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Copper(II) Triflate as a Source of Triflic Acid: Effective, Green Catalysis of Hydroalkoxylation Reactions

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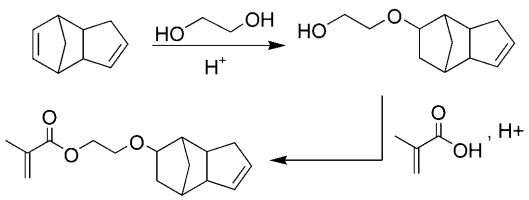
Abstract: The hydroalkoxylation of dicyclopentadiene (DCPD) and norbornene (NB) with 2-hydroxyethyl methacrylate (HEMA) for the synthesis of industrially relevant monomers has been investigated with various metal-based Lewis acids and strong Brønsted acids. In the absence of other additives, copper(II) triflate is the most efficient catalyst system. Kinetics, electron spin resonance (ESR), catalyst poisoning and cross experiments indicate that triflic acid (TfOH) is the true active catalyst in these reactions. This *in situ* generation of TfOH occurs *via* reduction of $Cu(OTf)_2$ by the olefin reagent (DCPD, NB). The copper ions present in the reaction mixture act as radical polymerization retardants, preventing polymerization of HEMA (which is observed with most other metal salts and strong Brønsted acids investigated), thus improving the selectivity and yield (up to 95%) for the desired products. These observations have led to the development of a highly effective green process, using bulk reagents (no solvent) and a cheap, metal-free catalyst system, based on TfOH and a phenolic radical inhibitor (2,5-di-*tert*-butylhydroxytoluene, BHT).

Keywords: Brønsted acids; copper; hydroalkoxylation; Lewis acids; triflate salts; triflic acid

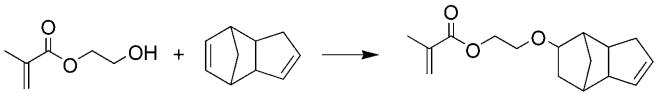
Introduction

Today's need for "green chemistry" such as 100% atom efficiency, energy saving, as well as the use of low amounts of non-toxic catalysts, is of crucial importance.[1] In this respect, the catalytic direct addition of E–Nu across multiple carbon-carbon bonds is the main atom-economic process for the synthesis of functionalized molecules.[2] Even though the controlled direct addition of O–H bonds across non-activated olefins to provide ethers or esters is, in principle, coproduct-free and energy-saving, only few examples of effective reactions are known. In recent years, Brønsted acids[3] or organometallic complexes[4–12] have been reported as efficient catalysts for intra- or intermolecular hydroalkoxylation reactions. Many of these catalytic systems are based on metal triflate salts, for example, of Ru(III) (*in situ*-formed),[6] Al(III),[7] Au^{I},[8] Fe(III) (*in situ*-formed),[9] Sn(IV),[10] Cu(II)[11] and Ir(III) (*in situ*-formed).[12] $Cu(OTf)_2$ and $Fe(OTf)_3$ are very attractive because they are air- and moisture-stable, non-toxic and relatively inexpensive. However, exact mechanistic pathways of such catalytic reactions are still unclear. Recent studies by Hartwig et al. suggest that metal triflates may actually be catalytically active through the formation of triflic acid (TfOH); although the formation pathway of TfOH was not addressed.[3a]

Dicyclopentenyloxyethyl methacrylate (DCPOMA) is a low volatile and low odor monomer largely used in industry for coating or molding.[13] The first industrial synthesis of DCPOMA has been developed by Rohm & Haas, *via* a two-step process (Scheme 1).[14] The monoetherified product is first obtained in 89% yield in the presence of a sulfonic acid resin, by reacting ethylene glycol (EG) and dicyclopentadiene (DCPD),[14a] followed by quantitative esterification with methacrylic acid and a catalytic amount of APTS and hydroquinone.[14b] Other acids have also been described for the monoetherification reaction such as $BF_3{\cdot}Et_2O$.[15] However, excess of EG (1.3 equiv.) and a purification step are needed to obtain the mono-



Scheme 1. Two-step synthesis of DCPOMA developed by Rohm & Haas.[14]



Scheme 2. One-step synthesis of DCPOMA from DCPD and HEMA.

etherified product in high yield. Moreover, removal of water during esterification in the second step, to yield quantitatively DCPOMA, is energy intensive.

In 1983, Hitachi Chemicals Co. developed an alternative synthesis of DCPOMA by the direct addition of 2-hydroxyethyl methacrylate (HEMA) across DCPD (Scheme 2).[16] DCPOMA is thus obtained in 84% yield at 80 °C in the presence of $H_3[PW_{12}O_{40}]\cdot 29\,H_2O$ (1.0 wt%) as catalyst and phenothiazine (0.05 wt%) as inhibitor of methacrylate polymerization. The limitations of this process lie in the use of a costly heteropolyacid catalyst and still moderate yield. On the basis of recent work in the field of Lewis acid catalysis,[3–12] we decided to develop a convenient green method for the catalytic synthesis of DCPOMA and to study carefully the reaction mechanism.

Results and Discussion

Chemoselectivity of the Addition of HEMA across DCPD

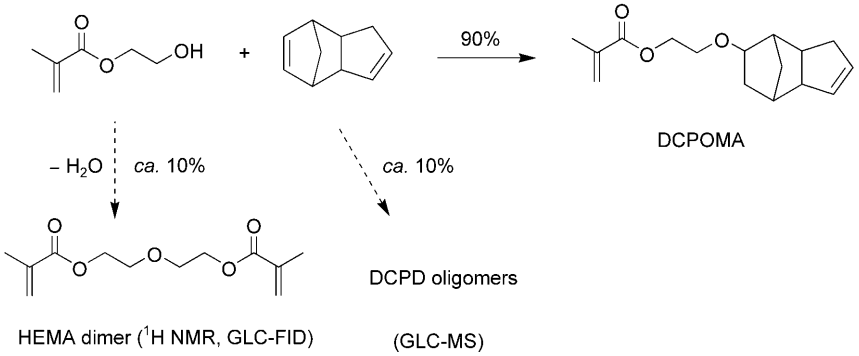
The addition of HEMA across DCPD (1:1 reaction) was preliminarily screened with a series of Lewis acids under Hii's conditions (1,4-dioxane, 80 °C, 2.5 mol% cat.).[11] We first focused on ubiquitous potential catalysts, especially air- and moisture-stable metal triflate salts, such as Cu(II), Zn(II) and rare earth (III) triflates. Representative results are summarized in Table 1.

