# Studies of Tetrazoles as Rubber Chemicals. I. Preparation and Characterization of Reactive Antioxidants Based on Tetrazoles

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## Synopsis

The novel reactive antioxidants based on tetrazoles that are stable at room temperature and convertible into the highly reactive nitrileimines by pyrolysis were prepared and the reactivity for carbon–carbon double bonds was evaluated. Antioxidants, i.e., 2-substituted phenyl-5-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)tetrazoles (PHPT) were prepared with the reaction of *p*-toluenesulfonylhydrazone of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde and substituted phenyl diazonium chloride in a mixed solvent of pyridine, ethanol, and water at −10°C to −20°C in 31–61% yields. To evaluate the reactivities of PHPT for carbon–carbon double bonds, *m*-chloro-substituted PHPT was pyrolyzed in an excess of styrene at 160–170°C for 0.5 h to give the 1-(3′-chlorophenyl)-3-(3″,5″-di-*tert*-butyl-4″-hydroxyphenyl)-5-phenyl-2-pyridazoline in a 44.1% yield by 1,3-dipolar addition reaction of the nitrileimine formed from the *m*-chloro-substituted PHPT. The thermogravimetric analysis of a mixture of proton isomer of PHPT and liquid polybutadiene showed that PHPT attached to liquid polybutadiene with an accompanying evolution of nitrogen.

## INTRODUCTION

Many antioxidants have been developed to prevent the oxidative degradation of rubber and plastics. However, common disadvantages of these antioxidants are their volatility and solvent extractability from a polymer matrix.[1] In order to improve these phenomena, high molecular weight antioxidants have been developed by using several synthetic procedures. For example, addition products of *p*-octyldiphenylamine with liquid SBR,[2] *p*-aminodiphenylamine with epoxydized BR,[3] terpolymer of styrene–divinylbenzene–maleic anhydride with hydroquinone,[4] and liquid BR or isoprene–butadiene copolymer with phenols[5] were reported, as well as the condensation products of aromatic amine antioxidants with hydroxyl-terminated liquid polybutadiene,[1(b)] 3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propionic acid with polyolefines containing hydroxyl groups,[6] or hydroxyl-terminated liquid polybutadiene.[7]

On the other hand, such antioxidants containing polymerizable groups as *N*-(4-anilinophenyl)methacrylamide,[8] *N*-(4-anilinophenyl)methacrylate,[9] 2-*tert*-butyl-4-methyl-6-allylphenol,[10] 3,5-di-*tert*-butyl-4-hydroxybenzyl acrylate,[11] *N*-(3,5-di-*tert*-butyl-4-hydroxybenzyl)acrylamide,[12] *N*-(3,5-di-*tert*-butyl-4-hydroxybenzyloxymethyl)acrylamide,[13] etc., were reported. Novel antioxidants containing reactive groups (reactive antioxidants) were also reported, i.e., 2,4-bis(*N*-isopropyl-*N*-4-anilinophenylamino)-6-mercapto-*s*-triazine,[14] *N*-(4-anilinophenyl)β-mercaptopropionamide,[15] γ-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl-β-mercaptopropionate,[16] nitrone compounds con-

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taining aromatic hydroxyl groups,[17] 2,4-di-*tert*-butyl-6-diazo-1,4-cyclohexa-diene-3-one,[18] and *p*-nitroso diphenylamine,[19] etc.

The authors have recently prepared novel reactive antioxidants based on tetrazoles. Tetrazoles (1) are expected to react with carbon–carbon double bonds in diene rubber, because they are convertible into nitrileimines (2) by pyrolysis and undergo 1,3-dipolar addition to dicyclopentadiene to give a 2-pyridazoline derivative (3)[20] [see eq. (1)].



