using a 6 ft × 2 mm (i.d.) glass column packed with CSP-20M. Peak areas were integrated by a HP 3390A recorder.

Photolysis of 1 in HCl. 1, 0.4 g (2.4×10^{-3} mol), was added to 20 mL of 1.3 M solution of HCl in ether and the mixture was irradiated for 16 h. The reaction mixture was diluted with water and the products were extracted twice with ether. The combined extracts were washed with sodium bicarbonate solution and water and dried over magnesium sulfate. The solvent was removed, and the crude product mixture was chromatographed on silica gel. Two fractions were collected. The first (120 mg) was a mixture of (*Z*)- and (*E*)-**2**: NMR ($CDCl_3$) δ 7.38 (phenyl), AB quartet with the outer pairs centered at 6.63 and 6.78 (*E* olefinic H) and AB quartet with the outer pairs centered at 6.08 and 6.63 (*Z* olefinic H). The second fraction contained 240 mg of the dichloride **3**: NMR ($CDCl_3$) δ 7.37 (s, 5 H), 5.87 (t, 1 H), 3.47 (d, 2 H). The overall product yield is found to be 93%.

Photolysis of 1 in DCl. A solution of 0.3 g of 1 (1.8×10^{-3} mol) and 15 mL of 1.5 M DCl in ether was irradiated for 16 h. The products were isolated as described before. Two components were obtained by column chromatography. One was a mixture of deuterated and undeuterated **2** (85 mg): MS, *m/e* 141 (2), 140 (11), 139 (5.5), 138 (33), 104 (14), 103 (100). The other component was a mixture of deuterated and undeuterated **3** (195 mg): MS, *m/z* 175 (7.02), 174 (3.2), 104 (12), 103 (15), 92 (8.4), 91 (100). The overall product yield is 95%.

Photolysis of 1 with Substrates. Products of reaction of 1 in HCl–TME and HCl–HOAC were isolated as described above and identified by comparison of their spectra with those of authentic samples.

Control Experiment. It has been observed that 1 does not react with HCl in the dark.

Photolysis of 1 in benzene without HCl yields the two isomeric β-chlorostyrenes in the ratio of 0.20 ((*Z*)-/(*E*)-**2**) which is independent of reaction time (0.3–3 h) and temperature (1–25 °C).

A mixture of **2** (5.0×10^{-3} M) and **3** (5.0×10^{-3} M) with excess HCl (1.2 M) in ether was irradiated under our experimental conditions for 10 h. Analysis of this mixture by GLC indicated that the composition remained unchanged.

A solution of **2** (5.0×10^{-2} M) and HCl (1.3 M) in ether was photolyzed for 10 h and analyzed by GLC. No addition or isomerization was found to occur.

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Registry No. 1, 88211-05-6; 2, 622-25-3; (*E*)-2, 4110-77-4; (*Z*)-2, 4604-28-8; 3, 4412-39-9; 4, 39773-55-2; 5, 97073-41-1; HCl, 7647-01-0; $C_6H_5CH_2CDCl_2$, 97073-40-0; $C_6H_5CH{=}CDCl$, 3947-94-2; benzylchlorocarbene, 88211-07-8.

Di-*tert*-butyl Hyponitrite as a Source of Alkoxyl Radicals for Dimerization

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The use of reactive radicals to couple organic molecules is an old approach that has been carried out extensively with di-*tert*-butyl peroxide[1-19] and also with benzoyl peroxide,[3,10,15] acetyl peroxide,[20-23] and Fenton's reagent.[24-26] The desired sequence (1)–(3) is usually accompanied to various extents by cage recombination and cross-coupling

$$\text{initiator} \rightarrow 2\text{In}\cdot \tag{1}$$

$$\text{In}\cdot + \text{RH} \rightarrow \text{In–H} + \text{R}\cdot \tag{2}$$

$$2\text{R}\cdot \rightarrow \text{R}_2 \tag{3}$$

of initiating radicals, induced decomposition of the initiator, scission of alkoxy radicals, disproportionation of substrate radicals and multiple sites for their recombination, and termination reactions of the radicals produced in secondary steps.

