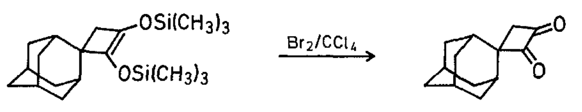
An Improved Method for the Preparation of Non-Enolisable *vic*-Diketones via Acyloin Condensation

J. Strating, S. Reiffers, and H. Wynberg

Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands

In a preliminary communication[1], we reported the nearly quantitative conversion of the bis-[trimethylsiloxy]-cyclobutene derivative **1** into the corresponding 1,2-dioxocyclobutane derivative **2**:



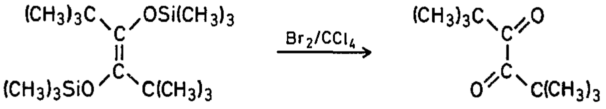
1 **2**

This oxidative cleavage[2] in aprotic medium may be of importance in the preparation of *vic*-diketones when an acyloin to be oxidized or the diketone is sensitive to protic solvents.

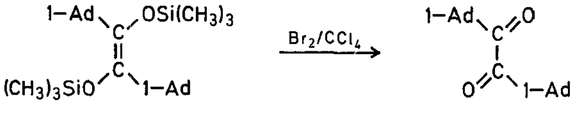
In this paper, we consider examples leading to the formation of non-enolisable *vic*-diones. Although in some cases chlorine and iodine were applied, it turned out that the procedure using *bromine* was the method of choice.

Acyclic Non-Enolisable *vic*-Diketones

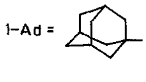
As representatives of this type of diones we chose 3,4-dioxo-2,2,5,5-tetramethylhexane (**4**, bipivaloyl)[3] and bis-[1-adamantyl]-ethanedione[4] (**6**). The starting compounds, 3,4-bis-[trimethylsiloxy]-2,2,5,5-tetramethyl-3-hexene (**3**) and 1,2-bis-[1-adamantyl]-1,2-bis-[trimethylsiloxy]-ethene (**5**), were prepared from ethyl pivaloate and ethyl adamantane-1-carboxylate[5] according to Schräpler and Rühlmann[6] in 42 and 60 % yields, respectively.



3 **4**

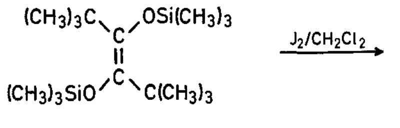


5 **6**

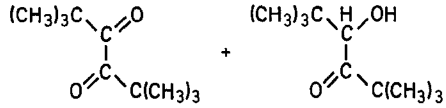


When a solution of *bromine* in carbon tetrachloride was added to a solution of **3** in the same solvent the bromine color was discharged immediately and the solution became yellow due to the formation of bipivaloyl (**4**). Compound **4** could be isolated in 81 % yield. Newman and Arkel[3] obtained **4** in 87 % yield by oxidation of pivaloin (**7**; prepared in 86 % yield) with chromic acid.

Treatment of **3** with *iodine* in dichloromethane for 30 min., followed by washing with aqueous sodium hydrogensulfite, afforded bipivaloyl (**4**, 53 %) and pivaloin (**7**, 30 %):



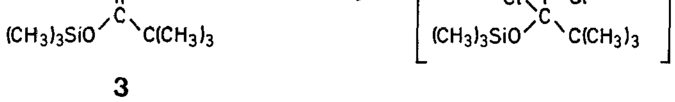
3



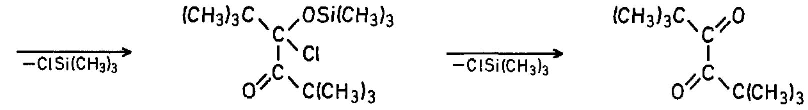
4 **7**

The formation of **7** may result from hydrolysis of the starting material **3** or of an iodine complex of **3**.

