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# α-CYCLOPROPYLIDENE-KETALS, -KETONES AND -ALDEHYDES

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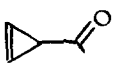
While cyclopropenyl- and vinylidene-cyclopropyl-carbonyl compounds of types a, b and c were amply described in literature (1) α-cyclopropylidene-carbonyl compounds of type d are practically unknown (2).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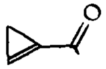
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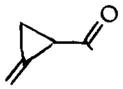
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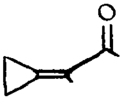
d

We wish to report in this communication a general method of preparation of aldehydes and ketones d, from α-ketoaldehyde and α-diketone monoketals by a Wittig reaction with cyclopropylidene triphenylphosphorane (3), followed by appropriate deketalisation (see Table I) ; the main spectral features of these particular conjugated carbonyl compounds are also presented.

Except for the commercially available ketoketal 1, the starting materials were prepared : 2 and 3, by the reaction of the corresponding diethylketal-pyruvates with MeMgCl and n-BuMgBr respectively in HMPT, according to a method recently described (4) ; 4 by the reduction of ethyl diethylketal-pyruvate with $LiAlH_4$ followed by oxidation with $CrO_3$, Pyridine, $CH_2Cl_2$ (5).

The preparation of α-cyclopropylidene-ketals 6 - 9 entails no comment ; they are relatively stable and may be isolated by distillation. The less stable, 9, undergoes partial decomposition at about 100°. Ketones 12 and 13 are also relatively stable which allows the hydrolysis of ketoketals 7 and 8 by trans ketalisation with $H_2SO_4$ as catalyst (6) (12 : 50% ; 13 : 95%). However deketalisation by hydrolysis on wet silicagel gives best result for 7 ⟶ 12. 11 and 14 are more instable and are obtained from 6 or 9 using mild conditions (6).

We also attempted to prepare ketone 14 from α-keto-thioketal 5 (7) via cyclopropylidene-thioketal 10 but only resinous products were obtained probably due in particular to the unstability of 14 in the hydrolysis conditions (Scheme I).

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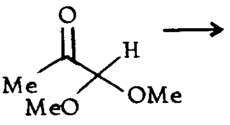
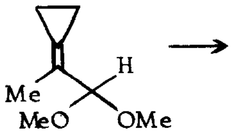
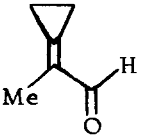
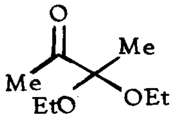
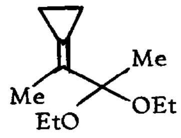
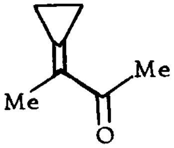
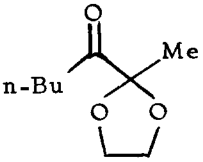
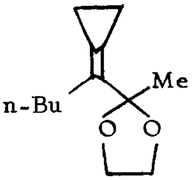
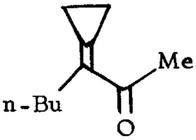
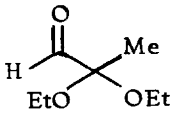
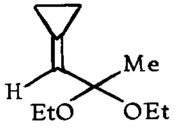
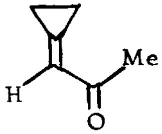
Table I. α-Cyclopropylidene-carbonyl compounds : preparation and spectral data

