# A Convenient Synthesis of 1,3-Diacetoxy-1,3-cycloalkadienes from Cyclic β-Diketones

A. Boháč,* P. Hrnčiar

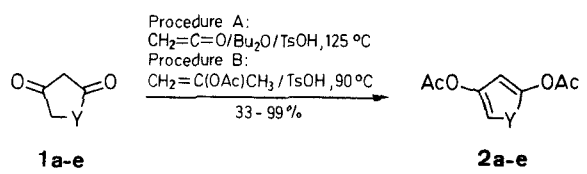
Department of Organic Chemistry, Comenius University, Mlynská dolina, 842 15 Bratislava, Czechoslovakia

An efficient method for preparing 1,3-diacetoxy-1,3-cycloalkadienes **2a–e**, from 1,3-cycloalkanediones **1a–e** by treatment with ketene in the presence of *p*-toluenesulfonic acid is described.

Little information can be found on the preparation of 1,3-disubstituted 1,3-cycloalkadienes in the literature. The Birch reduction of the corresponding aromatic derivatives is the most often used method.[1,2] In the remaining syntheses, β-dicarbonyl compounds (or their enol ethers) are the starting materials. Triethyloxonium tetrafluoroborate[3] or chlorotrimethylsilane[4,5] are reagents which are used to convert β-dicarbonyl compounds to the desired 1,3-cycloalkadiene derivatives. 1,3-Diacetoxy-1,3-cyclohexadiene was also observed in minor quantities (15%) when 1,3-cyclohexanedione was treated with isopropenyl acetate.[6] 1,3-Dialkoxy- or 1,3-diacetoxy-1,3-cycloalkadienes are synthetically valuable intermediates. Though, from the point of view of their structure they represent trapped forms of dienol tautomers of cyclic β-diketones, they undergo the same transformations as 1,3-cycloalkadienes. For example, 1,3-cycloalkadiene iron tricarbonyls[7] or their salts[8] can be easily prepared from 1,3-diacetoxy-1,3-cycloalkadienes. Such reactions broaden their synthetical use, as has been illustrated in the preparation of chiral organometallic compounds.[8]

We have found a simple and effective method for the preparation of 1,3-diacetoxy-1,3-cycloalkadienes from the corresponding 1,3-cycloalkanediones. Acetylation of 1,3-cyclohexanedione (**1b**), 5,5-dimethyl-1,3-cyclohexanedione (**1c**), 1,3-cycloheptanedione[9] (**1d**) and 1,3-cyclooctanedione[9] (**1e**) with ketene or isopropenyl acetate leads to the corresponding 1,3-diacetoxy-1,3-cycloalkadienes (**2b–e**) in excellent yield (90–99%).

In the case of 1,3-cyclopentanedione (**1a**), the yields are low, probably due to a variety of side reactions of compound **2a** (e.g. cycloaddition reaction with ketene,[10] dimerization, etc.). Cyclic 1,3-diketones with a high




**1a-e** **2a-e**

| 1,2 | Y | 1,2 | Y |
|---|---|---|---|
| **a** | $CH_2$ | **d** | $(CH_2)_3$ |
| **b** | $(CH_2)_2$ | **e** | $(CH_2)_4$ |
| **c** | $C(CH_3)_2CH_2$ | | |

content of enol form **1a–c**[11] react smoothly with ketene at elevated temperature and in the presence of *p*-toluenesulfonic acid. Isopropenyl acetate, however, proved to be a better acetylating agent for 1,3-cycloalkanediones with a low content of enol form **1d,e**.[11] In both cases the actual acetylating agent is probably a mixed anhydride, acetic *p*-toluenesulfonic anhydride.[12] An explanation for the different reactivity of **1a–c** on one hand, and **1d,e** on the other hand with ketene, can possibly lie in the rate determining step which seems to be an enolization of the parent carbonyl group. Concentration of an enol form of compounds **1d,e** remains low also at higher temperatures. Unsatisfactory results of the reactions of **1d,e** with ketene[13] (Table) prompted us to use isopropenyl acetate as an acetylating agent. Its advantage lies in the fact that it can be used in a large excess over the enol, therefore the equilibrium is shifted into desired direction.

