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PHOTOCYCLOADDITION OF THIOBENZOPHENONE TO OLEFINS

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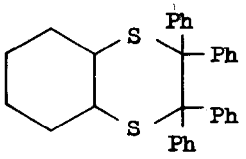
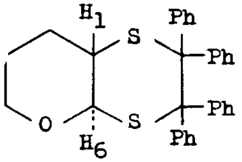
Thiocarbonyl compounds behave quite differently from their oxygen analogs in the photochemical reaction. When benzophenone is irradiated with ultra-violet light in isopropyl alcohol, a typical oxidation-reduction reaction takes place, giving dibenzpinacol and acetone.(1) Thiobenzophenone, however, on similar irradiation, affords dibenzhydryl disulfide and benzhydryl mercaptan as major products.(2) The photochemical addition of a carbonyl group to an olefin to form an oxetane is a well-known reaction.(3) The reaction of thiobenzophenone with 2-butene, on the other hand, does not give rise to a thietane derivative when irradiated with 2537A-light, but brings about a desulfurization reaction giving 1,1-diphenyl-1-propene.(4) We now wish to report a new type of photocycloaddition reaction involving a thiocarbonyl group to a carbon-carbon double bond to form a 1,4-dithiane derivative in good yield.

A solution of thiobenzophenone (4g) in cyclohexene (20g) was irradiated with a high pressure mercury lamp (Toshiba, H-400P) in a nitrogen atmosphere. The irradiation was continued for 25 hrs. until the blue color of the thioketone had completely disappeared. The cyclohexene was removed from the reaction mixture under a reduced pressure, and the residue was chromatographed on neutral alumina (Woelm, Activity Grade 1) with a benzene-petroleum ether mixture as an eluent. A crystalline solid (3.5g) was obtained and it gave, on recrystallization from benzene, a purified material: m.p. 174° dec (melt in blue color) ($C_{32}H_{30}S_2$ requires C, 80.29, H, 6.32; mol. wt., 478.7. Found: C, 80.40, H, 6.46%; mol. wt., 470 by cryoscopy in benzene); infrared absorption maxima (KBr) at 3090, 3055, 3035, 2930, 2860, 1600, 1575, 1480, 1448, 1440, 725, and 700 cm^{-1}; nmr (in $CDCl_3$, δ from TMS in ppm, s=singlet, t=triplet, m=multiplet) 7.53 m (4H), 7.24 m (4H), 7.01 m (12H), 3.09 m (2H), 1.73 m (4H), and 1.31 m (4H). These data as well as the following facts show the structure of this material to be 3,3,4,4-tetraphenyl-2,5-dithiabicyclo [4.4.0] decane (I). Reduction of (I) with zinc dust in acetic acid afforded diphenylmethane, tetraphenylethylene and tetraphenylethane in an approximate ratio of 1.3:1.0:0.03. Reaction of (I) with 4 equiv. of perbenzoic acid gave the corresponding sulfone: m.p. 178° C ($C_{32}H_{30}O_4S_2$ requires C, 70.82, H, 5.57. Found: C, 71.22, H, 5.77%); infrared (KBr) 1313, 1130 cm^{-1}; nmr (in $CDCl_3$, δ from TMS) 7.50 m (8H), 7.10 m (12H), 4.23 m (2H), 2.28-1.36 m (8H). Compound (I) decomposed when heated alone at the melting point. The decomposition products were thiobenzophenone and cyclohexene: the former was identified by its visible and ultraviolet absorption spectra and the latter by gas chromatography.



(I)

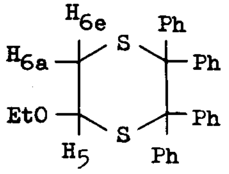
Similar reactions of thiobenzophenone were studied with 2,3-dihydropyran, ethyl vinyl ether and styrene. The reaction with 2,3-dihydropyran afforded 3,3,4,4-tetraphenyl-7-oxa-2,5-dithiabicyclo [4.4.0] decane (II) (70% based on thiobenzophenone), m.p. 147° ($C_{31}H_{28}OS_2$ requires C, 77.46, H, 5.87. Found: C, 77.62, H, 5.83%); infrared (KBr) 3080, 3050, 3025, 2930, 2850, 1070 (ether), 725, 700, 680 cm^{-1}; nmr (in $CDCl_3$, δ from TMS) 7.65-7.01 m (20H), 4.88 d (1H), 3.97 broad d (1H), 3.50 broad t (1H), 3.14 broad t (1H),



(II)

1.68 m (4H). Spin-decoupling study of the nmr of (II) revealed that the spin-coupling constant J(H_1-H_6) is 10.0 cps, and this value indicates that the two rings form a trans junction.