Table 1. Addition of HEMA across DCPD in dioxane at 80 °C.[a]

Entry	Catalyst (mol%)	Time [h]	DCPD conv. [%][b]	DCPOMA selectivity [%][b]
1	$Y(OTf)_3$ (2.5)	24	0	–
2	$Yb(OTf)_3$ (2.5)	24	0	–
3	$FeCl_3$ (2.5)	2	0	–
4	$Co(OAc)_2\cdot 4\,H_2O$ (2.5)	3.5	0	–
5	$Cu(OTf)_2$ (2.5)	2.5	100	90
6	$CuCl_2\cdot 2\,H_2O$ (2.5)	3.5	0	–
7	$Zn(OTf)_2$ (2.5)	24	0	–

[a] 1,4-dioxane (1.0 mL), 80 °C, HEMA = 1.00 mmol, DCPD = 0.98 mmol, 2.5 mol% cat.
[b] Determined by ^{1}H NMR

Surprisingly, we found that, among the series evaluated, $Cu(OTf)_2$ is the only active catalyst (precursor) (entry 5). Lanthanide triflates, which are known to be among the best Lewis acids,[17] are completely ineffective for the reaction under these conditions (entries 1, 2). Using $Cu(OTf)_2$ as the catalyst (precursor), and as observed with most other active systems apart from a few significant exceptions discussed hereafter, the addition of HEMA across DCPD proceeds quite selectively. The expected addition product DCPOMA is formed in *ca.* 90% yield (GLC and isolated yields), with complete consumption of both reagents. Analysis of the final reaction mixture by GLC-FID-MS and ^{1}H NMR revealed the formation of two main side-products, which account for the reaction balance: the etherification product of HEMA and oligomers of DCPD, both produced in *ca.* 10% yields (Scheme 3).[18]



Scheme 3. Main and side-products obtained from the reaction of DCPD and HEMA in bulk.

A kinetic monitoring of the reaction by ^{1}H NMR showed that, in the presence of 2.5 mol% of $Cu(OTf)_2$, the conversion reached 70% after 1.5 h and went to completion within 2.5 h. These data indicate that the addition reaction across DCPD proceeds *ca.* 5 times faster with a primary alcohol (HEMA) than with most reactive phenols or carboxylic acids in Hii's work.[11]

Process Optimization and Mechanistic Investigations

In order to optimize the process and make it industrially viable, new reaction conditions were selected. We decided to work at 100 °C, under air, with bulk reagents, that is, to eliminate any solvent (dioxane is especially toxic), in the presence of 1.0 mol% of catalyst. In addition to metal-based Lewis acids, a few strong Brønsted acids were also investigated. Representative results are summarized in Table 2.

We observed that, under such conditions, some catalyst systems, namely Co(II), Co(III) and Zn(II) triflates, and strong organic acids as well, reproducibly induce the polymerization of the methacrylic moiety of HEMA (entries 9–11, 17–21). This competitive process starts in the early stages of the reaction and plagues, or even sometimes completely hampers, the production of DCPOMA, due to the formation of large amounts of insoluble poly(HEMA). Consistent with the preliminary screening (Table 1), the results of Table 2 suggest that *both* Cu(II) and triflate ions are required for the hydroalkoxylation reaction to proceed effectively. In fact, even though no polymerization of HEMA was observed, $CuCl_2$ (entry 6), $Cu(OTf)\cdot(C_6H_6)$ (entry 15), $Cu(hfacac)_2$ (hfacac = hexafluoroacetylacetonate) (entry 16) are inactive. Only group 3 metal triflates, especially $Sc(OTf)_3$, proved to be also active and quite selective (entries 8 and 9), but they do not promote the reaction as efficiently as $Cu(OTf)_2$ does (entry 13) (*vide infra*). Actually, a low loading of the latter catalyst (0.1 mol%) is sufficient to perform the reaction within short time periods, still keeping a high selectivity for DCPOMA (entry 14).

Considering a Lewis acid-catalyzed pathway for the addition of alcohols across olefins, it was somewhat surprising to observe that $Cu(OTf)_2$ performs better than $Sc(OTf)_3$. On the other hand, as evidenced by Spencer,[19] protons can be the active catalysts in Lewis acid-mediated hetero-Michael addition reactions. Assuming that metal triflate species are able to generate *in situ* triflic acid, Hartwig pointed out the similar catalytic activity of triflic acid and metal triflates in olefin hydroamination or hydroalkoxylation reactions.[3a] Based on these considerations, we investigated in more detail the addition of HEMA across DCPD promoted by $Cu(OTf)_2$, to evidence a possible formation and contribution of triflic acid. For this purpose, we measured the relative reaction rates of different catalyst systems and performed catalyst poisoning experiments.

