Synthesis and Reactions of 1,6-Dithiocyanato- and 1,6-Diiodo-1,3,5-cycloheptatrienes

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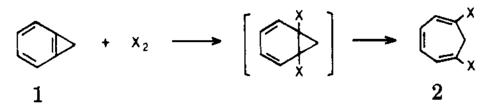
Photoreactions of benzocyclopropene (1) with thiocyanogen and iodine afforded 1,6-dithiocyanato- (4) and 1,6-diiodocycloheptatriene (7), respectively, in good yields, whereas thermal reactions gave 2-thiocyanatobenzyl thiocyanate (5) and 2-thiocyanatobenzyl isothiocyanate (6) from thiocyanogen and 2-iodobenzyl iodide (8) from iodine. Disodium 1,3,5-cycloheptatriene-1,6-dithiolate (9) obtained by reduction of 4 with sodium in liquid ammonia was converted into medium- to large-membered ring sulfur heterocycles (thiacrown compounds) 10–15 by reactions with diiodomethane, 1,2-dibromoethane, and *cis*-1,2-dichloroethylene. Metal-catalyzed cross coupling reactions of 7 with Grignard reagents gave mono- and dialkylcycloheptatrienes and the reactions of 7 with copper bis(trimethylsilyl)amide yielded 1-alkyl-6-[bis(trimethylsilyl)amino]-1,3,5-cycloheptatrienes. An improved procedure for the preparation of 1 was also described.

In connection with our study on bridged heterocyclic compounds,[1-3] we required a general synthetic method of cycloheptatrienes having a variety of substituents at the 1- and 6-positions. Although some examples of 1,6-disubstituted cycloheptatrienes have been reported,[4] no general synthetic method has been known. Recently Vogel and his co-workers reported a useful synthetic method of cycloheptatriene-1,6-dicarboxylic acid and its application to the preparation of some 1,6-disubstituted cycloheptatrienes,[5] but this method is mostly restricted to the synthesis of carbon-substituted derivatives. We have found that the photoreaction of benzocyclopropene (1) with thiocyanogen or iodine gives 1,6-dithiocyanato- or 1,6-diiodo-1,3,5-cycloheptatriene, respectively, in a good yield and these compounds can be converted into various kinds of 1,6-disubstituted cycloheptatrienes.[6,7]

Results and Discussion

Synthesis of 1,6-Dithiocyanato- and 1,6-Diiodocycloheptatrienes. If the activated "double bond" of benzocyclopropene (1) reacts with a reagent X_2 in such a way as shown in eq 1, it would provide a very useful approach to 1,6-disubstituted cycloheptatrienes. A literature survey suggests, however, that the reactions with electrophilic reagents X_2 lead to the formation of a product of type 3 instead of 2.[8] The only exception is the reaction with iodine which gives 1,6-diiodo-1,3,5-cycloheptatriene as a minor product, the major one being *o*-iodobenzyl iodide (vide infra).[9] It occurred to us that all the reactions so far reported are heterolytic reactions and a homolytic reaction might produce a desired type of compound 2. This expectation was indeed fulfilled. When 1 was allowed to react with thiocyanogen in benzene under irradiation of light from a medium-pressure mercury lamp for 30 min at room temperature, 1,6-dithiocyanato-1,3,5-cycloheptatriene (4) was formed as a major product (64%) along with *o*-thiocyanatobenzyl thiocyanate (5, 22%) and *o*-thiocyanatobenzyl isothiocyanate (6, 2%). In contrast, the reaction proceeded slowly in the dark and only 5 (14%) and 6 (9%) were formed after 20 h. It has been reported that photochemical reactions of thiocyanogen with olefins proceed in a homolytic fashion to give, depending on the structure of the olefins, α,β-dithiocyanates, allylic isothiocyanates, or mixtures of the two in high yields.[10] The



1 2 (1)

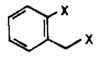


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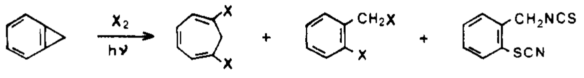
Table I. Reactions of Benzocyclopropene (1) with Iodine[a]

run	solvent	temp, °C	light source[b]	product yield,[d] %	
				7	8
1	CCl_4	0	A	0	87
2	CCl_4	0	B	2	89
3	CCl_4	0	C	5	87
4	C_6H_6	5–10	B	0	63
5	$C_6H_5CH_3$	−78	B	0	92
6	CH_2Cl_2	−78	B	5	63
7	n-C_5H_{12}	−78	B	7	58
8	n-C_5H_{12}	0	D	31	18
9	n-C_5H_{12}	0	E	47	21
10	n-C_7H_{16}	0	E	47	19
11	n-C_7H_{16}	0	F[c]	67	7

[a] The reactions were carried out with 1 (1.5–2 mmol) and iodine (1.6–2.1 mmol). [b] A, in the dark; B, normal diffused light; C, A 15-W fluorescent lamp was placed about 20 cm from the reaction flask; D, 100-W Hg lamp; E, 300-W halogen lamp; F, 400-W Hg lamp. [c] A filter solution of 0.1% aqueous K_2CrO_4 was circulated outside the lamp (see Experimental Section). [d] Isolated yield except runs 4–7 where the yields were estimated by NMR.



1 4, X = SCN 5, X = SCN 6
7, X = I 8, X = I

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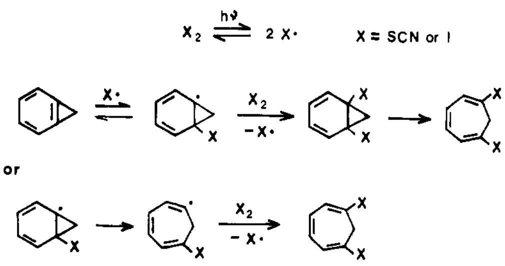
Scheme I



