Tetrahedron Letters No.33, pp. 3647-3650, 1968. Pergamon Press. Printed in Great Britain.

THE REACTION OF CARBON SUBOXIDE. FORMATION AND STRUCTURE OF PYRONES FROM ACETYLACETONE, BENZOYLACETONE AND ACETONE

A. Omori, N. Sonoda, S. Okano and S. Tsutsumi

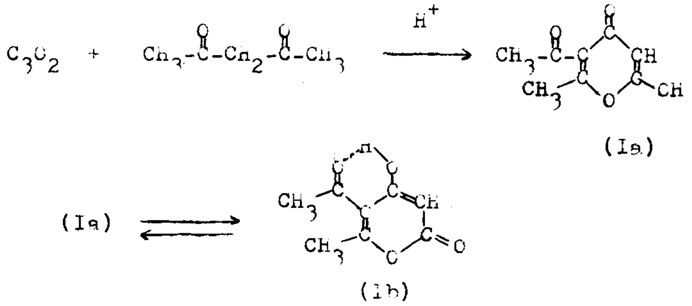
(Department of Chemical Technology, Faculty of Engineering,
Osaka University, Osaka, Japan)

(Received in Japan 6 May 1968; received in UK for publication 20 May 1968)

The reaction between carbon suboxide and benzaldehyde was reported to give benzalmalonic-benzylidenester,[1] whereas the reaction of carbon suboxide with β-di-ketones produced pyrono-pyrone derivatives, and pyrone (1:1 adduct) was not isolated.[2]

We found that pyrone (1:1 adduct) was prepared on the reaction of carbon suboxide with acetylacetone, and clarified some new facts on the structure and formation of pyrone or pyrono-pyrones from the reaction of carbon suboxide with acetylacetone, benzoylacetone and acetone.

In an ether solution, excess amount of acetylacetone reacted with carbon suboxide at 0-5° in the presence of catalytic amount of sulfuric acid to give a one to one adduct (I), m.p. 156-7°, in a 85% yield, to which we assigned a pyrone structure by the fact that treatment of (I) with ammonia gave 5-acetyl-4-hydroxy-6-methyl-2-pyridone.[3]



The infrared spectrum of (I) in a chloroform solution showed hydrogen-bonded OH-band at 3000cm^{-1} and strong absorption at 1739cm^{-1} due to the carbonyl stretch of α-pyrone.[4]

The hydroxyl proton shifts of the n.m.r. spectrum of (I) in a deutero-chloroform solution were relatively independent of the concentration and temperature (Table I,II), and molecular weight measurement by vapor pressure osmotic method using chloroform showed that (I) was monomeric in the solution.

TABLE I

Influence of Concentration of OH shifts [a)]

Concentration	τ value of OH
0.7 %	-2.10
1.2 %	-2.10
3.3 %	-2.08
5.3 %	-1.97

a) In $CDCl_3$ solution at 50°.

TABLE II

Influence of Temperature of OH shifts [b)]

Temperature	τ value of CH
20°	-2.10
50°	-2.02

b) In 1.9 % $CDCl_3$ solution.

The infrared spectrum in the solid phase (KBr disc) showed absorptions at 2600cm^{-1}(strong hydrogen-bonded ν OH) and at 1660cm^{-1} (νC=C of γ-pyrone) being different from that in the liquid phase.

These evidence suggests the structure (Ia, γ-pyrone) for the adduct in the solid state, and in the liquid phase this adduct may be present predominantly in the form of its tautomer (Ib, α-pyrone).*

To the solution of 2.2g (0.034mole) of carbon suboxide in 130ml of ether were added at -78°, benzoylacetone (7.9g;0.049mole) and conc. sulfuric acid (0.05ml). The reaction mixture was maintained at 0-5° for one day, and then the solid was filtered and recrystallized to give a compound(II)m.p. 252-4° (0.55g, yellow needles).

---

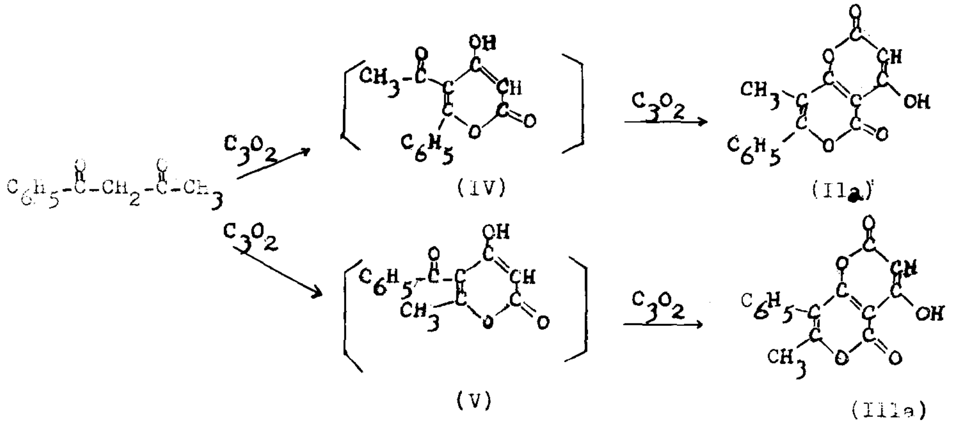
*Elvidge et al.[3] have discussed on the structure of (I) and concluded (Ia) based on the n.m.r. of (I) (in $CDCl_3$) and i.r. (nujol) , however, their treatment may be unlikly, because our observation shows that the structure of (I) in liquid phase is different from that of (I) in solid state.