1,3-Cycloalkanediones (**1a,b**) are obtained by hydrogenation of the corresponding unsaturated diones[14,15] and diketones **1d,e** by a three-step synthesis starting from diethyl adipate and diethyl pimelate,[9] respectively. The commercially available dimedone (**1c**) is purified by crystallization from acetone. Ketene is produced by pyrolysis of acetone vapors over the red-hot resistance wire in the ketene lamp (0.45 mol of ketene per hour).[16] Impurities accom-

**Table.** 1,3-Diacetoxy-1,3-cycloalkadienes **2** Prepared

| Product | Yield (%)[a] | Molecular Formula[b] | $n_D$ (20 °C) or mp (°C) | $R_f$[c] | IR ($CHCl_3$)[d] $\nu$ ($cm^{-1}$) | $^1$H-NMR ($CDCl_3$/TMS)[e] $\delta$, $J$ (Hz) | $^{13}$C-NMR ($CDCl_3$/TMS)[e] $\delta$ |
|---|---|---|---|---|---|---|---|
| **2a** | 33 | $C_9H_{10}O_4$ (182.2) | 95–100 | 0.86 | 1756 (br s), 1630 (m) | 2.17 (s, 6H), 3.16 (m, 2H), 5.55 (m, 1H), 6.13 (m, 1H) | 21.0 (q), 37.2 (t), 104.1 (d), 112.0 (d), 149.5 (s), 154.6 (s), 168.2 (s), 168.8 (s) |
| **2b** | 93[A] | $C_{10}H_{12}O_4$ (196.1) | 1.4864 | 0.78 | 1760 (s), 1674 (m) | 2.13 (s, 3H), 2.14 (s, 3H), 2.27–2.55 (m, 4H), 5.30 (m, 1H), 5.57 (d, 1H, $J$ = 1.5) | 20.8 (q), 21.0 (q), 21.7 (t), 25.4 (t), 108.2 (d), 110.2 (d), 144.7 (s), 150.8 (s), 168.4 (s), 169.0 (s) |
| **2c** | 90[A] (71[B]) | $C_{12}H_{16}O_4$ (224.2) | 1.4736 | 0.82 | 1753 (s), 1667 (m) | 1.12 (s, 6H), 2.11 (s, 3H), 2.13 (s, 3H), 2.30 (d, 2H, $J$ = 1.5), 5.10 (d, 1H, $J$ = 1.5), 5.60 (m, 1H) | 20.8 (q), 20.9 (q), 28.2 (q), 33.1 (s), 40.5 (t), 109.2 (d), 119.3 (d), 143.0 (s), 150.0 (s), 168.3 (s), 168.7 (s) |
| **2d** | 90[B] (57[A]) | $C_{11}H_{14}O_4$ (210.2) | 1.4899 | 0.85 | 1750 (br s), 1672 (m) | 1.67–2.80 (m, 6H), 2.11 (s, 6H), 5.41 (s, 1H), 5.56 (t, 1H, $J$ = 6) | 20.9 (q), 23.4 (t), 26.5 (t), 33.8 (t), 114.0 (d), 120.6 (d), 142.4 (s), 154.5 (s), 169.1 (s), 169.6 (s) |
| **2e** | 99[B] (57[A]) | $C_{12}H_{16}O_4$ (224.2) | 1.4880 | 0.95 | 1756 (br s), 1666 (m) | 1.35–1.90 (m, 4H), 1.90–2.55 (m, 4H), 2.10 (s, 3H), 2.13 (s, 3H), 5.38 (t, 1H, $J$ = 8), 5.45 (s, 1H) | 20.7 (t), 20.8 (q), 20.9 (q), 24.5 (t), 25.1 (t), 31.8 (t), 111.1 (d), 119.4 (d), 144.3 (s), 153.9 (s), 168.9 (s), 169.4 (s) |

[a] [A] Procedure A, [B] Procedure B.
[b] Satisfactory microanalyses obtained: C ± 0.25, H ± 0.09.
[c] TLC on silica gel; 50% EtOAc in light petroleum (bp 55–60 °C) as eluent.
[d] Recorded on a Specord IR-80 Infrared spectrophotometer.
[e] $^1$H-NMR were recorded on a Tesla BS 587 at 80 MHz and 20.1 MHz for $^{13}$C-NMR.

panying ketene are freezed out at − 40 °C prior to the reaction. The products and the time course of reactions are monitored by TLC (detection by $UV_{254}$ light).

