (**5**) and 2-(bromomethyl)-3,5-dioxahex-1-ene (**6**) from **2** by halide exchange reaction under PT catalytic conditions was investigated. Iodide **5** was obtained in yield of 74% by treating **2** with saturated aqueous potassium iodide at 80 °C for 3 h in the presence of sodium carbonate and a catalytic amount of tetrabutylammonium bisulfate. Iodide **5** was unstable and liberated a fair amount of iodine, and liquid **5** became dark yellow. GLC also showed the decomposition of **5** after 24 h at room temperature, but it is stable for about 1 month when stored in a refrigerator (below 0 °C). Preparation of the corresponding bromide **6** was also successful, and the conversion to **6** from **2** was 52%, estimated from GLC after a reaction period of 10 h under the same conditions as those for **5**.

Scheme III represents the acetonylation reactions investigated. The results are summarized in Table I.

(10) Gu, X.-P.; Ikeda, I.; Okahara, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 397.

Active proton-containing compounds such as a carboxylic acid (run 1), thiols (run 3, 4), alcohols (run 5–7), and a phenol (run 8) were alkylated with **2** in the presence of solid sodium hydroxide in dioxane under PT catalytic conditions to afford the corresponding allylated compounds **7**, which were further hydrolyzed in good to excellent overall yields (67–93%) to acetonyl compounds **8**. A secondary amine (run 2) was acetonylated under the same conditions as above but without PT catalyst, also in an excellent yield. Although the primary amine *n*-decylamine (run 17), as a typical example, was easily diallylated, the acidic hydrolysis in the next step was not successful by the usual procedure employed in this study.

In a reaction similar to our previous report concerning the stereoselective formation of allylic ethers by the reaction of epoxides with organic chlorides under liquid–solid phase-transfer catalysis,[11] *trans*-3-(phenylthio)allyl acetonyl ether (**17**, run 9) was also prepared by the reaction of **2** with phenyl glycidyl sulfide, followed by hydrolysis.

Acetonylation of active methylene compounds with **2** also proved successful. Malonate (run 10) and β-keto esters (run 11, 12) were readily monoalkylated with 1.1 equiv of **2** in the *t*-BuONa–*t*-BuOH system, giving good yields of allylated product. Hydrolysis to acetonyl compounds was also easily accomplished in dilute sulfuric acid. However, the allylation of a β-diketone (run 13) and indene (run 14) with 1.1 equiv of **2** had to be carried out in the presence of the PT catalyst even in the *t*-BuONa–*t*-BuOH system, followed by hydrolysis, to afford monoacetonyl compounds in good yields. In these cases, the monoacetonyl compounds were selectively formed. However when 2.2 equiv of **2** were used (another run of 12 in Table I), only a small amount (17%) of diacetonyl compound was obtained. On the contrary, fluorene (run 15) and phenylacetonitrile (run 16) gave mixtures of mono- and dialkylated compounds (about 1:1 estimated from the peak height of GLC) with the use of 1.1 equiv of **2**. Upon the use of 2.2 equiv of **2**, these compounds were easily dialkylated in the presence of the PT catalyst in the *t*-BuONa–*t*-BuOH system and afforded the corresponding diacetonyl compounds in good yields after hydrolysis.

As to the difference between these two groups of active methylene-containing compounds, it may be reasonable to assume that the second allylation of ethyl acetylacetate occurred mainly on oxygen and gave a complicated mixture on acidic hydrolysis due to intramolecular aldol condensation.