(1)



(2)



(1)

(3)
(Yield: 68%)
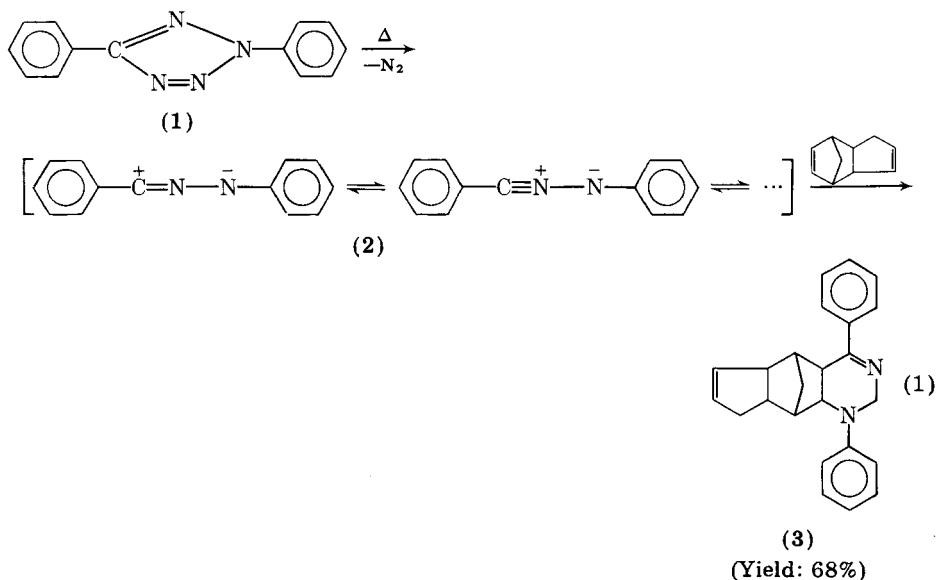
The bound antioxidants of nitrone compounds based on 1,3-dipolar addition reaction were reported.[17] However, those of tetrazole compounds were prepared for the first time by us and were ascertained to be convertible into the highly reactive nitrileimines by pyrolysis.

The present paper describes the preparation of novel reactive antioxidants derived from tetrazole and the reaction of the antioxidant with styrene as well as thermogravimetric analysis of the antioxidant in a liquid polybutadiene.

## EXPERIMENTAL

### Reagents

2,6-Di-*tert*-butylphenol supplied by the Ethyl Corp. was used without further purification. The liquid polybutadiene (LPBd) produced by the ARCO. Chemical Co., Ltd., Polybd R-45HT (hydroxyl equivalent: $8.3 \times 10^{-4}$ mol/g, molecular weight: about 2700, iodine value: 398, microstructure: *trans*-1,4 60 mol %, *cis*-1,4 20 mol %, 1,2-addition 20 mol %) was used without further purification. Other chemicals were supplied from Tokyo Kasei Kogyo Co., Ltd., or Junsei Chemical Co., Ltd., and used without further purification.

### Thermogravimetric and Qualitative Analyses

Thermogravimetric analysis was made at a heating rate of 10°C/min with a Rigaku Denki TG-DSC Standard Model under nitrogen stream. Elementary

analyses of carbon, nitrogen, and hydrogen were carried out with a Yanagimoto CHN Corder MT-II type and that of sulfur was done by dimethylsulfonazo-III method.[21] Infrared spectra (IR) were recorded with a Hitachi EPI-G$_3$ type on a nujol mull in a rock salt plate cell. $^1$H-NMR spectra were recorded with a Hitachi Perkin-Elmer R-24B type using tetramethylsilane as the internal standard.

### Preparations of Starting Materials, Hydrazone and Tetrazoles

**Starting Materials.** 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (BHBA) was prepared from 2,6-di-*tert*-butylphenol and hexamethylenetetramine according to G. A. Nikiforov et al.,[22] pale yellow crystal: mp 188.0–190.0°C (lit.,[22] mp 188–189°C). *p*-Toluenesulfonylhydrazide (TSH) was prepared from *p*-toluenesulfonylchloride and hydrazine hydrate according to Friedmann et al.,[23] colorless crystal: mp 106.5–108.5°C (lit.,[23] mp 109–110°C).

**_p_-Toluenesulfonylhydrazone of a 3,5-Di-_Tert_-Butyl-4-Hydroxyben-zaldehyde (THBA).** A mixture of BHBA (495 g, 2.118 mol), TSH (394 g, 2.118 mol), 4.2 L of methanol and 83 mL of glacial acetic acid was refluxed with stirring for 3.5 h and cooled in an ice bath to afford THBA, crystallized in colorless crystalline scale. THBA obtained was filtered, washed several times with methanol, and dried in a desiccator. Yield: 575.2 g (67.6%), decomp point 205.5–206.5°C. The product was of adequate purity and used without further purification.