The kinetics of DCPOMA formation were monitored by ^{1}H NMR for reactions conducted in the presence of 0.1 mol% of catalyst at 100 °C (Figure 1). As aforementioned, $Sc(OTf)_3$, in spite of its high Lewis

Table 2. Addition of HEMA across DCPD in bulk.[a]

Entry	Catalyst	mol%	Temp. [°C]	Time [h]	P(HEMA) [%][b]	DCPD conv. [%][c]	DCPOMA selectivity [%][c]
8	$Sc(OTf)_3$	1.0	100	3.5	–	95	85
9	$Yb(OTf)_3$	1.0	100	8	20	100	85
10	$Co(OAc)_2\cdot 4H_2O$	1.0	100	2	solid[b]	nd	-
11	$Co(acac)_3$	1.0	100	1	solid[b]	nd	-
12	$Cu(OTf)_2$	1.0	80	2	–	100	90
13	$Cu(OTf)_2$	1.0	100	0.5	–	100	90
14	$Cu(OTf)_2$	0.1	100	4.5	–	100	90
15	$Cu(OTf)\cdot(C_6H_6)$	1.0	100	1	–	0	
16	$Cu(hfacac)_2\cdot H_2O$	1.0	100	3	–	0	
17	$Zn(OTf)_2$	1.0	100	1	30	0	–
18	H_2SO_4	7.5	100	2.5	20	100	70
19	H_2SO_4	1.0	100	0.5	50	0	–
20	H_2SO_4	1.0	80	1.5	50	0	–
21	Amberlite[d]	10 wt%	100	16	solid[b]	nd	–
22	TfOH/BHT	0.1/0.01	100	4	–	100	90

[a] HEMA = 3.85 mmol, DCPD = 3.78 mmol.
[b] Conversion of HEMA to poly(HEMA), as determined by ^{1}H NMR in the presence of biphenyl as internal standard; "solid" refers to solidification of the reaction medium due to heavy precipitation of poly(HEMA)
[c] Determined by ^{1}H NMR
[d] Amberlite IR-120, hydrogen form

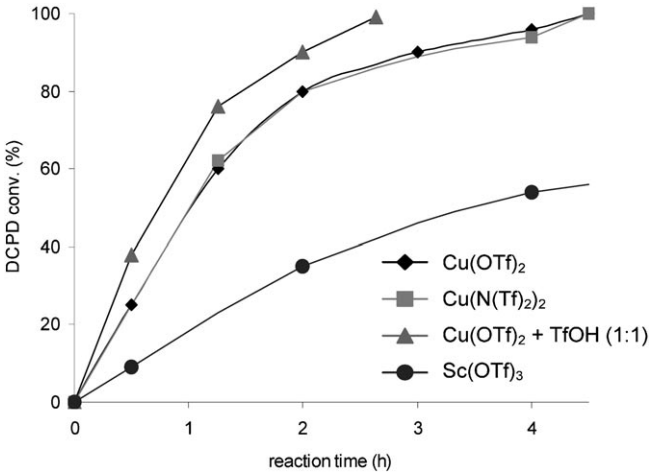


Figure 1. Rate of conversion of DCPD (0.1 mol% cat., 100 °C).

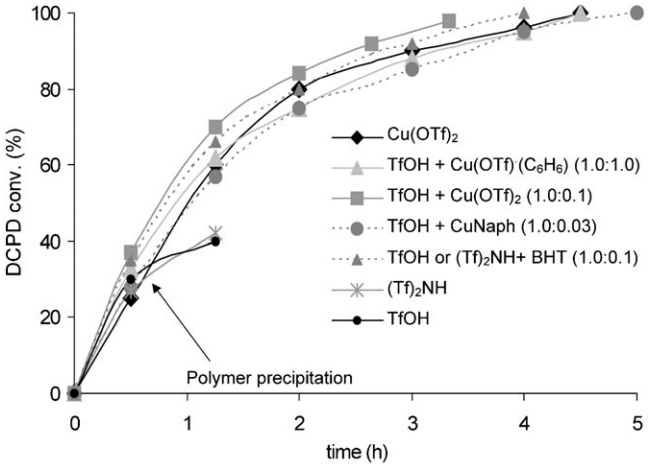


Figure 2. DCPD conversion as a function of time (0.1 mol% cat., 100 °C).

acidity, is a moderately active catalyst; only 50% conversion was reached in 4 h, after which time periods polymerization of HEMA was often observed to take place to a significant extent. Using $Cu(OTf)_2$, the reaction was selectively completed after 4.5 h, showing a maximum TOF of 480 h^{-1}; after 2 h, the reaction rate decreased, which possibly arises from mass transfer limitation due to the high viscosity of the mixture, and/or from the presence of increasing amounts of water (*vide infra*; Table 3 and Scheme 3). Copper triflimidate $[Cu(N(Tf)_2)_2]$, which is slightly more Lewis acidic than $Cu(OTf)_2$)[20] and known to catalyze Friedel–Crafts acylation[21] and Diels–Alder reactions,[20] exhibits strictly identical activity as $Cu(OTf)_2$. It is noteworthy that the activity of the latter catalyst precursor can be improved by adding one equivalent of triflic acid (Figure 1).[21] This increase in activity can be accounted for, in principle, by two phenomena: (*i*) a ligand effect, in which excess ligand (TfO^-) would improve the global reaction rate by stabilizing the active (metal) species, and/or (*ii*) a higher concentration of triflic acid as the actual catalytically active species. As revealed hereafter, it is this second hypothesis that is operative in this system.

The performance of $Cu(OTf)_2$ and triflic acid were next compared (Figure 2). After 30 min, triflic acid turns out to be as active as $Cu(OTf)_2$ for the hydroalkoxylation of DCPD. Expectedly, the strong Brønsted triflimidic acid $[(Tf)_2NH]$,[22] which is known to catalyze organic transformations such as Michael additions,[23] features the same performance as TfOH and $Cu(OTf)_2$. However, both TfOH and Tf_2NH induce the parallel formation of poly(HEMA) (most likely *via* a cationic pathway), leading to complete gelation of the reaction mixture after *ca.* 1 h and poor final yields of DCPOMA.

