

reaction mixture. GLC analysis established a 96% yield of 2,2,6,6-tetramethylcyclohexanone.

Using this procedure, cyclobutanone, cyclopentanone, cyclohexanone, and acetophenone are nearly quantitatively permethylated in 15 min at 25 °C (see Table I). 4-Heptanone and cycloheptanone give cleanly the trimethylated product and acetone the pentamethylated product under these conditions. In these latter cases, the reason for incomplete methylation is slow reaction of the penultimate methylated ketone with KH. With acetone and cycloheptanone, refluxing the reaction mixture for 1 h followed by cooling and addition of the final equivalent of methyl iodide gives the permethylated ketones in good yields. However, this latter procedure is ineffective with 4-heptanone. In fact, no hydrogen was evolved when a sample of 3,3,5-trimethyl-4-heptanone was refluxed for 6 h with KH and the starting ketone was recovered quantitatively after addition of methyl iodide.

**Reduction of 2,2,6,6-Tetramethylcyclohexanone with KH.** When reaction mixtures for the permethylation of cyclohexanone were allowed to stir for periods of an hour or more prior to workup, small amounts of a side product identified as the methyl ether of 2,2,6,6-tetramethylcyclohexanol were detected. Evidently, a slow reduction of the permethylated ketone by KH occurs.<sup>7</sup> This was confirmed by stirring mixtures containing equivalent amounts of KH and 2,2,6,6-tetramethylcyclohexanone at room temperature and analyzing quenched aliquots periodically for 2,2,6,6-tetramethylcyclohexanol. Ten percent of the starting ketone was reduced in 5 h and 50% in 24 h.

### Experimental Section

<sup>1</sup>H-NMR spectra were recorded on a Varian T-60 with Me<sub>4</sub>Si internal standard. Infrared spectra were recorded using a Perkin-Elmer 237B grating spectrometer. GLC analyses and preparative chromatography were obtained with a Varian 920 using 6 ft × 0.25 in. stainless steel columns packed with 1.5% OV-101 on Chromosorb GHP. THF was distilled from the sodium ketyl of benzophenone just prior to use. KH was obtained as a mineral oil suspension (Alpha) and used directly. Methyl iodide and all ketones were distilled and stored under an argon atmosphere. Caution: the paper by Brown<sup>6</sup> should be consulted before handling KH.

**Reaction of KH with Methyl Iodide.** A 50-mL round-bottomed flask equipped with a magnetic stirring bar, septum inlet, and mercury bubbler was flushed with argon and attached to a gas buret. The flask was charged with 1.86 mL (10 mmol) of KH suspension and 10 mL of THF. Methyl iodide (0.6 mL, 10 mmol) was injected. A total of 93 mL (3.7 mmol) of gas was evolved in 1 min. No further gas was evolved in 2 h. GLC analysis (2.5% AgNO<sub>3</sub>, and 7% paraffin on Al<sub>2</sub>O<sub>3</sub>) of a sample of the gas indicated the presence of methane. 1-Pentane (10 mmol) was added to the reaction mixture as internal standard and GLC analysis (1.5% OV-101) of an aliquot established the presence of 6.3 mmol of methyl iodide.

**Permethylation of Ketones.** Because of the volatility of methyl iodide, it was found best to use a dry ice condenser on the reaction flask. The following procedure for the permethylation of cyclohexanone is representative of the general technique. A 500-mL round-bottomed flask was equipped with a magnetic stirring bar, septum inlet, and dry ice condenser and flushed with argon. The flask was charged with 40 mL (216 mmol) of KH in mineral oil. The flask was then immersed in a water bath maintained at 25 °C. THF (220 mL) was injected followed by dropwise addition of cyclohexanone (5.2 mL, 50 mmol) over a 5-min period. After 5 min of additional stirring, methyl iodide (13.5 mL, 216 mmol) is added dropwise over a 15-min period. After an additional 15 min of stirring, the reaction mixture is treated cautiously with 15 mL of water. The aqueous layer is extracted with one 15-mL portion of ether and the combined organic layers are dried over anhydrous K<sub>2</sub>CO<sub>3</sub>. The organic layer is subjected to simple distillation to obtain 6.25 g, 81% yield, of 2,2,6,6-tetramethylcyclohexanone: bp 183–185 °C; <sup>1</sup>H NMR (CCl<sub>4</sub>, internal Me<sub>4</sub>Si) δ 1.6 (s, 6 H), 1.1 (s, 12 H); IR (neat) 1700 cm<sup>-1</sup> (C=O). Using this procedure, the following compounds were obtained (all new products gave satisfactory C, H elemental analysis):

**2,2,4,4-Tetramethylcyclobutanone:** isolated yield, 65%; bp 130–133 °C; <sup>1</sup>H NMR (CCl<sub>4</sub>, internal Me<sub>4</sub>Si) δ 1.7 (s, 2 H), 1.2 (s, 12 H); IR (neat) 1780 cm<sup>-1</sup> (C=O).

