J. Org. Chem. **1997,** *62,* 3849−3857 **3849**

Ingold−Fischer "Persistent Radical Effect", Solvent Effect, and Metal Salt Oxidation of Carbon-Centered Radicals in the Synthesis of Mixed Peroxides from *tert*-Butyl Hydroperoxide

Anna Bravo, Hans-René Bjørsvik, Francesca Fontana, Lucia Liguori, and Francesco Minisci*

Dipartimento di Chimica del Politecnico, via Mancinelli 7, I-20131 Milano, Italy

Received January 17, 1997[⊗]

Mixed peroxides are formed from *tert*-butyl hydroperoxide (TBH), *tert*-butyl peroxalate (TBP), and a variety of substrates (*p*-cresol, cyclohexene, styrene, α-methylstyrene, acrylonitrile, 2-methylcyclohexanone). Also, the oxidation of THF in the presence of acrylonitrile under the same conditions gives the mixed peroxide, generated by addition of the tetrahydrofuranyl radical to the double bond and the cross-coupling of the radical adduct with the *tert*-butylperoxyl radical. Similarly, benzoyl peroxide, TBH, and acrylonitrile give the mixed peroxide by oxidative arylation of the double bond. Paradoxically, TBH acts as effective inhibitor of the polymerization of vinyl monomers (acrylonitrile, styrene). An overall kinetic evaluation suggests that the conditions for the Ingold−Fischer "persistent radical effect", characterized by the simultaneous formation of a persistent and a transient radical, are fulfilled in all cases. The reactions are strongly affected by solvents, which form hydrogen bonds with TBH. Catalytic amounts of Cu(II) and Fe(III) salts influence the selectivity; the possibility that the mixed peroxides can also be generated by metal salt oxidation of carbon-centered radicals is discussed.

Introduction

The formation of mixed peroxides has been observed in a variety of reactions of hydroperoxides catalyzed by metal salts complexes (copper,[1,2] manganese,[1] iron,[3,4] including Gif[5] and metalloporphyrin[6] catalysis, etc.). The interest of these reactions is also related to the fact that hydroperoxides are intermediates in one of the most important reactions of organic chemistry, the autoxidation, in which transition-metal salts often play a key catalytic role. Occasionally, the prevailing formation of mixed peroxides has been observed in reactions of hydroperoxides also in the absence of transition-metal salts, but in the presence of different sources of radicals, such as acetyl peroxide[7] (a clean source of methyl radicals) or di-*tert*-butyl hyponitrite[8] (a convenient source of *tert*-butoxyl radical at moderate temperature). In these latter cases, the only reasonable mechanism for the mixed peroxide formation is based on the Ingold−Fischer "persistent radical effect",[4,8,9] characterized by the fact that two radicals are generated at similar rates and one of these is transient[10] while the other is persistent:[10] the main reaction product is formed by cross-coupling between transient (R_t) and persistent (R_p) radicals (eq 1).

$$R_t^{\bullet} + R_p^{\bullet} \rightleftarrows R_tR_p \tag{1}$$

In preliminary communications,[2,5,6,11] we have reported new synthetic approaches to mixed peroxides from hydroperoxides concerning phenols, simple and conjugated alkenes, and alkylbenzenes, always catalyzed by metal−salt complexes, and we have explained their formation by a ligand-transfer oxidation of carbon-centered radicals according to the original Kochi interpretation[12] (eq 2).

$$R^{\bullet} + \mathrm{MOOBu}\text{-}t \rightarrow \mathrm{ROOBu}\text{-}t + \mathrm{M} \tag{2}$$

$$\mathrm{M} = \mathrm{Cu(I)},\ \mathrm{Fe(II)},\ \mathrm{Mn(II)}$$

In this paper, we describe new methods of synthesis of mixed peroxides, catalyzed by metal salt complexes, further new synthetic developments in the absence of metal salt catalysis, a macroscopic solvent effect, and a comparison between the catalytic and noncatalytic routes in an attempt to define whether the metal salt oxidation of the carbon-centered radical (eq 2) is a possible mechanism, considering that more recently[13] Kochi has seemingly abandoned the idea that mixed peroxides are formed via a ligand-transfer process (eq 2).

Results and Discussion

Mixed Peroxide from *p*-Cresol. We have recently reported, in a preliminary communication,[11] the oxidation of phenols bearing unsubstituted *p*-positions to *p*-quino-

---

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

[1] Kharasch, M. S.; Fono, A. *J. Org.Chem.* **1958**, *23,* 324; **1959**, *24,* 72.

[2] Araneo, S.; Fontana, F.; Minisci, F.; Recupero, F.; Serri, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1399.

[3] Leising, R. A.; Norman, R. E.; Que, L., Jr. *Inorg. Chem.* **1990**, *29,* 2553. Leising, R. A.; Zang, Y.; Que, L., Jr. *J. Am. Chem. Soc.* **1991**, *113,* 8555. Kojima, T.; Leising, R. A.; Yan, S.; Que, L., Jr. *J. Am. Chem. Soc.* **1993**, *115,* 11328. Leising, R. A.; Kim, J.; Pérez, M. A.; Que, L., Jr. *J. Am. Chem. Soc.* **1993**, *115,* 9524.

[4] Arends, I. W. C. E.; Ingold, K. U.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117,* 4710.

[5] Minisci, F.; Fontana, F.; Araneo, S.; Recupero, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1823.

[6] Minisci, F.; Fontana, F.; Araneo, S.; Recupero, F.; Banfi, S.; Quici, S. *J. Am. Chem. Soc.* **1995**, *117,* 226.

[7] Kharasch, M. S.; Fono, A.; Nudenberg, W. *J. Org. Chem.* **1950**, *15,* 753.

[8] MacFaul, P. A.; Arends, I. W. C. E.; Ingold, K. U.; Wayner, D. D. M. *J. Chem. Soc., Perkin Trans. 2,* in press. We thank K. U. Ingold for the personal communication and the useful suggestions about the Ingold-Fischer effect.

[9] Fischer, H. *J. Am. Chem. Soc.* **1986**, *108,* 3925. Daikh, B. E.; Finke, R. G. *J. Am. Chem. Soc.* **1992**, *114,* 2938.

[10] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9,* 13.

[11] Bravo, A.; Fontana, F.; Minisci, F. *Chem. Lett.* **1996**, 401.

[12] Kochi, J. K. *Tetrahedron* **1962**, *18,* 483. Kochi, J. K.; Mains, H. E. *J. Org. Chem.* **1965**, *30,* 1862.

[13] Srinavasan, K.; Perrier, S.; Kochi, J. K. *J. Mol. Catal.* **1986**, *38,* 297.