Since $Cu(OTf)\cdot(C_6H_6)$ is inactive (Table 2) and $Cu(OTf)_2$ is the most active and selective catalyst precursor, we assumed that triflic acid is generated by

Table 3. Catalyst poisoning experiments in the addition of HEMA across DCPD in bulk at 100 °C.

Entry	Catalyst system (mol%)	Additive (mol%)	Time [h]	DCPD conv. (mol%)[a]
23	$Cu(OTf)_2$ (1.0)	–	0.5	100[b]
24	$Cu(OTf)_2$ (1.0)	H_2O (10)	0.5	53
25	$Cu(OTf)_2$ (1.0)	2,6-(t-Bu)$_2$pyridine (1.1)	4	0
26	TfOH/BHT (1.0/0.1)	2,6-(t-Bu$_2$)pyridine (1.1)	4	0
27	$Cu(OTf)_2$ (1.0)	Phenothiazine (5.0)	1.25	42
			2.25	70
			3	80
28	TfOH (1.0)	Phenothiazine (5.0)	1.5	60
			2.5	80
			5	96
29	$Cu(OTf)_2$ (0.1)	TEMPO (0.1)	8	0
30	TfOH (0.1)	TEMPO (0.1)	4	0

[a] Determined by ^{1}H NMR; selectivity for DCPOMA = 90% in all cases.
[b] 80% conv. in 10 min.

the *in situ* reduction of $Cu(OTf)_2$ in the presence of a hydrogen donor DH_2 [Eq. (1)].

$$2\,Cu(OTf)_2 + DH_2 \longrightarrow 2\,CuOTf + 2\,TfOH + D \quad (1)$$

Indeed, we observed that a 1:1 mixture of $Cu(OTf)\cdot(C_6H_6)$ (0.1 mol%) and TfOH (0.1 mol%) performs identically (within experimental uncertainty) to $Cu(OTf)_2$ (0.1 mol%) (Figure 2); most noteworthy, no polymerization of HEMA was detected in this reaction. These observations support that TfOH is the real active catalyst in this process and suggest that copper [Cu(I), Cu(II), *vide supra*) plays a key role in inhibiting polymerization of HEMA. The latter hypothesis was confirmed by reproducing the performance of $Cu(OTf)_2$ by carrying out the reaction in the presence of TfOH (0.1 mol%) and adding either $Cu(OTf)_2$ (0.1 equiv. *vs.* TfOH, i.e., 0.01 mol%) or even less of Cu(II) naphthenate (0.003 mol%, 0.03 equiv. *vs.* TfOH) (Figure 2). The slightly higher reaction rate observed with the TfOH/$Cu(OTf)_2$ (0.1/0.01 mol%) system, as compared to $Cu(OTf)_2$ (0.1 mol%), further supports the generation of TfOH from $Cu(OTf)_2$ [a 10% increase in the reaction rate would be expected if $Cu(OTf)_2$ is quantitatively transformed to TfOH according to Eq. (1)]. The positive role of copper as polymerization/radical inhibitor[24] in the reaction has been highlighted by its replacement with BHT (2,5-di-*tert*-butylhydroxytoluene); in fact, the hydroalkoxylation reaction proceeds equally well with metal-free systems such as TfOH/BHT (Figure 2, and Table 2, entry 22) or Tf_2NH/BHT (0.1/0.01 mol%) (Figure 2). Under these conditions, the turnover frequency reaches 480 h^{-1} (at 50% conversion) and can be improved up to 1500 h^{-1} by increasing the temperature to 120 °C (reaction completed within 2 h), without affecting significantly the selectivity of the reaction. Also, the phenolic BHT inhibitor in this catalytic system can obviously be varied, for example, replacement with hydroquinone (HQ), without affecting the selectivity and activity.

To further support that TfOH is the real active species in this process, the reaction of HEMA with DCPD was carried out in the presence of TfOH poisons, such as water, weak Lewis and/or Brønsted bases[19] (Table 3). The reference reaction was carried out in the presence of $Cu(OTf)_2$ (1.0 mol%) and complete conversion of DCPD was observed after 0.5 h (entry 23). Addition of a fairly large amount of water with respect to the catalyst dramatically slowed down the reaction rate (entry 24), probably by buffering the triflic acid liberated, as observed by Spencer.[19] Moreover, the use of a bulky Brønsted base such as 2,6-di-*tert*-butylpyridine, which is too sterically hindered to coordinate metal ions,[25] totally inhibited the hydroalkoxylation reaction promoted by $Cu(OTf)_2$ (entry 25) or TfOH/BHT (entry 26). As the bulky pyridine can only interact with protons, this result strongly supports a Brønsted acid to be the active species.

The weak Lewis and Brønsted base phenothiazine, which also plays the role of radical polymerization inhibitor (thus avoiding the use of BHT), only decreased the rate of the reaction promoted by $Cu(OTf)_2$ (entry 27) or TfOH (entry 28). It is noteworthy that the inhibition effect was almost identical using either $Cu(OTf)_2$ or TfOH, consistent with the inhibition of the same active species in both cases. On the other hand, TEMPO, which is known to react irreversibly with TfOH by disproportionation,[26] completely inhibited the catalytic reaction (entries 29 and 30).