thermal reaction of 1 with iodine (in carbon tetrachloride) is reported[9] to give 1,6-diiodocycloheptatriene (7) as described above. We repeated this reaction but never more than 2% of 7 was obtained when the reaction was conducted under normal diffused light. We found, however, that irradiation of the reaction solution remarkably increases the yield of 7 at the expense of that of *o*-iodobenzyl iodide (8). The yield of 7 was also highly dependent on the solvent and reaction temperature. Among many attempts carried out to improve the yield of 7, some examples are listed in Table I. The results of runs 1–3 appeared to suggest that the formation of 7 was a photoreaction and that of 8 was a thermal reaction. Among solvents studied (runs 2, 4–7) pentane gave the best result probably due to the slow rate of the thermal reaction which allowed the photoreaction leading to desired 7 to occur concurrently. The ratio of 7 to 8 was dramatically increased by irradiation (runs 8–10) and the best result was obtained (run 11) when a heptane solution of 1 and iodine was irradiated at 0 °C by a medium-pressure mercury lamp through a filter solution of 0.1% aqueous potassium chromate which transmitted light only above 450 nm. Under these conditions iodine (λ_{max} 530 nm) is a sole species to absorb light, thus the photodecomposition of 7 formed being prevented. In this case the isolated yield of 7 was 67%. Heptane was used instead of pentane because the solubility of iodine is higher in the former solvent. Although the photoreaction of 1 with bromine in pentane at low temperatures was attempted, the product was only *o*-bromobenzyl bromide. This clearly suggests that the thermal reaction leading to the benzyl bromide is very fast in the reaction with bromine even at low temperatures.

The photoreactions leading to cycloheptatrienes 4 and 7 most likely proceed via a radical chain mechanism as described in Scheme I, since the reaction with thiocyanogen was inhibited by oxygen or 2,6-di-*tert*-butyl-4-methylphenol. The thiocyanates 5 and 6 are probably formed via a thermal heterolytic pathway as in the case of the formation of 8 in the reaction with iodine.

The reaction with iodine was much slower than that with thiocyanogen in keeping with the thermochemical data shown in eq 2.[11] The success of the addition of iodine to

$$CH_2{=}CH_2 + RS\cdot \rightarrow RSCH_2CH_2\cdot$$

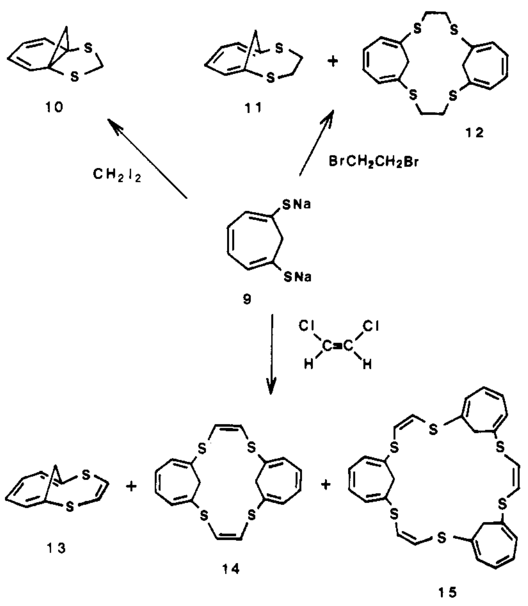
$$\Delta H = -14 \text{ kcal/mol}$$

$$CH_2{=}CH_2 + I\cdot \rightarrow ICH_2CH_2\cdot$$

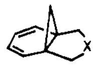
$$\Delta H = 7 \text{ kcal/mol} \tag{2}$$

1 under thermodynamically unfavorable (endothermic) conditions is obviously due to the release of high strain energy (68 kcal mol^{-1}) of the fused cyclopropene ring.[8c]

Scheme II



Synthesis of 1,6-Disubstituted Cycloheptatrienes and Related Compounds from Dithiocyanatocycloheptatriene (4). The dithiocyanate (4) is readily reduced with sodium in liquid ammonia into dithiolate 9,[7] which reacts with diiodomethane, 1,2-dibromoethane, and *cis*-1,2-dichloroethylene to give 10 (80%), 11 (46%), and 12 (7%), and 13 (11%), 14 (13%), and 15 (11%), respectively (Scheme II). That 10 has a tricyclic structure, whereas 11 and 13 have a bicyclic one, was established by their NMR spectra. The ^{13}C NMR spectrum of 10 shows two peaks due to the olefinic carbons, whereas those of 11 and 13 exhibit three and four peaks in the olefinic region, respectively. It is known that the vicinal coupling constant of the bridge methylene protons of a tricyclic compound of type 16 and that of a bicyclic compound of type 17 are 4–6 and 9–12 Hz, respectively.[12] The values of 6 Hz for 10 and 12 Hz for 11 and 13 are in keeping with the conclusion obtained from the ^{13}C NMR.



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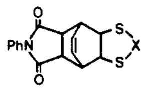
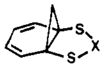


18, X = CH_2
19, X = CH_2CH_2
20, X = CH=CH



23, X = CH=CH
24, X = CH_2CH_2

The difference in structure between tricyclic 10 and bicyclic 11 and 13 is also reflected in the reactivity of the Diels–Alder reaction of these compounds. Reaction of 10 with *N*-phenylmaleimide in ether at room temperature afforded a 1:1 adduct (18) in 48% yield, whereas the reactions of 11 and 13 required refluxing in xylene (4 days

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[11] These values of ΔH's are estimated by using the bond energies given by Pauling. Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, New York, 1960; Chapter 3. Since the reaction, $XCH_2CH_2\cdot + X_2 \rightarrow XCH_2CH_2X + X\cdot$, has a negative ΔH value, the ease with which the addition reaction in Scheme II proceeds is determined by the ΔH's of the reaction of X· with an olefin (i.e., eq 2).

[12] (a) Vogel, E. *Pure Appl Chem.* **1969**, *20*, 237. (b) Vogel, E.; Wiedeman, W.; Roth, H. D.; Eimer, J.; Günther, H. *Liebigs Ann. Chem.* **1972**, *759*, 1. (c) Schäfer-Ridder, M.; Wagner, A.; Schwamborn, M.; Schreiner, H.; Devrout, E.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 853. (d) Gölz, H. J.; Muchowski, J. M.; Maddox, M. L. *Ibid.* **1978**, *17*, 855. (e) Lipa, W. J.; Crawford, H. T.; Radlick, P. C.; Helmkamp, G. K. *J. Org. Chem.* **1978**, *43*, 3813.