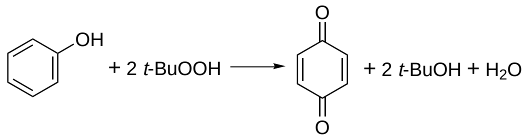
S0022-3263(97)00094-7 CCC: $14.00

Table 1. Oxidation of *p*- and *m*-Cresols by TBH and TBP

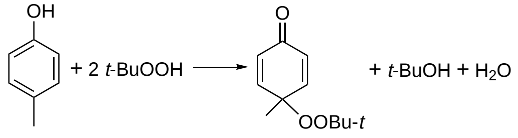
cresol (mmol)	TBH (mmol)	TBP (mmol)	metal salt (mmol)	solvent (mL)	conversn[a] (%)[a]	T (°C)	**1** (%)	**2** + **3** (%)
para (1)	1	1		benzene (5)	30	45	78.3	21.7
para (5)	1	1		benzene (5)	37	45	21.8	78.2
para (1)	1	1		CH_2Cl_2 (5)	13	45	89.3	10.7
para (5)	10			benzene (10)		45		
para (5)		1		benzene (5)	16	45		100
para (5)[b]	10		FeTPPCl (10^{-3})	benzene (10)	100	20	87.4	12.6
para (5)[b]	10		FeTPPCl (10^{-3})	benzene (10)	98	70	82.2	17.8
para (25)[b]	10		FeTPPCl (10^{-3})	benzene (10)	88	20	10.6	89.4
para (5)[b]	10		FeTPPCl (10^{-3})	benzene (10)	66	20	87	13
para (5)[b]	10		MnTDClPPCl (10^{-3})	benzene (10)	38	20	89	11
para (5)	10		$Cu(OAc)_2$ (0.5)	benzene (10)	18	20	100	
para (5)	10		$Cu(OAc)_2$ (0.5)	benzene (10)	64	50	100	
meta (5)[b]	10		FeTPPCl (10^{-3})	benzene (10)	82	20	2-methyl-*p*-benzo-quinone **4** (80%)	

[a] Conversion based on peroxides. [b] 0.3 mmol of pyridine are added.

nes by TBH, catalyzed by the metalloporphyrins Fe-tetraphenylporphyrin chloride (FeTPPCl) and Mn-tetrakis-(dichlorophenyl)porphyrin chloride (MnTDClPPCl) (eq 3).



(3)

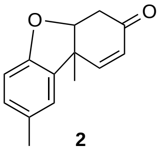


(4)

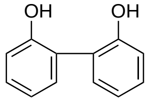
1

In order to understand the mechanism of this oxidation, we have particularly investigated the oxidation of *p*-cresol under the same conditions in which phenols with free *p*-positions are converted into benzoquinones.

The main reaction product is the mixed peroxide **1** with a stoichiometric ratio of *p*-cresol and TBH (1:2, eqs 3 and 4) (Table 1). The Pummerer ketone **2** and the diphenol **3** are byproducts (Table 1).



2



3

Clearly, compounds **1**−**3** are formed by a free-radical mechanism involving the phenoxyl radical intermediate.

Recently, we[6,14] have reported evidence concerning the involvement of t-BuO$^\bullet$ and t-BuOO$^\bullet$ radicals in the oxidation and halogenations of alkanes, alkenes, and alkylbenzenes by TBH, catalyzed by Fe(III) and Mn(III) porphyrins. The *tert*-butoxyl radical would be generated by the oxidation of the metalloporphyrin (PFe(III)) with TBH (eq 5).

$$\mathrm{PFe(III)} + t\text{-BuOOH} \rightarrow \mathrm{PFe(IV)} + t\text{-BuO}^\bullet + \mathrm{OH}^- \quad (5)$$

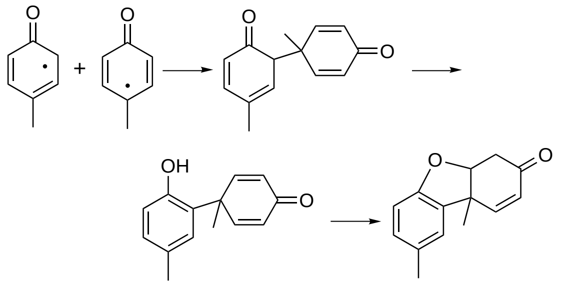
Alkoxyl radicals react very rapidly with TBH (i.e., the rate constant of H-abstraction by cumyloxyl radical from TBH has been evaluated[15] at 1.3×10^8 M^{-1} s^{-1} in benzene at 298 K) giving the *tert*-butylperoxyl radical (eq 6).

$$\mathrm{RO}^\bullet + t\text{-BuOOH} \rightarrow \underset{\mathbf{4}}{t\text{-BuOO}^\bullet} + \mathrm{ROH} \quad (6)$$

On the other hand, the rate constant for hydrogen abstraction from phenol by cumyloxyl radical has been evaluated[15] at 2.8×10^8 M^{-1} s^{-1} in benzene at 298 K (eq 7).

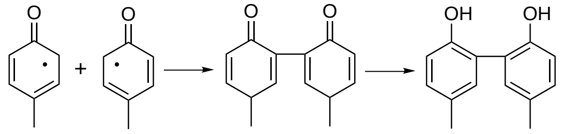
$$\mathrm{RO}^\bullet + \mathrm{ArOH} \rightarrow \underset{\mathbf{5}}{\mathrm{ArO}^\bullet} + \mathrm{ROH} \quad (7)$$

By using a 2:1 ratio (stoichiometric ratio of eqs 3 and 4) between TBH and phenol, one of the two conditions for the Ingold−Fischer “persistent radical effect” is plainly fulfilled (the peroxyl radical **4** and the phenoxyl radical **5** are generated at the same rate). Moreover, the bimolecular self-reactions of the phenoxyl radical leading to the Pummerer ketone **2** and the diphenol **3** (eqs 8 and 9) are very fast reactions (transient radicals),[16] whereas the bimolecular self-reaction of *tert*-butylperoxyl radical is a relatively slow radical−radical reaction (persistent radical) (a value of 4×10^2 M^{-1} s^{-1} has been evaluated for eq 10 in CCl_4 at 303 K).[17]



2

(8)



3

(9)

$$2\ t\text{-BuOO}^\bullet \longrightarrow t\text{-BuOOBu-}t + O_2 \quad (10)$$

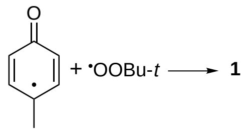
---

(14) Minisci, F.; Fontana, F.; Zhao, L.; Banfi, S.; Quici, S. *Tetrahedron Lett.* **1994**, *35*, 8033.

(15) Avila, D. V.; Ingold, K. U.; Lusztyk, J.; Green, W. A.; Procopio, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 2929.

(16) Howard, A.; Scaiano, J. C. *Landolt-Börnstein*; 1984; Vol. 13, p 143.

Thus, the other condition for a radical cross-coupling (eq 11) is also fulfilled.



(11)

Actually, the dimers **2** and **3** of the phenoxyl radical become the main reaction products by increasing the phenol:TBH ratio, whereas the mixed peroxide **1** is a minor product of the reaction (Table 1).

In order to obtain direct evidence concerning the mechanism of reaction 11, we have carried out the same reaction with TBH in the absence of metalloporphyrins, but using TBP (di-*tert*-butyl peroxyoxalate) as a clean source of *tert*-butoxyl radical at moderate temperature (40 °C) (eq 12).

$$t\text{-BuOOCOCOOOBu-}t \rightarrow 2\ t\text{-BuO}^{\bullet} + 2\ \text{CO}_2 \quad (12)$$

The results were similar to those obtained for the reaction catalyzed by metalloporphyrins: **1**−**3** were the reaction products, but the ratio between the mixed peroxide **1** and the dimers of the phenoxyl radical (**2** and **3**) is somewhat lower compared to the one observed in the catalyzed reaction. Again, the amount of phenoxyl radical, and consequently of its dimers (**2** and **3**), is increased by increasing the *p*-cresol/TBH ratio (Table 1).

The formation of **2** and **3** by oxidation of *p*-cresol with a variety of monoelectron oxidants ($K_3Fe(CN)_6$, Ce(IV), Mn(III), Ag(I)) is well-known,[18] and the ratio between the ketone **2** and the diphenol **3** depends on temperature, solvent, concentration, and nature of the oxidant. This variation has been attributed to the reversibility of the coupling step (eqs 8 and 9).