The reaction of **3** with *chlorine* in carbon tetrachloride was rapid and led to the formation of a colorless product. The spectral data of this substance were consistent with the structure of 3-chloro-4-oxo-2,2,5,5-tetramethyl-3-(trimethylsiloxy)-hexane (**8**):



3



8 **4**

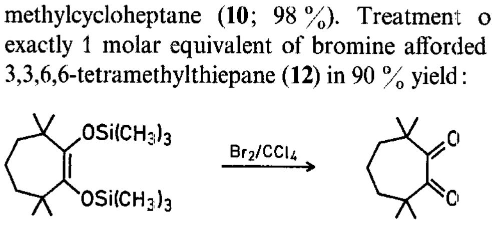
On standing, **8** slowly became yellow, indicating a decomposition to give bipivaloyl (**4**). Compound **4** was produced in 75 % yield when **8** was refluxed without solvent for 30 min.

Treatment of compound **5** with bromine in carbon tetrachloride afforded bis-[1-adamantyl]-ethanedione (**6**) in 98% yield.

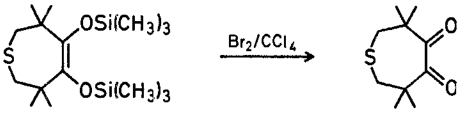
Cyclic Non-Enolisable *vic*-Diketones

The starting materials **9** and **11** have hitherto not been described. 1,2-Bis-[trimethylsiloxy]-3,3,7,7-tetramethylcycloheptene (**9**) was prepared in 50 % yield by Feith[7] employing the method of Gream and Worthley[8]. 4,5-Bis-[trimethylsiloxy]-3,3,6,6-tetramethyl-2,3,6,7-tetrahydrothiepin (**11**) was obtained in 60 % yield following the procedure of Rühlmann, Seefluth, and Becker[9].

Treatment of **9** with bromine in the usual way yielded gaschromatographically pure 1,2-dioxo-3,3,7,7-tetramethylcycloheptane (**10**; 98 %). Treatment of **11** with exactly 1 molar equivalent of bromine afforded 5,6-dioxo-3,3,6,6-tetramethylthiepane (**12**) in 90 % yield:



9 **10**



11 **12**

The oxidation of **11** with iodine in dichloromethane afforded 42 % of **12** and 52 % of the corresponding acyloin. From the reaction mixture obtained by treatment of **11** with chlorine in carbon tetrachloride, the dione **12** could not be isolated. The N. M. R. spectrum of the product indicated that chlorination in α-position to the sulfur atom and ring opening had occurred. The preparation of **10** from the corresponding acyloin by oxidation with chromium(VI)-oxide has been described[10]; the dione **12** has previously been obtained by oxidation of the corresponding acyloin with lead(IV)-acetate in pyridine[11].

The m.p. and b.p. given are uncorrected. N.M.R. spectra were run using a Varian A-60 and trimethylsilane as an internal standard. I.R. spectra were recorded on a Perkin-Elmer spectrophotometer model 257. Microanalyses were carried out in the Analytical Department of this laboratory (W. M. Hazenberg).

The *vic*-bis-[trimethylsiloxy]-alkenes were prepared according to the procedure of Rühlmann et al.[6,9]. All reactions were carried out in boiling toluene under a nitrogen atmosphere.

Starting Materials

3,4-Bis-[trimethylsiloxy]-2,2,5,5-tetramethyl-3-hexene (3):
Yield: 42%; b.p. 88–95°/1 mm. Crystallization from ether at −70° gave the analytically pure compound; m.p. 47–49°.

$C_{16}H_{36}O_2Si_2$	calc.	C 60.7	H 11.46
(316.63)	found	60.4, 60.4	11.3, 11.4

I.R. (nujol): $\nu_{max} = 1255$ (s) and 1270 cm^{-1} (m), C—Si; 840 (s) and 860 cm^{-1} (s), O—Si; 1160 cm^{-1} (s).
N.M.R. (CCl_4): $\tau = 8.86$ (s, 18 H), 9.75 (s, 18 H).