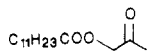
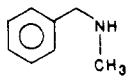
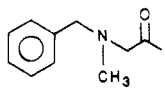
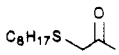
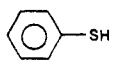
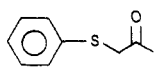
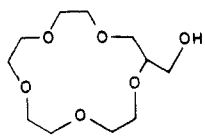
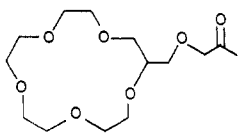
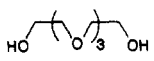
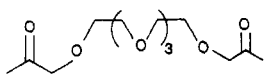
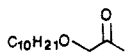
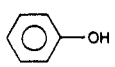
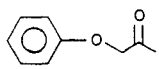
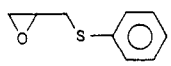
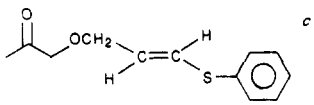
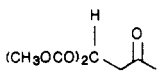
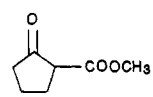
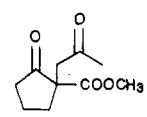
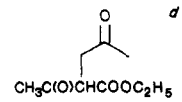
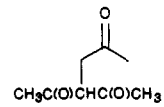
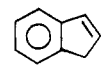
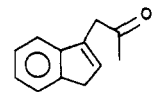
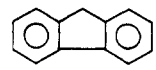
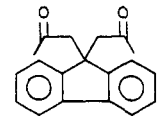
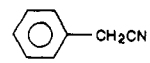
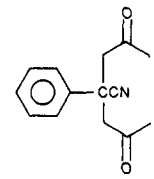
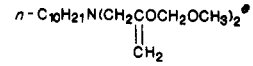
In the case of indene, the product obtained was 3-acetonylindene[12] rather than 1-acetonylindene. The product may result from the migration of the C=C double bond of a 1-substituted indene intermediate by proton shift.

In an another run for acetonylation of 2-(methoxycarbonyl)cyclopetanone (run 11), the allylation reaction with **2** was carried out in the presence of potassium iodide. Athough the yield is almost the same as that without potassium iodide, the reaction time was markedly shortened from 20 h to 2 h. This result may show that **5**, which is very reactive to allylation, is rapidly formed by halide exchange reaction. This fact is very favorable because it

(11) Gu, X.-P.; Ikeda, I.; Okahara, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 667.

(12) In order to confirm the substitution position, indene was methylated with iodomethane under the same reaction conditions as those for acetonylation. The product was confirmed to be 3-methylindene by comparison with the reported spectral data (*J. Org. Chem.* **1970**, *35*, 1876). However, the possibility of substitution at the 2-position cannot be excluded, since 1-acetonylideneindane was not observed which was reported to exist in equilibrium with 3-acetonylindene after treatment under acidic conditions (*J. Chem. Soc. C* **1969**, 944).

**Table I. Acetonylation[a] of Active Proton-Containing Compounds**

| run | starting material | product | yield, % |
|---|---|---|---|
| 1 | $C_{11}H_{23}COOH$ |  **9** | 93 |
| 2 |  |  **10** | 80 |
| 3 | $C_8H_{17}SH$ |  **11** | 82 |
| 4 |  |  **12** | 90 |
| 5 |  |  **13** | 80 |
| 6[b] |  |  **14** | 63 |
| 7 | $C_{10}H_{21}OH$ |  **15** | 74 |
| 8 |  |  **16** | 67 |
| 9 |  |  **17** [c] | 78 |
| 10 | $(CH_3OCO)_2CH_2$ |  **18** | 71 |
| 11 |  |  **19** | 61 |
| 12 | $CH_3C(O)CH_2CO$-$OC_2H_5$ |  **20** [d] | 68 |
| 13 | $CH_3C(O)CH_2$-$C(O)CH_3$ |  **21** | 64 |
| 14 |  |  **22** | 70 |
| 15[b] |  |  **23** | 78 |
| 16[b] |  |  **24** | 61 |
| 17 | $n$-$C_{10}H_{21}NH_2$ |  **25** [e] | 50 |

[a] 1.1 equiv of **2** were used. [b] 2.2 equiv of **2** were used. [c] The formation of allyl ethers by the rearrangement of epoxides was discussed in ref 11. [d] When 2.2 equiv of **2** were used, ethyl diacetonylacetylacetate was obtained in a yield of 17%. [e] Diallylated decylamine **25** was isolated in a yield of 50%. However, GLC showed the acidic hydrolysis product comprised a complicated mixture.

is unnecessary to prepare especially unstable **5** beforehand.