To confirm the afore-suggested generation of TfOH by reduction of $Cu(OTf)_2$ in the presence of DCPD [reaction mixtures of HEMA and DCPD, using either $Cu(OTf)_2$ or TfOH as catalysts, turn progressively dark brown after a few minutes; the same brown coloration is also observed by reacting $Cu(OTf)_2$ and DCPD (i.e., without adding HEMA), suggesting that generation of TfOH may occur thanks to DCPD], we followed the reaction by ESR spectroscopy (Figure 3).[27] This study showed the disappearance of the paramagnetic signal assigned to Cu(II), confirming that the latter is reduced into Cu(I) in the presence of DCPD at 70 °C [control experiments confirmed that reduction of Cu(II) to Cu(I) proceeds only in the presence of olefin DCPD]. Under the con-

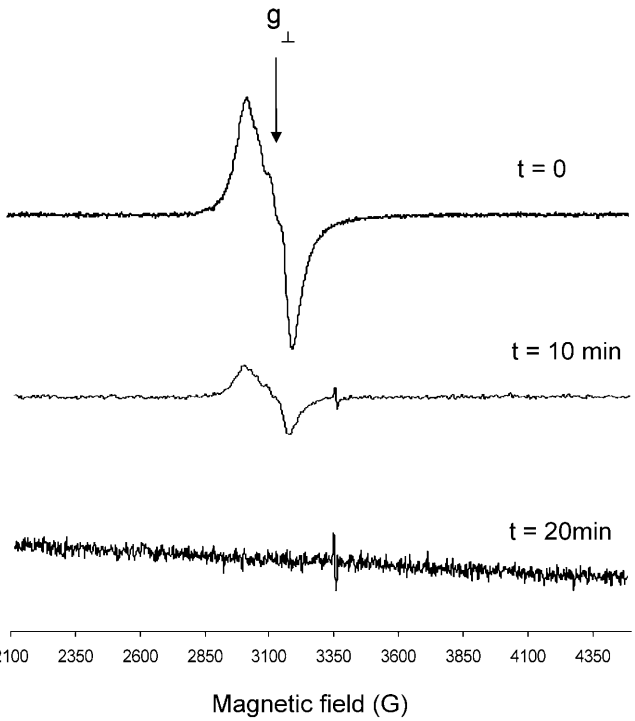
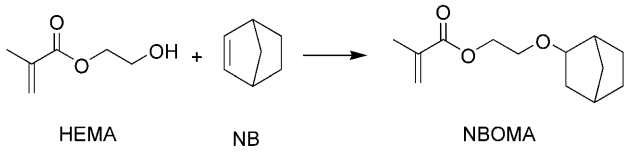


Figure 3. ESR monitoring of the reaction of $Cu(OTf)_2$ with DCPD (1/4) in CH_3CN at 70 °C showing the disappearance of the Cu(II) signal.

ditions of this analytical investigation ($[Cu]_{tot}=0.0675\,M$ in CH_3CN, [DCPD]/[Cu] = 4), the reduction is completed within 20 min. A possible mechanism for the reduction of $Cu(OTf)_2$ into CuOTf by DCPD, and concomitant generation of TfOH, is olefin dehydrogenation through a radical pathway.[28] ^1H NMR monitoring of the reaction between $Cu(OTf)_2$ and DCPD (1/1) at 70 °C in CD_3CN revealed the appearance, after a few minutes, of new signals including a broad singlet at $\delta = 14.95$ ppm, which was assigned to TfOH;[29] many new resonances were also observed in the aliphatic area, but due to their complexity and severe overlapping, these proved uninformative about the nature of the DCPD oxidation products.[30]

In order to explore the generality of this *in situ* generation of TfOH from $Cu(OTf)_2$, we investigated the addition of HEMA across norbornene (NB) (Scheme 4). The corresponding hydroalkoxylation



Scheme 4. Addition of HEMA across norbornene.

product (NBOMA) is also an industrially relevant monomer.[31] As shown in Table 4, the reaction with NB proceeds more slowly as compared to that of DCPD, but the reaction is more selective (entries 23 and 31). The etherification dimer of HEMA was formed in lower amounts, as revealed by NMR and GLC analysis. Also, NB is less prone to oligomerization reactions. As previously observed by Hii[11] and Hartwig,[3a] NBOMA is obtained selectively as the *exo*-isomer.

The formation of NBOMA was monitored by ^1H NMR, with the same catalyst systems and reaction conditions as those used with DCPD (0.1 mol% cat., 100 °C, bulk) (Figure 4). Using $Cu(OTf)_2$ as the catalyst precursor, the conversion of NB reached 40% after 4 h, which is to be compared with 90% over the same time for DCPD. However, when the reaction was carried out with TfOH/$Cu(OTf)_2$ (0.1/0.01 mol%)

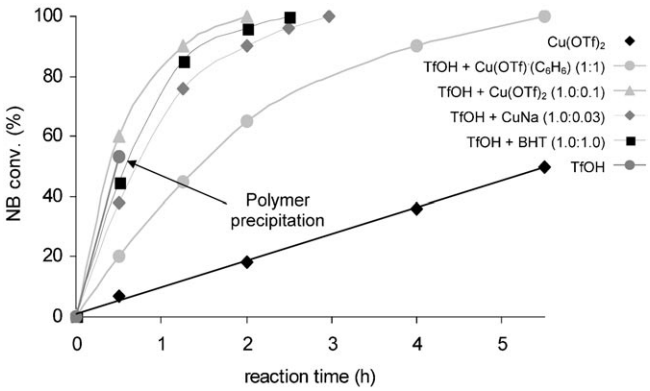


Figure 4. NB conversion as a function of time (0.1 mol% cat., 100 °C).

or TfOH/BHT (0.1/0.1 mol%), the hydroalkoxylation of NB was completed within 2.5 h. Surprisingly, TfOH/$Cu(OTf)\cdot(C_6H_6)$ showed an in-between activity and the addition of an excess of Cu(I) (1.5 equiv.) with respect to TfOH dramatically slowed down the reaction rate (conversion of NB = 6 mol% after 2 h).

The lower activity of $Cu(OTf)_2$ in the hydroalkoxylation of NB, as compared to that of DCPD, can be accounted for by a slower formation of TfOH. That has been confirmed by ESR analyses carried out under similar conditions as in the case of DCPD: we observed a slower disappearance of the Cu(II) signal in the presence of 4 equivalents of NB; only after 105 min (instead of 20 min. in the case of DCPD), did the signal of paramagnetic Cu(II) disappear completely.