**2,2,5,5-Tetramethylcyclopentanone:** isolated yield, 83%; bp 153 °C; <sup>1</sup>H NMR (CCl<sub>4</sub>, internal Me<sub>4</sub>Si) δ 1.7 (s, 4 H), 1.0 (s, 12 H); IR (neat) 1745 cm<sup>-1</sup> (C=O).

**2,2,7-Trimethylcycloheptanone:** isolated by preparative GLC; <sup>1</sup>H NMR (CCl<sub>4</sub>, internal Me<sub>4</sub>Si) δ 2.6–3.0 (m, 1 H) [1.2–2.0 (m, 8 H), 1.0 (s, 6 H), 0.9 (α, 3 H)]; IR (neat) 1710 cm<sup>-1</sup> (C=O).

**2,2,4-Trimethyl-3-pentanone:** isolated by preparative GLC; <sup>1</sup>H NMR (CCl<sub>4</sub>, internal Me<sub>4</sub>Si) δ 3.0 (heptet, 1 H, *J* = 8 Hz), 1.1 (s, 9 H), 1.0 (d, 6 H, *J* = 8 Hz); IR (neat) 1705 cm<sup>-1</sup> (C=O).

**2,2-Dimethylpropiophenone:** isolated yield, 81%; bp (5 Torr) 85–90 °C; <sup>1</sup>H NMR (CCl<sub>4</sub>, internal Me<sub>4</sub>Si) δ 7.5 (m, 2 H), 7.2 (m, 3 H), 1.3 (s, 9 H); IR (neat) 1675 cm<sup>-1</sup> (C=O).

**3,3,5-Trimethyl-4-heptanone:** isolated yield, 66%; bp 187 °C; <sup>1</sup>H NMR (CCl<sub>4</sub>, internal Me<sub>4</sub>Si) δ 2.7 (m, 1 H), 1.4 (m, 4 H), 1.0 (s, 6 H), 1.8 (m, 3 H); IR (neat) 1695 cm<sup>-1</sup> (C=O).

The following compounds were obtained by a modification of the above procedure by which the reaction mixture was heated to reflux for 1 h after addition of one less than the theoretical equivalent of methyl iodide. The reaction flask was then immersed in a water bath at 25 °C and the final equivalent of methyl iodide was injected dropwise. Workup was as described above.

**2,2,7,7-Tetramethylcycloheptanone:** isolated yield, 50%; bp 195 °C; <sup>1</sup>H NMR (CCl<sub>4</sub>, internal Me<sub>4</sub>Si) δ 1.6 (s, 8 H), 1.1 (s, 12 H).

**2,2,4,4-Tetramethyl-3-pentanone:** isolated yield, 60%; bp 157 °C; <sup>1</sup>H NMR (CCl<sub>4</sub>, internal Me<sub>4</sub>Si) δ 1.2 (s); IR (neat) 1670 cm<sup>-1</sup>.

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**Registry No.**—KH, 7693-26-7; methyl iodide, 74-88-4.

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### Thiol-Olefin Cooxidation Reaction. 6. A New Convenient Route to 1-Substituted Indenes. Indenone as Dienophile in Diels-Alder Reactions