**Tetrazoles: General Procedure.** A solution of sodium nitrite (method A, 0.1 mol, method B, 0.3 mol) in 40 mL (method A) or 120 mL (method B) of water was added dropwise to a solution of substituted anilines (method A, 0.1 mol; method B, 0.3 mol) and 26 mL (method A) or 78 mL (method B) of 35% concentrated hydrochloric acid in 160 mL (method A) or 320 mL (method B) of 50% aqueous ethanol below 10°C. The solution of substituted phenyldiazonium chloride thus obtained was added dropwise to a stirred solution of THBA (method A, 0.1 mol; method B, 0.2 mol) in 400 mL (method A) or 800 mL (method B) of pyridine at such a rate that the temperature was maintained between −20°C and −10°C. Additional stirring was continued at −20−−10°C for 3–5 h and at 0–10°C for 6–8 h. Tetrazoles crystallized from the solution. The product was filtered, washed several times with a cold mixed solution of pyridine, ethanol, and water (volume ratio: 5:1:1), and purified by recrystallization, followed by drying in a desiccator.

### Reaction of *m*-Chloro-Substituted PHPT with Styrene

A mixture of *m*-chloro-substituted PHPT (3.90 g, 0.010 mol) and styrene (20.8 g, 0.20 mol) was stirred at 130–140°C for 2 h. After dilution with benzene (50 mL), the reaction mixture was poured into 500 mL of methanol with vigorous stirring to separate polystyrene. The polystyrene was filtered and washed several times with methanol, and the combined filtrate was evaporated under a reduced pressure to give the solid residue. The residue obtained was recrystallized from a mixed solvent of methanol, acetone, and a small amount of water to afford a 2.05 g (44.1%) of 2-pyridazoline derivative of light orange crystal, mp 157.5–160.5°C.

## RESULTS AND DISCUSSION

### Synthesis of THBA

THBA (6) was synthesized from BHBA (4) and TSH (5) by a condensation reaction using acetic acid as a catalyst in the usual way [see eq. (2)].[24]



**(4)**                     **(5)**

**(6)**
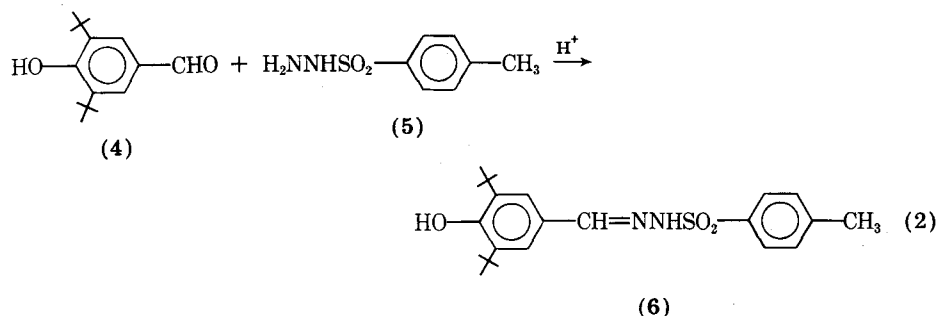
As will be discussed later, the corresponding reaction product was identified as the expected hydrazone by elementary analysis, IR and $^1$H-NMR spectra.  The found values of elementary analysis agreed with the calculated values.

ANAL.  Found: C, 65.80; H, 7.38; N, 7.13; S, 8.51%.  Calcd for $C_{22}H_{30}N_2SO_3$:  C, 65.64; H, 7.51; N, 6.96; S, 7.96%.