Table II. Metal-Catalyzed Cross Coupling Reactions of 7 with Grignard Reagents[a]

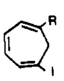
run	R in RMgX	molar ratio RMgX/7	catalyst[b]	yield, % 25	yield, % 26
1	$CH_2{=}CH$	1.6	A	88	
2	$CH_2{=}CH$	1.2[c]	B		67
3	$CH_2{=}CH$	1.5[d]	C	18	11
4	$n\text{-}C_4H_9$	1.4	A	51	
5	$n\text{-}C_4H_9$	2.0	A	34	23
6	$(MeO)_2CHCH_2CH_2$	1.4	A	60	
7	$CH_2{=}CHCH_2$	1.1	A	84	4
8	$CH_2{=}CHCH_2$	2.0	A		67

[a] The reactions were carried out at −55 to −70 °C for 1.5 h except runs 2 and 3. [b] A, Li_2CuCl_4; B, $Ni(Ph_2PCH_2CH_2CH_2PPh_2)Cl_2$; C, $Pd(Ph_3P)_4$. [c] The reaction was done in refluxing THF for 2.5 h and 7 (33%) was recovered. [d] The reaction was done in refluxing THF for 5 h and 7 (29%) was recovered.

for **11** and 2 h for **13**) to give adducts **19** (77%) and **20** (59%), respectively. A similar great difference in the reactivity between tricyclic and bicyclic compounds has also been reported for carbocyclic derivatives **21** ($X = CH_2$ in **16**) and **22** ($X = CH_2CH_2$ in **17**); the conditions reported for the reaction with maleic anhydride in ether being 0 °C for 4 h for **21** and 34 °C for 2 h for **22**.[12b] It is noteworthy that **13** reacts with *N*-phenylmaleimide much faster than **11**. This probably results from a higher equilibrium concentration of **23** (in **13** ⇄ **23**) than that of **24** (in **11** ⇄ **24**) due to the bracketing effect of the shorter carbon–carbon double bond in **13**. The higher concentration of the tricyclic structure (**23**) makes the cycloaddition more favorable as in the case of **10**.

The formation of **12**, **14**, and **15** is interesting, since these are the first examples of polythiaethers (thiacrown compounds) having cycloheptatriene units in the macrocyclic ring.[13]

Synthesis of a Variety of 1,6-Disubstituted Cycloheptatrienes from Diiodocycloheptatriene (7). Since the iodine atom of vinyl iodides is known to be converted into various other functional groups, **7** is expected to be a good starting material for a variety of substituted cycloheptatrienes. For example, a halogen atom of vinyl halides is known to undergo a metal-catalyzed cross coupling reaction with Grignard reagents to give an alkyl- or aryl-substituted olefin.[14] The cross coupling reaction of the diiodide **7** afforded 1-alkyl-6-iodo- (**25**) and/or 1,6-dialkyl-1,3,5-cycloheptatrienes (**26**) depending on the reaction conditions and the results are shown in Table II. Use of copper catalyst, Li_2CuCl_4,[15] and a small excess of Grignard reagents gave the monoalkylated product **25** as a main product, whereas use of excess Grignard reagents resulted in the formation of a mixture of **25** and **26** (run 5) or in the exclusive formation of **26** (run 8). In order to minimize the dialkylation, it is important to choose an appropriate reaction time by monitoring the reaction (TLC or GLC). In contrast, use of nickel catalyst, $Ni(Ph_2PCH_2CH_2CH_2PPh_2)Cl_2$,[16] led to only **26** (run 2) even when a small excess of Grignard reagent was used. Palladium catalyst, $Pd(Ph_3P)_4$,[17] was least satisfactory, since the selectivity with regards to monoalkylation is poor and the reaction was not completed even after prolonged heating.



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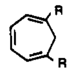

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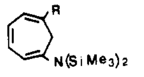
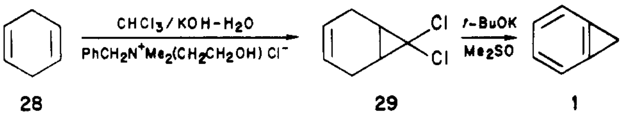


27

a, $CH_2{=}CH$; b, *n*-Bu; c, $(MeO)_2CHCH_2CH_2$; d, $CH_2{=}CHCH_2$

The iodine atom of **25b–d** was converted into a bis(trimetylsilyl)amino group by using copper bis(trimethylsilyl)amide to give amine **27b–d** (**27b**, 27%; **27c**, 37%; **27d**, 13%).

Improved Procedure for the Synthesis of Benzocyclopropene (1). In the course of the present study we needed an efficient synthetic method of **1** suitable for a large scale preparation. Although **1** is usually prepared by the method of Billups,[18] i.e., dehydrochlorination of 7,7-dichlorobicyclo[4.1.0]hept-3-ene (**29**), the yield of **1** from **28** via **29** is 12–16% (**28** → **29**, 38–39%; **29** → **1**, 32–41%).[18b]



28 **29** **1**

We have found a modified procedure for the preparation of **1** which raises the total yield from **28** up to 28–35%. The modified points are as follows: (1) A phase-transfer catalyst $[KOH\text{–}PhCH_2N(CH_3)_2(CH_2CH_2OH)^+\ Cl^-]$ is used instead of relatively expensive potassium *tert*-butoxide in the generation of dichlorocarbene. The present method is not only more economical and experimentally simpler than the Billups' method but also increases the yield of **29** from **2**, up to 50–55%. (2) **1** is pumped out from the reaction mixture by using a vacuum sealed stirrer (<0.5 mmHg) with efficient stirring. The yield of **1** from **29** increases up to 56–64% by this method. This suggests that the dehydrochlorination of **29** is a fairly clean reaction. More than 40 g of **1** can be obtained in one operation by this procedure (cf. 4.4–5.5 g in the literature[18b]).

Experimental Section

All the reactions were carried out under an argon or nitrogen atmosphere. Melting and boiling points were uncorrected.

Preparation of Benzocyclopropene (1). (a) Preparation of **29**. In a 3-L three-necked flask was placed sodium hydroxide (695 g, 17.4 mol), water (695 mL), benzyldimethyl(2-hydroxyethyl)ammonium chloride (30.8 g, 0.145 mol),[19] 1,4-cyclohexadiene (232 g, 2.90 mol), and methylcyclohexane (30 mL, internal standard for GLC analysis). The reaction was monitored by GLC. To the mixture whose temperature was raised to 50 °C with vigorous stirring was added chloroform (460 mL, 5.77 mol) over a period of 1.5 h (exothermic). The reaction temperature was kept at about 55 °C with external cooling. After completion of addition, the reaction mixture was stirred for 1 h and then two portions of chloroform (100 mL each) was added with an interval of about 1 h. After stirring for a further 40 min, the mixture was cooled to room temperature and washed with 2 L of water. After filtration of insoluble diadduct (4,4,8,8-tetrachlorotricyclo[$5.1.0^{1,7}.0^{3,5}$]octane), the aqueous layer was extracted with chloroform twice and the extract was combined with the organic layer. The combined organic layer was concentrated and the residue

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(19) Hiyama, T.; Sawada, H.; Tsukanaka, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, 3013.

was distilled under reduced pressure (44–46 °C (1.5 mmHg)) to give **29** (258 g, 1.58 mol, 54.5%).