The relatively slow generation of triflic acid in the NB/HEMA/$Cu(OTf)_2$ system and its impact on the reaction rate is also confirmed by experiments conducted in the presence of known reducing agents DH_2 [Eq. (1)]. In fact, the addition of one equivalent of $PhNHNH_2$[27] or BHT[19] accelerates dramatically the reaction rate (entries 33 and 34), eventually reaching the high activity of the TfOH/BHT system (entry 32). Obviously, in these systems, rapid reduction of $Cu(OTf)_2$ with concomitant liberation of one equivalent of TfOH takes place at the beginning of the reaction.

Table 4. Addition of HEMA across NB *vs.* DCPD in bulk at 100 °C.

Entry	Catalyst (mol%)	DH_2 (mol%)	Time [h]	Olefin (conv.) [mol%][a]	Product (yield) [mol%][a]
23	$Cu(OTf)_2$ (1.0)	–	0.5	DCPD (100)	DCPOMA (90)
31	$Cu(OTf)_2$ (1.0)	–	1	NB (100)	NBOMA (95)
32	TfOH/BHT (0.1/0.1)	–	2.5	NB (100)	NBOMA (95)
33	$Cu(OTf)_2$ (0.1)	$PhNHNH_2$ (0.1)	3	NB (100)	NBOMA (95)
34	$Cu(OTf)_2$ (0.1)	BHT (0.1)	3	NB (100)	NBOMA (95)

[a] Determined by ^1H NMR.

In order to confirm the reducing role of NB, the reaction between $Cu(OTf)_2$ and NB (1/1) was monitored by ^1H NMR. At 70 °C in CD_3CN, a highly deshielded broad resonance appeared at $\delta = 15.3$ ppm, as in the case of DCPD, which was assigned to TfOH.[29] Other new signals could also be observed in the aliphatic region, while the signal for the "HC=CH" hydrogens disappeared after 5 h.[30]

A most practical aspect of this reaction is the possibility to use air- and moisture-stable catalyst systems (metal triflates, triflic acid) with "used as received" reagents, without any purification or special care, to perform efficiently the hydroalkoxylation reaction. The presence of phenolic stabilizers (BHT, …) in commercial/technical reagents such as olefins (DCPD, NB) and/or solvents (dioxane) could turn out to be of particular importance in the present chemistry. Actually, the generation of TfOH could be also envisioned by the reaction of such residual phenols[32] with reducible metal triflates [Cu(II), Fe(III) and Ru(II)]. Also, as proposed by Spencer,[19] the presence of water in reagents/solvents or formed *in situ* by side reactions (e.g., etherification of HEMA) could generate small amounts of triflic acid as well. However, control ESR experiments ruled out significant contribution of these alternative pathways for generating of TfOH. Indeed, quantitative reduction of Cu(II) to Cu(I) takes place at olefin/$Cu(OTf)_2$ ratios as low as 4/1 (rapidly for DCPD, more slowly for NB), that is, in the almost total absence of water and phenol derivatives.

Conclusions

We have demonstrated the *in situ* formation of triflic acid in the hydroalkoxylation of dicyclopentadiene and norbornene with 2-hydroxyethyl methacrylate promoted by $Cu(OTf)_2$. Kinetics, ESR, and catalyst poisoning experiments indicate that triflic acid is the true active catalyst in these reactions. Reduction of $Cu(OTf)_2$ by the olefin reagent (DCPD, NB), is the main (if not exclusive) pathway for generating triflic acid.

The copper ions have been shown to have a serendipitous beneficial role on the hydroalkoxylation, acting as methacrylic radical polymerization retardants, thus improving the selectivity and yield of the reaction. These observations have led to the development of an improved and green synthesis of industrially relevant monomers such as DCPOMA and NBOMA using bulk reagents. The best performing catalyst system, based on triflic acid and a phenolic radical inhibitor such as BHT, is cheap, metal-free, and highly effective.

Experimental Section

General Considerations

All reactions were carried out without specific precautions, with reagents used as received and in air, unless otherwise stated. Dioxane and acetonitrile (CH_3CN, CD_3CN) were distilled over Na/benzophenone or CaH_2, respectively, and degassed with argon prior to use. Glassware was dried in an oven prior to use. Dicyclopentadiene (DCPD, stabilized with 250 ppm BHT) and 2-hydroxyethyl methacrylate (HEMA; stabilized with 300 ppm MEHQ) were purchased from Aldrich and used as received. Norbornene (purum) was purchased from Fluka and used as received. All other reagents were purchased from Aldrich, Fluka or Strem and used as received. $Cu(NTf_2)_2$ was prepared by a literature method.[21] Deuterated solvents were purchased from Euriso-top.

NMR spectra were recorded on a Bruker 500 MHz spectrometer. Chemical shifts are reported in ppm, and were calibrated using residual ^1H and ^{13}C resonances of deuterated solvents. Coupling constants (J) are expressed in Hertz. Mass spectra were recorded at the CRMPO, University of Rennes 1. ESR spectra were recorded on a Bruker EMX spectrometer. GLC-FID and GLC-MS analyses were recorded on a Shimadzu GC-2014 and a Shimadzu GC-2010/GC-MS2010S apparatus, respectively.

Typical Procedure for the Addition of HEMA across DCPD in Dioxane (Table 1)

DCPD (0.10 mmol, 132 mg) and HEMA (0.10 mmol, 130 mg) were weighed in air and added under argon to a solution of the catalyst (2.5×10^{-5} mol) in dioxane (1.0 mL). The reaction mixture was heated at 80 °C in an oil bath and stirred for the desired time period. The solution was then cooled to room temperature and the conversion was determined by ^1H NMR (by comparing the integral ratio between DCPD and DCPOMA, especially the disappearance of the DCPD double bond signal and the appearance of the signal of the DCPOMA double bond).

