The Reaction of Dicarbonyl Compounds with Potassium in the Presence of Trimethylsilyl Chloride

Takashi MURAKAWA, Koji FUJII, Shinji MURAI, and Shigeru TSUTSUMI

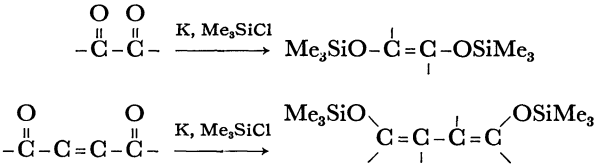
Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka

(Received February 24, 1972)

The reaction of dicarbonyl compounds with potassium in the presence of trimethylsilyl chloride was studied. The carbonyl compounds were benzil (II), 9,10-phenanthroquinone (III), *p*-benzoquinone (IV), disodium salt of tetrahydroxy-*p*-benzoquinone (V), and *trans*-dibenzoylethylene (VI), as well as benzophenone (I). I and II gave bistrimethylsiloxy compounds in good yields, but III did not react under the same conditions. 1,4-Bistrimethylsiloxybenzene and 1,4-diphenyl-1,4-bistrimethylsiloxybutadiene were obtained from IV and VI respectively. A similar conjugate reductive silylation was successful with V affording hexakistrimethylsiloxybenzene in 35% yield.

In the presence of trialkylsilyl chlorides, monoketones undergo reductive dimerization to pinacol bissilyl ethers with magnesium or alkali metals.[1-3] 1,2-Bistrimethylsiloxy alkenes were obtained when acyloin condensation was carried out in the presence of trimethylsilyl chloride.[4,5] Since the modified acyloin condensation is very likely to involve reductive silylation of 1,2-diketone intermediates,[6] it seems to be of interest to study the reduction of dicarbonyl compounds with alkali metal in the presence of trimethylsilyl chloride. A few studies have been reported on the reductive silylation of diketones. Rühlman treated benzil with alkali metal and trimethylsilyl chloride to give two isomeric enediol-disilyl ethers. However, no effort was made to establish the structure of each isomer.[4a] Recently Bouas-Laurent reported the reductive silylation of quinones with magnesium, bistrimethylsiloxy arenes being obtained.[7]

The present work deals with the reaction of dicarbonyl compounds with potassium in the presence of trimethylsilyl chloride. The compounds studied were benzil (II), 9,10-phenanthroquinone (III), *p*-benzoquinone (IV), disodium salt of tetrahydroxy-*p*-benzoquinone (V),[8] and *trans*-dibenzoylethylen (VI), as well as benzophenone (I). The following conjugate reductive silylation would be expected for the 1,2- and 1,4-dicarbonyl compounds:



Potassium was used as a reducing metal because it melts above 64°C and can provide a clean metal surface during the course of reaction. The standard procedure of the reaction is as follows. Trimethylsilyl chloride in a slight excess was added to a mixture of a ketone, melted potassium and a solvent over a period of 2 hr at 60—70°C. When the total amount of trimethylsilyl chloride was added at the beginning of the reaction, the same products were obtained but in a lower yield probably because of impurities formed on the metal surface. The results are shown in Table 1.

Benzophenone (I) gave VII which was identical with that prepared separately by the trimethylsilylation of benzopinacol. The observed wide range of melting point might be attributed to the dissociation of VII into diphenyl(trimethylsiloxy)methyl radical as suggested by Calas *et al.*[1] From benzil (II), *cis*- and *trans*-1,2-bistrimethylsiloxy-1,2-diphenylethylene (VIIIa and VIIIb respectively) were obtained in good yields. The assignment of the isomer was based on the IR spectra. The *cis*-isomer VIIIa showed an absorption due to the double bond at 1620 cm^{-1}, while the *trans*-isomer VIIIb showed no double bond absorption usually observed for a double bond at the center of symmetry.[9] The high melting point of VIIIb might also support this assignment. The ratio of VIIIa to VIIIb was 70: 30. The predominant formation of VIIIa could be explained by the stabilization of *cis*-radical-anion.[10] 9,10-Phenanthroquinone (III) which is considered to have *s-cis* configuration of II resisted completely to react under the present con-

1) R. Calas, N. Duffaut, C. Bourges, F. Pisiotti, and J. Dunognes, *Acad. Sci., Paris, Ser, C*, **267**, 322 (1968).

2) C. L. Fryl, R. M. Salinger, and T. J. Patin, *J. Amer. Chem. Soc.*, **88**, 2343 (1966).

3) a) R. A. Calas, J. Dunogues, N. Duffant, and C. Biran, *Acad. Sci., Paris, Ser, C*, **267**, 494 (1968). b) K. Rühlmann, A. Sitzki, and C. Michael, *Chem. Ber.*, **101**, 285 (1968).