All the spectral data and elemental analyses obtained were consistent with the structures of acetonyl compounds **8** and the intermediate allyl compounds (**7**), which were also isolated by distillation at reduced pressure. Characterization of the intermediate allyl phenol was described in run 8 as a representative case.

2-(Chloromethyl)-3,5-dioxahex-1-ene (**2**) can be regarded as a superior acetonylation reagent from the following points: the easy and effective process for its preparation and isolation; its stability; and its high reactivity and versatility in allylation and the ready hydrolysis of the allylated intermediates to the acetonyl compounds.

## Experimental Section

$^1H$ NMR spectra were recorded on a JEOL-PS-100 instrument in $CDCl_3$ with $Me_4Si$ as internal standard. Mass spectra were measured on a Hitachi RMU-6E spectrometer. Infrared spectra were obtained on a Hitachi 260-10 spectrometer. All the reagents were of reagent grade and were used without further purification. 2-Chloro-1-(chloromethyl)ethyl methoxymethyl ether (**1**) was prepared according to ref 10. Evaporative distillation (Kugelrohr distillation) was performed from bulb to bulb by a glass tube oven Model GTO-250RS.

**Preparation of 2-(Chloromethyl)-3,5-dioxahex-1-ene (2).** Into a 200-mL, three-necked flask equipped with a thermometer and a Vigreaux column connected to a receiver flask through a Liebig condenser were added sequentially 2-chloro-1-(chloromethyl)ethyl methoxymethyl ether (**1**) (69.2 g, 0.40 mol), pulverized sodium hydroxide (24 g, 0.60 mol), and tetrabutylammonium bisulfate (6.8 g, 5% based on **1**). The mixture was stirred with a magnetic stirrer and heated to 80 °C (bath temperature) at reduced pressure (about 30 Torr), and the distillate was collected from 50 °C to dryness in the flask (2.5 h). A small amount of water that distilled out together with the product was removed in a separatory funnel, and the remaining liquid was dried over anhydrous magnesium sulfate. After filtration, **2** was obtained in a yield of 85% (46.4 g) as a colorless liquid, bp 62–63 °C/35 Torr: $^1H$ NMR ($CDCl_3$) $\delta$ 3.44 (s, 3 H), 3.96 (s, 2 H), 4.40 (s, 2 H), 5.00 (s, 2 H); MS, $m/e$ (relative intensity) 136 ($M^+$), 138 ($M^+$), 45 (100); IR (neat) 2950, 1640, 1300, 1150, 1100, 1020, 840, 740 $cm^{-1}$. Anal. Calcd for $C_5H_9ClO_2$: C, 43.90; H, 6.64; Cl, 25.96.

Found: C, 43.60; H, 6.78; Cl, 25.82.

**2-(Iodomethyl)-3,5-dioxahex-1-ene (5).** A heterogeneous mixture of **2** (27.2 g, 0.2 mol), potassium iodide (66.4 g, 0.4 mol), sodium carbonate (21.8 g, 0.2 mol), and tetrabutylammonium bisulfate (3.4 g, 0.01 mol) in 200 mL water was stirred at 80 °C for 3 h. After extraction with ether and drying over magnesium sulfate, **5** was obtained, by distillation at reduced pressure, as a pale yellow liquid in a yield of 74%, bp 74–75 °C/18 Torr: $^1$H NMR ($CDCl_3$) $\delta$ 3.48 (s, 3 H), 3.80 (s, 2 H), 4.35–4.45 (d, 2 H), 5.00 (s, 2 H); MS, *m/e* (relative intensity) 228 ($M^+$), 45 (100), 101 (40); IR (neat) 2950, 1640, 1290, 1020 cm$^{-1}$.