A part of a general study of alkyl hyponitrites, we have investigated the use of di-*tert*-butyl hyponitrite as a potentially more convenient source of reactive radicals via reaction 4:

$$t\text{-BuON{=}NOBu-}t \rightarrow \text{N}_2 + 2t\text{-BuO}\cdot \tag{4}$$

The results of our study are summarized in Table I along with previous approaches with other initiators. Except for the cases with Fenton's reagent, the use of the hyponitrite results in a substantial reduction of reaction time. The yields with hyponitrite were improved over literature procedures in four cases, although we did not make extensive attempts at optimization. Substitution of *tert*-amyl for *tert*-butyl hyponitrite led to a lower yield of dimer from diphenylmethane.

Rather surprisingly, benzaldehyde gave no detectable benzil with di-*tert*-butyl hyponitrite. With a twofold excess of aldehyde a complicated mixture was formed, while with excess aldehyde an interesting tetramer, derived from addition of benzoyl radical to benzaldehyde, crystallized from the reaction mixture. This compound had been isolated previously[10,15] from a high-temperature reaction

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Table I. Dimerization with Free Radicals

reactant	dimer	initiator (mM)[a]	ratio (molar) RH:In	T (°C)	time	yield (%)[t]	manner[b] isolated
CH_3CH_2OCHO	$[CH_3CH_2OCO-]_2$	$B_2N_2O_2$ (3.7)	11.4	reflux	8.5 h	n.d.	
$(CH_3)_2NCHO$	$[(CH_3)_2NCO-]_2$	$B_2N_2O_2$ (5.4)	10.3	67	2 h	n.d.	
		B_2O_2 (550)	14.9	132	43 h	3.9[c]	
		Fe^{2+}/H_2O_2 (75)	4.8	0–10	1 h	77[d]	
$(CH_3)_3CNHCHO$	$[(CH_3)_3CNHCO-]_2$	$B_2N_2O_2$ (14)	2.0[e]	75	30 m	49	ppt
		B_2O_2 (44)	11.2	140	20 h	73[c]	
H_2NCHO	$[H_2NCO-]_2$	$B_2N_2O_2$ (29)	2.0[e]	80	1 h	53	ppt
CH_3NHCHO	$[CH_3NHCO-]_2$	$B_2N_2O_2$ (17)	2.0[e]	80	30 m	n.d.	
CH_3COOH	$[HOOCCH_2-]_2$	$B_2N_2O_2$ (7.1)	10	52	16 h	n.d.	
		B_2O_2 (–)	41	117	117 h	12[f]	
		Ac_2O_2 (144)	35	85–95		50[g]	
		Fe^{2+}/H_2O_2 (400)	12	25	20 m	4[h]	
$(CH_3)_3CCOOCH_3$	$[(CH_3)_3CCOOCH_2-]_2$	$B_2N_2O_2$ (12)	2.0	80	30 m	n.d.	
CH_3COCH_3	$[CH_3COCH_2-]_2$	$B_2N_2O_2$ (14)	10	reflux	16 h	59	GC (A)
		B_2O_2 (–)	20	135	22 h	30[f]	
		Fe^{2+}/H_2O_2 (103)	6	25	25 m	4[h]	
CD_3COCD_3	$[CD_3COCD_2-]_2$	$B_2N_2O_2$ (6.7)	10	reflux	16 h	5.5	GC (B)
$(CH_3)_3COCH_3$	$[CH_3)_3COCH_2-]_2$	$B_2N_2O_2$ (8)	20	reflux	16 h	59	GC (B)
		$B_2O_2/h\nu$ (104)	0.1	40	95 h	45[i]	
		B_2O_2 (27)	10	140	60 h	n.d.[i]	
		$(PhCOO)_2$ (50)	10	55	7 d	4[i]	
$(CH_3)_3COH$	$[HOC(CH_3)_2CH_2-]_2$	$B_2N_2O_2$ (15.7)	14[e]	80–100	2 h	n.d.	
		Fe^{2+}/H_2O_2 (103)	9.5	10–20	20 m	36[h,j]	
$(CH_3)_2CHCN$	$[(CH_3)_2C(CN)-]_2$	$B_2N_2O_2$ (7.6)	20	reflux	1 h	61	subl.
		B_2O_2(–)	20	140		84[k]	
Ph_2CH_2	$[Ph_2CH-]_2$	$B_2N_2O_2$ (11)	5.4[e]	90	30 m	96	ppt, (EtOH)
		$Am_2N_2O_2$ (7.5)[l]	4	90	30 m	22	ppt, (EtOH)
		Ac_2O_2 (465)	6.4	140		38.9[m]	
		B_2O_2 (26)	19	140	48 h	61.7[n]	
$PhCH_3$	$[PhCH_2-]_2$	$B_2N_2O_2$ (4.6)	40	50	20.5 h	61.6	(EtOH)
		B_2O_2 (–)	41	110	105 h	46[f]	
		B_2O_2 (27)	37	110	72 h	31[n]	
$PhCH(CH_3)_2$	$[Ph(CH_3)_2C-]_2$	$B_2N_2O_2$ (6.9)	9.7	80	30 m	54.5	(MeOH)
		Ac_2O_2 (436)	4.6	125	4 h	62[o]	
		B_2O_2 (68)	26.5	140	48 h	61[n]	
$PhOCH_3$	$[PhOCH_2-]_2$	$B_2N_2O_2$ (4.6)	40	40	21.5 h	≤3	
		$B_2O_2/h\nu$ (30)	10	40–45	96 h	11[p]	
		B_2O_2 (30)	10	140	60 h	n.d.[p]	
$PhCHO$	$[PhCOOCH(Ph)-]_2$	$B_2N_2O_2$ (12)	6.8	90	30 m	meso 5.6	ppt, washed hot EtOH
		$(PhCOO)_2$ (90)	11	80	18 h	meso 15.6[a]	
		B_2O_2 (274)	7.3	130	30 h	85[q]	
		B_2O_2 (68)	6.9	140	24 h	meso 22 racem. 26[r]	
$PhCH_2COCH_3$	$[CH_3COCH(Ph)-]_2$	$B_2N_2O_2$ (10.4)	4[e]	90	30 m	meso 14.6	ppt, MeOH–EtOH
		Ac_2O_2 (170)	4.8	125–130		meso 14 racem. 13[s]	
		B_2O_2 (–)	30	140	16 h	meso 33 racem. 16[f]	
$PhCH_2CN$	$[Ph(CN)CH-]_2$	$B_2N_2O_2$ (10.4)	4[e]	90	30 m	meso 18	ppt, (EtOH)
		B_2O_2 (–)	30	140	18 h	meso 58 racem. 15[f]	