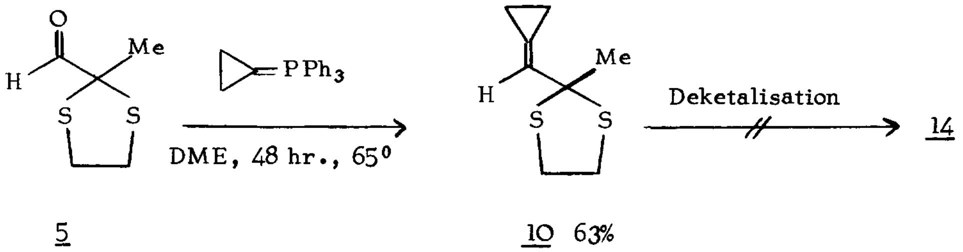
| α-keto-ketals | α-cyclopropylidene-ketals [a] | α-cyclopropylidene-carbonyl compounds [b] | |
|---|---|---|---|
| | | | IR, UV, NMR [c] |
| <br>1 | <br>6 56% | <br>11 85% | 1680 and 1745 cm$^{-1}$.<br>230 (>7000) and 327 (> 20).<br>1.32 (m, 4H) ; 1.86 (m, 3H) ; 9.68 (s, 1H). |
| <br>2 | <br>7 79% | <br>12 85% | 1675 and 1755 cm$^{-1}$.<br>229 (14000) and 320 (31).<br>1.35 (m, 4H) ; 1.88 (m, 3H) ; 2.26 (s, 2H). |
| <br>3 | <br>8 50% | <br>13 95% | 1675 and 1745 cm$^{-1}$.<br>231 (13000) and 323 (42).<br>0.90 - 1.35 (7H) ; 1.35 (m, 4H) ; 2.26 (s, 3H). |
| <br>4 | <br>9 65% | <br>14 85% | 1675 and 1745 cm$^{-1}$.<br>219 (12000) and 325 (28).<br>1.38 (m, 4H) ; 2.20 (s, 3H) ; 6.31 (m, 1H). |

a) Obtained from keto-ketals 1 - 4 by Wittig reaction with two equivalents of  PPh$_3$ (3) in DME (6 and 9 :48hr., 65°) (7 and 8 : 96hr., 75°). The products were isolated : 6 and 7 by bulb to bulb distillation, 90° - 140°/10 torr ; 9 by flash distillation 75° - 80°/0.07 torr ; 8 by column chromatography on silicagel.

b) Deketalisation of 6 - 9 into ketones and aldehyde 11 - 14 was conducted by hydrolysis on wet silicagel in CH$_2$Cl$_2$ or transketalisation (6).

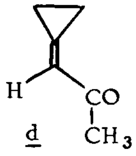
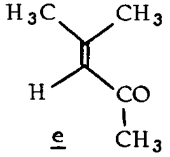
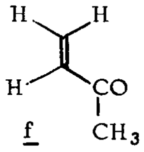
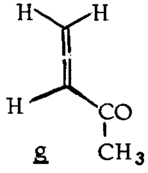
c) IR spectra in CCl$_4$ : $\nu_{C=O}$ and $\nu_{C=C}$ in order; in all the spectra of 11 - 14 the $\nu_{C-H}$ band of the cyclopropylidene group at 3060 cm$^{-1}$ is also present). UV spectra in cyclohexane λ max ( $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$) in nm ($\varepsilon$). NMR spectra in CCl$_4$ : $\delta$ ppm. 14 was recently described (2).

Scheme I



As a comparison main IR and UV features of a typical ketone d : 14 and related enones : isopropylidene-ketone e, vinyl-ketone f and allenyl-ketone g are gathered in table II. In the d (cyclopropylidene-ketone) spectrum, $\nu_{C=O}$ band frequency is lower than in the spectra of the others (e, g, f) and in contrast to latter two, there is a single band, probably because only one conformation s-cis or s-trans is present. On the other band, the $\nu_{C=C}$ frequency of aldehyde and ketones d (11 - 14) is higher, i.e. in the position expected for the double bond of alkylidenecyclopropanes. The n $\longrightarrow \pi^*$ transitions of all these enones occur at $\sim$ 320 nm ; on the contrary, $\pi \longrightarrow \pi^*$ transitions depend on the structure. Maximum wavelength is longer in cyclopropylidene-ketone (d) than in vinyl-ketone (f) and allenyl-ketone (g), but lower than in isopropylidene-ketone e .