**Preparation of Acetonyl Laurate (9).** A mixture of lauric acid (10 g, 0.05 mol), 30 mL dioxane, and 30 mL methanol was added into a solution of sodium hydroixde (2.4 g, 0.06 mol) in 10 mL of water. After the solvents were removed to dryness by a rotary evaporator at reduced pressure, 100 mL of dioxane, **2** (7.5 g, 0.055 mol), and tetrabutylammonium bisulfate (0.85 g, 5% based on lauric acid)[13] were added into the residue, and the mixture was stirred at 100 °C for 5 h. The solid material was removed by filtration and about 80% of the dioxane was distilled out at reduced pressure. Then, 10 mL of 1% aqueous sulfuric acid was added, and mixture was stirred at 80 °C for 1 h. The product was extracted with ether and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent, **9** was isolated by Kugelrohr distillation at reduced pressure in a yield of 93% (11.9 g) as a colorless oil, which turned immediately to white needles in the receiver, bp 120 °C/0.04 Torr; mp 33–34 °C: $^1$H NMR ($CDCl_3$) $\delta$ 0.78–1.00 (t, 3 H), 1.20–1.80 (m, 18 H), 2.14 (s, 3 H), 2.30–2.50 (t, 2 H), 4.64 (s, 2 H); MS, *m/e* (relative intensity) 257 ($M^+ + 1$), 183 (100), 98 (48), 57 (64), 43 (79); IR (neat) 2950, 1740, 1180 cm$^{-1}$. Anal. Calcd for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01. Found: C, 69.88; H, 11.24.

**Acetonylbenzylmethylamine (10).** A mixture of methylbenzylamine (6.06 g, 0.05 mol), **2** (7.5 g, 0.055 mol), sodium hydroxide (5.0 g, 0.125 mol, pellet), and 20 mL of dioxane was stirred at 80 °C for 5 h. After the solid material was removed, the mixture was hydrolyzed with 10% aqueous sulfuric acid mixed with dioxane (1:1, v/v) at 80 °C for 4 h and neutralized to weak alkalinity with 5% aqueous sodium hydroxide. After the usual workup, **10** was obtained by Kugelrohr distillation at reduced pressure in a yield of 80% (7.1 g) as a colorless liquid, bp 50 °C/0.06 Torr: $^1$H NMR ($CDCl_3$) $\delta$ 2.11 (s, 3 H), 2.28 (s, 3 H), 3.12 (s, 2 H), 3.55 (s, 2 H), 7.28 (s, 5 H); MS, *m/e* (relative intensity) 177 ($M^+$), 134 (45), 91 (100); IR (neat) 2800, 1720, 1460, 1035, 760, 720 cm$^{-1}$. Anal. Calcd for $C_{11}H_{15}NO$: C, 74.53; H, 8.53; N, 7.90. Found: C, 74.23; H, 8.62; N, 7.71.

**General Procedure A for the Preparation of 11–17. Acetonyl Octyl Sulfide (11).** A mixture of octanethiol (7.3 g, 0.05 mol), **2** (7.5 g, 0.055 mol), sodium hydroxide (5.0 g, 0.125 mol, pellet), tetrabutylammonium bisulfate (0.85 g), and 20 mL of dioxane was stirred at 60 °C for 2 h. After removing the solid material by filtration through a short column filled with silica gel and evaporating off the solvent, 10 mL of 1% aqueous sulfuric acid and 10 mL of dioxane were added into the residue, and mixture was stirred at 80 °c for 1 h. The product was extracted with ether and isolated by Kugelrohr distillation at reduced pressure. **11** was obtained in a yield of 82% (8.3 g) as a colorless liquid, bp 70 °C/0.1 Torr: $^1$H NMR ($CDCl_3$) $\delta$ 0.75–1.05 (t, 3 H), 1.10–1.80 (m, 12 H), 2.28 (s, 3 H), 2.35–2.60 (t, 2 H), 3.18 (s, 2 H); MS, *m/e* (relative intensity) 202 ($M^+$), 159 (30), 69 (100), 61 (65), 55 (52), 43 (57); IR (neat) 2925, 1730, 1370, 1250 cm$^{-1}$. Anal. Calcd for $C_{11}H_{22}OS$: C, 65.30; H, 10.96; S, 15.85. Found: C, 64.97; H, 11.08; S, 15.57.