[a] $B_2N_2O_2$ = di-*tert*-butyl hyponitrite, B_2O_2 = di-*tert*-butyl peroxide. [b] Gc(A) or Gc(B) refers to gas chromatographic columns A and B described in experimental section. Ppt = product precipitated from reaction mixture. (Solvent) indicates solvent for recrystallization. [c] Reference 1. [d] Reference 25. [e] These reactions were carried out by slow addition of the hyponitrite to the heated reactants. [f] Reference 16. [g] Reference 20. [h] Reference 24. [i] Reference 3. [j] Reference 26. [k] Reference 12. [l] *tert*-Amyl hyponitrite (this work). [m] Reference 23. [n] Reference 8. [o] Reference 21. [p] Reference 2. [q] Reference 15. [r] Reference 10. [s] Reference 22. [t] n.d. = not detected.

of benzaldehyde and di-*tert*-butyl peroxide. A more soluble, racemic isomer was also reported. We did not study the reaction products further, although with liquid chromatography we could show the presence of at least two additional products in the mother liquors.

Since the primary isotope effect favors H over D abstraction, we thought that free-radical dimerization of a deuterated substrate should preferentially deplete any residual nondeuterated material from the starting material. This potential advantage, however, was greatly offset with acetone-d_6 by the substantially lower yield. Moreover, the product underwent exchange with protons during gas chromatographic isolation, even though the column had been pretreated with D_2O.

Since di-*tert*-butyl hyponitrite is resistant to induced decomposition even at high concentrations,[29] we initially sought to optimize the use of the reactants with a 2:1 (or with benzaldehyde, 4:1) ratio of substrate to initiator. This approach was not uniformly successful. We did not examine the product mixtures in detail, but a number of reasons can be imagined all of which are less important in dilute solutions.