(b) Preparation of 1. Dry potassium *tert*-butoxide prepared from *tert*-butyl alcohol (1350 mL, 14.4 mol) and potassium (96.2 g, 2.46 mol) in a 2-L three-necked flask equipped with a vacuum sealed stirrer was dissolved in 1 L of dry dimethyl sulfoxide at about 55 °C. After cooling to room temperature, **29** (134 g, 0.82 mol) was added over 20 min with external cooling (ice–water) and the mixture was stirred for 3 h at room temperature. The crude product was pumped out (0.2–0.5 mmHg) directly into an ethanol–dry ice trap with stirring. To the distillate was added ice–water and the organic layer was washed with water two times to remove *tert*-butyl alcohol and dimethyl sulfoxide. The product was dried by filtration through $MgSO_4$ column. The distillation was continued until the distillate no longer contained an appreciable amount of 1, usually three times exchange of the cold trap being necessary. The total yield of 1 was 42.2 g (0.47 mol, 57.3%). The product thus obtained contained only a small amount of *tert*-butyl alcohol as impurity (NMR).

Photoreaction of 1 with Thiocyanogen. To a benzene solution (100 mL) of thiocyanogen, prepared from lead(II) thiocyanate (17.84 g, 0.0552 mol) and bromine (8.00 g, 50.0 mmol)[23] was added 1 (3.83 g, 35.7 mmol) in benzene (6 mL). The mixture was irradiated by a medium-pressure mercury lamp (100 W) through a Pyrex filter at room temperature for 30 min. The resulting solution was filtered to remove orange precipitates (polymer of thiocyanogen) and concentrated. Chromatography (silica gel, 2:1 hexane–ether) of the residual oil afforded 4 (4.70 g, 64%), 5 (1.62 g, 22%), and 6 (147 mg, 2%). 4: mp 78.5–79.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.03 (s, 2 H), 6.66 (s, 4 H); IR (KBr) 2150 cm^{-1}; MS, *m/e* 206 (M^+, 55), 148 (37), 121 (100). Anal. Calcd for $C_9H_6N_2S_2$: C, 52.40; H, 2.93; N, 13.58; S, 31.09. Found: C, 52.44; H, 2.69; N, 13.81; S, 30.74. 5: a colorless oil; ^{1}H NMR ($CDCl_3$) δ 4.27 (s, 2 H), 7.30–7.85 (m, 4 H); IR (neat) 2150 cm^{-1}; MS, *m/e* 206 (M^+, 10), 148 (47), 121 (100); exact mass, *m/e* 205.9942, calcd for $C_9H_6N_2S_2$, *m/e* 205.9972. 6: a colorless oil; ^{1}H NMR ($CDCl_3$) δ 4.88 (s, 2 H), 7.05–7.84 (m, 4 H); IR (neat) 2160, 2095 cm^{-1}; MS, *m/e* 206 (M^+, 10), 148 (61), 121 (100); exact mass, *m/e* 205.9950, calcd for $C_9H_6N_2S_2$, *m/e* 205.9972.

Thermal Reaction of 1 with Iodine. To a carbon tetrachloride solution (10 mL) of 1 (137 mg, 1.52 mmol) cooled with ice–water bath was added a carbon tetrachloride solution (32 mL) of iodine (405 mg, 1.60 mmol) over a period of 30 min in the dark, and the solution was stirred at 0 °C for 5 h. The resulting solution was washed with aqueous sodium thiosulfate to remove the excess iodine, dried ($MgSO_4$), and concentrated. Chromatography (silica gel, pentane) gave 453 mg (87%) of *o*-iodobenzyl iodide (8), but 1,6-diiodo-1,3,5-cycloheptatriene (7) was not detected by NMR spectroscopy. When the reaction in a similar scale was carried out under normal sunlight, 465 mg (89%) of 8 was obtained and a trace of 7 was detected by NMR. When a similar reaction was carried out under 15-W fluorescent light, 455 mg (87%) of 8 and 28 mg (5%) of 7 were obtained. The reactions in other solvents were conducted similarly and the results are given in Table I.

Photoreaction of 1 with Iodine. (a) In pentane (run 8 in Table I). A pentane solution (90 mL) of 1 (217 mg, 2.41 mmol) was irradiated with an immersed medium-pressure mercury lamp (100 W). To this was added a pentane solution (80 mL) of iodine (648 mg, 2.55 mmol) during 2 h at 0 °C. After irradiation for an additional 2.5 h at the same temperature, the solution was shaken with 5% aqueous sodium thiosulfate. The organic layer was dried ($MgSO_4$) and concentrated to give 543 mg (65%) of a mixture of 7 and 8, the ratio of which was determined to be 2 to 1 by ^{1}H NMR. Chromatography (silica gel, pentane) gave 7 (258 mg, 31%) and 8 (149 mg, 18%). 7: mp 37–38 °C (lit.[9] 37–38 °C); ^{1}H NMR (CCl_4) δ 3.43 (s, 2 H), 6.20–6.35 (m, 2 H), 6.70–6.85 (m, 2 H). 8: mp 71–72 °C (lit.[9] 72 °C); ^{1}H NMR (CCl_4) δ 4.47 (s, 2 H), 6.70–7.90 (m, 4H). Photoreactions under other conditions (runs 9–11 in Table I) were conducted similarly.

(b) A large scale synthesis in heptane. The reaction was carried out with the apparatus shown in Figure 1.

A typical procedure is as follows. To a heptane solution (200 mL) of 1 (2.72 g, 30.2 mmol) cooled with ice–water was added a heptane solution (1000 mL) of iodine (8.06 g, 31.7 mmol) over a period of 3.6 h, during which time the solution was irradiated with light (a 400-W medium-pressure mercury lamp) through a circulating filter solution (1 cm long) of 0.1% aqueous K_2CrO_4 cooled to about 10 °C with a dry ice–ethanol bath. After the addition of iodine, the solution was irradiated until the characteristic odor of 1 disappeared. Workup of the reaction solution in a similar manner to that described in a afforded 7 (7.09 g, 68%) and 8 (0.91 g, 9%). A similar photoreaction of 1 (8.05 g, 89.4 mmol in 600 mL of heptane) with iodine (23.5 g, 92.5 mmol in 2.2 L of heptane) could also be conducted with the apparatus in Figure 1 to give 17.8 g (58%) of 7.