**Acetonyl Phenyl Sulfide (12).** Upon application of the general procedure described above but without the PT catalyst, **12** was isolated in a yield of 90% (7.5 g, 0.05-mol scale) as a colorless liquid, bp 125 °C/5 Torr: $^1$H NMR ($CDCl_3$) $\delta$ 2.25 (s, 3 H), 3.65 (s, 2 H), 7.30 (s, 5 H); MS, *m/e* (relative intensity) 166 ($M^+$), 123 (100), 45 (60); IR (neat) 1720, 1580, 1480, 1440, 1360, 1230, 1150, 1120, 750, 700 cm$^{-1}$. Anal. Calcd for $C_9H_{10}OS$: C, 65.03; H, 6.06; S, 19.29. Found: C, 65.15; H, 6.18; S, 18.92.

**[(Acetonyloxy)methyl]-15-crown-5 (13).** (Hydroxymethyl)-15-crown-5 was prepared by a reported method.[14] The allylation reaction was carried out at 60 °C for 3 h without the PT catalyst according to the general procedure. Hydrolysis was accomplished with 1% aqueous sulfuric acid for 1 h at room temperature. **13** was obtained in a yield of 80% (2.4 g, 0.01 mol scale) as a colorless liquid, bp 140 °C/0.02 torr: $^1$H NMR ($CDCl_3$) $\delta$ 2.16 (s, 3 H), 3.60–3.90 (m, 21 H), 4.00–4.16 (d, 2 H); MS, *m/e* (relative intensity) 306 ($M^+$), 101 (95), 87 (90), 57 (85), 45 (100); IR (neat) 2900, 1730, 1350, 1125 cm$^{-1}$. Anal. Calcd for $C_{14}H_{26}O_7$: C, 54.88; H, 8.56. Found: C, 54.73; H, 8.69.

**Tetraethylene Glycol Diacetonyl Ether (14).** By the same procedure used for **13**, except for the use of 2.2 equiv of **2**, **14** was obtained in a yield of 63% (9.7 g, 0.05-mol scale) as a colorless liquid, bp 150 °C/0.06 Torr: $^1$H NMR ($CDCl_3$) $\delta$ 2.14 (s, 6 H), 3.60–3.80 (d, 16 H), 4.10 (s, 4 H); MS, *m/e* (relative intensity) 306 ($M^+$), 101 (100), 57 (83), 45 (31); IR (neat) 2950, 1740, 1140 cm$^{-1}$. Anal. Calcd for $C_{14}H_{26}O_7$: C, 54.88; H, 8.56. Found: C, 54.50; H, 8.71.

**Acetonyl Decyl Ether (15).** By the general procedure described above, **15** was obtained in a yield of 74% (7.9 g, 0.05-mol scale) as a colorless liquid, bp 50 °C/0.05 Torr: $^1$H NMR ($CDCl_3$) $\delta$ 0.75–1.05 (t, 3 H), 1.10–1.80 (m, 16 H), 2.16 (s, 3 H), 3.40–3.60 (t, 2 H), 4.00 (s, 2 H); MS, *m/e* (relative intensity) 214 ($M^+$), 57 (100), 43 (90); IR (neat) 2925, 1720, 1130 cm$^{-1}$. Anal. Calcd for $C_{13}H_{26}O_2$: C, 72.84; H, 12.33. Found: C, 73.09; H, 12.41.

**Acetonyl Phenyl Ether (16).** The allylating reaction was carried out at 80 °C for 5 h. By the general workup described above, allylic ether **7** (Y = PhO) was obtained in a yield of 76% by Kugelrohr distillation at reduced pressure as a colorless oil, bp 150 °C/30 Torr: $^1$H NMR ($CDCl_3$) $\delta$ 3.40 (s, 3 H), 4.45 (s, 4 H), 5.00 (s, 2 H), 6.90–7.05 (m, 3 H), 7.20–7.40 (m, 2 H); MS, *m/e* (relative intensity) 194 ($M^+$), 45 (100); IR (neat) 2950, 1660, 1500, 1230, 1140, 760, 700 cm$^{-1}$. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.03; H, 7.34. **16** was obtained in a yield of 67% (5.0 g, 0.05-mol scale) as a colorless liquid after hydrolysis of the allylic ether **7**, bp 130 °C/30 Torr: $^1$H NMR ($CDCl_3$) $\delta$ 2.20 (s, 3 H), 4.47 (s, 2 H), 6.75–7.10 (m, 3 H), 7.10–7.36 (m, 2 H); MS, *m/e* (relative intensity) 150 ($M^+$), 107 (70), 77 (100), 43 (77); IR (neat) 1740, 1610, 1525, 1240, 1190, 770, 700 cm$^{-1}$. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.75; H, 6.92.