The results obtained with TBH and TBP represent unequivocal evidence of the Ingold−Fischer "persistent radical effect"; the only reasonable explanation for the mixed peroxide formation is eq 11. By mere chance, the stoichiometric ratio between phenol and TBH (eqs 3 and 4) corresponds to the same rates of eqs 6 and 7, thus fulfilling the conditions for the Ingold−Fischer effect; the increase of this ratio is reflected by an increase of the rate of eq 7 and of the amount of phenoxyl radical dimers **2** and **3**.

If the cross-coupling (eq 11) is the only mechanism for the mixed peroxide formation, then a fundamental question arises: considering that the ratio between the catalyst and TBH is 1:10^4, what is the operating mechanism for the metalloporphyrin catalysis? We can envisage two possible explanations:

(i) The Fe(IV) complex generated in eq 5 could abstract hydrogen from both the phenol and TBH (eqs 13 and 14)

$$\text{PFe(IV)=O} + \text{HOAr} \rightarrow \text{PFe(III)OH} + {}^{\bullet}\text{OAr} \quad (13)$$

$$\text{PFe(IV)=O} + \text{HOOBu-}t \rightarrow \text{PFe(III)OH} + {}^{\bullet}\text{OOBu-}t \quad (14)$$

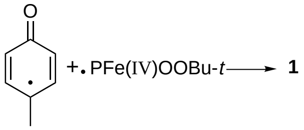
with similar rates, thus regenerating the Fe(III) complex and giving rise, consequently, to a Fe(IV)/Fe(III) redox chain.

(ii) The Fe(III) complex could oxidize TBH to the peroxyl radical, thus generating a Fe(III)/Fe(II) redox chain (eqs 15 and 16).

$$\text{PFe(III)} + \text{HOOBu-}t \rightarrow \text{PFe(II)} + {}^{\bullet}\text{OOBu-}t + \text{H}^+ \quad (15)$$

$$\text{PFe(II)} + \text{HOOBu-}t \rightarrow \text{PFe(III)} + {}^{\bullet}\text{OBu-}t + \text{OH}^- \quad (16)$$

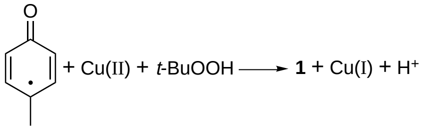
A further possible mechanism, which could superimpose to the cross-coupling, is related to the original Kochi interpretation of the phenoxyl radical oxidation (eq 17), with the generation of a different Fe(IV)/Fe(III) redox chain.



(17)

In order to have further indications about the catalytic mechanism by metal salts, we have investigated the catalysis by $Cu(OAc)_2$ in the oxidation of *p*-cresol under the same conditions utilized with metalloporphyrins. The reaction is slower at room temperature, and it requires a much higher amount of catalyst (5−10%), but it is completely selective: the mixed peroxide **1** is the only reaction product. By increasing the temperature to 50 °C, the oxidation is obviously faster, but always quite selective. This represents a new type of catalysis in the oxidation of phenols by TBH.

A simple explanation of this result could be related to a superimposition of the phenoxyl radical oxidation (eq 18), according to the original Kochi mechanism, to the cross-coupling of eq 11. This way, all of the phenoxyl radicals, which exceed the cross-coupling, are scavenged by Cu(II) salt, thus preventing the formation of **2** and **3**; the Cu(I) salt is oxidized by TBH, generating *tert*-butoxyl radical and giving a Cu(II)/Cu(I) redox chain (eq 19).



(18)

$$\text{Cu(I)} + t\text{-BuOOH} \longrightarrow \text{Cu(II)} + t\text{-BuO}^{\bullet} + \text{OH}^- \quad (19)$$

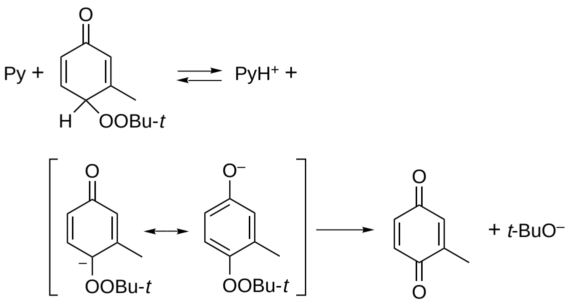
However, the cross-coupling (eq 11) could still be the only mechanism for the formation of **1** also in this case, if we admit that the Cu(II) catalysis is different from the one provided by metalloporphyrins and that the copper salt is more effective in generating a higher steady-state concentration of peroxyl radicals. It is anyway quite difficult to envisage a redox chain leading to the peroxyl radical, in which Cu(I) and the *tert*-butoxyl radical are not involved.

In any case, these results clarify the mechanism of *p*-benzoquinone formation when the para-position of phenol is free (i.e., oxidation of *m*-cresol): it occurs by *t*-BuOH elimination from the mixed peroxide. The reaction is more selective in the presence of small amounts of pyridine, which catalyzes this elimination (eq 20).

---

(17) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3797. Adamic, K.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3803.

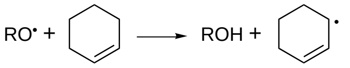
(18) Anderson, R. A.; Dalgleish, D. T.; Nonhebel, D. C.; Pauson, P. L. *J. Chem. Res., Synop.* **1977**, 12.



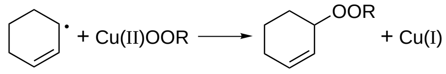
(20)

Mixed Peroxide from Cyclohexene. The synthesis of mixed peroxides from alkenes and hydroperoxides by the Kharasch reaction is well-known.[1] The original Kochi interpretation involves a Cu(I)/Cu(II) redox chain with formation of alkoxyl radicals (eq 21), allylic hydrogen abstraction (eq 22), and a ligand transfer oxidation of the allyl radical (eq 23).

$$\mathrm{ROOH + Cu(I) \longrightarrow RO^{\bullet} + Cu(II)OH} \qquad (21)$$



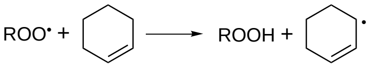
(22)



(23)

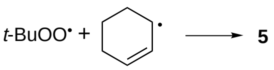
5

Recently, we have reported[6,19] that this mechanism is not consistent with the chemoselectivity of the reaction and that, at least, eq 22 should be substituted by eqs 6 and 24 in solvents that do not form hydrogen bonds with hydroperoxides.



(24)

However, in a much more recent work, Kochi[13] apparently abandoned the idea that mixed peroxides were formed via ligand transfer. Thus, the same two questions, discussed above for phenols, also arise with alkenes: are the conditions for the Ingold−Fischer effect fulfilled for the cross-coupling formation of the mixed peroxide **5** (eq 25)? What is the mechanism for the metal salt catalysis if eq 23 is not involved?