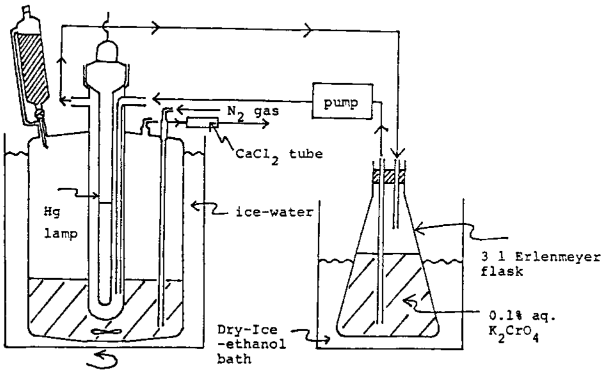

Figure 1. Apparatus for the photochemical reaction of benzocyclopropene (1) with iodine.

7,9-Dithiatricyclo[4.3.1.0^{1,6}]deca-2,4-diene (10). To a suspension of 4 (206 mg, 1.00 mmol) in liquid NH_3 (25 mL) was added sodium (93 mg, 4.04 mmol) at −78 °C until a blue color persisted. After addition of absolute ethanol (ca. 5 mL) to destroy a small excess of sodium, the ammonia was evaporated. The reduction mixture containing dithiolate (9) was dissolved in THF (10 mL) containing hexamethylphosphoric triamide (HMPA) (0.5 mL), and to the solution was added diiodomethane (0.08 mL, 1 mmol). The solution was stirred at room temperature for 1.5 h and then concentrated. The residue was extracted with ether and the ether layer was washed with water, dried over $MgSO_4$, and concentrated. The residual oil was subjected to chromatography (Florisil, hexane) to give 10 (205 mg, 81%), which was unstable to air (presumably due to oxidation): a colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.54 (d, *J* = 6 Hz, 1 H), 2.25 (d, *J* = 6 Hz, 1 H), 3.68 (d, *J* = 10.8 Hz, 1 H) 4.20 (d, *J* = 10.8 Hz, 1 H), 5.90–6.70 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 127.2, 120.5, 52.9, 37.3, 26.1; IR (neat 3040, 2980, 2920, 1675, 1540, 1420, 1380, 1220, 1090, 980 cm^{-1}; MS, *m/e* (relative intensity) 168 (M^+, 90%), 167 (100), 122 (58), 121 (69), 78 (40), 77 (30); exact mass, *m/e* 168.0085, calcd for $C_8H_8S_2$, *m/e* 168.0067.

7,10-Dithiabicyclo[4.4.1]undeca-1,3,5-triene (11) and 2,5,12,15-tetrathiatricyclo[14.4.1.1^{6,11}]docosa-6,8,10,16,18,20-hexaene (12). To 4 (158 mg, 0.77 mmol) in liquid NH_3 (20 mL) was added sodium (71 mg, 3.1 mmol) at −78 °C. After evaporation of NH_3,the residual yellowish solid was dissolved in THF (10 mL) containing HMPA (0.5 mL). To the solution was added 1,2-dibromoethane (0.1 mL, 1.15 mmol) with stirring. Stirring was continued for 1 h at room temperature and the solution was then concentrated. The reaction mixture was transferred to a separatory funnel with 110 mL of CH_2Cl_2 and 30 mL of water. The organic layer was washed with 10 mL of water, dried over $MgSO_4$, and concentrated. Chromatography (TLC, silica gel, CCl_4) of the residual oil afforded 11 (65 mg, 46%) and 12 (21 mg, 15%). 11: a colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.04 (d, *J* = 12 Hz, 1 H), 3.29 (d, *J* = 12 Hz, 1 H), 2.43–2.88 (m, 2H), 3.12–3.6 (m, 2 H), 6.22–6.75 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 131.2, 127.6, 118.6, 42.9, 33.7; IR (neat) 3000, 2900, 1595, 1490, 1440, 1410, 1280, 1260, 1085, 880, 835, 770, 730 cm^{-1}; MS, *m/e* 182 (M^+, 89%), 154 (84), 153 (100), 121 (37), 78 (88), 77 (42), 76 (68); exact mass, *m/e* 182.0205, calcd for $C_9H_{10}S_2$, *m/e* 182.0222. 12: mp 138–140 °C; ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 4 H), 2.94 (s, 8 H), 5.95–6.45 (m, 8 H); IR (KBr) 2950, 1590, 1505, 1495, 1320, 1090, 835, 780, 730 cm^{-1}; MS, *m/e* 364 (M^+, 40%), 207 (61), 155 (89), 121 (100). Anal. Calcd for $C_{18}H_{20}S_4$: C, 59.30; H, 5.53; S, 35.18. Found: C, 59.48; H, 5.72; S, 34.91.

7,10-Dithiabicyclo[4.4.1]undeca-1,3,5,8-tetraene (13), 2,5,12,15-Tetrathiatricyclo[14.4.1.1^{6,11}]docosa-3,6,8,10,13,16,18,20-octaene (14), and 2,5,12,15,22,25-Hexathiatetracyclo[24.4.1.1^{6,11}.1^{16,21}]tritriaconta-3,6,8,10,13,16,-18,20,23,26,28,30-dodecaene (15). To a solution of 4 (206 mg, 1 mmol) in liquid NH_3 (20 mL) was added sodium (92 mg, 4 mmol) at −78 °C. Sodium disappeared slowly and the resulting yellow solution gave the yellow solid after evaporation of NH_3. The residue was dissolved in THF (12 mL) containing HMPA (0.5 mL) and then to the solution was added *cis*-1,2-dichloroethylene (0.076 mL, 1 mmol). Stirring was continued for 5 h at room temperature and the solvent was evaporated. The residue was washed with water and the resulting precipitates were chromatographed (silica gel, CS_2) to give **13** (19 mg, 11%), **14** (24 mg, 13%), and **15** (21 mg, 11%).