4) a) K. Rühlmann and S. Poredda, *J. Prakt. Chem.*, **12**, 18 (1960). b) U. Schrapler and K. Rühlmann, *Chem. Ber.*, **96**, 2780 (1963). c) *ibid.*, **97**, 1383 (1964). d) *ibid.*, **98**, 1352 (1965). e) K. Rühlmann, H. Seefluth, and H. Becker, *ibid.*, **100**, 3820 (1967).

5) a) J. J. Bloomfield, *Tetrahedron Lett.*, **1968**, 587. b) *ibid,*. **1968**, 591. c) *ibid.*, **1968**, 5647. d) G. E. Green and S. Worthley, *ibid.*, **1968**, 3319. e) J. M. Conia and J. M. Denis, *ibid.*, **1969**, 3545. f) G. A. Russell and G. W. Holland, *J. Amer. Chem. Soc.*, **91**, 3968 (1969). g) T. Mori, T. Nakahara, and H. Nozaki, *Can. J. Chem.*, **47**, 3266 (1966). h) C. Ainsworth and F. Chen, *J. Org. Chem.*, **35**, 1272 (1970).

6) S. M. McElvain, "Organic Reactions," Vol. 4, p. 257. (1949).

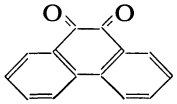
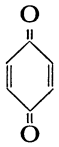
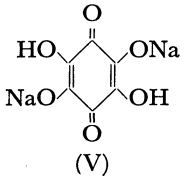
7) H. Bouas-Laurent, R. Lapouyade, C. Brigand, and J. P. Desvergne, *Acad. Sci., Paris, Ser, C*, **270**, 2167 (1970).

8) A preliminary result obtained for V has been reported. S. Murai, T. Murakawa, and S. Tsutsumi, *Chem. Commun.*, **1970**, 1329.

9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y. (1958), p. 38.

10) a) N. L. Bauld, *J. Amer. Chem. Soc.*, **84**, 4345 (1962). b) *ibid.*, **87**, 4748 (1965).

TABLE 1. REDUCTIVE SILYLATION OF CARBONYL COMPOUNDS

Exp. No.	Material	Solvent	Product	Yield (%)
1	$C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5$ (I)	Toluene	$\left(Me_3Si{-}O{-}\overset{\|}{\underset{C_6H_5}{\underset{\|}{C}}}{-}\right)_2$ (VII)	72
2	$C_6H_5\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}C_6H_5$ (II)	Benzene	$C_6H_5(C_6H_5)C{=}C(OSiMe_3)(Me_3SiO)$ (VIIIa); $C_6H_5(Me_3SiO)C{=}C(C_6H_5)(OSiMe_3)$ (VIIIb)	88 *cis/trans*=70/30
3	 (III)	Benzene	No reaction	
4	 (IV)	Benzene	No reaction	
		THF	$Me_3SiO{-}C_6H_4{-}OSiMe_3$ (IX)	28
5	 (V)	THF	$(Me_3SiO)_3C_6H_3(OSiMe_3)$ (X)	35
6	$C_6H_5\overset{O}{\overset{\|}{C}}{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}C_6H_5$ (VI)	Benzene	$C_6H_5(H)C{=}C(OSiMe_3)(Me_3SiO){-}C(H){=}C(H)C_6H_5$ (XIa) or $Me_3SiO(H)C{=}C(C_6H_5){-}C(C_6H_5)(H){=}C(H)OSiMe_3$ (XIb)	12

ditions.[11] The double bond in the dianion of ene-diol formed by reduction in the case of II might bring the originally separated two phenyl groups into one π-net work increasing *ca.* 18 kcal/mol of the delocalization energy of the system.[10] On the other hand, two phenyl groups of III are originally coupled and the effect of introducing a double bond at 9,10-position by the reduction with alkali metal might decrease the delocalization energy as compared with that of III.[12] The reaction of *trans*-dibenzoylethylene (VI), a 1,4-diketone, gave a bistrimethylsiloxybutadine (XI) whose NMR spectra showed one sharp singlet due to the trimethylsilyl group. Of the three possible isomers for XI, *trans-trans*- or *cis-cis*-1,4-diphenyl-1,4-bistrimethylsiloxybutadine (XIb or XIa) is consistent with the NMR data, but not for the *cis-trans* isomer with two nonequivalent trimethylsilyl groups. The low yield of XI might be due to polymerization of the product.

The 1,6-conjugate reductive silylation was extended to *p*-quinones. The reaction of *p*-benzoquinone (IV) in benzene gave 1,4-bistrimethylsiloxybenzene (IX) when tetrahydrofuran was used as a solvent. A similar conjugate reductive silylation was successful with disodium salt of tetrahydroxy-*p*-benzoquinone (V) affording hexakistrimethylsiloxybenzene (X) is 35% yield. Inspection of a model of X revealed the existence of two representative structures; one with

11) However, III was reported to undergo reductive silylation with magnesium.[7] The difference from potassium and magnesium is not clear.

12) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemist," John Wiley & Sons, Inc., New York, N. Y. (1961), p. 251.

Table 2. Properties of silylated products

Products	Mp °C (Bp °C/mmHg)	Formula	Analyses (%) Found (Calcd) C	H	NMR[a] τ	IR cm^{-1}
VII	130—135[d]	$C_{32}H_{38}O_2Si_2$	75.28 (75.29)	7.43 (7.45)	9.98 (*s*, 18H) 2.89 (*s*, 20H)	1250, 830 (Me_3Si) 1105 (C–O–Si)
VIIIa	(160—161/8)[e]	$C_{20}H_{28}O_2Si_2$	67.74 (67.41)	8.18 (7.87)	9.95 (*s*, 18H) 3.20 (*s*, 10H)	1250, 850 (Me_3Si) 1150 (C–O–Si) 1620 (C=C)
VIIIb	108—110[f]	$C_{20}H_{28}O_2Si_2$	67.55 (67.41)	7.97 (7.87)	10.23 (*s*, 18H) 2.07 (*s*, 10H)	1250, 850 (Me_3Si) 1150 (C–O–Si)
IX	48—50[g]	$C_{12}H_{22}O_2Si_2$	56.76 (56.65)	8.69 (8.65)	9.76 (*s*, 18H) 3.36 (*s*, 4H)	1225, 1255, 840 (Me_3Si) 925 (C–O–Si)
X	220[c]	$C_{24}H_{54}O_6Si_6$	47.39 (47.47)	9.12 (8.96)	9.86 (*s*)	1250, 840 (Me_3Si)[b] 1040 (C–O–Si)
XI	128—130	$C_{22}H_{30}O_2Si_2$	68.73 (69.07)	7.82 (7.73)	9.75 (*s*, 18H) 3.63 (*s*, 2H) 2.70 (*m*, 10H)	1245, 870 (Me_3Si) 1580, 1555 (C=C–C=C) 1060 (C–O–Si)

a) Obtained in CCl_4. *s*: singlet, *m*: multiplet. b) There was an additional strong absorption at 890 cm^{-1}. c) The mass and UV spectroscopic data were reported elsewhere.[8] d) Lit,[1] 158°C decomp. e) Lit,[4a] bp 142—143.5/2 mmHg f) Lit,[4a] 109.5—110°C. g) Lit [7] 49—50°C.

all the silicon and oxygen atoms in the same plane of benzene ring and the other in which only the six oxygen atoms lie in the plane of the ring leaving the six silicon atoms outside (alternatively above and below) the plane. Low temperature NMR study was carried out in the hope of obtaining information on the non-equivalent methyl groups which might arise. However, the one sharp singlet (τ 9.86 in CCl_4 at room temperature) remained unchanged even at −100°C (in ether-pentane). This could be accounted for in different way, such as (a) as being due to the methyl protons lying too far apart to be affected by aromatic π-electrons or (b) to free rotation about the bonds in trimethylsilyl groups. No conclusive evidence of the structure of X has so far been obtained.

The reductive silylation has been proven to be a good synthetic method for compounds such as X and XI which might be otherwise difficult to obtain.

Experimental

The starting materials, ketone, diketones, and quinones were commercially available except for *trans*-1,2-dibenzoylethylene.[13] All the reactions were carried out under dry nitrogen. Boiling and melting points were uncorrected.

General Procedure. To a rapidly stirred mixture of 0.1 mol of carbonyl compound and potassium (0.1 g atom for I and 0.2 g atom for II—IV, and VI, and 0.4 g atom for V) in an appropriate solvent was added a slight excess of trimethylsilyl chloride (above the amount of potassium used) over a period of 2 hr at 60—70°C. The reaction mixture was then cooled to room temperature and left to stand overnight. Filtration of potassium chloride followed by evaporation of the solvent afforded the product mixture. This was found to contain merely starting carbonyl compounds in the case of Expts. 3 and 4 (in benzene). In Expts. 1, 4 (in THF), 5, and 6, the resulting product mixture was solids and was recrystallized from hexane to give pure silylated compounds VII, IX, X, and XI, in the yields shown in Table 1. In Expt. 2, the product mixture was a yellow liquid which on standing partially crystallized. The solids were collected by filtration and crystallized from hexane to give VIIIb, colorless rhombic crystals. The filtrate was distilled under reduced pressure and afforded VIIIa, a colorless liquid, bp 160—161°C/8 mmHg. The *cis*/*trans* ratio was determined from the NMR spectrum of the mixture.

The authors are indebted to Shin-etsu Kagaku Kogyo Co. Ltd. for the supply of trimethylsilyl chloride.

13) R. E. Lutz, "Organic Syntheses," Coll. Vol. III, p. 248 (1955).