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
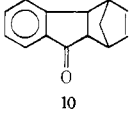
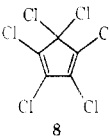
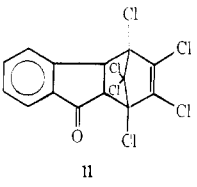
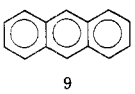
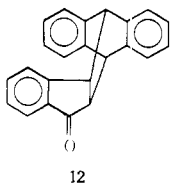
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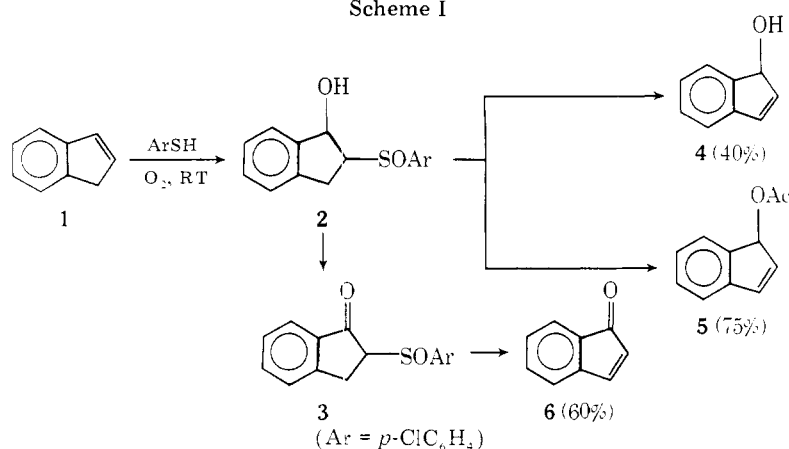
A recent publication<sup>1</sup> concerning the use of indenone ketals as dienophiles in a Diels-Alder reaction with butadiene (to give adducts that then serve as starting materials for the synthesis of degradation products of the plant stimulant gibberellic acid) prompts us to report the use of indenone itself in the cycloaddition reaction and its convenient preparation from indene as well as of other 1-substituted indenones (4–6). The facile conversion of indene by means of the TOCO reaction to a mixture of three isomeric β-hydroxy sulfoxides<sup>2,3</sup> followed by their oxidation to β-keto sulfoxides<sup>4</sup> was coupled with the ready elimination of the sulfoxide moiety to give the 1-substituted indenones as shown in Scheme I.

The formation of 4 requires refluxing overnight in toluene as compared to a 4-h period of reflux for the formation of 5 and 6. The longer time required for the elimination of the sulfoxide moiety in the case of the formation of 4 suggests the stabilization of 2 by intra- and intermolecular hydrogen bonding.

Table I. Diels–Alder Adducts of Indenone 6

Diene	Registry no.	Product	Registry no.	Mp, °C	Yield %
	542-92-7		65495-96-7	Liquid	53
	97-47-4		65495-97-8	158–60	30
	120-12-7		37069-90-2	198–200	68

Scheme I



The conversion of indene to **5** is a one-pot reaction but the intermediate  $\beta$ -acetoxy sulfoxide can also be isolated.

Numerous methods are available for the preparation of substituted indenones,<sup>1,5–8</sup> but there are very few methods available for a specific synthesis of **6**.<sup>7,9,10</sup> Our reaction sequence is highly convenient because **6** can be easily separated from the *p*-chlorophenyl disulfide and other sulfur-containing products. The Diels–Alder reaction can be attained by carrying out the elimination in the presence of dienes and without the need to separate *p*-chlorophenyl disulfide. In this way the chance of dimerization to truxone is reduced. In our hands **4** and **5** fail to give Diels–Alder adducts, even under vigorous conditions (reflux in toluene 48 h), whereas **6** forms Diels–Alder adducts<sup>10</sup> as summarized in Table I.

### Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian A-60A spectrometer using tetramethylsilane as an internal standard. Indene was distilled under vacuum. *p*-Chlorothiophenol was recrystallized from aqueous ethanol. Cyclopentadiene was distilled just before use. Hexachlorocyclopentadiene and anthracene were used directly as supplied commercially. Melting points are uncorrected.

**2-(*p*-Chlorophenylsulfinyl)-1-indanone (3).** Jones reagent, prepared by dilution with water of a solution of 26.72 g of chromium trioxide in 23 mL of concentrated sulfuric acid to the volume of 100 mL, was added dropwise to a solution of 2 g of **2** in 40 mL of reagent grade acetone until the color of the top layer changed from green to brown. The solvent was removed under vacuum and the residue was extracted with chloroform. The extract was washed with water until the top layer was clear, dried over anhydrous sodium sulfate, and

evaporated to give **3** (yield 1.5 g) (75%) recrystallized from 95% ethanol to white needles: mp 160–61 °C (lit.<sup>4</sup> mp 160–62 °C); NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>)  $\delta$  3.55 (d, 2), 4.9 (t, 1), 7.75 (m, 8).

On addition of a drop of NaOD in D<sub>2</sub>O the triplet at  $\delta$  4.9 disappeared completely and the doublet at  $\delta$  3.55 changed to a singlet.<sup>11</sup>

**1-Hydroxyindene (4).** A solution of 1 g of **2** in 20 mL of toluene was refluxed overnight. The solvent was removed under vacuum and the residue was chromatographed on 30 g of alumina (F-20). The material was eluted with hexane, a mixture of hexane and benzene, and finally benzene. The hexane fraction gave *p*-chlorophenyl disulfide and the benzene fraction produced **4**: yield 180 mg (40%); mp 57–59 °C (lit.<sup>12</sup> mp 57–58 °C).