1,2-Bis-[1-adamantyl]-1,2-bis-[trimethylsiloxy]-ethene (5):
Yield: ~55% (determined by G.L.C.). Recrystallization from ether and hexane afforded the analytically pure compound; m.p. 159–161°.

$C_{28}H_{48}O_2Si_2$	calc.	C 71.12	H 10.23
(472.86)	found	71.2, 71.4	10.1, 10.2

Mass spectrum: $M^+ = 472$.
I.R. (KBr): $\nu_{max} = 1250$ (s) and 1265 cm^{-1} (s), C—Si; 840 (s) and 860 cm^{-1} (s), O—Si; 1165 cm^{-1} (s).
N.M.R. (CCl_4): $\tau = 9.74$ [s, 18 H, OSi($C\underline{H}_3)_3$], 8.0–8.5 (m, 30 H, adamantyl protons).

1,2-Bis-[trimethylsiloxy]-3,3,7,7-tetramethylcycloheptene (9)[7]:
Yield: 50%; b.p. 141°/10 mm; n_D^{20}: 1.4648.

$C_{17}H_{36}O_2Si_2$	calc.	62.13	H 11.04
(328.65)	found	62.1, 62.4	10.8, 10.8

I.R. (neat): $\nu_{max} = 1615$ cm^{-1} (m), C=C; 840 cm^{-1} (s), O-Si.
N.M.R. (CCl_4): $\tau = 8.39$ (s, 6 H), 8.96 (s, 12 H), 9.86 [s, 18 H, OSi($C\underline{H}_3)_3$].

4,5-Bis-[trimethylsiloxy]-3,3,6,6-tetramethyl-2,3,6,7-tetrahydrothiepin (11):
Yield: 61%; b.p. 102–105°/0.25 mm.

$C_{16}H_{34}O_2Si_2S$	calc.	C 55.43	H 9.89	S 9.25
(346.68)	found	55.6, 55.5	9.8, 9.8	9.1, 9.1

I.R. (neat): $\nu_{max} = 1250$ cm^{-1} (s), C—Si; 880 (s) and 845 cm^{-1} (s), O—Si.

N.M.R. ($CDCl_3$): $\tau = 9.80$ [s, 18 H, OSi($C\underline{H}_3)_3$], 8.74 (s, 12 H, —$C\underline{H}_3$), 7.40 (s, 4 H, S—$C\underline{H}_2$—).

Reaction of the Bis-[trimethylsiloxy]-ethene Derivatives with Halogen

Reaction with Bromine: To a stirred solution of the alkene in carbon tetrachloride was added dropwise a solution of bromine in carbon tetrachloride until no further decolorisation of bromine occurred, or until exactly one equivalent of bromine was added. The solvent was then removed under reduced pressure and the residue was distilled or recrystallized.

3,4-Dioxo-2,2,5,5-tetramethylhexane (4, Bipivaloyl):
From **3**; yield: 81%; b.p. 58–60°/13 mm (Ref.[10], b.p. 59 to 62°/14 mm).

Bis-[1-adamantyl]-ethanedione (6):
From **5**; yield: >95%; crystallized from ethanol, m.p. 211–214° (Ref.[4], m.p. 219°).

1,2-Dioxo-3,3,7,7-tetramethylcycloheptane (10):
From **9**; yield: 95%; gaschromatographically pure; micro-distilled at 12 mm, bath temperature 120° (Ref.[10], b.p. 87–91°/6 mm).

5,6-Dioxo-3,3,6,6-tetramethylthiepane (12):
From **11**; yield: 90%; b.p. 120–122°/12 mm (Ref.[10], b.p. 68°/0.36 mm).