In the IR spectrum ranging from 1500 to 4000 cm$^{-1}$, THBA exhibits three characteristic peaks at 3640, 3190, and 1605 cm$^{-1}$ assigned to the hindered phenolic —OH group, $>$NH group and $>$C$=$N— group, respectively.  In the $^1$H-NMR spectrum, each proton of THBA appears at one of eight positions as a singlet or doublet as follows:



**(3)**
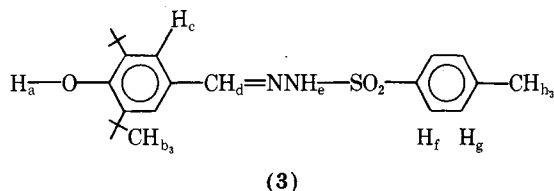
—H$_a$, 6.3 (s); —H$_b$, 1.4 (s); —H$_c$, 7.4 (s); —H$_d$, 7.9 (s); —H$_e$, 9.7 (s); —H$_f$, 7.8 (d, $j$ = 8.7); —H$_g$, 7.3 (d, $j$ = 8.7); —H$_h$, 2.4 ppm (s).  The peak patterns are designated in parentheses.  The designations, (s), (d) and ($j$) indicate singlet, doublet, and coupling constant, respectively.

### Syntheses of Reactive Antioxidants Based on Tetrazoles

2-Substituted phenyl-5-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)tetrazoles (PHPT, 8) were obtained as crystals by allowing THBA (6) in pyridine to react with substituted phenyl diazonium chloride (7) in aqueous ethanol solution at −10−−20°C, according to the procedure of Ito et al.[25] [see eq. (3)]:



**(6)**                              **(7)**

$$HO-\text{(ring)}-C\overset{N}{\underset{N=N}{\diagdown}}N-\text{(ring)}-Y \quad (3)$$

(8)
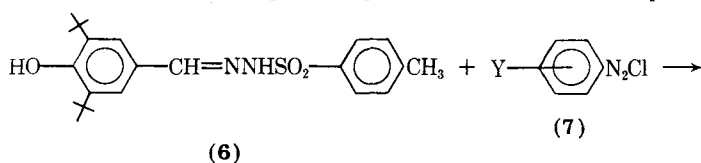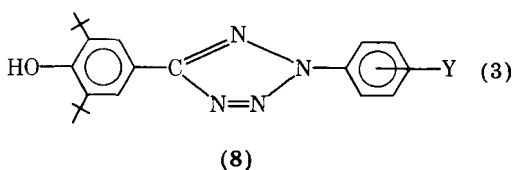
The reaction products were identified by elementary analyses, IR and $^1$H-NMR spectra, as will be discussed later. The results are shown in Table I.

Satisfactory yields of the tetrazoles were obtained at a molar ratio of the substituted phenyl diazonium chloride to that of THBA (6) of 1.5. The values obtained by elementary analyses for all the tetrazoles agreed with the calculated values (see Table II). In the IR spectra, all the tetrazoles exhibit four characteristic peaks at 3600–3630 (strong), 1600–1625 (medium), 1505–1530 (medium), and 995–1020 cm$^{-1}$ (strong), assigned to the hindered phenolic —OH group, the $>$C=N— group, phenyl group, and the tetrazole ring system.[25] In the $^1$H-NMR spectra, all the tetrazoles exhibit three singlet peaks at 1.51–1.52, 5.47–5.57, and 8.00–8.07 ppm, assigned to the protons of the tert-butyl group, the proton of the hindered phenolic —OH group and the aromatic protons of the 5-aryl group, respectively. Furthermore, all the tetrazoles exhibit a few peaks at 7.01–8.30 ppm as a doublet or multiplet that can be assigned to the aromatic protons of the 2-aryl group. In the case of the alkyl or alkoxy derivatives of PHPT, on the other hand, the absorptions that can be assigned to the protons of the alkyl or alkoxy groups were observed at reasonable positions. These results are shown in Table II.

## Model Reaction

To evaluate the reactivity of PHPT towards carbon–carbon double bonds, $m$-chloro-substituted PHPT (9) was pyrolyzed in an excess of styrene to afford a light orange crystal (mp 157.5–160.5°C). Elementary analysis of the product gave the following results:

ANAL. Found: C, 76.13; H, 7.68; N, 6.29. Calcd for $C_{29}H_{33}N_2OCl$: C, 75.55; H, 7.21; N, 6.08.