(25)

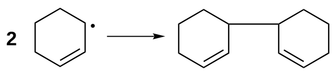
First, we have investigated the possibility that **5** could be formed in the absence of metal salt catalysis by using the same methodology reported above for phenols. Thus, the decomposition of TBP in benzene solution at 45 °C in the presence of cyclohexene and TBH cleanly leads to the mixed peroxide **5**; the process is even more selective than the Kharasch reaction (Table 2). The only reasonable explanation for this result is the decomposition of TBP according to eq 12, followed by hydrogen abstraction from TBH by the *tert*-butoxyl radical (eq 6) and from cyclohexene by the *tert*-butyl peroxyl radical (eq 24), and finally the cross-coupling between cyclohexenyl and peroxyl radicals (eq 25). The known absolute rate constants for eqs 6, 22, and 24 indicate that the Ingold−Fischer "persistent radical effect" is fulfilled. In benzene solution at room temperature the rate constant for eq 6 has been evaluated[15] at $1.3 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$, whereas those for eqs 22 and 24 are, respectively,[20] $5.7 \times 10^{6}\ \mathrm{M^{-1}\ s^{-1}}$ and $3.7 \times 10^{-1}\ \mathrm{M^{-1}\ s^{-1}}$. Thus, a persistent radical (t-BuOO$^{\bullet}$) and a transient radical (cyclohexenyl) are simultaneously formed, even with a 20:1 ratio of cyclohexene/TBH.

Table 2. Solvent and Concentration Effects in the Oxidation of Cyclohexene by TBH (1 mmol) and TBP (0.5 mmol)[a]

cyclohexene (mmol)	solvent (mL)	**5** (%)	**6** (%)
5	benzene (6)	100	
10	benzene (6)	100	
20	benzene (6)	97	3
5[b]	benzene (6)		
5[c]	benzene (6)		100
5	CH_2Cl_2 (6)	100	
5	*t*-BuOH (6)	68	32
5	benzene (4) pyridine (2)	86	14
5	benzene (3) pyridine (3)	66	34
10	benzene (3) pyridine (3)	57	43
5	benzene (2) pyridine (4)	44	56
5	pyridine (6)	24	76
20	pyridine (10)	15	85

[a] The conversions of cyclohexene, based on the peroxides, are in the range 40−50%. [b] In the absence of TBP. [c] In the absence of TBH.

Reaction 6 is strongly affected by the nature of the solvent, the rate constant being $6.7 \times 10^{6}\ \mathrm{M^{-1}\ s^{-1}}$ at room[15] temperature in *t*-BuOH solution. Reactions 22 and 24 are substantially unaffected by the solvent, so that reaction 22 should become competitive with reaction 6 in *t*-BuOH solution. In agreement with these rate constants, the reaction in *t*-BuOH solution gives the mixed peroxide **5** as the main reaction product (68%) but also forms a significant amount of dicyclohexenyl (**6**) (32%) by using the same ratio cyclohexene/TBH, 5:1, utilized in benzene solution. Under these conditions, reaction 22 is somewhat faster than reaction 6, which explains the prevailing formation of cyclohexenyl radical and its homocoupling (eq 26), in competition with the cross-coupling (eq 25).



(26)

6

The effect of the solvent on the rate of eq 6 is due[6,15,19] to hydrogen bond formation between the solvent and TBH. We have recently observed, while discussing the mechanism of the Gif reaction,[6,19] that this solvent effect is particularly marked in pyridine, which forms strong hydrogen bonds with TBH (evaluated[21] at 8 kcal/mol). Thus, we have investigated the behavior of cyclohexene with TBH and TBP in benzene solution in the presence of pyridine. The ratio **5**:**6** decreases as the concentration

---

(19) Minisci, F.; Fontana, F.; Araneo, S.; Recupero, F.; Zhao, L. *Synlett* **1996**, 119.

(20) Howard, A.; Scaiano, J. C. *Landolt-Börnstein*; 1984; Vol. 13, p 19. Encina, M. V.; Rivera, M.; Lissi, E. A. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1709. Paul, H.; Small. R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520. Encina, M. V., Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393. Chenier, J. H. B.; Tong, S. B.; Howard, J. A. *Can. J. Chem.* **1978**, *56*, 3047.

(21) Yablonskii, O. P.; Kobiakov, A. K.; Beolyaev, V. A. *Neftekhimiya* **1974**, *14*, 449.

Table 3. Oxidation of Cyclohexene by TBH (1 mmol) and TBP (0.5 mmol) in the Presence of $Cu(OAc)_2$ and $Fe(OAc)_2OH$[a]

cyclohexene (mmol)	metal salt (mmol)	solvent	**5** (%)	**6** (%)	**7** (%)
5	$Cu(OAc)_2$ (0.05)	benzene	100		
10	$Cu(OAc)_2$ (0.05)	benzene	100		
5	$Cu(OAc)_2$ (0.05)	*t*-BuOH	77	2	11
10	$Cu(OAc)_2$ (0.05)	*t*-BuOH	75	3	12
5	$Cu(OAc)_2$ (0.2)	*t*-BuOH	57		43
5	$Cu(OAc)_2$ (0.05) AcOH (0.1)	*t*-BuOH	68		32
5	$CuSO_4$ (0.05)	pyridine	97	3	
5	$Cu(OAc)_2$ (0.05)	pyridine	75	2	13
20	$Cu(OAc)_2$ (0.05)	pyridine	74	3	13
5	$Cu(OAc)_2$ (0.2)	pyridine	54		46
5[b]	$Fe(OAc)_2OH$ (0.05)	pyridine	70	18	2

[a] The conversions of cyclohexene, based on the peroxides, are in the range 60−70%. [b] 10% of cyclohexenyl alcohol is also formed.

of pyridine increases; in pyridine solution **6** is largely prevailing on **5** (Table 2).

If we assume that reaction 22 is not substantially influenced by the solvent,[22] we can evaluate from the results of Table 2 that the rate constant for eq 6 is roughly four times smaller in pyridine than in *t*-BuOH, in agreement with the stronger hydrogen bond. Thus, the rate constant for reaction 6 in pyridine can be approximately evaluated at $1.6 \times 10^6\ M^{-1}\ s^{-1}$, compared with $1.3 \times 10^8\ M^{-1}\ s^{-1}$ and $6.7 \times 10^6\ M^{-1}\ s^{-1}$, respectively, in benzene[15] and *t*-BuOH.[15]

However, the presence of a catalytic amount of $CuSO_4$ in pyridine solution completely changes the reaction course: the mixed peroxide **5** is the main reaction product (97%) and only 3% of the dicyclohexenyl **6** is formed, *vs* 24% of **5** and 76% of **6** in the absence of $CuSO_4$ under the same conditions. If $CuSO_4$ is substituted by $Cu(OAc)_2$ under the same conditions, the formation of **6** is again minimized (2%) and **5** is the main reaction product, but a significant amount of cyclohexenyl acetate **7** is also formed. **6** is minimized (3%) in pyridine solution and $Cu(OAc)_2$ catalysis even with a large excess of cyclohexene (20:1 ratio cyclohexene/TBH), whereas in the absence of $Cu(OAc)_2$ **6** is the main reaction product (85%) (Tables 2 and 3). The **5**:**7** ratio decreases by increasing the amount of $Cu(OAc)_2$ or of AcOH. The presence of a catalytic amount of $Fe(OAc)_2OH$ has a similar effect in pyridine solution: **6** becomes a minor reaction product, whereas **5** is the main product, with a smaller amount of cyclohexenol and traces of **7** (Table 3).

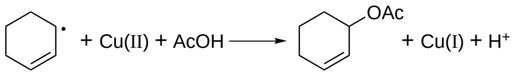
The reaction takes place with TBH also in the absence of TBP, but in the presence of $CuSO_4$, $Cu(OAc)_2$, or CuCl, and the results are quite similar in *t*-BuOH, pyridine, or benzene solutions. In all cases, **6** is formed in traces or it is absent; **7** is not formed in benzene solution, but it is an increasing reaction product as the amount of $Cu(OAc)_2$ increases or by increasing the amount of AcOH at low Cu(II) salt concentration in *t*-BuOH or pyridine solution (Table 4).