**1-Acetoxyindene (5).** A mixture of 2 g of **2**, 2 g of sodium acetate, 20 mL of acetic anhydride, and 60 mL of toluene was refluxed for 4 h. The solvent was removed under vacuum and the residue was chromatographed on 100 g of silica gel G. The material was eluted with hexane, a mixture of hexane and benzene, and finally benzene. The benzene fraction produced **5**: yield 0.88 g (74%); bp 50–52 °C (3 mm) (lit.<sup>12</sup> bp 118–22 °C (12 mm)); NMR (CDCl<sub>3</sub>)  $\delta$  2.1 (s, 3), 6.2–6.9 (m, 3), 7.2–7.4 (m, 4).

The intermediate  $\beta$ -acetoxy sulfoxide was isolated and characterized as follows. The isomeric mixture of 2 g of **2** was treated overnight with a mixture of 2 g of sodium acetate and 40 mL of acetic anhydride at room temperature. The mixture was concentrated in vacuo and the residue was suspended in benzene. The unreacted sodium acetate was filtered and the removal of benzene gave a gummy product which was crystallized from 95% ethanol to give 1-acetoxy-2-(*p*-chlorophenylsulfinyl)indane: yield 1.74 g (76%); mp 143–45 °C; NMR (CDCl<sub>3</sub>)  $\delta$  1.9 (s, 3), 3.2–3.6 (m, 3), 6.7 (d, 1), 7.2–7.6 (m, 8). Anal. Calcd for C<sub>17</sub>H<sub>15</sub>ClO<sub>3</sub>S: C, 60.89; H, 4.52. Found: C, 60.74; H, 4.56.

**1-Indenone (6).** A solution of 2 g of **3** in 50 mL of toluene was heated to reflux for 4 h. The solvent was removed under vacuum and

the residue was chromatographed from 60 g of alumina (F-20). The material was eluted with hexane, a mixture of hexane and benzene, and finally benzene. The hexane fraction gave *p*-chlorophenyl disulfide and the benzene fraction produced **6** (yield 0.52 g) (58%), which was characterized by its yellow color, its biting lachrymatory odor, and 2,3-dibromoindanone: mp 62–63 °C (lit.<sup>13</sup> mp 64–65 °C); NMR (CDCl<sub>3</sub>) δ 6.4–6.9 (m, 2), 7.4–7.8 (m, 4). **6** readily dimerizes to truxone in the presence of a trace of acid catalyst.

**Typical Procedure for Diels–Alder Reactions.** A solution of 0.5 g (1.7 × 10<sup>-3</sup> mol) of **3** and a small excess of diene (3 × 10<sup>-3</sup> mol) in 30 mL of toluene was heated to reflux for 8–10 h. The solvent was removed under vacuum and the crude residue was transferred onto a column of 100 g of alumina (F-20) in hexane containing 0.3 to 0.5 mL of toluene. The material was eluted with hexane, 75:25 and 50:50 mixtures of hexane and toluene, and finally toluene. The hexane fraction yielded *p*-chlorophenyl disulfide, the hexane–toluene fraction gave the Diels–Alder adduct in the case of the cyclopentadiene, and the toluene fraction gave the Diels–Alder adduct in the case of hexachlorocyclopentadiene and anthracene.

**Cyclopentadiene adduct (10):** yield 180 mg (53%); colorless liquid; NMR (CDCl<sub>3</sub>) δ 1.9 (br s, 2), 2.9–4 (m, 4), 5.3 (q, 1), 5.9 (q, 1), 7.2–7.4 (m, 4). Anal. Calcd for C<sub>14</sub>H<sub>12</sub>O: C, 85.69; H, 6.26. Found: C, 85.34, H, 6.61.

**Hexachlorocyclopentadiene adduct (11):** yield 210 mg (30%); mp 158–60 °C; NMR (CDCl<sub>3</sub>) δ 2.7 (d, 1), 3.2 (d, 1), 7.2–7.5 (m, 4). Anal. Calcd for C<sub>14</sub>H<sub>6</sub>Cl<sub>6</sub>O: C, 41.78; H, 1.49; Cl, 52.79. Found: C, 42.00; H, 1.59; Cl, 53.09.

**Anthracene adduct (12):** yield 360 mg (68%); mp 198–200 °C; NMR (CDCl<sub>3</sub>) δ 3.1 (q, 1), 3.9 (q, 1), 4.6 (d, 1), 4.8 (d, 1), 6.9–7.5 (m, 12). Anal. Calcd for C<sub>23</sub>H<sub>16</sub>O: C, 89.58; H, 5.22. Found: C, 89.39; H, 5.36.