TABLE I
Syntheses of the Reactive Antioxidants Based on Tetrazoles

$$HO-\text{(ring)}-C\overset{N}{\underset{N=N}{\diagdown}}N-\text{(ring)}-Y$$
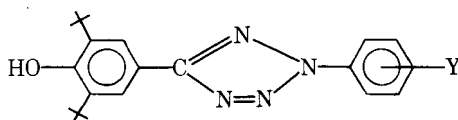
| Tetrazole | Yield (%)[a] | | DP | | |
| —Y | Method A | Method B | (°C) | Solvent[b] | Appearance |
|---|---|---|---|---|---|
| —H | 41.1 | 54.6 | 171.0–172.0 | IP-T | Light yellow |
| $p$-CH$_3$ | 37.4 | 54.0 | 188.0–189.5 | IP-T | Light yellow |
| $p$-OC$_2$H$_5$ | 36.7 | 60.6 | 165.5–168.5 | IP-T | Orange |
| $p$-Cl | 30.6 | 55.8 | 169.0–171.0 | B | Light yellow |
| $p$-$n$-C$_4$H$_9$ | 27.6 | — | 129.0–130.0 | IP-T | Light yellow |
| $m$-CH$_3$ | 29.1 | 53.5 | 156.5–158.5 | M-B | Light yellow |
| $m$-Cl | 19.0 | 30.8 | 136.0–138.8 | B | Light yellow |

[a] Yields (isolated) based on THBA.
[b] Solvent for recrystallization. IP = isopropanol, T = toluene, B = benzene, M = methanol.

TABLE II
Elementary Analyses and IR and ¹H-NMR Spectral Data for The Tetrazoles
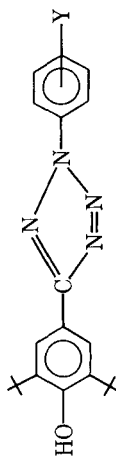


| Tetrazole —Y | Molecular formula | Elementary analysis (%) | | | IR (Nujoll mull) (cm⁻¹) | ¹H-NMR in CDCl₃ (ppm)ᵃ |
|---|---|---|---|---|---|---|
| | | C | H | N | | |
| —H | $C_{21}H_{26}N_4O$ | Calcd 71.97 | 7.48 | 16.00 | 1010, 1505, 1525 | 1.51 (s), 5.48 (s) |
| | | Found 72.11 | 7.53 | 16.37 | 1610, 1620, 3630 | 7.29–7.70 (m), 8.02 (s), 7.95–8.30 (m) |
| (p)-CH₃ | $C_{22}H_{28}N_4O$ | Calcd 72.50 | 7.74 | 15.37 | 1015, 1530, 1625 | 1.51 (s), 2.41 (s), 5.47 (s) |
| | | Found 72.07 | 7.81 | 15.21 | 3620 | 7.29 (d, $j$ = 8.4), 8.00 (s), 8.03 (d, $j$ = 8.4) |
| (p)-OC₂H₅ | $C_{23}H_{30}N_4O_2$ | Calcd 70.07 | 7.66 | 14.20 | 1005, 1520, 1600 | 1.52 (s), 1.45 (t, $j$ = 7.0) |
| | | Found 69.82 | 6.82 | 13.64 | 1615, 3630 | 4.08 (q, $j$ = 7.0), 5.50 (s), 7.01 (d, $j$ = 9.0), 8.03 (s), 8.07 (d, $j$ = 9.0) |
| (p)-Cl | $C_{21}H_{25}N_4OCl$ | Calcd 65.53 | 6.55 | 14.56 | 1000, 1500, 1520 | 1.52 (s), 5.50 (s) |
| | | Found 65.25 | 6.71 | 14.41 | 1620, 3600 | 7.49 (d, $j$ = 8.6), 8.01 (s), 8.12 (d, $j$ = 8.6) |
| (p)-n-C₄H₉ | $C_{25}H_{34}N_4O$ | Calcd 73.86 | 8.43 | 13.78 | 1015, 1530, 1625 | 1.01 (b), 1.40 (b), 1.52 (s) |
| | | Found 74.45 | 8.76 | 13.89 | 3630 | 2.72 (b), 5.51 (s), 8.08 (s), 7.36 (d, $j$ = 9.0), 8.11 (d, $j$ = 9.0) |
| (m)-CH₃ | $C_{22}H_{28}N_4O$ | Calcd 72.50 | 7.74 | 15.37 | 995, 1505, 1530 | 1.52 (s), 2.47 (s), 5.48 (s) |
| | | Found 72.31 | 7.77 | 15.23 | 1605, 1625, 3625 | 7.09–7.56 (m), 8.04 (s), 7.80–8.20 (m) |
| (m)-Cl | $C_{21}H_{25}N_4OCl$ | Calcd 65.53 | 6.55 | 14.56 | 1020, 1520, 1600 | 1.52 (s), 7.25–7.66 (m) |
| | | Found 65.27 | 6.64 | 14.27 | 1620, 3625 | 5.52 (s), 8.00–8.15 (m), 8.07 (s) |