Typical Procedure for the Addition of HEMA across DCPD in Bulk (Table 2 and Table 3)

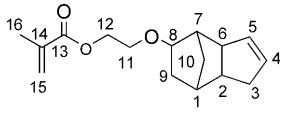
In a Schlenk tube, DCPD (3.78 mmol, 500 mg), HEMA (3.85 mmol, 500 mg) and biphenyl (NMR internal standard, 0.38 mmol, 61 mg) (and the catalyst poison for specific experiments) were added over the catalyst (3.78×10^{-5} mol) in air [except for $Sc(OTf)_3$, $Yb(OTf)_3$, $Zn(OTf)_2$, which were weighed in a glove box]. The reaction mixture was vigorously stirred and heated at 100 °C in an oil bath for the desired time period. The solution, which turned dark brown when $Cu(OTf)_2$ and $Sc(OTf)_3$ were used as the catalysts, was cooled to room temperature and the conversion was determined by ^1H NMR.

Typical Procedure for the Addition of HEMA across DCPD in Bulk with 0.1 mol% of Catalyst

In a Schlenk tube, DCPD (35.34 mmol, 4.666 g) or NB (35.74 mmol, 3.360 g) and HEMA (35.89 mmol, 4.666 g) were added onto the metal catalyst (3.53×10^{-5} mol). When

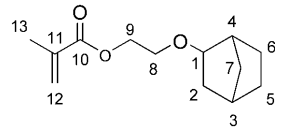
strong acids (TfOH, Tf_2NH, …) were used as catalysts, they were added at the very end to the reaction mixture under vigorous stirring to avoid the formation of polymer. Then, the reaction mixture was vigorously stirred and heated at 100 °C. The conversion was determined by ^1H NMR analysis of aliquots sampled over regular time periods. When the reaction was completed, the mixture was cooled to room temperature and analyzed by ^1H NMR and GC-MS. The crude reaction mixture was diluted in pentane (*ca.* 50 mL) and washed with 1 M aqueous NaOH. The organic layer was dried over $MgSO_4$ and filtered through celite. Volatiles were removed under vacuum to give impure DCPOMA as a brown oil (yield: *ca.* 90%). This crude product was purified by column chromatography on silica gel (heptane/ethyl acetate: 6/1; $R_f = 0.75$) to give DCPOMA as a pale yellow oil (isolated yield: 85%).

DCPOMA



^1H NMR (500 MHz, 25 °C, $CDCl_3$): δ = 6.15 (s, 1H, H-15), 5.89 (m, 1H, H-5), 5.59 (s, 1H, H-15), 5.47 (m, 1H, H-4), 4.28 (br t, $^3J = 5$ Hz, 2H, H-12), 3.66 (m, 2H, H-11), 3.46 (m, 1H, H-8), 2.70–2.40 (m, 2H, H-3, H-6), 2.2–1.8 (m, 4H, H-1, H-2, H-3, H-7), 1.96 (s, 3H, H-16), 1.8–1.55 (m, 1H, H-9), 1.45–1.10 (m, 3H, H-9, H-10); ^{13}C NMR (125 MHz, 25 °C, $CDCl_3$): δ = 167.40, 136.25, 132.49, 132.13, 132.12 131.15, 126.61, 82.80 , 82.15 , 66.19 , 66.15 , 64.09, 55.24, 51.28, 47.62, 44.97, 43.10, 41.70, 39.28, 39.25, 39.16, 28.41, 28.31, 18.32; MS (EI): $m/z = 224$ (M^+).

***exo*-NBOMA**



^1H NMR (500 MHz, 25 °C, $CDCl_3$): δ = 6.13 (s, 1H, H-12), 5.57 (m, 1H, H-12), 4.26 (t, $^3J = 5$ Hz, 2H, H-9), 3.63 (m, 2H, H-8), 3.39 (d, $^3J = 6.8$ Hz,1H, H-1), 2.32 (d, $^3J = 4.7$ Hz, 1H, H-4), 2.23 (br. s, 1H, H-7), 1.95 (s, 3H, H-13), 1.60–1.35 (m, 5H, H-3, H-5, H-6, H-2), 1.12–0.92 (m, 3H, H-5, H-6, H-7); ^{13}C NMR (125 MHz, 25 °C, $CDCl_3$): δ = 167.37 (C-10), 136.25 (C-11), 125.58 (C-12), 82.84 (C-1), 65.96 (C-9), 64.09 (C-8), 40.35 (C-4), 39.49 (C-7), 35.12 (C-2), 34.83 (C-3), 28.53 (C-5), 24.51 (C-6), 18.31 (C1-3); MS (EI): $m/z = 262$ (M^+).

For experiments conducted in the presence of phenylhydrazine, the latter reagent was added directly onto solid $Cu(OTf)_2$. The resulting brown solid was mixed for ten minutes, and then NB and HEMA were added. The reaction mixture was vigorously stirred for 2 h at room temperature and then heated at 100 °C.

ESR Studies

In a typical experiment, in the glove box, $Cu(OTf)_2$ (2.7×10^{-5} mol, 10.0 mg) was dissolved in degassed CH_3CN (*ca.* 0.4 mL) and added over degassed DCPD (1.1×10^{-4} mol, 15.0 mg) or degassed NB (1.1×10^{-4} mol, 10.0 mg) in a ESR tube. The mixture was heated to 70 °C for the given time period and EPR spectra were recorded at room temperature.

