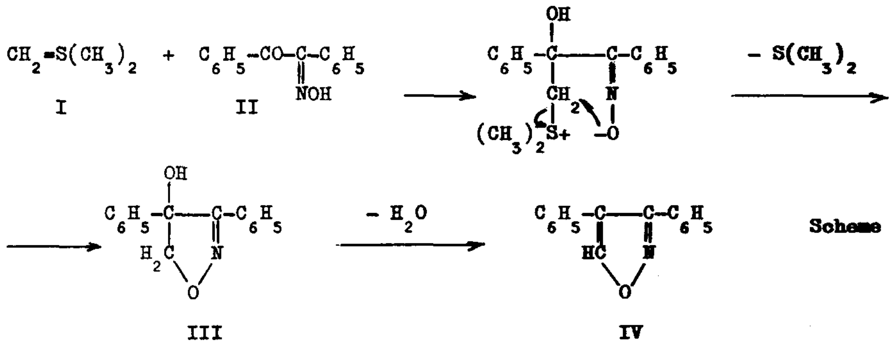
Tetrahedron Letters, No.37, pp. 3223-3226, 1970. Pergamon Press. Printed in Great Britain.

THE REACTION OF DIMETHYLSULPHONIUM METHYLIDE WITH BENZIL MONO-OXIME

P.Bravo, G.Gaudiano and C.Ticozzi
Istituto di Chimica del Politecnico di Milano, 20133 Milano, Italy

(Received in UK 25 June 1970; accepted for publication 9 July 1970)

We have recently reported several examples of syntheses of heterocycles based on the reaction of sulphur ylides with 1,3-dipoles and other appropriate substrates (1,2). We also pointed out that such reactions and other similar reactions recorded in the literature all follow a common general scheme (1,3). We consequently thought that the reaction of dimethylsulphonium methylide (I) with α-benzil mono oxime (II) would lead to 3,4-diphenylisoxazole, according to the scheme :



Scheme 1

However, the reaction between I and II is less straightforward than expected. When a THF solution of II was added to a 3.5 molar excess of I, prepared in DMSO from $(CH_3)_3\overset{+}{S}.I^-$ (V) and NaH according to the literature (4), a slow reaction took place which was complete after about 24 hours at −10°C.[•] The main product of the reaction was 3,4-diphenyl-

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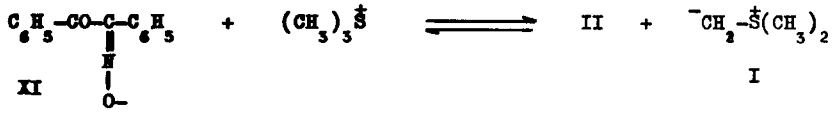
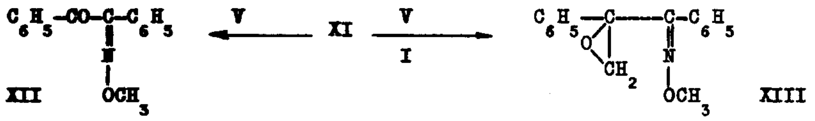
[•] The reaction occurs also when I is generated from V by butyllitium in THF.





The reaction of I and other ylides with α-oximino ketones as a possible route to isoxazoles is under investigation.

Acknowledgment. We thank Prof. A. Quilico for his interest in this work.

References

1. P.Bravo, G.Gaudiano and A.Umani-Ronchi, Tetrahedron Letters, 1969, 679 and references therein.
2. P.Bravo, G.Gaudiano and M.G.Zubiani, J.Heterocycl.Chem., in the press.
3. P.Bravo, G.Gaudiano and A.Umani-Ronchi, Gazz.chim.ital., 100, in the press.
4. E.J.Corey and M.Chaykovsky, J.Am.Chem.Soc., 87, 1535 (1965).
5. B.Holt and P.A.Lowe, Tetrahedron Letters, 1966, 683.
6. a) A.C.Cope, P.A.Trumbull and E.R.Trumbull, J.Am.Chem.Soc., 80, 2844 (1958).
   b) J.Bornstein, M.A.Joseph and J.E.Shields, J.Org.Chem., 30, 801 (1965).
7. M.C.Henry and G.Wittig, J.Am.Chem.Soc., 82, 563 (1960).
8. J.L.Pierre, R.Guidotti and P.Arnaud, Bull.soc.chim.France, 1967, 1439.
9. a) H.König, H.Metzger and K.Seelert, Ber., 98, 3724 (1965).
   b) P.Bravo, G.Gaudiano, C.Ticozzi and A.Umani-Ronchi, Gazz.chim.ital., 99, 549 (1969).

Tetrahedron Letters No.37, pp. 3227-3228, 1970. Pergamon Press. Printed in Great Britain.