From the mother liquor, a compound (III) m.p. 226-8° (0.34g, white needles, benzene) was isolated.

The compound (II) $C_{16}H_{10}O_6$ has λ_{max}^{EtOH} (in mμ) 245, 278, 357 (log ε, 4.20, 4.20 4.16) ; ν_{max}^{KBr} (in cm^{-1}) 1750(s)-$\overset{O}{\overset{\|}{C}}$-O-(α-pyrone) ; 1690(s)-$\overset{O}{\overset{\|}{C}}$-O-(α-pyrone) ; 1640 (s)-$\overset{O}{\overset{\|}{C}}$- ; enolic-OH group (by $FeCl_3$ test).

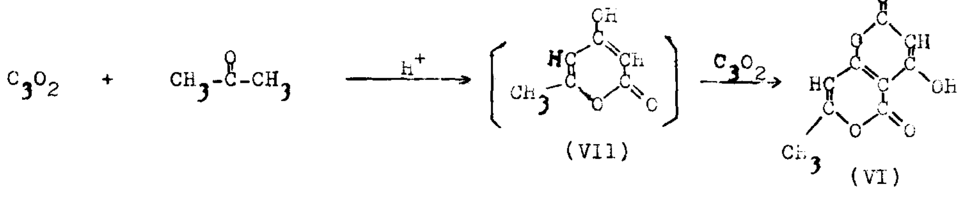
The compound (III) $C_{16}H_{10}O_6$ λ_{max}^{EtOH}(in mμ) 255, 315 (log ε, 4.09, 3.77) ; ν_{max}^{KBr}(in cm^{-1}) 1750(s)-$\overset{O}{\overset{\|}{C}}$-O-(α-pyrone) ; 1702(s)-$\overset{O}{\overset{\|}{C}}$-O-(α-pyrone) ; 1670(s)-$\overset{O}{\overset{\|}{C}}$- ; $\tau_{T.M.S.}^{CDCl_3}$ 2.5(m) ph- ; 4.5(s)-C=CH- ; 7.7(s)-CH_3- ; enolic-OH group (by $FeCl_3$ test).

The compound (II) can be assigned the structure as (IIa), and (III) is suggested to be (IIIa) , based on u.v. spectrum.



Excess amount of acetone reacted with carbon suboxide in an ether solution in the presence of the catalytic amount of sulfuric acid to give a one to two adduct, m.p. 225° , in a 8% yield, (Anal. Found:C. 55.81;H. 3.04. Calcd. for $C_9H_6O_5$:C, 55.68;H, 3.14: M(Rast Method), 180. Calcd. for $C_9H_6O_5$: 194).

The adduct was identified as (VI) by its i.r. νmax (KBr disc) 1762cm^{-1} (C=O), 1695cm^{-1} (C=O) , n.m.r. spectrum ($CDCl_3$) τ 7.60(singlet) CH_3;4.50(singlet) C=CH- ; 3.78(singlet) C=CH- . and u.v. λ_{max}(EtOH) 271, 330 mμ(log ε, 4.15, 3.93) which was in good agreement with that of an authentic sample.[5]



The facts that acetylacetone gave pyrone and the other ketones gave pyronopyrones in the same reaction conditions suggested the pyrone(Ib) may be stabilized by intramolecular hydrogen bond and less reactive for carbon suboxide than (IV) , (V) and (VII). In the cases of (IV) and (V) , the intramolecular hydrogen bonding may be unfavorable to form by the steric hindrance between phenyl and acetyl groups.

Additional studies of the reaction of carbon suboxide with β-diketones will be reported elsewhere.

REFERENCES

1. H. Hopff and G. Hegar, *Helv. Chim. Acta*, **44**, 2016 (1961).
2. F. Haadetzky and E. Ziegler, *Monatsh Chem.*, **97**, 398 (1966).
3. M. A. Butt and Y. A. Elvidge, *J. Chem. Soc.*, 4483 (1963).
4. D. Herbst, W. B. Moro, O. R. Gattlieb and C. Djerassi, *J. Am. Chem. Soc.* **81**, 2427 (1959).
5. T. Money, I. H. Qureshi, G. B. Webster and A. I. Scott, *J. Am. Chem. Soc.* **87**, 3004 (1965).