A similar reaction carried out in a more diluted solution resulted in the formation of **13** as a main product. The maximum yield of **13** (32%) was attained under the following reaction conditions: the dithiolate (**9**) (3 mmol) and *cis*-1,2-dichloroethylene (4 mmol) were dissolved in THF (100 mL) and the mixture was stirred for 1 week at room temperature. **13**: ^1H NMR ($CDCl_3$) δ 2.66 (d, J = 12 Hz, 1 H), 3.92 (dt, J = 12 Hz, 1.4 Hz, 1 H), 5.69 (s, 2 H), 6.1–6.7 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 133.33, 125.8, 116.1, 113.0, 45.7; IR (neat) 3000, 1590, 1540, 1480, 1415, 1295, 1075, 910, 840, 730, 695, 660 cm^{-1}; MS, *m/e* 180 (M^+, 15%), 147 (100), 135 (22), 121 (13); exact mass, *m/e* 180.0083, calcd for $C_9H_8S_2$, *m/e* 180.0068. **14**: mp 257 °C dec; ^1H NMR (CS_2) δ 2.81 (s, 4 H), 6.45 (bs, 8 H), 6.59 (s, 4 H); IR (KBr) 3000, 1590, 1540, 1480, 1415, 1295, 1075, 910, 840, 730, 720, 695, 660 cm^{-1}; MS, *m/e* 360 (M^+, 56%), 179 (43), 147 (100), 135 (34), 121 (36), 91 (49), 89 (57). Anal. Calcd for $C_{18}H_{16}S_4$: C, 59.96; H, 4.47; S, 35.57. Found: C, 60.10; H, 4.31; S, 35.70. **15**: mp 219 °C dec; ^1H NMR (CS_2) δ 2.72 (s, 6 H), 6.47 (s, 6 H), 6.15–6.55 (m, 12 H); IR (KBr) 3000, 1580, 1540, 1490, 1420, 1300, 1080, 900, 830, 720, 690, 660 cm^{-1}; MS, *m/e* 540 (M^+, 7%), 147 (100), 135 (30), 121 (40), 91 (44), 89 (33), 78 (44). Anal. Calcd for $C_{27}H_{24}S_6$: C, 59.96; H, 4.47; S, 35.57. Found: C, 59.84; H, 4.22; S, 35.53.

Reactions of 10, 11, and 13 with *N*-Phenylmaleimide. A mixture of **10**, **11**, or **13** (1 mmol) and *N*-phenylmaleimide (1 mmol) was allowed to react in ether (room temperature, 3 days for **10**) or in refluxing xylene (4 days for **11** and 2 h for **13**). After these periods **10**, **11**, and **13** were consumed as judged by TLC. The Diels–Alder adducts **18**, **19**, and **20** were obtained in 48%, 77%, and 59% yields, respectively, after chromatographic purification (silica gel, CH_2Cl_2) and recrystallization from CH_2Cl_2–MeOH. The reactions with **11** and **13** did not occur in boiling benzene or dioxane. **18**: mp 261–262 °C; ^1H NMR ($CDCl_3$) δ 1.27 (d, J = 6.6 Hz, 1 H), 1.82 (d, J = 6.6 Hz, 1 H), 3.43–3.95 (m, 4 H), 3.95 (d, J = 10.8 Hz, 1 H), 4.41 (d, J = 10.8 Hz, 1 H), 5.87–6.27 (q, 2 H), 6.93–7.50 (m, 5 H); IR (KBr) 1780, 1715, 1495, 1385, 1190, 805, 760, 735, 695, 660, 630 cm^{-1}; MS, *m/e* 341 (M^+, 1%), 168 (100), 153 (60), 135 (50). Anal. Calcd for $C_{18}H_{15}NO_2S_2$: C, 63.32; H, 4.43; N, 4.10; S, 18.78. Found: C, 63.04; H, 4.19; N, 4.28; S, 18.59. **19**: mp 270–271 °C; ^1H NMR ($CDCl_3$) δ 0.91 (d, J = 6 Hz, 1 H), 1.54 (d, J = 6 Hz, 1 H), 2.70 (bs, 4 H), 3.20–3.55 (m, 2 H), 3.70–3.83 (m, 2 H), 5.90–6.15 (m, 2 H), 7.00–7.55 (m, 5 H); IR (KBr) 1780, 1710, 1495, 1390, 1190, 805, 790, 755, 720, 695, 635 cm^{-1}; MS, *m/e* 355 (M^+, 14%), 327 (21), 182 (100), 154 (27). Anal. Calcd for $C_{19}H_{17}NO_2S_2$: C, 64.20; H, 4.82; N, 3.94; S, 18.04%. Found: C, 63.95; H, 4.64; N, 3.99; S, 18.05. **20**: mp 257–258 °C; ^1H NMR ($CDCl_3$) δ 1.12 (d, J = 6 Hz, 1 H), 1.68 (d, J = 6 Hz, 1 H), 3.26–3.66 (m, 4 H), 5.93–6.13 (m, 2 H), 6.63 (s, 2 H), 6.90–7.50 (m, 5 H); IR (KBr) 1780, 1710, 1490, 1390, 1185, 815, 760, 740, 690, 660, 640 cm^{-1}; MS, *m/e* 353 (M^+, 15), 180 (100), 179 (40), 147 (48), 135 (38), 128 (69). Anal. Calcd for $C_{19}H_{15}NO_2S_2$: C, 64.56; H, 4.28; N, 3.96; S, 18.14. Found: C, 64.83; H, 3.98;; N, 4.14; S, 18.66.

Reactions of 1 with Grignard Reagents. 1-Iodo-6-vinyl-1,3,5-cycloheptatriene (25a).[20] (a) With nickel catalyst. To a solution of **7** (172 mg, 0.5 mmol) and $Ni(Ph_2PCH_2CH_2CH_2PPh_2)Cl_2$[21] (4.8 mg, 0.005 mmol) in ether (3 mL) was added vinylmagnesium bromide (0.58 mmol) in THF (1 mL) at room temperature. After the mixture was refluxed for 2.5 h, 2 M hydrochloric acid (3 mL) was added. The product was extracted with ether, washed with water, dried over $MgSO_4$, and concentrated. Chromatography (silica gel, pentane) of the residual oil gave a mixture of **26a** (48 mg, 67%) and **7** (57 mg, 33%) as judged by NMR. **26a**:[22] ^1H NMR (CCl_4) δ 2.52 (s, 2 H), 5.04 (d, 1 H, J = 11 Hz), 5.43 (d, 1 H, J = 17 Hz), and 5.82–6.58 (m, 5 H).