STEROIDS XVI[1]. BROMINATION OF STEROIDAL 3-KETO-1,4,6-TRIENES

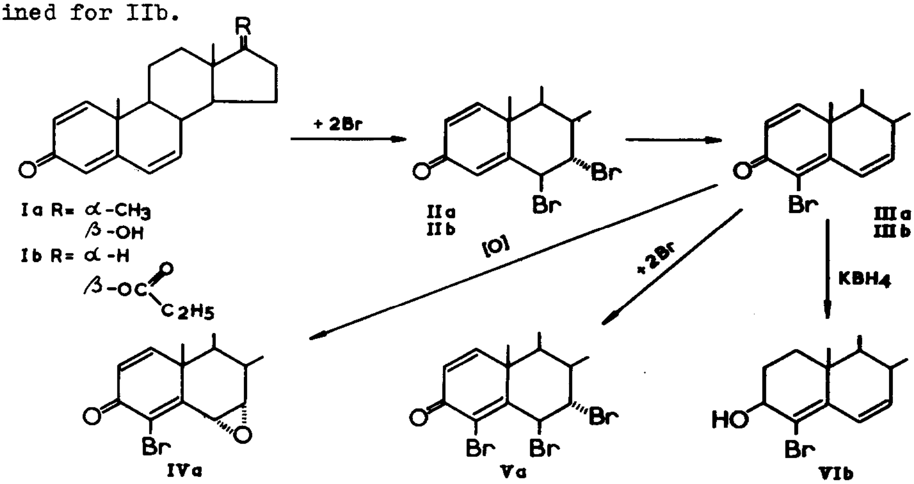
M. Kocór and M. Gumułka

Institute of Organic Chemistry of the Polish Academy of Sciences, Warsaw

(Received in UK 10 June 1970; accepted for publication 9 July 1970)

In the course of our investigations of the reactivity of steroidal 3-keto-1,4,6-trienes[1] Ia and Ib we have found an interesting dehydrobromination reaction which is the subject of the present communication.

The bromination of Ia and Ib with molecular bromine or with N-bromoamides, gave only diaxial addition products, i.e. 6β,7α-dibromo-3-keto-1,4-dienes : IIa, m.p. 152-153,5°, and IIb, m.p. 135-137° (NMR[2] of IIa : H-1 7.05, H-2 6.30, $J_{12}=J_{21}=10$ Hz, H-4 6.32, H-6 5.15, H-7 6.60). Very similar values were obtained for IIb.



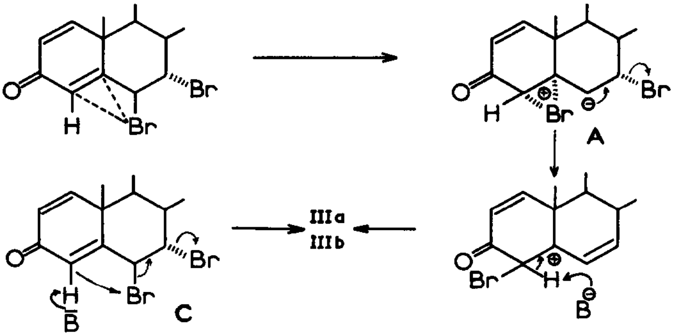
Bromination or chlorination of Ia and Ib with N-haloamides gave no trace of allylic halogenation.

Dehydrobromination of IIa and IIb with organic bases yielded 4-bromo-3-keto-1,4,6-trienes (IIIa, m.p. 97-101°, or IIIb, m.p. 102-106°) instead of the expected 6-bromo-derivatives. The structure of IIIa was supported by its spectra : UV, λ_{max} 202,230,314 nm; IR, 1660 (C=O), 1610-1620 (C=C) cm^{-1}; NMR : H-1 7.04, $J_{12}=9.5$ Hz, H-6 6.36, $J_{67}=9.5$ Hz, $J_{68}=2.8$ Hz, H-2 6.78, $J_{21}=9.5$ Hz, H-7 6.18, $J_{78}=2.8$ Hz. Similar values were observed for IIIb.

Further evidence for the proposed 4-bromo-structure was obtained by epoxidation of IIIa to the 6α,7-epoxide IVa (λ_{max} 251 nm and NMR : H-1 6.90, H-2 6.30, $J_{12}=J_{21}=10$ Hz, H-6 4.92, H-7 4.40) and by bromination of IIIa to the tribromocompound Va (λ_{max} 259 nm and NMR : H-1 7.10, H-2 6.40, $J_{12}=J_{21}=10$ Hz, H-6 6.18, H-7 4.60). The bromotrienone IIIb could be also reduced by means of $NaBH_4$ to give the unsaturated 3β-alcohol VIb, m.p. 122-124° (λ_{max} 248,255, 264 nm; NMR, H-6 6.36, H-7 5.80, $J_{67}=J_{76}=10$ Hz, $J'=3$ Hz, H-17 4.64, H-3 4.24).

We exclude classical or nonclassical carbonium ion mechanisms involving the formation of positive charge on C-4 for this unexpected dehydrobromination.

We propose that the geometry of the molecule allows overlap of the π-orbitals of 4,5-double bond with the valence orbitals of Br-6, giving rise to a bromine shift to the slightly negative C-4 to produce A. The latter is stabilised in the presence of bases in the normal way to give the 4-bromo compound : IIIa or III b



The possibility of an alternative concerted mechanism C is supported by the fact that we could not capture the plausible ionic transition state A by the use of an excess of the other ions (Cl^-, CN^-) in the reaction medium.

References :

1) Steroids XV, M. Kocór and M. Gumułka, in press

2) All NMR chemical shifts are given in δ(ppm); the signals of $C\underline{H}_3$ protons have the normal values.