***trans*-1-(Phenylthio)-6-oxo-4-oxahept-1-ene (17)** was prepared by the reaction of phenyl glycidyl sulfide[11] (8.3 g, 0.05 mol) with **2** (9.6 g, 0.07 mol) under the same conditions as used for **11**, in a yield of 78% (8.7 g) as a colorless liquid, bp 120 °C/0.05 Torr: $^1$H NMR ($CDCl_3$) $\delta$ 2.12 (s, 3 H), 4.00–4.30 (m, 4 H), 5.65–5.95 (m, $J$ = 15 Hz, 1 H), 6.38–6.58 (m, $J$ = 15 Hz, 1 H), 7.15–7.40 (m, 5 H); MS, *m/e* (relative intensity) 222 ($M^+$), 149 (100), 43 (80); IR (neat) 2875, 1730, 1580, 1480, 1440, 1360, 1130, 750, 700 cm$^{-1}$. Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35; S, 14.42. Found: C, 64.47; H, 6.37; S, 14.24.

**General Procedure B for the Preparation of 18–24. Dimethyl Acetonylmalonate (18).** After metallic sodium (1.3 g, 0.055 mol) was dissolved in 50 mL of *tert*-butyl alcohol, dimethyl malonate (6.6 g, 0.05 mol) was added gradually at 60 °C. Then **2** (7.5 g, 0.055 mol) was added dropwise, and the mixture was stirred at the same temperature for 3 h. The solid material was removed by filtration through a short column filled with silica gel, and the solvent was evaporated off at reduced pressure. Hydrolysis was carried out with 1% aqueous sulfuric acid at room temperature for 1 h. The product was extracted with dichloromethane and isolated by Kugelrohr distillation at reduced pressure to give **18** in a yield of 71% (6.7 g) as a colorless liquid, bp 110 °C/7 Torr: $^1$H NMR ($CDCl_3$) $\delta$ 2.20 (s, 3 H), 3.00–3.15 (d, 2 H), 3.75 (s, 6 H), 3.80–4.00 (t, 1 H); MS, *m/e* (relative intensity) 188 ($M^+$), 125 (67), 114 (50), 43 (100); IR (neat) 2900, 1740, 1440, 1170, 820 cm$^{-1}$. Anal. Calcd for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 51.23; H, 6.50.

**2-Acetonyl-2-(methoxycarbonyl)cyclopentanone (19).** The allylation reaction was carried out at 80 °C for 20 h in the presence of the PT catalyst under similar conditions as used for **18**, and hydrolysis was carried out at 80 °C for 1 h in a mixture of dilute aqueous sulfuric acid and dioxane (1:1, v/v). **19** was obtained in a yield of 61% (6.1 g) as a colorless liquid, bp 145 °C/10 Torr:

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$^1$H NMR ($CDCl_3$) δ 2.10 (s, 3 H), 1.90–2.60 (m, 6 H), 3.00–3.20 (d, 2 H), 3.70 (s, 3 H); MS, *m/e* (relative intensity) 198 ($M^+$), 166 (45), 95 (35), 43 (100); IR (neat) 3000, 1760 $cm^{-1}$. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.34; H, 7.34.

In an another run, the allylation reaction was also carried out in the presence of patassium iodide (18 g, 2.0 equiv to CDOH). The reaction time was shortened to 2 h, and product **19** was obtained in a yield of 60%.