ᵃ Peak patterns and coupling constants are designated in parentheses:  s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad band.
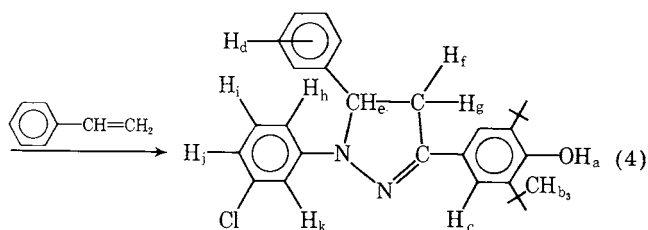
This result indicates that the product is 1-(3'-chlorophenyl)-3-(3'',5''-di-*tert*-butyl-4''-hydroxyphenyl)-5-phenyl-2-pyridazoline (CPP, **11**) formed by 1,3-dipolar addition reaction of the nitrileimine (**10**) with styrene [see eq. (4)]:
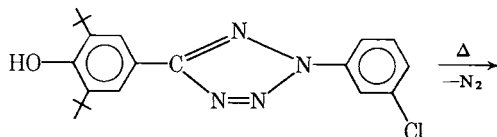
(9)
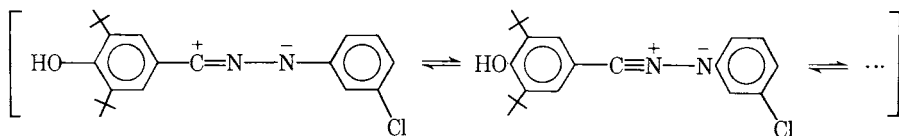
(10)

(11)

As will be discussed later, IR and $^1$H-NMR spectra of the product proved this equation. In the IR spectrum, the product exhibited four characteristic peaks at 3630 (strong), 1600 (strong), 1565 (medium), and 1490 cm$^{-1}$ (strong), assigned to the hindered phenolic —OH group, the $>$C$=$N— group and the benzene rings. The $^1$H-NMR spectrum of the product in acetone-$d_6$ is shown in the Figure 1. Each peaks belong to the protons of the 2-pyridazoline derivative assigned to $H_a$, 6.25, $H_b$, 1.48, $H_c$, 7.62, $H_d$, 7.29, $H_h$, $H_i$, $H_j$, $H_k$, 6.45–7.15 ppm. The protons of $H_e$, $H_f$, and $H_g$ are discussed later. The enlarged $^1$H-NMR spectra in the range
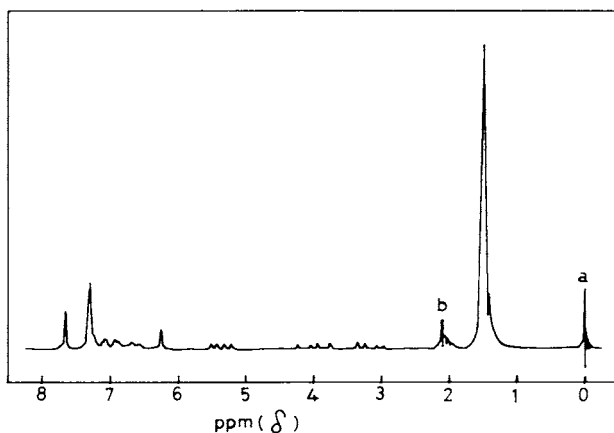


Fig. 1. $^1$H-NMR spectrum of the reaction product of *m*-chloro derivative of PHPT and styrene in CDCl$_3$: (a) (CH$_3$)$_4$Si; (b) CH$_3$COCH$_3$.
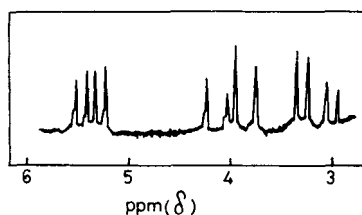
Fig. 2. Enlarged ^{1}H-NMR spectrum of the reaction product of *m*-chloro derivative of PHPT and styrene in CDCl₃.