Cyclohexenyl acetate **7** cannot be formed by a cross-coupling process: it is difficult to envisage a mechanism for the acetoxyl radical formation, but above all the fast decarboxylation of acetoxyl radical ($\sim 10^9\ s^{-1}$)[23] prevents its intermolecular reactions. The reasonable mechanism for the formation of **7** is therefore the oxidation of cyclohexenyl radical by Cu(II) salt (eq 27).

Table 4. Oxidation of Cyclohexene by TBH (1 mmol) and Copper Salts[a]

cyclohexene (mmol)	copper salt (mmol)	solvent	*T* (°C)	**5** (%)	**6** (%)	**7** (%)
50	$Cu(OAc)_2$ (0.1)	benzene	70	87	13	
5	$Cu(OAc)_2$ (0.05)	benzene	45	100		
5	$Cu(OAc)_2$ (0.05)	benzene	70	100		
5	$Cu(OAc)_2$ (0.05)	CH_3CN	70	93	<1	6
5	$CuSO_4$ (0.05)	pyridine	70	96	4	
20	$CuSO_4$ (0.05)	pyridine	70	91	9	
5	$Cu(OAc)_2$ (0.05)	pyridine	45	80	<1	19
5	$Cu(OAc)_2$ (0.2)	pyridine	45	51		49
5	CuCl (0.01)	*t*-BuOH	70	93	7	
5	$Cu(OAc)_2$ (0.05)	*t*-BuOH	70	79		21
20	$Cu(OAc)_2$ (0.05)	*t*-BuOH	70	76	5	19
5	$Cu(OAc)_2$ (0.1)	*t*-BuOH	70	66		34
5	$Cu(OAc)_2$ (0.15)	*t*-BuOH	70	61		39
5	$Cu(OAc)_2$ (0.2)	*t*-BuOH	70	47		53
5	$Cu(OAc)_2$ (0.5)	*t*-BuOH	70	5		95
20	$Cu(OAc)_2$ (0.5)	*t*-BuOH	70	6		94
5	$Cu(OAc)_2$ (0.1) AcOH (0.1)	*t*-BuOH	70	49		51
5	$Cu(OAc)_2$ (0.1) AcOH (0.2)	*t*-BuOH	70	32		68
5	$Cu(OAc)_2$ (0.1) AcOH (0.5)	*t*-BuOH	70	5		95
5	$Cu(OAc)_2$ (0.1) AcOH (4)	*t*-BuOH	70	<1		99

[a] The conversions of cyclohexene, based on TBH, are in the range 60−65%.

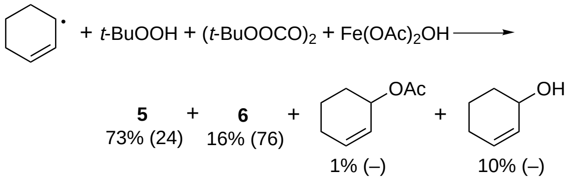


(27)

7

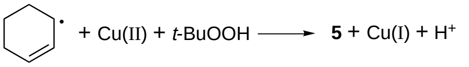
The Cu(I) is rapidly oxidized to Cu(II) by the peroxides, generating *tert*-butoxyl radical and a Cu(II)/Cu(I) redox chain.

The $Fe(OAc)_2OH$ catalyst appears to be less effective and selective compared with $Cu(OAc)_2$ in pyridine solution. The cyclohexenyl radical is less effectively scavenged, and minor amounts of **7** and of cyclohexenol are formed (eq 28) (in parentheses are the results in the absence of iron catalyst under the same conditions).



(28)

All of these results indicate that the Ingold−Fischer "persistent radical effect" is certainly operating in the formation of the mixed peroxide **5** (eq 25) in the absence of metal salt catalysis, depending on the ratios between cyclohexene and TBH and on the nature of the solvent, but they strongly suggest that **5** can be also formed by oxidation of the cyclohexenyl radical by Cu(II) or Fe(III) salt (eqs 28 and 29). On the other hand, if eq 27 represents the mechanism for cyclohexenyl acetate formation, we do not see any reason why a similar reaction (eq 29) could not occur with TBH, even if clearly reaction 29 appears to be slower than reaction 27.



(29)

---

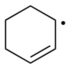
[22] Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115,* 466.

[23] Hilborn, J. W.; Pincock, J. A. *J. Am. Chem. Soc.* **1991**, *113,* 2683. Pincock, J. A. *Acc. Chem. Res.* **1997**, *30,* 43.

Moreover, the redox chains (eqs 30–32 and 33–34), which can be envisaged with copper salt catalysis, always involve both alkoxyl and peroxyl radical. This is not consistent with the results of Tables 3 and 4, if we exclude the involvement of eq 29 or the analogous eq 32.

$$\mathrm{Cu(II)} + t\text{-BuOOH} \longrightarrow \mathrm{Cu(III)} + t\text{-BuO}^{\bullet} + \mathrm{OH}^- \qquad (30)$$

$$\mathrm{Cu(III)} + t\text{-BuOOH} \longrightarrow \mathrm{Cu(II)} + t\text{-BuOO}^{\bullet} + \mathrm{H}^+ \qquad (31)$$



$$+ \mathrm{Cu(III)} + t\text{-BuOOH} \longrightarrow \mathbf{5} + \mathrm{Cu(II)} + \mathrm{H}^+ \qquad (32)$$

$$\mathrm{Cu(II)} + t\text{-BuOOH} \longrightarrow \mathrm{Cu(I)} + t\text{-BuOO}^{\bullet} + \mathrm{H}^+ \qquad (33)$$

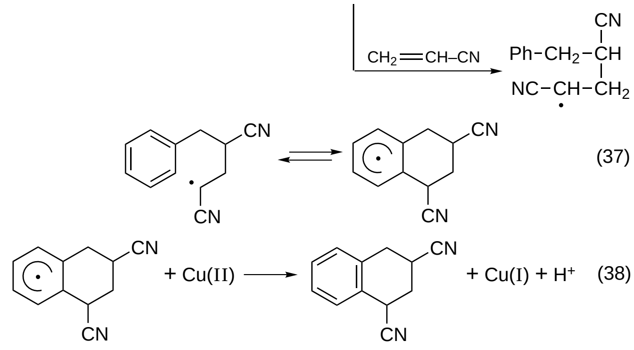
$$\mathrm{Cu(I)} + t\text{-BuOOH} \longrightarrow \mathrm{Cu(II)} + t\text{-BuO}^{\bullet} + \mathrm{OH}^- \qquad (34)$$

An open problem concerns the ligand-transfer or electron-transfer character of the cyclohexenyl oxidation (eqs 27–29 and 32). The original Kochi mechanism[12] was related to a ligand-transfer process (eq 23). The following results and discussions would suggest a more likely "inner-sphere" electron-transfer mechanism.