**Ethyl Acetonylacetylacetate (20).** By the general procedure B described above, **20** was obtained in a yield of 68% (6.4 g, 0.05-mol scale) as a colorless liquid by the reaction of ethyl acetylacetate with 1:1 equiv of **2**, bp 60 °C/0.1 Torr: $^1$H NMR ($CDCl_3$) δ 1.20–1.35 (t, 3 H), 2.18 (s, 3 H), 2.37 (s, 3 H), 2.98–3.45 (m, 2 H), 3.95–4.35 (m, 3 H); MS, *m/e* (relative intensity) 187 ($M^+ + 1$), 101 (30), 55 (25), 43 (100); IR (neat) 3000, 1750, 1400, 1080 $cm^{-1}$. Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.65; H, 7.66.

With 2.2 equiv of **2**, ethyl diacetonylacetylacetate was also obtained in a yield of 17% as a colorless liquid by distillation at reduced pressure, bp 80 °C/0.1 Torr: $^1$H NMR ($CDCl_3$) δ 1.02–1.49 (t, 3 H), 2.13 (s, 9 H), 3.35 (s, 4 H), 3.39–4.44 (q, 2 H); MS, *m/e* (relative intensity) 242 ($M^+$), 199 (30), 111 (100), 43 (60); IR (neat) 2950, 1720, 1360, 1200, 1020 $cm^{-1}$. Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.23; H, 7.56. In this reaction, 10% of monoacetonylacetylacetate was also obtained together with a substantial amount of unidentified substances.

**3-Acetonylacetylacetone (21).** By the general procedure B described above, **21** was obtained in a yield of 64% (5.0 g) as a colorless liquid, bp 130 °C/10 Torr: $^1$H NMR ($CDCl_3$) δ 2.00–2.40 (m, 9 H), 2.70 (s, 0.2 H), 2.99–3.02 (d, 1.6 H), 3.40 (s, 0.4 H), 4.10–4.28 (t, 0.8 H); MS, *m/e* (relative intensity) 156 ($M^+$), 96 (20), 71 (40), 43 (100); IR (neat) 2950, 1720, 1380, 1180 $cm^{-1}$. Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.15; H, 7.85.

**3-Acetonylindene (22).** By the same procedure used for **18**, **22** was obtained in a yield of 70% (6.0 g, 0.05-mol scale) as a slightly yellowish liquid, bp 80 °C/0.05 Torr: $^1$H NMR ($CDCl_3$) δ 2.16 (s, 3 H), 3.40 (s, 2 H), 3.64 (s, 2 H), 6.40 (s, 1 H), 7.10–7.52 (m, 4 H); MS, *m/e* (relative intensity) 172 ($M^+$), 129 (100), 43 (65); IR (neat) 3100, 2900, 1750, 1640, 1400 $cm^{-1}$. Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83,21; H, 7.07.

**9,9-Diacetonylfluorene (23).** The diacetonylation was carried out by treating fluorene (8.3 g, 0.05 mol) with **2** (15.0 g, 0.11 mol) at 30 °C for 4 h in the presence of the PT catalyst and conditions similar to those used for **18**, followed by hydrolysis with a mixture of dilute aqueous sulfuric acid and dioxane at 60 °C for 1 h to afford **23** in a yield of 78% (10.9 g) as a yellowish waxy solid, bp 130 °C/0.05 Torr; mp 61–62 °C: $^1$H NMR ($CDCl_3$) δ 1.90 (s, 6 H), 3.21 (s, 4 H), 7.20–7.40 (m, 4 H), 7.50–7.80 (m, 4 H); MS, *m/e* (relative intensity) 278 ($M^+$), 221 (25), 179 (30), 43 (100); IR (neat) 3050, 2925, 1740, 1480, 1360, 1200, 1140, 980, 800, 760 $cm^{-1}$. Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.03; H, 6.41.

**Diacetonylphenylacetonitrile (24).** The diacetonylation was carried out at 60 °C for 3 h, and hydrolysis was accomplished in a manner similar to that used for **23**. **24** was obtained in a yield of 61% (7.0 g, 0.05-mol scale) as a yellowish waxy solid, bp 120 °C/0.05 Torr; mp 105–106 °C: $^1$H NMR ($CDCl_3$) δ 2.10 (s, 6 H), 3.40 (s, 4 H), 7.20–7.60 (m, 5 H); MS, *m/e* (relative intensity) 229 ($M^+$), 143 (40), 82 (50), 43 (100); IR (neat) 2900, 2240, 1740, 1180 $cm^{-1}$. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.60; N, 6.11. Found: C, 73.72; H, 6.53; N, 6.04.