The lower yield of tetraphenylethane with di-*tert*-amyl hyponitrite is consistent with steric retardation[30] of the alkoxyl H-abstraction together with an enhanced rate of alkoxyl β-scission,[31] in comparison to the corresponding reactions of *tert*-butoxyl.

The reaction temperature may be associated with difference in yield for some of the other examples in Table I. We also point out that experimental details are lacking

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in some of the literature cited.

The side reactions in some of the other unsuccessful cases led to very complicated mixtures as indicated by the HPLC traces. In addition, several of the substrates can undergo attack at multiple sites, which can lead to dimers other than the ones searched for. Finally, the facile loss of carbon monoxide from radicals derived from formates is consistent with the absence of ethyl oxalate among the products from ethyl formate.[32]

Several attempts to carry out the coupling of diphenylmethane with di-*tert*-butyl hyponitrite at 25 °C with ultrasound were unsuccessful.

Our initial reactions in this project were accompanied by a few irregularities. A stoichiometric mixture of *tert*-butylformamide and di-*tert*-butyl hyponitrite, which did not dissolve completely, underwent a sudden exotherm after being placed in a bath at 60 °C, and most of the contents of the tube were ejected as a small, mushroom-shaped cloud. The reaction was more successful when hyponitrite was added in small portions to the prehteated amide following the decomposition by the evolution of nitrogen. On another occasion, a loud pop was emitted from a tube containing a 2:1 formamide and undissolved di-*tert*-butylformamide under nitrogen in a bath at 70 °C. Thereafter we used diluents (frequently the substrate) or slow addition to insure that the hot solutions were always homogeneous. We took the additional precaution of flushing the mixture with an inert gas since di-*tert*-butyl hyponitrite is rather volatile.[28]

Experimental Section

Di-*tert*-butyl hyponitrite[27] was recrystallized from a mixture of ethanol and methanol at −60 °C. The substrates were usually reagent grade and were purified by conventional techniques of the oxidative propensity (aldehydes, ethers) or age suggested the presence of impurities. Reactions with small volumes of high-boiling substrates were carried out in screw-threaded test tubes (Ace glass) with a serum cap pierced by a syringe needle for relief of pressure. The tube was flushed with argon or nitrogen before being placed in an oil bath maintained at constant temperature with a Thermo-watch. The reaction mixtures were stirred magnetically. A slow stream of inert gas was passed into the liquid phase when a portionwise addition of hyponitrite was required.

Reactions with excess, volatile substrates were refluxed in the conventional manner after flushing initially with inert gas. The dimers were generally isolated by removing volatiles at 20 torr followed by purification of the residue as described in Table I. Product identification was made with IR and NMR techniques. Chromatographic isolation was carried out with a Sigma 3B and a $^{1}/_{4}$ in. × 25 ft column with Carbowax 20M (column A), a HP5830A and a 2 mm × 6 ft column of 3% SP-2250 DADA on 100–120-mesh Supelcoport (column B), or with a hybrid LC system and a Sphirogel 8 mm × 30 cm size exclusion column.

Note Added in Proof: *tert*-Butyl hyponitrite (8.74 mmol) and *tert*-butylformamide (35.5 mmol) in CCl_4 (10 mL) at 50 °C for 16 h precipitated crystalline *tert*-butylamine hydrochloride (12.8 mmol, mp 296 °C dec, ionic Cl 32.12%; lit.[33] mp 270–290 °C subl).