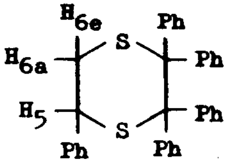
The reaction with ethyl vinyl ether resulted in the formation of 2,2,3,3-tetraphenyl-5-ethoxy-1,4-dithiane (III) (73% based on thiobenzophenone), m.p. 140° ($C_{30}H_{28}OS_2$ requires C, 76.88, H, 6.02. Found: C, 76.46, H, 5.89%); infrared (KBr) 3080, 3050, 3015, 2965, 2910, 2860, 1072 (ether), 732, 718, 701 cm^{-1}; nmr (in $CDCl_3$, δ from TMS) 8.05-6.93 m (20H), 4.80 t (1H), 4.27 quintet (1H), 3.50 quintet (1H), 2.76 m (2H), 1.45 t (3H). In spin-decoupling with H at 4.80 being irradiated, the multiplet at 2.76 appeared as an AB quartet. Since the quintets at 4.27 and at 3.50 appear to be spin-coupled with each other and both of them with the triplet at 1.45, these three signals should be assigned to the protons in the ethoxy group, in which we assume that the two methylene protons are non-equivalent.(6) These results leave no doubt that the multiplet at 2.76 is assigned to H_{6a} and H_{6e}, and the triplet at 4.80 to H_5. Spin-coupling constants J(H_5-H_{6a}) and J(H_5-H_{6e}) are 3.0 cps, indicating H_5 to be in the equatorial position.(5) When compound (III) was dried in an Abderhalden at the temperature of boiling benzene, elimination of a molecule of ethanol took place and 4,4,5,5-tetraphenyl-3,6-dithiacyclohexene was produced, m.p. 184° ($C_{28}H_{22}S_2$ requires C, 79.58, H, 5.25. Found: C, 79.19, H, 5.20%); infrared (KBr) 3060, 3030, 3015, 1550, 730, 700 cm^{-1}; nmr (in $CDCl_3$, δ from TMS) 7.45-7.10 m (20H), 6.31 s (2H).



(III)

The reaction with styrene was carried out in a n-hexane solution, and 2,2,3,3,5-pentaphenyl-1,4-dithiane (IV) was produced in 20% yield, m.p. 154° ($C_{34}H_{28}S_2$ requires C, 81.56, H, 5.64. Found: C, 81.89, H, 5.56%); infrared (KBr) 3080, 3050, 3020, 2945, 2915, 2900, 735, 720, 695 cm^{-1}; nmr (in $CDCl_3$, δ from TMS) 7.89-7.05 m (25H), 4.86 quartet (1H), 3.21 t (1H), 2.90 quartet

(1H). On the basis of the result of spin-decoupling study, the quartet at 4.86, the triplet at 3.21 and the quartet at 2.90 are assigned to H_5, H_{6a} and H_{6e}, respectively. The coupling constant values, $J(H_5-H_{6a})$ 11.8, $J(H_5-H_{6e})$ 4.2, and $J(H_{6a}-H_{6e})$ 14.0 cps, are consistent with structure (IV), in which H_5 is in the axial position.(5)



(IV)

Similar irradiation of thiobenzophenone in 1-hexene, gave, as the only isolable product, 3,3,5,5-tetraphenyl-1,2,4-trithiacyclopentane (16% based on thiobenzophenone), m.p. 124°, (lit.(7) 124°). No reaction took place with acrylonitrile inspite of prolonged irradiation. Thus, in both cases, the products expected from the cycloaddition reaction were not isolated. It therefore seems likely that the cycloaddition reaction of thiobenzophenone takes place only with the carbon-carbon double bonds activated with electron-releasing groups.

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