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CYCLOPROPANONES. XI[1a] REACTION OF 2,2-DIMETHYLCYCLOPROPANONE WITH $CH_2=C(OCH_3)_2$. A NOVEL ORTHOESTER AND ITS UNUSUAL DIMERIZATION.*

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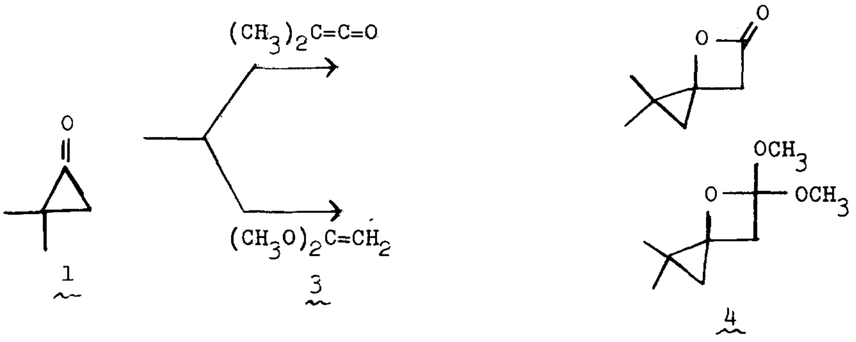
There has been considerable recent interest in the syntheses and chemistry of small rings.[2] 2,2-Dimethylcyclopropanone (1) undergoes both 3+ 2 (6π electron) → 5 membered ring and 3 + 4 (6π electron) → 7 membered ring cycloadditions,[3] which are allowed from orbital symmetry considerations, to be concerted.[4] Thermal 2 + 2 (4π electron) → 4 membered ring cycloadditions, however, are expected to be two step reactions.[5,6] Nevertheless, 1 reacts with the C=C bond of dimethylketene to yield[7] the cyclic lactone 2. We report now that the cycloaddition of 1 to 1,1-dimethoxy ethylene (3) yields the novel orthoester 4. In addition, 4 undergoes an unusual dimerization to yield the eight membered ring heterocycle, 5.



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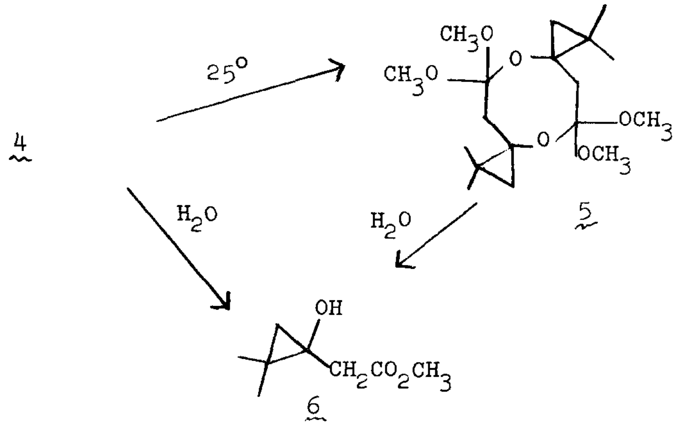
Addition of 3 to a CH_2Cl_2 solution of 1 yields 4 (90% by NMR). Compound 4 shows NMR (CH_2Cl_2, TMS internal) δ 0.47 (2 H, AB, $\Delta\nu'_{AB}$ = 12.0 Hz, J = 6.8 Hz), 0.97 (3 H, S), 1.12 (3 H, S), 2.73 (2 H, AB, $\Delta\nu'_{AB}$ = 9.1 Hz, J = 11.5 Hz), 3.31 (6 H, S); IR (CCl_4) No OH, No C=O; MS 75 ev (m/e, %) 172 (24, M^+), 157 (57), 143 (25), 141 (24), 130 (18), 125 (12), 115 (88), 88 (82), 85 (15), 84 (12), 83 (21), 82 (11), 81 (30) and 43 (100) inter alia.