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Registry No. DMF, 68-12-2; $B_2N_2O_2$, 14976-54-6; B_2O_2, 110-05-4; Fe^{2+}, 15438-31-0; H_2O_2, 7722-84-1; $[PhC(O)O]_2$, 94-36-0; $Am_2N_2O_2$, 24251-13-6; Ac_2O_2, 110-22-5; NH_2CHO, 75-12-7; CH_3NHCHO, 123-39-7; CH_3CO_2H, 64-19-7; $(CH_3)_3CC(O)OCH_3$, 598-98-1; $CH_3C(O)CH_3$, 67-64-1; CH_3CH_2OCHO, 109-94-4; $(CH_3)_3CNHCHO$, 2425-74-3; $(CH_3)_2CHCN$, 78-82-0; Ph_2CH_2, 101-81-5; $CD_3C(O)CD_3$, 666-52-4; $(CH_3)_3COCH_3$, 1634-04-4; $(CH_3)_3COH$, 75-65-0; $PhCH_3$, 108-88-3; $PhCH(CH_3)_2$, 98-82-8; CH_3OPh, 100-66-3; PhCHO, 100-52-7; $PhCH_2C(O)CH_3$, 103-79-7; $PhCH_2CN$, 140-29-4; $[CH_3CH_2OC(O)]_2$, 95-92-1; $[(CH_3)_2NC(O)]_2$, 1608-14-6; $[(CH_3)_3CNHC(O)]_2$, 37486-48-9; $[H_2NC(O)]_2$, 471-46-5; $[CH_3NHC(O)]_2$, 615-35-0; $(HO_2CCH_2)_2$, 110-15-6; $[(CH_3)_3CC(O)OCH_2]_2$, 20267-20-3; $[CH_3C(O)CH_2]2$, 110-13-4; $[CD_3C(O)CD_2]_2$, 97135-07-4; $[(CH_3)_3COCH_2]_2$, 26547-47-7; $[HOC(CH_3)_2CH_2]_2$, 110-03-2; $[(CH_3)_2C(CN)]_2$, 3333-52-6; $(Ph_2CH)_2$, 632-50-8; $(PhCH_2)_2$, 612-00-0; $[Ph(CH_3)_2C]_2$, 1889-67-4; $(PhOCH_2)_2$, 104-66-5; *meso*-$[PhC(O)OCH(Ph)]_2$, 38036-63-4; (±)-$[PhC(O)OCH(Ph)]_2$, 86703-60-8; *meso*-$[CH_3(O)CH(Ph)]_2$, 69373-33-7; (±)-$[CH_3C(O)CH(Ph)]_2$, 69373-32-6; *meso*-$[PhCH(CN)]_2$, 15146-07-3; (±)-$[PhCH(CN)]_2$, 19657-49-9.

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Strained Benzene Derivatives by Copper-Catalyzed *tert*-Butylation

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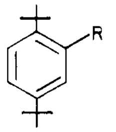
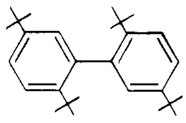
During our research on long-range deuterium isotope effects in ^{13}C NMR spectra[1] we became interested in an isotopomer of 1,2,4-tri-*tert*-butylbenzene (**1a**) bearing a perdeuterated *tert*-butyl group specifically at carbon atom 2, **1b**. The parent compound **1a** has been prepared by cobalt-mediated trimerization of *tert*-butylacetylene and photochemically induced isomerization of 1,3,5-tri-*tert*-butylbenzene.[2,3] Along these routes, however, the preparation of **1b**, free of regioisotopomers, is not possible. Any novel approach to the strained hydrocarbon **1a** thus has to accommodate this regiochemical problem, and for economic reasons, the introduction of the perdeuterated *tert*-butyl group in the last step is most attractive.



1a, R = $C(CH_3)_3$
1b, R = $C(CD_3)_3$
1c, R = Br
1d, R = H
1e, R = OH



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We report here on a method of introducing a *tert*-butyl group adjacent to a preexisting one in a single step, starting from ortho brominated precursors.

2,5-Di-*tert*-butylbromobenzene (**1c**) obtained[4] from commercially available 1,4-di-*tert*-butylbenzene (**1d**) gave halogen/lithium exchange in tetrahydrofuran on addition of 2.5 equiv of *tert*-butyllithium in pentane at −78 °C. To this mixture of anions, cuprous iodide was added to create a solution containing mixed homocuprates. Subsequently the copper reagents were oxidized with molecular oxygen at −78 °C.[5,6]

GLC–MS analysis of the crude product revealed 1,2,4-tri-*tert*-butylbenzene (**1a**) to be present as the main product accompanied by 1,4-di-*tert*-butylbenzene (**1d**),

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[†] Dedicated to Professor K. Dimroth on the occasion of his 75th Birthday.

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