(b) With palladium catalyst. To a solution of **7** (172 mg, 0.5 mmol) and $Pd(Ph_3P)_4$ (17.5 mg, 0.015 mmol) in benzene (5 mL) stirred for 5 h at room temperature was added vinylmagnesium bromide (0.75 mmol) in THF (0.73 mL) at room temperature. The temperature was raised gradually to refluxing temperature of THF during 6 h. After the reflux was continued for an additional 1 h, an excess of the Grignard reagent was quenched with water. The organic layer was washed with water, separated, dried over $MgSO_4$, and concentrated. The residual oil was a mixture of **25a**[7] (22 mg, 18%), **26a** (8 mg, 11%), and **7** (49 mg, 29%) as analyzed by NMR.

1-Butyl-6-iodo-1,3,5-cycloheptatriene (25b). To **7** (344 mg, 1 mmol) in THF (3 mL) cooled to −25 °C was added a solution of butylmagnesium bromide (1.4 mmol) in ether. A THF solution of Li_2CuCl_4 (0.03 mmol)[15a] was added to the above mixture at −20 °C. Stirring was continued for 1 h and then the temperature was raised gradually to room temperature. After the usual workup the crude products were chromatographed on silica gel (pentane) to give **25b** (124 mg, 51%) and recovered **7** (41 mg, 12%). When 2 equiv of the Grignard reagent was used at −78 °C, **25b** and **26b** were obtained in 34% and 23%, respectively. **25b**: a pale yellow oil; ^1H NMR (CCl_4) δ 0.7–1.9 (m, 9 H), 2.90 (s, 2 H), 5.80–6.80 (m, 4 H); IR (neat) 3060, 2950, 1600 cm^{-1}; MS, *m/e* 274 (M^+, 5%), 147 (38), 105 (100), 91 (28); exact mass, *m/e* 274.0178, calcd for $C_{11}H_{15}I$, *m/e* 274.0218. **26b**: a colorless oil; ^1H NMR (CCl_4) δ 0.6–2.6 (m, 18 H), 2.25 (s, 2 H), 5.70–6.40 (m, 4 H); IR (neat) 3040, 1595 cm^{-1}; MS, *m/e* 204 (M^+, 14%), 147 (42), 105 (100), 91 (32); exact mass, *m/e* 204.1858, calcd for $C_{15}H_{24}$, *m/e* 204.1878.

1-Iodo-6-(3,3-dimethoxypropyl)-1,3,5-cycloheptatriene (25c). The reaction of **7** (1.38 g, 4.02 mmol) with (3,3-dimethoxypropyl)magnesium bromide (5.6 mmol) was conducted in a similar manner to that described for **25b** to afford **25c** (0.77 g, 60%): a pale yellow oil; ^1H NMR (CCl_4) δ 1.50–1.96 (m, 2 H), 2.06–2.46 (m, 2 H), 2.90 (s, 2 H), 3.16 (s, 6 H), 4.23 (t, J = 5 Hz, 1 H), 5.73–6.63 (m, 4 H); IR (neat) 3015, 2950, 1625, 1595, 1525 cm^{-1}; MS, *m/e* 288 (M^+ − MeOH, 14%), 230 (100), 167 (47), 129 (74), 115 (31), 103 (74), 75 (43).

1-Allyl-6-iodo-1,3,5-cycloheptatriene (25d). The reaction of **7** (3.44 g, 10.0 mmol) with allylmagnesium chloride (10.7 mmol) was carried out in a similar manner described for **25b** to give **25d** (2.17 g, 84%), **26d** (670 mg, 4%), and recovered **7** (133 mg, 4%). When 2 equiv of the Grignard reagent was used, only **26d** was obtained in 67% yield. **25d**: a pale yellow oil; ^1H NMR (CCl_4) δ 2.90 (s, 2 H), 3.00 (bd, J = 7 Hz, 2 H) 4.90–6.80 (m, 7 H); IR (neat) 3000, 1620, 1595, 1520, 1420 cm^{-1}; MS, *m/e* 258 (M^+, 27%), 217 (53), 203 (7), 131 (100), 116 (38), 91 (91), 90 (50); exact mass, *m/e* 257.9924, calcd for $C_{10}H_{11}I$, *m/e* 257.9908. **26d**: ^1H NMR (CCl_4) δ 2.20 (s, 2 H), 2.89 (bd, J = 6 Hz, 4 H), 4.80–6.42 (m, 10 H); IR (neat) 3070, 1635, 1620 cm^{-1}; MS, *m/e* 172 (M^+, 20%), 131 (100), 129 (23), 91 (60); exact mass, *m/e* 172.1249, calcd for $C_{13}H_{16}$, *m/e* 172.1251.

1-Alkyl-6-[bis(trimethylsilyl)amino]-1,3,5-cycloheptatriene (27). General Procedure. Butyllithium (1.2 mmol) in hexane was added with stirring to a solution of bis(trimethylsilyl)amine (193 mg, 1.2 mmol) in 2 mL of THF at room temperature and the mixture was refluxed for 1 h. Powdered anhydrous copper(I) iodide (229 mg, 1.2 mmol) was added in one portion to the solution cooled to ca. −40 °C. The copper salt dissolved when the temperature of the reaction mixture was raised to 0 °C. After refluxing for an additional 1 h, THF was removed under reduced pressure. A pyridine (2 mL) solution of **25** (1.06 mmol) was added and the mixture was refluxed for 8 h. The resulting solution was cooled to ca. 70 °C and hexane (10 mL) was added with rapid stirring. After cooling to room temperature, precipitates formed were removed by filtration and the filtrate was distilled (Kugelrohr) to give **27**.

1-Butyl-6-[bis(trimethylsilyl)amino]-1,3,5-cycloheptatriene (27b). Yield 27%; a colorless oil; bp 105 °C (0.95 mmHg); ^1H NMR (CCl_4) δ 0.10 (s, 18 H), 0.6–1.6 (m, 9 H), 2.20

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(20) For a reaction using a copper catalyst, see ref 7.

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(s, 2 H), 5.3–6.2 (m, 4 H); IR (neat) 3000, 2940, 2920, 2850, 1590, 1175, 1140, 1100, 1065, 995, 930, 885, 840, 735, 675, 620 cm^{-1}; MS, *m/e* 307 (M$^+$, 32%), 234 (28) 105 (55), 73 (100); exact mass, *m/e* 307.2138, calcd for $C_{17}H_{33}NSi_2$, *m/e* 307.2151.