Mixed Peroxides from Acrylonitrile. In preliminary communications, we have reported[2,24] how the copper salt catalysis can substantially modify the free-radical polymerization of acrylonitrile. When the polymerization is carried out by using a large amount of benzoyl peroxide as radical source in the presence of $\mathrm{Cu(OAc)_2}$, significant amounts of the dinitrile **8** (two stereoisomers) have been isolated. We have explained[24] the formation of **8**, which is not formed in the absence of $\mathrm{Cu(OAc)_2}$, by a reversible intramolecular homolytic aromatic addition (eqs 35–37); Cu(II) salt determines a fast irreversible oxidation of the cyclohexadienyl radical (eq 38), shifting the equilibrium of eq 37 to the right.

$$\mathrm{(PhCOO)_2} \longrightarrow 2\mathrm{Ph}^{\bullet} + 2\,\mathrm{CO_2} \qquad (35)$$

$$\mathrm{Ph}^{\bullet} + 2\,\mathrm{CH_2{=}CHCN} \longrightarrow \mathrm{PhCH_2CHCN} \qquad (36)$$



8

In the absence of Cu(II) salt, the equilibrium of eq 37 is shifted to the left by irreversible acrylonitrile polymerization. In the presence of TBH, under the same conditions, neither the polymerization nor the formation of **8** take place, and the mixed peroxide **9** is the main reaction product. We have explained[2] its formation by the oxidation of the radical adduct by Cu(II) salt (eq 39), which would favorably compete with the polymerization.

$$\mathrm{PhCH_2\dot{C}HCN} + t\text{-BuOOH} + \mathrm{Cu(II)} \rightarrow \underset{\mathbf{9}}{\mathrm{PhCH_2CH(OOBu}\text{-}t\mathrm{)CN}} + \mathrm{Cu(I)} + \mathrm{H}^+ \qquad (39)$$

9 easily loses *t*-BuOH, giving the ketonitrile (eq 40).

$$\mathbf{9} \rightarrow \mathrm{PhCH_2COCN} + t\text{-BuOH} \qquad (40)$$

In order to verify if the Cu(II) catalysis is really necessary for the formation of **9**, we have now carried out the same reaction in benzene solution, but in the absence of $\mathrm{Cu(OAc)_2}$. No polymerization occurs, but **9** is the main reaction product from acrylonitrile. Biphenyl and phenyl benzoate are byproducts, clearly arising from the homolytic phenylation of benzene and the cage coupling of the phenyl and benzoyloxyl radicals. The diperoxide **10** is a minor reaction product; its formation will be discussed later. *The paradox of these results is that the presence of TBH (an usual free-radical initiator, particularly in association with metal salts) completely inhibits the free-radical polymerization of acrylonitrile by benzoyl peroxide either in the presence or in the absence of copper salt catalysis.*

Again, the only reasonable explanation in the absence of Cu(II) salt is the Ingold–Fischer effect, leading to the cross-coupling of the α-cyanoalkyl and peroxyl radicals (eq 41).

$$\mathrm{PhCH_2\dot{C}H(CN)} + t\text{-BuOO}^{\bullet} \rightarrow \underset{\mathbf{9}}{\mathrm{PhCH_2CH(CN)OOBu}\text{-}t} \qquad (41)$$

The peroxyl radical would be generated according to eq 42.

$$\mathrm{PhCOO}^{\bullet}\ (\mathrm{Ph}^{\bullet}) + \mathrm{HOOBu}\text{-}t \rightarrow \mathrm{PhCOOH}\ (\mathrm{PhH}) + t\text{-BuOO}^{\bullet} \qquad (42)$$

We expect reaction 42 to be very fast and to compete with the decarboxylation of benzoylperoxyl radical on the basis of fast reaction 6 ($\sim 10^8\ \mathrm{M^{-1}\ s^{-1}}$ in benzene),[15] mainly due to enthalpic effects (bond energies 88, 103, and 110 kcal/mol, respectively, for ROOH, ROH, and ArCOOH): Thus, the kinetic conditions for the Ingold–Fischer effect would be fulfilled also in this case. The persistent radical effect will operate when the addition of phenyl to acrylonitrile is about as fast as the reaction of phenyl with TBH.

We have not obtained any evidence that reaction 39 could be an alternative mechanism to eq 41: no acetate or benzoate **11** has been observed by the use of increasing amounts of $\mathrm{Cu(OAc)_2}$, AcOH, or PhCOOH in various solvents (benzene, *t*-BuOH, pyridine), contrary to the behavior of cyclohexene (eq 27).

$$\mathrm{PhCH_2CH(CN)OCOR}$$

11

R = Me, Ph

This is not surprising, if an electron-transfer process is involved in eqs 27, 28, 29, and 32, considering the electrophilic character of the α-cyanoalkyl radical. Equation 41 would be the mechanism for the formation of **9** also with Cu(II) catalysis.

We have obtained further evidence of this behavior by reaction of acrylonitrile with TBP. A fast polymerization of the monomer takes place in benzene solution; however,

---

[24] Araneo, S.; Fontana, F.; Minisci, F.; Recupero, F.; Serri, A. *Tetrahedron Lett.* **1995**, *36*, 4307.

in the presence of TBH the polymerization is again inhibited and the mixed peroxide **10** is cleanly formed (eq 43).

$$CH_2{=}CHCN + (t\text{-}BuOOCO)_2 + 2\ t\text{-}BuOOH \rightarrow \underset{\mathbf{10}}{t\text{-}BuOOCH_2CH(CN)OOBu\text{-}t} + 2\ CO_2 + 2\ t\text{-}BuOH \quad (43)$$

The Ingold–Fischer effect is again responsible for the formation of **10**. The peroxyl radical, generated according to eq 6, adds to acrylonitrile (eq 44), and the radical adduct is trapped by another peroxyl radical (eq 45)

$$t\text{-}BuOO^{\bullet} + CH_2{=}CHCN \rightarrow t\text{-}BuOOCH_2\dot{C}H(CN) \quad (44)$$

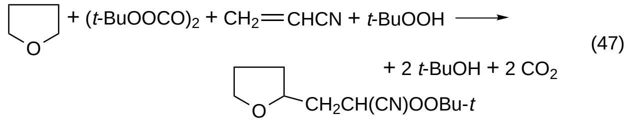
$$t\text{-}BuOOCH_2\dot{C}H(CN) + {}^{\bullet}OOBu\text{-}t \rightarrow \mathbf{10} \quad (45)$$

The presence of variable amounts of $Cu(OAc)_2$ and AcOH does not modify the reaction course in various solvents (benzene, t-BuOH, pyridine): no acetic ester is formed. This supports the hypothesis that no oxidation takes place according to eqs 27–29, always due to the electrophilic character of the α-cyanoalkyl radical.

The formation of **10** smoothly takes place also in the absence of TBP, but only if Cu(II) catalysis[2] is present (eq 46).

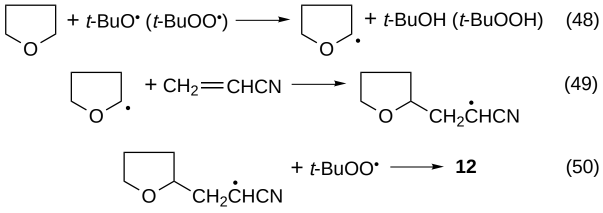
$$3\ t\text{-}BuOOH + CH_2{=}CHCN \xrightarrow{Cu(II)} \mathbf{10} + t\text{-}BuOH + H_2O \quad (46)$$

On the grounds of the above results, we believe that also for reaction 46 only eqs 44 and 45 are responsible for the formation of **10**, contrary to our preliminary communication,[2] in which eq 46 was explained by a ligand-transfer oxidation of the radical adduct. A further synthetic development has been achieved by carrying out the reaction in THF solution (eq 47).



12

Also, the formation of **12** (two stereoisomers in about 1:1 ratio) is clean, and it is well explained by hydrogen abstraction from THF (eq 48), fast addition of the nucleophilic radical to acrylonitrile (eq 49), and cross-coupling of the radical adduct with the peroxyl radical (eq 50).