Table II. IR and UV data of different types of enones.

| |  |  |  |  |
|---|---|---|---|---|
| $\nu^{CCl_4}_{C=O}$ (cm$^{-1}$) | 1675 (8a) | 1694 (s-cis) | 1706 (s-cis)<br>1686 (s-trans) | 1686 and 1677 (8e)<br>($C_2Cl_4$) |
| $\nu_{C=C}$ (cm$^{-1}$) | 1745(8a) | 1623 (8b) | 1617 (8b) | |
| $\lambda^{alkane}_{max}$ $\pi \rightarrow \pi^*$ nm ($\varepsilon$) | 219 (12000)(8a) | 231 (11500)(8c) | 208 (8200)(8d) | 200.5 (13500)(8f) |

The preparation and characterisation of other $\alpha$-cyclopropylidene-ketones and -aldehydes are in progress.

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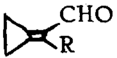
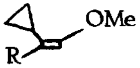
1) See for instance : R. Breslow, Angew. Chem. Internat. Ed., 7, 565 (1968) ; E.F. Ullman and W.J. Fanshawe, J. amer. chem. Soc., 83, 2379 (1961) ; H. Monti and M. Bertrand, Tetrahedron Letters, 1235 (1969) ; M. Franck-Neumann and C. Buchecker, ibid., 15 (1969) ; M. Vidal, M. Vincens and P. Arnaud, Bull. Soc. chim., 657, 665 (1972) ; M. Vidal and P. Arnaud, ibid., 675 (1972) ; and references therein.

2) Except for α-cyclopropylidene-acetone 14 recently pointed out as formed by photoisomerisation of 2-acetyl-methylenecyclopropane (Z. Goldschmidt and S. Mauda, Tetrahedron Letters, 4183 (1976)), cyclopropylidene-malonaldehyde-diketal (C. Reichardt, W. Pressler and E.U. Wurthweim, Angew. Chem. Internat. Ed., 15, 112 (1976), three α-cyclopropylidene-aldehydes :  obtained in this laboratory from  by photooxygenation then reduction (G. Rousseau, P. Le Perchec and J.M. Conia, submitted for publication in this journal) and esters (E.F. Ullman, J. amer. chem. Soc., 81, 5386 (1959); E.F. Ullman, ibid., 82, 505 (1960) ; W.v.E.Doering and H.D. Roth, Tetrahedron, 26, 2825 (1970) ; R. Barlet, Thesis, Grenoble, 1976, A.O. CNRS 12142).

3) K. Utimoto, M. Tamura and K. Sisido, Tetrahedron, 29, 1169 (1973).

4) F. Huet, M. Pellet and J.M. Conia, Tetrahedron Letters, 3579 (1976).

5) R. Ratcliffe and R. Rodehorst, J. org. Chem., 35, 4000 (1970).

6) 2 g $SiO_2$, 0,2 g $H_2O$, 1 g 7 or 9 ketoketals, 4 $cm^3$ $CH_2Cl_2$ are stirred for 10 min. at room temperature then filtrated, washed with $CH_2Cl_2$ and evaporated. With more resistant to hydrolysis 6, 50 mg of COOH-COOH are previously added to the mixture. Otherwise 13 may be obtained by transketalisation of 8 (1g 8, 50 $cm^3$ acetone, 20 mg $H_2SO_4$ , 10 min., 56°, neutralisation by $Na_2CO_3$, filtration, evaporation). 11 is obtained either by hydrolysis on wet silicagel or by mild transketalisation (1 g 6, 50 $cm^3$ acetone, 50 mg COOH-COOH, 60 hr. 25°). Concerning deketalisation by wet silicagel, see F. Huet, A. Lechevallier, M. Pellet and J.M. Conia, to be published.

7) T.L. Fridinger and K.R. Henery-Logan, J. Heterocycl. Chem., 8, 469 (1971).

8) a) Present paper ; b) J.M. Conia and J. Gore, in Structure et Proprietés Moléculaires, J.M. Conia and coll., Masson Ed., 1973, p. 44 ; c) J.P. Doucet, ibid, p. 223 ; d) R. Mecke and K. Noack, Chem. Ber., 93, 210 (1960) ; e) J. Chouteau, G.Davidovics, M. Bertrand, J. Le Gras, J. Figarella and M. Santelli, Bull. Soc. chim., 2562 (1964) ; f) J. Le Gras, Thesis, Marseille, 1966.