**1,3-Diacetoxy-1,3-cyclohexadiene (2b); Typical Procedure A:**
Into a suspension of 1,3-cyclohexanedione (**1b**, 0.80 g, 7.13 mmol), of TsOH (100 mg) and of $Bu_2O$ (70 mL), kept at 125 °C (oil bath temperature), ketene[16] is introduced during 5 h. The solvent is removed at 25 °C/13 Pa and the residue is subjected to flash chromatography[17] (silica gel, EtOAc, petroleum ether bp 55–60 °C, 1:1); yield: 1.30 g (93%) of **2b** (Table).

**1,3-Diacetoxy-1,3-cyclooctadiene (2e); Typical Procedure B:**
A mixture of 1,3-cyclooctanedione (**1e**, 1.15 g, 8.20 mmol), isopropenyl acetate (75 mL) and TsOH (300 mg) is stirred and heated in an oil bath at 90 °C under nitrogen. The acetone formed during the reaction is continuously removed through a 20 cm vacuum-jacketed silvered column. After 71 h when no more acetone distills, the mixture is cooled and worked-up as described in A; yield: 1.82 g (99%) of **2e** (Table).

**1,3-Diacetoxy-1,3-cyclopentadiene (2a):**
Ketene is introduced during 4.5 h into a solution of 1,3-cyclopentanedione (**1a**, 1.00 g, 10.19 mmol) and TsOH (100 mg) in $CHCl_3$ (100 mL) at r.t. The mixture was worked-up as described in A; yield: 0.61 g (33%) of **2a** (Table).

Received: 27 February 1991; revised: 19 June 1991

(1) Baxter, I.; Phillips, W.R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2374.
(2) Birch, A.J.; Butler, D.N.; Effenberger, R.; Rickards, R.W. *J. Chem. Soc., Perkin Trans. 1* **1979**, 807.
(3) Rizzardo, E. *J. Chem. Soc., Chem. Commun.* **1975**, 644.
(4) Torkelson, S.; Ainsworth, C. *Synthesis* **1977**, 431.
(5) Hanson, L.; Carlson, R. *Acta Chem. Scand.* **1989**, *43*, 304.
(6) Cimarusti, C.M.; Wolinsky, J. *J. Am. Chem. Soc.* **1968**, *90*, 113.
(7) Birch, A.J.; Kelly, L.F.; Thompson, D.J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1006.
(8) Hashmi, M.A.; Munro, J.D.; Pauson, P.L.; Williamson, J.M. *J. Chem. Soc. (A)* **1967**, 240.
(9) Šraga, J.; Hrnčiar, P. *Acta Fac. Rerum. Nat. Univ. Comenianae, Chim.* **1981**, *29*, 105; *C.A.* **1982**, *96*, 122261.
(10) Rey, M.; Roberts, S.M.; Dreiding, A.S.; Roussel, A.; Vanlierde, H.; Toppet, S.; Ghosez, L. *Helv. Chim. Acta* **1982**, *65*, 703.
(11) Neilands, O.J.; Kalnina, S.V.; Stradinš, J.P.; Silinš, E.A. *Structure and Tautomerism of β-Dicarbonyl Compounds*, Zinatne, Riga 1977, p. 50, 61 and 66.
(12) Modi, N.N.; Ramegowda, N.S.; Koul, A.K.; Narang, C.K.; Mathur, N.K. *Indian J. Chem.* **1973**, *11*, 1049.
(13) Boháč, A.; Hrnčiar, P. *Coll. Czech. Chem. Commun.*, in press.
(14) Šraga, J.; Hrnčiar, P. *Synthesis* **1977**, 282.
(15) Thompson, R.B. *Org. Synth.* **1955**, *3*, 278.
(16) Williams, J.W.; Hurd, C.D. *J. Org. Chem.* **1940**, *5*, 122.
(17) Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.