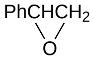


We believe that eq 50 is responsible for the formation of **12** also from TBH with Cu(II) catalysis, as we have reported in a recent preliminary communication.[2]

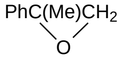
Mixed Peroxides from Styrenes. When TBP is decomposed in benzene solution in the presence of styrene or α-methylstyrene, the polymerization of the alkene occurs. If TBH is added to the solution, the polymerization is again inhibited, and diperoxides **13** and **14**, epoxides **15** and **16**, and the corresponding rearranged aldehydes **17** and **18** are significant reaction products.

PhCH(OOBu-t)CH$_2$OOBu-t **13**

PhC(Me)(OOBu-t)CH$_2$OOBu-t **14**



15



16

PhCH$_2$CHO **17**

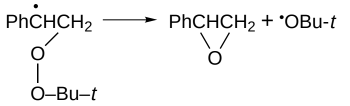
PhCH(Me)CHO **18**

Moreover, benzaldehyde, acetophenone, and minor amounts of the alkoxylperoxyl derivatives **19** and **20** are respectively formed from styrene and α-methylstyrene.

$$\underset{\mathbf{19}}{PhCH(OOBu\text{-}t)CH_2OBu\text{-}t}$$

$$\underset{\mathbf{20}}{PhC(Me)(OOBu\text{-}t)CH_2OBu\text{-}t}$$

13 and **14** are clearly formed by the same mechanism reported above with acrylonitrile (eqs 6, 12, 44, and 45); **15** and **16** arise from the fragmentation of the radical adduct in a chain process according to eq 51, which competes with the formation of the diperoxides.



(51)

The aldehydes **17** and **18** are well-known products of the rearrangement of epoxides **15** and **16**; benzaldehyde and acetophenone arise from oxidative degradation, probably through *β*-scission of benzyloxyl radicals, and **19** and **20** are generated by addition of *tert*-butoxyl radical to the alkene, in competition with eq 6, followed by cross-coupling of the radical adduct with the peroxyl radical.

As with cyclohexene, the reaction is strongly affected by the solvent and the metal salt catalysis. In benzene solution in the presence of Fe(III)- or Mn(III)-porphyrins, **13** is the main reaction product (~90%) with styrene, whereas **19** is a minor product (~10%).[6] In solvents, which form hydrogen bonds with TBH, the rate of reaction 6 is lower and the main reaction products in the presence of iron, manganese, or copper salt catalysis are **19** (pyridine),[6] **21** (acetic acid),[12,25] and **22** (methanol).[25]

$$\underset{\mathbf{21}}{PhCH(OAc)CH_2OBu\text{-}t} \qquad \underset{\mathbf{22}}{PhCH(OMe)CH_2OBu\text{-}t}$$

Under these conditions, the addition of *tert*-butoxyl radical to styrene (eq 52) prevails on reaction 6; the benzylic radical adduct, due to its nucleophilic character, is oxidized by the metal salt (eq 53), as is the allyl radical in eqs 27–29.

---

[25] Minisci, F.; Cecere, M.; Galli, R; *Gazz. Chim. Ital.* **1963**, *93*, 1288.

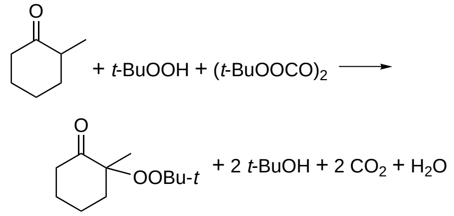
$$\mathrm{PhCH{=}CH_2} + {}^{\bullet}\mathrm{OBu}\text{-}t \rightarrow \mathrm{Ph\dot{C}HCH_2} - \mathrm{OBu}\text{-}t \quad (52)$$

$$\mathrm{Ph\dot{C}HCH_2OBu}\text{-}t + \mathrm{M(II)} + \mathrm{ROH} \rightarrow \mathrm{PhCH(OR)CH_2OBu}\text{-}t + \mathrm{M(I)} + \mathrm{H^+} \quad (53)$$

$$\mathrm{M(II)} = \mathrm{Fe(III), Mn(III), Cu(II)}$$
$$\mathrm{ROH} = t\text{-}\mathrm{BuOOH, AcOH, MeOH}$$

Thus, also with styrene, as with cyclohexene, there is evidence that two mechanisms of formation of mixed peroxides might be operating: a cross-coupling between the benzyl and peroxyl radicals when the Ingold−Fischer conditions are fulfilled and an oxidation of the intermediate nucleophilic benzyl radical by metal salts.

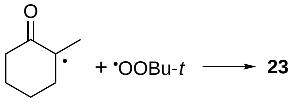
Mixed Peroxides from 2-Methylcyclohexanone. In benzene solution at 45 °C, 2-methylcyclohexanone reacts with TBH and TBP only in traces, giving the mixed peroxide **23**. However, at 67 °C the reaction gives **23** with good conversion and selectivity (eq 54).



(54)

23

At 45 °C, the homolysis of TBP is fast, and a lack of reaction, contrary to the behavior of phenols, cyclohexene, acrylonitrile, styrene, and THF, must be ascribed to slow hydrogen abstraction from 2-methylcyclohexanone by peroxyl radical. At 67 °C, this hydrogen abstraction effectively takes place, and once again, the conditions for the Ingold−Fischer effect are fulfilled, so that cross-coupling according to eq 55 leads to **23**.



(55)

The same peroxide **23** was obtained by the Kharasch reaction[1] for 7 h at 70 °C, but not at 45 °C. No acetic ester was obtained in the presence of $\mathrm{Cu(OAc)_2}$ or AcOH. We believe that, also in the copper-catalyzed reaction, **23** is formed by eq 55, the only role of the copper salt being the generation of alkoxyl and peroxyl radicals from TBH. This is due to the electrophilic character of the α-ketoalkyl radical, which prevents its oxidation by metal salts, as previously discussed for α-cyanoalkyl radicals from acrylonitrile.

Conclusions

The bimolecular self-reactions, the hydrogen abstractions, and the additions to unsaturated substrates are relatively slow reactions for tertiary peroxyl radicals. This fulfills the conditions for the Ingold−Fischer "persistent radical effect" with several compounds (phenols, cyclohexene, acrylonitrile, THF and acrylonitrile, styrenes, 2-methylcyclohexanone, and certainly a large variety of other substrates) in thermal and catalytic reactions for the synthesis of mixed peroxides from hydroperoxides by cross-coupling of peroxyl with carbon-centered radicals (eqs 11, 25, 41, 45, 50, and 55). This would be the only mechanism with electrophilic carbon-centered radicals, whereas with nucleophilic carbon-centered radicals there is evidence that the oxidation by metal salts is a viable alternative mechanism (eqs 29, 32, and 53). The nature of the solvent plays a fundamental role in fulfilling the Ingold−Fischer conditions and, therefore, in determining the cross-coupling or the oxidation mechanism.

Experimental Section

General Methods. Mass spectra were performed on a GLC-MS Finnigan TSQ70 instrument, using a Varian 3700 gas chromatograph, equipped with a SBP-1 fused silica column (30 m × 0.2 mm i.d., 0.2 μm film thickness) and helium as carrier gas.

GLC analyses were performed on a Dani 6500 capillary gas chromatograph, equipped with SBP-5 fused silica column (25 m × 0.25 mm i.d., 1 μm film thickness) at a hydrogen flow rate of 8 $\mathrm{cm^3\ min^{-1}}$, PTV injector, flame ionization detector.