TABLE III
Chemical Shifts and Coupling Constants of 2-Pyridazoline Protons in CPP and TPP

| 2-Pyridazoline (solv) | $H_e$ | $H_f$ | $H_g$ | $j_{gem}$ | $j_{cis}$ | $j_{trans}$ |
|---|---|---|---|---|---|---|
| CPP (acetone-d₆) | 5.36 | 3.34 | 3.71 | \|17.2\| | \|11.1\| | \|7.4\| |
| TPP[27] (CDCl₃) | 5.19 | 3.06 | 3.75 | −16.2 | 12.1 | 7.7 |

of 2.5–6.0 ppm are shown in Figure 2. This peak pattern indicates the typical ABX type. The chemical shifts and coupling constants calculated by the usual way,[26] agreed with those of the 1,3,5-triphenyl-2-pyridazoline (TPP)[27] formed by 1,3-dipolar addition reaction of the diphenylnitrileimine with styrene. Table III shows the chemical shifts and coupling constants of CPP and TPP, respectively.

These results obtained indicate that the nitrileimine reacts with the carbon–carbon double bond of styrene by 1,3-dipolar addition reaction, but not with the hindered phenolic —OH group owing to steric hindrance, though Huisgen et al.[20] reported that the nitrileimine formed from 2,5-diphenyltetrazole reacted with phenol to yield a benz-*N,N*-diphenylhydrazide in a 79% of yield.

Thus, the expectation to be drawn from these results is that PHPT would be allowed to react with diene rubber, retaining the hindered phenolic —OH group, which is closely related to the antioxidation activity. It is from this aspect that we have undertaken an investigation reported in a subsequent paper.
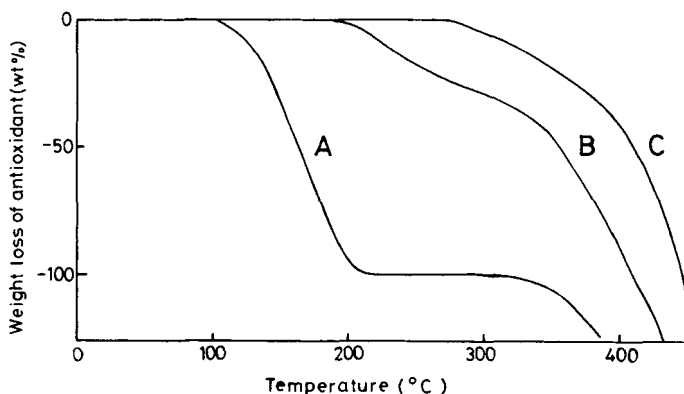


Fig. 3. Thermogravimetric analysis curve of a mixture of unsubstituted PHPT and LPBd: (A) a mixture of BHT (2.20 g, 0.01 mol) and LPBd (10.8 g); (B) a mixture of unsubstituted PHPT (3.50 g, 0.01 mol) and LPBd (10.8 g); (C) LPBd.

## Thermogravimetric Analysis of a Mixture of PHPT and LPBd

Thermogravimetric analyses curves of a mixture of unsubstituted PHPT and LPBd, 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT)–LBPd mixture and LPBd are shown in Figure 3.   BHT volatilized easily at temperatures of 112–223°C. However, the weight loss of unsubstituted PHPT was not observed in the case of a mixture of unsubstituted PHPT and LPBd, though the weight losses corresponding to nitrogen evolution and decomposition of LPBd were observed. These results indicate that unsubstituted PHPT was converted to the nitrileimine, with concomitant nitrogen evolution, by pyrolysis and immediately underwent 1,3-dipolar addition reaction with the carbon–carbon double bonds of LPBd.

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