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The Diels-Alder Reaction of 1,3,5-Cycloheptatriene with Thiobenzophenone

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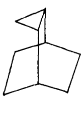
1,3,5-Cycloheptatriene (CHT) is known to undergo the Diels-Alder reaction with various dienophiles. In most cases, the structure of the adduct thus formed has tricyclo[3.2.2.0^{2,4}]nonane skeleton, **1**, instead of simple (2+4) cycloadduct, **2**.1–4) There are two exceptions, one of which is the cycloadduct of CHT with nitrosobenzene and the other is that of CHT with acrolein. The structure of the former cycloadduct was initially thought to have **2**-type skeleton, but recently it was re-examined and found to have **3**-type skeleton, or a (2+6) cycloadduct.5) The latter adduct, which was formed in minor (~10%) yield along with major (~30%) tricyclic **1**-type adduct, is believed to have a skeleton of **2**-type, but, unfortunately, the position of the formyl group in this adduct was not determined because its formation was confirmed after hydrogenation.6)

We have found that the Diels-Alder reaction of CHT with thiobenzophenone affords **2**-type cycloadduct with regiospecificity.7) Regiospecific formation of a bicyclic Diels-Alder adduct from unsubstituted CHT has never been reported in earlier papers.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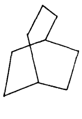
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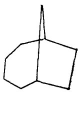
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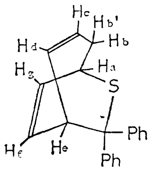
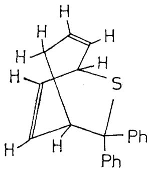
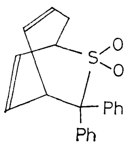


4a



4b



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Results and Discussion

Thiobenzophenone does not react with CHT at room temperature without light.8) However, from the reaction mixture at 90—100 °C, the Diels-Alder adduct, **4a**, was isolated in 40% yield along with some unidentified materials. The structure of **4a** was confirmed by the 100 MHz NMR spectrum (Fig. 1) with the decoupling technique and by the oxidation to the corresponding sulfone, **5**.

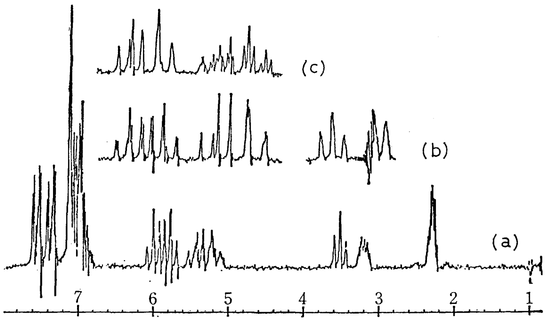

Fig. 1. The NMR spectra of (a) 6,6'-diphenyl-7-thiabicyclo-[3.2.2]nona-3,8-diene, **4a**, in benzene-d_6; (b) that with irradiation at H_b; and (c) that with irradiation at H_a. Spectra (b) and (c) are recorded with doubled scale.

The spectrum is consistent with the structure **4**, but inconsistent with any those of other cycloadducts. Although structures **4a** and **4b** are possible for the adduct, the former structure is prefered over the latter by the following reason; in **4b**, the phenyl ring at the *exo*-position should cause larger difference than that observed here in the chemical shift of signals due to H_b and H_b'. Namely, the signal at δ 2.30 in benzene-d_6 appears as an AA'XY-type multiplet. The double irradiation at the resonance positions of H_a and H_c simplifies this signal to an AA'-type quartet. Contrary the spectrum of **5** shows the large difference in chemical shifts of H_b (δ 3.13 in $CDCl_3$) and H_b' (δ 2.38 in $CDCl_3$). In addition, the signal from H_a (δ 3.94 in $CDCl_3$) in the sulfone appears at more down-field than that from H_a (δ 3.65 in $CDCl_3$) in the sulfide and the reverse is true for H_e protones in the sulfide and sulfone.