1-[Bis(trimethylsilyl)amino]-6-(3,3-dimethoxypropyl)-1,3,5-cycloheptatriene (27c). Yield 36%; a colorless oil; bp 125 °C (0.95 mmHg); ^{1}H NMR (CCl_4) δ 0.23 (s, 18 H), 2.26 (s, 2 H), 1.55–2.26 (m, 4 H), 3.24 (s, 6 H), 4.31 (t, *J* = 5 Hz, 1 H), 5.40–6.30 (m, 4 H); IR (neat) 3000, 2940, 2880, 2820, 1595, 1505, 1440, 1380, 1175, 1125, 1080, 1070, 1055, 990, 950, 930, 910, 890, 840, 820, 760, 740, 680, 660 cm^{-1}; MS, *m/e* 353 (M$^+$, 3%), 321 (36), 248 (22), 73 (100); exact mass, *m/e* 353.2220, calcd for $C_{18}H_{35}NO_2Si_2$, *m/e* 353.2206.

1-Allyl-6-[bis(trimethylsilyl)amino]-1,3,5-cycloheptatriene (27d). Yield 13%; a colorless oil; bp 110 °C (0.65 mmHg); ^{1}H NMR (CCl_4) δ 0.10 (s, 18 H), 2.16 (s, 2 H), 2.80 (bd, *J* = 6 Hz, 2 H), 4.65–6.15 (m, 7 H); IR (neat) 3075, 3000, 2950, 2880, 1590, 1550, 1445, 1170, 1130, 990, 960, 930, 910, 880, 840, 820, 755, 740, 700, 680, 620 cm^{-1}; MS *m/e* 291 (M$^+$, 35%), 218 (33) 73 (100); exact mass, *m/e* 291.1860, calcd for $C_{16}H_{29}NSi_2$, *m/e* 291.1838.

Trapping Free Radicals Formed in the Reaction of Ozone with Simple Olefins Using 2,6-Di-*tert*-butyl-4-cresol (BHT)

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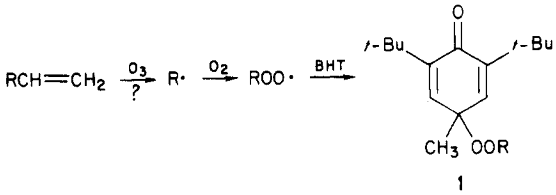
Free radicals are detected from the ozonation of a series of olefins using a BHT trapping technique. We have determined the structure of the adduct when 3,3-dimethylbutene (*tert*-butylethylene) is ozonated at −78 °C and then warmed in the presence of BHT. The adduct can be rationalized as arising from trapping *tert*-butylperoxyl radicals by BHT to give 2,6-di-*tert*-butyl-4-(*tert*-butylperoxy)-4-methyl-2,5-cyclohexadienone (1).

Ozone, one of the most ubiquitous of environmental toxins, causes damage to biological systems both by Criegee ozonolysis (which presumably does not involve free radicals) and by a process that generates free radicals.[1,2] The production of free radicals from ozone/olefin reactions in solution has been somewhat controversial,[3] and it is important to establish unambiguously that free radicals actually are produced. We have used spin trapping techniques to demonstrate radical production,[2a,3] but these data are not entirely satisfactory for two reasons. First, nitrones and nitroso compounds can be converted to nitroxide radicals by processes that do not involve the trapping of free radicals; in other words, ESR spectra of spin adducts can arise by artifactual reactions. Second, spin trapping is difficult to quantify, and we were only able to show that the yield of free radicals from ozone/olefin reactions lies between 0.01 and 10%.[2b] In this communication we report results on the trapping of free radicals from ozone/olefin reactions using BHT as the radical trap. While BHT is not a "spin trap" in the strictest definition of the term, it is a well-known scavenger of oxy radicals, and the structure of the BHT adduct of peroxyl radicals has been elucidated in several cases.[4-7]

We have previously shown that ozone reacts with simple olefins to give peroxyl radicals, and we suggested that these radicals arise from a hydrotrioxide (ROOOH) that is the immediate radical precursor.[2a] One possible mechanism by which olefin/ozone reactions could produce hydrotrioxides is by reaction of ozone at the allylic hydrogen, and we have demonstrated that this type of reaction can occur, using cumene as a model for an olefin with an allylic hydrogen.[8] However, olefins that do not possess allylic hydrogens cannot react by this mechanism; nevertheless, our original study[2] showed that at least one such olefin, 3,3-dimethylbutene (*tert*-butylethylene), gives radicals on reaction with ozone. As a probe of the mechanism in this case, we have studied *tert*-butylethylene by the BHT trapping method. We here present evidence that olefins of the structure $RCH{=}CH_2$ or $RCH{=}CMe_2$ (where R is *tert*-butyl) react with ozone to give an intermediate that is stable at −78 °C. This intermediate appears to decompose on warming to give alkyl radicals that subsequently react with oxygen to give peroxyl radicals; if BHT is present, these peroxyl radicals are then trapped by BHT to give adducts as shown in eq 1.



(1)

1

Experimental Section

Instrumentation. Proton NMR spectra were recorded with a Varian A-60 NMR spectrometer and both ^{1}H and ^{13}C NMR spectra with a Bruker WP-200 spectrometer. Mass spectra were obtained on a Hewlett-Packard 5985A mass spectrometer; electron-impact (70 eV) and chemical-ionization (methane) spectra were obtained by a direct-insertion method. Infrared spectra were

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(2) (a) Pryor, W. A.; Prier, D.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 2883–2888. (b) In systems where radicals are generated directly (and cleanly) from initiators, PBN appears to demonstrate a high efficiency in trapping radicals. However, in systems in which peroxyl radicals may be trapped (and where peroxyl spin adducts subsequently rearrange to give alkoxyl spin adducts), the efficiency of spin trapping by PBN appears to be much lower. This describes the spin trapping problem faced with ozone, which appears to produce a mixture of oxy-radicals that are ultimately observed as alkoxyl spin adducts.[2a] We have discussed these aspects of quantitating radical yields by spin trapping, as has E.G. Janzen, K.U. Ingold, and M.V. Merritt and R.A. Johnson (see references cited in reference 2a).

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