All of the solvents and the reagents were obtained from commercial sources and were used without further purification.

tert-Butyl peroxalate (TBP) was prepared according to the literature procedure.[26] All of the reaction products were known compounds; some of them were commercially available, while others were prepared following the literature procedures; they were then used for the qualitative identification and the quantitative analyses (GLC and GLC-MS): **1**,[11] **2**,[18] **3**,[18] **5**,[1] **8**,[24] **9**,[2] **11**,[2] **12**,[2] **13**,[5] **14**,[5] **19**,[5] **20**,[5] **21**,[25] **22**,[26] and **23**.[1] Commercially available: **4**, **6**, **7**, **15**, **16**, **17**, and **18**.

General Procedures for the Oxidation of *p*- and *m*-Cresols. (A) By TBH and TBP. *p*-Cresol, TBP, and TBH in the ratios and with the solvents reported in Table 1 were stirred for 2 h at 45 °C under $\mathrm{N_2}$. The solution was directly analyzed by GLC (biphenyl as internal standard) and GLC−MS. Authentic samples of **1**, **2**, and **3** were utilized for the identification and the quantitative analysis of the reaction products. In the absence of TBP no reaction takes place, whereas in the absence of TBH **2** and **3** were the only reaction products. **(B) By TBH and Metalloporphyrins.** *p*- or *m*-cresols, TBH, FeTPPCl (commercial product), or MnTDClPPCl (prepared according to the literature procedure)[27] in the ratios and with the solvents reported in Table 1 were stirred for 5 h at 20 °C or for 2 h at 70 °C under $\mathrm{N_2}$ in the presence of 0.03 mmol of pyridine for mmol of TBH. The solution was directly analyzed as in A. *m*-Cresol does not lead to mixed peroxides or dimers of the phenoxyl radical, but 2-methylbenzoquinone **4** was the substantial reaction product; it was identified by comparison with an authentic sample. **(C) By TBH and $\mathrm{Cu(OAc)_2}$.** *p*-Cresol, TBH, and $\mathrm{Cu(OAc)_2}$ in the ratios reported in Table 1 in benzene solution were stirred at 20 °C under $\mathrm{N_2}$; after 5 h the conversion was 3% and after 72 h it was 18%. **1** is the only reaction product. At 50 °C under the same conditions the conversions were 23% after 3 h and 64% after 20 h; again, **1** was the only reaction product.

The results are reported inTable 1.

General Procedure for the Oxidation of Cyclohexene. (A) By TBH and TBP. One mmol of TBH, 0.5 mmol of TBP, and the amounts of cyclohexene and solvents reported in Table 2 were stirred for 3 h at 45 °C under $\mathrm{N_2}$. The solution was directly analyzed by GLC (biphenyl as internal standard) and GLC−MS. Authentic samples of **5** and **6** were utilized for the identification and the quantitative analysis of the reaction products. The conversions of cyclohexene are in the range 40−50%. In the absence of TBP no reaction occurs under the same conditions, whereas in the absence of TBH **6** is the only reaction product. The results are reported in Table 2. **(B) By TBH and TBP in the Presence of Metal Salts.** The reaction was carried out as in A in the presence of $\mathrm{Cu(OAc)_2}$

---

[26] Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762.

[27] Banfi, S.; Maiocchi, A.; Montanari, F.; Quici, S. *Gazz. Chim. Ital.* **1990**, *120*, 123. Quici, S.; Banfi, S.; Pozzi, G. *Gazz. Chim. Ital.* **1993**, *123*, 597.

and $Fe(OAc)_2OH$, as reported in Table 3. Cyclohexenyl acetate **7** is formed in addition to **5** and **6**. The conversions of cyclohexene, based on the peroxides, are in the range 60−70%. The results are reported in Table 3. **By TBH and Copper Salts.** One mmol of TBH, cyclohexene, and copper salts in the solvents reported in Table 4 were stirred for 2 h at 70 °C or for 4 h at 45 °C under N_2. The solution was directly analyzed as in A and B, and the results are reported in Table 4.

Oxidation of Acrylonitrile by Benzoyl Peroxide and TBH. Ten mmol of acrylonitrile, 10 mmol of TBH, and 10 mmol of benzoyl peroxide were refluxed for 4 h in 6 mL of benzene under N_2. The solution was washed with 10% aqueous NaOH in order to separate benzoic acid, and then the benzene solution was analyzed by GLC ($PhCH_2CH_2CN$ as internal standard) and GLC−MS. The four reaction products (**9**, 34.9%; **10**, 20.6%, biphenyl, 27.5%, and phenyl benzoate, 16.9%), obtained in overall 58% yield, were identified by comparison with authentic samples.

Oxidation of Acrylonitrile by TBP and TBH. (A) Five mmol of acrylonitrile and 0.5 mmol of TBP in 5 mL of benzene were stirred for 2 h at 45 °C under N_2. Only polymerization of acrylonitrile took place. (B) As in A, in the presence of 1 mmol of TBH. No polymerization occurred, but **10** (identified by comparison with an authentic sample) was the only reaction product from acrylonitrile; the conversion (based on the peroxides, GLC) was 27%. (C) Five mmol of TBH, 25 mmol of acrylonitrile, and 0.25 mmol of $Cu(OAc)_2$ in 25 mL of benzene were stirred for 18 h at 50 °C under N_2. GLC revealed a yield of 55% of **10** based on TBH. No polymerization of acrylonitrile took place.

Oxidation of Acrylonitrile by TBP and TBH in THF. (A) Ten mmol of acrylonitrile, 5 mmol of TBH, and 5 mmol of TBP in 5 mL of THF and 5 mL of benzene were stirred for 2 h at 45 °C under N_2. GLC analysis (biphenyl as internal standard) revealed a yield of 63% of **12** (two stereoisomers in 45:55 ratio) as the only reaction product from acrylonitrile: **12** was identified by comparison with an authentic sample. (B) Five mmol of TBH, 25 mmol of acrylonitrile, and 0.25 mmol of $Cu(OAc)_2$ in 25 mL of benzene and 5 mL of THF were stirred for 18 h at 50 °C under N_2. GLC revealed a yield of 80% of **12** based on THF.

Oxidation of Styrenes by TBH and TBP. (A) Five mmol of styrene or α-methylstyrene and 0.5 mmol of TBP in 5 mL of benzene were stirred for 2 h at 45 °C under N_2. Only the polymerization of the monomers took place. (B) As in A, in the presence of 1 mmol of TBH. **Styrene.** No polymerization occurred. The reaction solution was directly analyzed by GLC (biphenyl as internal standard) and GLC−MS by using authentic samples for the identification of the main reaction products: **13** (32.2%), **15** (23.1%), **17** (9.8%), **19** (6.5%), and benzaldehyde (22.5%); yields are based on the peroxides. (C) As in B. **α-Methylstyrene.** The main reaction products were analyzed by GLC and GLC−MS (comparison with authentic samples): **14** (10.1%), **16** (19.7%), **18** (10.3%), **20** (4.5%), and acetophenone (41.1%); yields are based on the peroxides.

Oxidation of 2-Methylcyclohexanone by TBP and TBH. Five mmol of 2-methylcyclohexanone, 1 mmol of TBH, and 0.5 mmol if TBP in 5 mL of benzene were stirred for 2 h at 67 °C under N_2. An authentic sample of **23** was utilized for the identification of the reaction product. The direct GLC analysis of the reaction mixture revealed the presence of 77% yield of **23**. At 45 °C under the same conditions only traces of **23** were formed.

JO9700944