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**Registry No.**—**2**, 62967-56-0; **3**, 62937-76-2; **4**, 61463-21-6; **5**, 35116-20-2; **6**, 480-90-0; 1-acetoxy-2-(*p*-chlorophenylsulfanyl)indine, 65495-98-9; 2,3-dibromoindanone, 50870-59-2.

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### Radical Anions of Substituted Cyclobutene-1,2-diones<sup>1</sup>

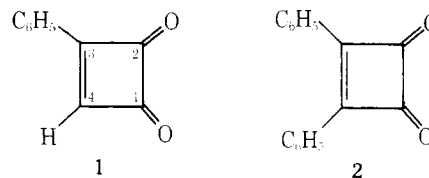
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A recent report<sup>2</sup> on the observation of a paramagnetic reduction product of phenylcyclobutene-1,2-dione (**1**) prompts us to describe some observations we have made in this and other systems.

We have observed that the reduction of **1** in a static system at 25 °C yields the spectrum reported by Concepcion and Vincow ( $a^H = 11.25$ ,  $a^C = 8.5$ , 4.5 G) in hexamethylphosphoramide (HMPA)–lithium, in dimethyl sulfoxide (Me<sub>2</sub>SO)–potassium *tert*-butoxide, or in dimethylformamide (DMF)–electrolysis. We have hesitated upon assigning this species to



**1**<sup>-</sup> for several reasons. The half-life of the species in Me<sub>2</sub>SO was several hours which is inconsistent with structure **1**<sup>-</sup>, particularly in view of the high spin density of ~11.25/27 on C-4.<sup>3</sup> If the spin densities at C-3 and C-4 were to be equated, it would appear that the semidione function is nearly devoid of spin density. We have been unable to prepare alkyl derivatives in this system, for example, by the treatment of 1,2-dimethylcyclobutene-1,2-dione with basic Me<sub>2</sub>SO,<sup>3</sup> but still the reported spectrum indicates little spin delocalization by the aromatic ring. Finally, under flow conditions with basic Me<sub>2</sub>SO, **1** was observed to yield an ESR spectrum (Chart I) more consistent with the hyperfine splitting constants (hfsc) expected for **1**<sup>-</sup> and also consistent with the spectrum observed for **2**<sup>-</sup> when **2** is continuously electrolyzed in DMF. Under stopped-flow conditions the species we assign as **1**<sup>-</sup> disappeared in seconds as did **2**<sup>-</sup> when electrolysis was halted. The observed hfsc constants for **1**<sup>-</sup> are quite consistent with the Hückel spin density calculations reported by Concepcion and Vincow<sup>2</sup> with all  $\beta_{cc}$  values equal (the predicted values of  $a^H$  being<sup>2</sup>  $a_4^H = -7.5$ ,  $a_3^H = -2.05$ ,  $a_m^H = -0.11$ , and  $a_p^H = -2.45$  G).<sup>14</sup>

Reduction of **2** with HMPA–lithium or HMPA–(trimethylsilyl)sodium<sup>5</sup> presented some complications which may be related to the observation of the species with  $a^H = 11$ –12 G from **1**. With alkali metal reducing systems at 25 °C the radical attributed to **2**<sup>-</sup> was the major species detected, but a second radical anion with  $a^H = 3.00$  (2), 2.4 (4), and 0.8 (4) G was observed. Upon irradiation with a low-pressure UV lamp **2**<sup>-</sup> disappeared and only the spectrum of the second radical anion remained. The second radical anion appears to be benzophenone ketyl but without the usually observed metal hfsc.<sup>6</sup> Reduction of benzophenone (0.25 M) by HMPA–(trimethylsilyl)sodium yielded a spectrum with  $a^H = 3.5$  (2), 2.5 (4), and 0.75 (4) G and  $a^{Na} = 0.75$  G, consistent with literature values of benzophenone ketyl in dimethoxyethane<sup>7</sup> or HMPA.<sup>7</sup>

We presume that the 11.25-G doublet arising from the reduction of **1** and benzophenone ketyl from **2** arise from 1,2 migrations in the cyclobutene-1,2-dione system. Attack by traces of hydroxide ion could initiate a benzylic acid type of rearrangement (Scheme I). Reduction of **1a** to the radical trianion **3** is feasible but now H-4 would be in the nodal plane of the allylic system and a small hfsc would be expected. On the other hand, loss of an electron from **1a** to yield **4** would give a semitriene for which  $a^H$  might reasonably be 11 G, and the

Chart I. Observed Hyperfine Splitting Constants

