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PHOTOCYCLOADDITIONS OF AROMATIC THIONES TO ALLENES

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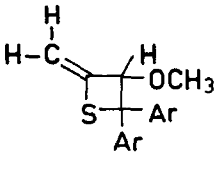
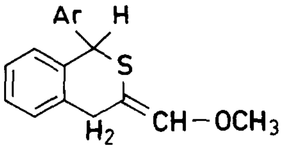
The communications of Gotthardt[1] prompt us to publish our results in this field (compare also [2]).

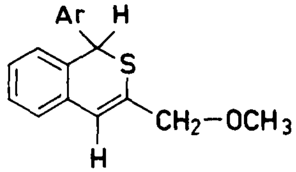
After irradiation of thiobenzophenone (0.025 mole) with methoxyallene (0.100 mole) in 250 ml of benzene during 20 minutes with a high pressure mercury lamp (HPK 125 W) through a $K_2Cr_2O_7$-filter solution two isomeric adducts $C_{17}H_{16}OS$ could be isolated by crystallization and chromatography. One isomer was the alkylidenethietane I (Ar = C_6H_5); oil; IR 1650 cm^{-1} (C=C); PMR (in CCl_4) δ=3.21 (s, OCH_3), δ=4.91 (t, J=2.3 Hz, =CH-), δ=5.24 (t, J=2.3, =CH-), δ=5.35 (t, J=2.2, >CH-O) and δ=6.9-7.5 (10 aromatic H).



I



II



III

The other isomer was the thiopyran derivative II (Ar = C_6H_5); m.p.>124° (decomp.); IR in KBr 1650 cm^{-1} (C=C); PMR (in $CDCl_3$) δ=3.42 (s, broad, $>CH_2$), δ=3.54 (s, OCH_3), δ=5.27 (s, >CH-S), δ=6.12 (t, J=1.4, =CH-O) and δ=7.1-7.6 (9 aromatic H). Both isomers were formed in yields of 15-20 %.

By heating of II (Ar = C_6H_5) at 140° during 5 minutes it almost quantitatively isomerized to III (Ar = C_6H_5); oil; IR 1650 cm^{-1} (C=C), 1590 cm^{-1} (Ar-C=C); PMR (in CCl_4) δ=3.16 (s, OCH_3), δ=4.00 ("t", "J"=1, OCH_2), δ=5.14 (s, >CH-S), δ=6.71 ("q", "J"=1.0 en "J"=1.7, =CH-), $\delta\approx$7.2 (9 aromatic H).

In the reaction of thiobenzophenone with some acetylenes also ortho-ringclosure with a benzene-ring has been observed[3].

With xanthene-9-thione (0.010 mole) and methoxyallene (0.020 mole) adduct I ($Ar_2 = O(C_6H_4)_2$) was formed in 34 % yield after 2½ h, m.p.85°; IR in KBr 1640 cm^{-1} (C=C); PMR (in $CDCl_3$) δ=2.86 (s, OCH_3), δ=4.93 (t, J=2.3, =CH-), δ=5.10 (t, J=2.4, =CH-), δ=5.52 (t, J=2.2, >CH-O), δ=7.0-8.4 (m, 8 aromatic H); MS, m/e 282 (P^+) and 58 ($H_2C{=}C{=}S^+$). No appreciable amount of II could be detected.

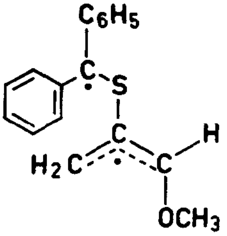
Irradiation of allene with thiobenzophenone gave a mixture of products from which a (2:1)-adduct $C_{29}H_{24}S_2$, m.p.196-198° was isolated; PMR (in CCl_4) δ=3.57 (s, 2H), δ=3.62 (s, 2H) and δ=6.7-7.3 (20 aromatic H). The structure of this compound could not yet be resolved.

Irradiation of tetramethylallene with thiobenzophenone gave results analogous to those of Gotthardt[1].

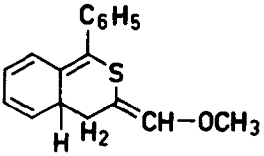
Mechanism

It is assumed that triplet[2] thiobenzophenone attacks methoxyallene at the central carbon atom[4] with formation of the biradical IV[5,6]. After spin inversion this can cyclize to the thietane I (Ar = C_6H_5) or to the thiopyran derivative V, which will isomerize to II.

In the case of the more rigid xanthene-9-thione no ortho-attack on the benzene-ring occurs and only the thietane is formed.



IV



V

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