Reaction with Chlorine:

3-Chloro-4-oxo-2,2,5,5-tetramethyl-3-(trimethylsiloxy)-hexane (8):
To a stirred solution of **3** in carbon tetrachloride was added with external cooling (icebath) an excess of chlorine in carbon tetrachloride. The reaction mixture was concentrated, below 20° under reduced pressure, to yield an instable, colorless oil.

I.R. (neat): $\nu_{max} = 1705$ cm^{-1} (s), C=O; 1260 cm^{-1} (s), C—Si; 850 cm^{-1}, O—Si.

N.M.R. (CCl_4) $\tau = 9.70$ (s, 9 H), 8.72 (s, 9 H), 8.91 (s, 9 H).

When the oil was heated, chlorotrimethylsilane [$ClSi(CH_3)_3$] was eliminated rapidly and bipivaloyl (**4**) was formed.

3,4-Dioxo-2,2,5,5-tetramethylhexane (4, Bipivaloyl):
From **8**. Compound **8** was refluxed without solvent for 30 min. and the resultant product distilled in vacuo; yield 75% (calculated on **3**); b.p. 57–59°/11 mm.

Reaction with Iodine:

Bipivaloyl (4) and 3-Hydroxy-4-oxo-2,2,5,5-tetramethylhexane (7, Pivaloin) from 3:
To a stirred solution of **3** in dichloromethane, one molar equivalent of iodine was added slowly. The color of the iodine disappeared fairly rapidly until ~0.5 equivalent of iodine was added. The mixture turned dark. The rest of the iodine was added and the mixture stirred for additional 30 min. The solvent was removed in vacuo and the residue taken up in ether. The ether solution was washed with aqueous sodium hydrogen sulfite, then with aqueous sodium hydrogencarbonate, and dried over magnesium sulfate. The solvent was removed and the residual yellowish oil distilled in vacuo; yield: 53% of *bipivaloyl* (**4**); b.p. 59 to 65°/13–14 mm. From the residue of the distillation, *pivaloin* (**7**) could be isolated by sublimation; yield: 30%; m.p. 76–78° (Ref.[10], m.p. 80–80.5°).

5,6-Dioxo-3,3,6,6-tetramethylthiepane (12) from 11:
Using the same procedure as described above, a mixture of **12** (42%) and the corresponding acyloin (4-hydroxy-5-oxo-3,3,6,6-tetramethylthiepane, 52%) was obtained. The yields were calculated from the N. M. R. spectrum of the mixture.

Received: December 3, 1970

---

[1] H. WYNBERG, J. STRATING, S. REIFFERS, Rec. Trav. Chim. **89**, 982 (1970).

[2] K. RÜHLMANN, S. POREDDA, J. prakt. Chem. [4] **12**, 18 (1960). These Authors proved the existence of the double bond in bis-[trimethylsiloxy]-alkenes by decolorisation of a bromine solution; in the case of 1,2-diphenyl-1,2-bis- [trimethylsiloxy]-ethene, they obtained benzil in 98% yield.

[3] M. S. NEWMAN, A. ARKELL, J. Org. Chem. **24**, 385 (1959).

[4] H. STETTER, E. RAUSCHER, Chem. Ber. **93**, 1161 (1960).

[5] H. STETTER, M. SCHWARZ, A. HIRSCHHORN, Chem. Ber. **92**, 1629 (1959).

[6] U. SCHRÄPLER, K. RÜHLMANN, Chem. Ber. **96**, 2780 (1963).

[7] H. FEITH, this laboratory, unpublished work.

[8] G. E. GREAM, S. WORTHLEY, Tetrahedron Letters **1968**, 3319.

[9] K. RÜHLMANN, H. SEEFLUTH, H. BECKER, Chem. Ber. **100**, 3820 (1967).

[10] N.J. LEONARD, P.M. MADER, J. Amer. Chem. Soc. **72**, 5388 (1950).

[11] A. deGROOT, H. WYNBERG, J. Org. Chem. **31**, 3954 (1966).