**Bis(2-methylene-3,5-dioxahexyl)decylamine (25).** Decylamine (4.7 g, 0.03 mol) was treated with **2** (9.5 g, 0.07 mol) under the same conditions used for **10**. After the usual workup, the diallylic amine (bis(2-methylene-3,5-dioxahexyl)decylamine) was obtained by Kugelrohr distillation at reduced pressure in a yield of 50% (5.4 g) as a colorless liquid, bp 140 °C/0.07 Torr: $^1$H NMR ($CDCl_3$) δ 0.74–1.00 (t, 3 H), 1.10–1.80 (m, 16 H), 2.40–2.60 (m, 2 H), 3.17 (s, 4 H), 3.43 (s, 6 H), 4.25 (s, 4 H), 4.96 (s, 4 H); MS, *m/e* (relative intensity) 357 ($M^+$), 230 (75), 45 (100); IR (neat) 2950, 1640, 1460, 1160, 1110, 1040 $cm^{-1}$.

Treatment of bis(2-methylene-3,5-dioxahexyl)decylamine in acidic water–dioxane ($H_2SO_4$) afforded a complicated mixture (by GLC).

**Registry No.** 1, 70905-45-2; **2**, 105104-40-3; **5**, 108270-19-5; **7**, 105104-43-6; **9**, 108270-20-8; **10**, 23982-57-2; **11**, 20233-08-3; **12**, 5042-53-5; **13**, 108270-21-9; **14**, 108270-22-0; **15**, 40657-11-2; **16**, 621-87-4; **17**, 108270-23-1; **18**, 24889-15-4; **19**, 92825-45-1; **20**, 41892-81-3; **21**, 42781-07-7; **22**, 103556-85-0; **23**, 108270-24-2; **24**, 108270-25-3; **25**, 108270-26-4; $C_{11}H_{23}COOH$, 143-07-7; $C_8H_{17}SH$, 111-88-6; $C_{10}H_{21}OH$, 112-30-1; $(CH_3OCO)_2CH_2$, 108-59-8; $CH_3C(O)CH_2COOC_2H_5$, 141-97-9; $CH_3C(O)CH_2C(O)CH_3$, 123-54-6; $n$-$C_{10}H_{21}NH_2$, 2016-57-1; methylbenzylamine, 103-67-3; benzenethiol, 108-98-5; (hydroxymethyl)-15-crown-5, 75507-25-4; tetraethylene glycol, 112-60-7; phenol, 108-95-2; phenyl glycidyl sulfide, 5296-21-9; 2-(methoxycarbonyl)cyclopentanone, 10472-24-9; ethyl diacetonylacetylacetate, 85288-60-4; indene, 95-13-6; fluorene, 86-73-7; phenylacetonitrile, 140-29-4.

# Metacyclophanes and Related Compounds. 19. Reaction of 8-Methoxy[2.2]metacyclophanes with Iodine in Benzene Solution. A Preparative Route of Pyrenes[1]

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When 8-methoxy[2.2]metacyclophanes are treated with iodine in boiling benzene, the corresponding tetrahydropyrenes (**8**) are obtained in good yield. The $AlCl_3$-catalyzed trans-*tert*-butylation of **8** effected loss of the *tert*-butyl group to give **10a–c**, which were easily dehydrogenated with DDQ to afford the corresponding pyrene derivatives.

Although reaction of 8,16-unsubstituted [2.2]metacyclophanes with iodine in boiling benzene afforded the corresponding hexahydropyrenes,[2,3] 8,16-disubstituted [2.2]metacyclophanes did not react with iodine under similar conditions.[4] These results prompted us to investigate the reaction of 8-monosubstituted [2.2]metacyclophanes with iodine.

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