Treatment of 4 with H_2O yields 6 (85%). NMR ($CDCl_3$, TMS internal) δ 0.43 (2 H, AB, $\Delta\nu_{AB}$ = 14.5 Hz, J = 5.5 Hz), 1.04 (3 H, S), 1.27 (3 H, S), 2.70 (2 H, AB, $\Delta\nu_{AB}$ = 14.0 Hz, J = 17.0 Hz), 3.49 (1 H, S, ex. D_2O) and 3.73 (3 H, S); IR ($CDCl_3$) cm^{-1} 3600, 3550 (free and intramolecular assoc. OH, resp.), 3068 (CH, cyclopropyl), 1730 (C=O); MS 75 ev (m/e, %) 158 (7, M^+), 143 (56), 140 (12), 127 (4), 125 (5), 111 (8), 88 (11), 86 (63), and 84 (100), inter alia. Compound 4 and 6 decomposed on standing after several hours at room temperature, precluding analysis.

Upon standing at room temperature (2 weeks) 4 undergoes decomposition in hexane.[8] The dimer 5 (39%) slowly crystallizes from concentrated hexane solution. Compound 5 shows NMR ($CDCl_3$, TMS internal) 0.87 (4 H, AB, $\Delta\nu'_{AB}$= 19.2 Hz, J = 5.5 Hz), 1.06 (6 H, S), 1.23 (6 H, S), 2.39 (4 H, AB, $\Delta\nu_{AB}$ = 21.8 Hz, J = 16.0 Hz), 3.17 (6 H, S) and 3.22 (6 H, S); IR (CCl_4) No OH, No C=O; MS 75 ev (m/e,%) 344 (.4, M^+), 155 (100) inter alia. Anal. Calc. $C_{18}H_{32}O_6$: C, 62.77; H, 9.36; Found: C, 62.74; H, 9.17. Treatment of 5 with H_2O also yields 6 (84%).



Compound 4 appears to be the first four membered ring orthoester to have been prepared and characterized.[9] The dimerization of 4 to yield the unusual[10] 1,5-dioxacyclooctane 5 is also apparently without precedent.[9]

REFERENCES

(1) (a) Part X. N.J. Turro and S.S. Edelson, *J. Am. Chem. Soc.*, 90, 4499 (1968).
    (b) Alfred P. Sloan Fellow 1966-1970.
    (c) National Institutes of Health Postdoctoral Fellow 1967-1968.

(2) (a) L.L. Muller and J. Hammer, "1,2-Cycloaddition Reactions," Interscience, New York, New York 1967.
    (b) M.Y. Lukina, *Russian Chem. Rev.*, 31, 419 (1962).
    (c) W.A. Bernett, *J. Chem. Ed.*, 44, 17 (1967).
    (d) R. Breslow, in "Molecular Rearrangements" Part I, ed. P. deMayo, Interscience, New York, New York, 1963, p. 233.

(3) N.J. Turro, S.S. Edelson, J.R. Williams and T.R. Darling, *J. Am. Chem. Soc.* 90, 1926 (1968).

(4) (a) R.B. Woodward and R. Hoffmann, *ibid.*, 87, 4388 (1965) and earlier papers.
    (b) R. Huisgen, *Angew. Chem.* (intern. ed. Eng.) 7, 321 (1968).

(5) P.D. Bartlett, *Science*, 159, 833 (1968).

(6) A concerted reaction with an asymmetrical transition state is also possible and difficult to distinguish from a two-step mechanism, especially for cycloadditions involving highly polar (or polarizable) addends: S. Proskow, H.E. Simmons and T.L. Cairns, *J. Am. Chem. Soc.*, 88, 5254 (1966).

(7) W.B. Hammond and N.J. Turro, *J. Am. Chem. Soc.*, 88, 2880 (1966). Although cycloaddition reactions of ketenes to C=O groups are known (R.N. Lacey, in "The Chemistry of Alkenes," ed. S. Patai, Interscience, New York, New York, 1964) no corresponding cycloaddition of 3 or its derivatives to C=O groups have been reported. Diphenylketene does react with ketene acetals, but across the C=C bond: R. Scarpati and D. Sica, *Gazz. Chim. Ital.*, 92, 1073 (1962).

(8) NMR Analyses of the deoomposition of 4 shows that at least two new compounds containing cyclopropane rings are formed.

(9) (a) S. Searles, Jr. in Heterocyclic Compounds, ed. A. Weissberger, vol. 19 part II, Interscience, New York, 1964, p. 983.
    (b) H. Meewein, in Methoden der Organischen Chemie, (Houben. Weyl) vol. 6 (3), Verlag, Stuttgart, 1965.

(10) M. Bodanszky and M.A. Ondetti, *Chem. and Ind.*, 26 (1966).