It is known that thiobenzophenone is a good dienophile.9) The formation of the tricyclic Diels-Alder adducts from CHT is accounted for by two ways: the one proposes lower reactivity of CHT than that of norcaradiene, which is in equilibrium with the triene.10,11) The other, based on kinetics, prefers to propose C_2–C_7 bond formation at the transition state of the cycloaddition from CHT itself.12) Although we cannot discuss the mechanism of the cycloaddition in

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1) G. H. Wahl, Jr., *J. Org. Chem.*, **33**, 2158 (1968).
2) C. J. Rostek and W. M. Jones, *Tetrahedron Lett.*, 3957 (1969).
3) M. J. Goldstein and A. H. Gevirtz, *ibid.*, 4413, 4417 (1965).
4) K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, **92**, 4143 (1970).
5) a) G. Kresze and G. Schultz, *Tetrahedron*, **12**, 7 (1967); b) J. Hutton and W. A. Waters, *Chem. Commun.*, 634 (1966); c) P. Burns and W. A. Waters, *J. Chem. Soc., C*, 27 (1969).
6) E. M. Mil'vitskaya and A. F. Plate, *Zh. Obshch. Khim.*, **32**, 2566 (1962); *Chem. Abstr.*, **58**, 8927e (1963).
7) For a symmetric dienophile, see H. Ishitobi, H. Tanida, K. Tori, and T. Tsuji, This Bulletin, **44**, 2993 (1971).
8) Results on the photo-reaction of CHT with thiobenzophenone will be published elsewhere.

9) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron*, **25**, 871 (1969).
10) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1454 (1967).
11) G. Maier, *Angew. Chem. Int. Ed. Engl.*, **6**, 385 (1967).
12) T. Tsuji, S. Teratake, and H. Tanida, This Bulletin, **42**, 2033 (1969).

detail,[13] the present result suggests that the existence of reactive norcaradiene, if any, does not necessarily mean the formation of tricyclic Diels-Alder cycloadducts.

Experimental

Reaction of Thiobenzophenone with CHT. A mixture of thiobenzophenone (1.0 g) and CHT (15 ml) in an ampoule was degassed and sealed. The sample was heated at the temperature of boiling water until complete decolorization of thiobenzophenone took place (2.5 days). After excess CHT had been evaporated, the residue was chromatographed on a column of silica gel with elution by a mixture of *n*-hexane and benzene (4: 1 v/v). The first elution gave 0.26 g of unidentified material. From the second elution 0.67 g of crystals were obtained. Recrystallizations of crystals from a mixture of benzene and *n*-hexane gave **4a** in 40% yield; mp 170—172 °C.

The structure of **4a** was confirmed by the following data: NMR (δ from TMS, benzene-d_6)[14] 3.23 (H_a), 2.36 (H_b or H_b'), 2.23 (H_b' or H_b), 5.20 (H_c), 5.46 (H_d), 3.55 (H_e), 6.04 (H_f), 5.81 (H_g), and 6.8—7.7 (H_{ar}). Coupling constants (J_{xy}, Hz) 2.0 (ab), 3.2 (bc), 11.6 (cd), 8.0 (de), 7.0 (ef), 9.0 (fg), 6.0 (ag), 1.0 (eg), 1.0 (af), 18.0 (bb′). Irradiation at the resonance position of $H_b(H_b')$ made signals from H_a, H_c, and H_d to be broad doublet, doublet, and doublet of doublet, respectively, with no change for signals from H_e, H_f, and H_g. On irradiation at H_a, H_c appeared as double triplets, H_g as doublet, and H_f as doublet of doublet, but the signal from H_d did not change. Mass spectrum (*m/e*) 290 (M^+), 200, 199, 198 (Ph_2CS^+, base), 197, 121, 92, 91, and 77.

Found: C, 82.50; H, 6.34; S, 10.91%. Calcd for $C_{20}H_{18}S$: C, 82.50; H, 6.25; S, 11.40%.

*Oxidation of **4a**.* A solution composed of **4a**, (100 mg) and two equivalents of *m*-chloroperbenzoic acid in 10 ml of dichloromethane was stirred for a day at room temperature. After working-up and recrystallizations from *n*-hexane–benzene, **5** was obtained in quantitative yield: mp 260 °C. IR: 1135 and 1305 cm^{-1}.

Found: C, 74.54; H, 5.66; S, 10.14%. Calcd for $C_{20}H_{18}O_2S$: C, 74.53; H, 5.63; S, 9.93%.

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[13] Note that thiobenzophenone has a heteropolar double bond and two-step mechanism is possible to this compound.

[14] The spectrum in chloroform-*d* did not show well-resolved signals.