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References

[1] M. Poliakoff, P. Licence, *Nature* **2007**, *450*, 810.
[2] a) *Catalytic Heterofunctionalization*, (Eds.: A. Togni, H. Grützmacher), Wiley-VCH, Weinheim, **2001**; b) M. Beller, J. Seayad, A. Tillack, H. Jiao, *Angew. Chem.* **2004**, *116*, 3448; *Angew. Chem. Int. Ed.* **2004**, *43*, 3368.
[3] *Triflic acid*: a) D. C. Rosenfeld, S. Shekhar, A. Takemiya, M. Utsunomiya, J. F. Hartwig, *Org. Lett.* **2006**, *8*, 4179; b) Z. Li, J. Zhang, C. Brouwer, C.-G. Yang, N. W. Reich, C. He *Org. Lett.* **2006**, *8*, 4175; c) R. T. Mathers, C. LeBlond, K. Damodaran, D. I. Kushner, V. A. Schram, *Macromolecules* **2008**, *41*, 524; d) L. Coulombel, E. Dunach, *Green Chem.* **2004**, *6*, 499; *Sulfonic acid derivatives*: e) P. J. Linares-Palomino, S. Salido, J. Altarejos, A. Sãnchez, *Tetrahedron Lett.* **2003**, *44*, 6651; f) Y. Gu, F. Shi, Y. Deng, *J. Mol. Catal. A: Chem.* **2004**, *212*, 71; *Sulfamic acid*: g) B. Wang, Y. Gu, L. Yang, J. Suo, O. Kenichi, *Catal. Lett*. **2004**, *96*, 71.
[4] *Palladium:* K. M. Gligorich, M. J. Schultz, M. S. Sigman, *J. Am. Chem. Soc.* **2006**, *128*, 2794.
[5] *Platinum*: H. Qian, X. Q. Han, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2004**, *126*, 9536.
[6] *Ruthenium*: a) Y. Oe, T. Ohta, Y. Ito, *Chem. Commun.* **2004**, 1620; b) Y. Oe, T. Ohta, Y. Ito, *Synlett* **2005**, 179.
[7] *Aluminium*: L. Coulombel, M. Rajzmann, J.-M. Pons, S. Olivero, E. Dunach, *Chem. Eur. J.* **2006**, *12*, 6356.
[8] *Gold*: a) C.-G. Yang, C. He, *J. Am. Chem. Soc.* **2005**, *127*, 6967; b) C. G. Yang, N. W. Reich, Z. J. Shi, C. He, *Org. Lett.* **2005**, *7*, 4553; c) X. Zhang, A. Corma, *Chem. Commun.* **2007**, 3080.
[9] *Iron*: a) K. Komeyama, T. Morimoto, Y. Nakayama, K. Takaki, *Tetrahedron Lett.* **2007**, *48*, 3529; b) J.-C. Choi, K. Kohno, D. Masuda, H. Yasuda, T. Sakakura, *Chem. Commun.* **2008**, 777.
[10] *Tin:* a) L. Coulombel, I. Favier, E. Dunach, *Chem. Commun.* **2005**, 2286; b) P. Lemechko, F. Grau, S. Antoniotti, E. Dunach, *Tetrahedron Lett.* **2007**, *48*, 5731.
[11] *Copper*: a) J. G. Taylor, N. Whittall, K. K. M. Hii, *Chem. Commun.* **2005**, 5103; b) K. K. M. Hii, *WO Pat. Appl.* 2007/007084, **2007**.
[12] *Iridium*: V. H. Grant, B. Liu, *Tetrahedron Lett.* **2005**, *46*, 1237.
[13] a) Y. Hoshino, (Denki Kagaku Kogyo Co.), Japanese Patent 2004256765, **2004**; *Chem. Abst.* **2004**; 639130; b) Y. Ubutame, M. Watanabe, (Hitachi Chemical Co.), Japanese Patent 2004161814, **2004**; *Chem. Abst.* **2004**; 472358; c) Y. Ubutame, M. Watanabe, (Hitachi Chemi-

cal Co.), Japanese Patent 2003171430, **2003**; *Chem. Abst.* **2003**; 470523; d) W. D. Weir, (Rohm & Haas Co.), U.S. Patent 6,509,494, **2003**, *Chem. Abst.* **2003**; 53547; e) K. Ogoshi, Y. Ubutame, (Hitachi Chemical Co.), Japanese Patent 2002020441, **2004**; *Chem. Abst.* **2002**; 63525; f) S. Iwasa, K. Maeda, E. Hasegawa, (NEC Corp. Japan), U.S. Patent 6,437,052, *Chem. Abst.* **2000**; 344470; g) T. Aoki, Y. Namatame, K. Tanaka, (Hitachi Chemical Co.), Japanese Patent 09059330, *Chem. Abst.* **1997**; 303048; h) T. Aoki, Y. Namatame, (Hitachi Chemical Co.), Japanese Patent 08193108, *Chem. Abst.* **1996**; 618138; i) K. Tanaka, Y. Namatame, T. Aoki, (Hitachi Chemical Co.), Japanese Patent 08193109, *Chem. Abst.* **1996**: 595817; j) K. Tanaka, T. Aoki, Y. Namatame, (Hitachi Chemical Co.), Japanese Patent 08059761, *Chem. Abst.* **1996**; 345506; k) F. Tashiro, K. Nomaguchi, (Hitachi Chemical Co.), Japanese Patent 03093864; *Chem. Abst.* **1992**; 7977; l) F. Tashiro, K. Nomaguchi, (Hitachi Chemical Co.), Japanese Patent 03066765; *Chem. Abst.* **1991**; 34791; m) J. A. Lavelle, (Rohm & Haas Co.), *Chem. Abst.* **1986**; 554249; n) Hitachi Chemical Co. , Japanese Patent 58179214; *Chem. Abst.* **1984**; 175904; o) W. D. Emmons, K. Nyi, (Rohm & Haas Co.; *U.S. Patent* 4,261,872, *Chem. Abst.* **1981**; 463875; p) Rohm & Haas Co, NL Patent 7806577; *Chem. Abst.* **1980**; 40957.

[14] a) K. Nyi, A. W. Kohr, (Rohm & Haas Co.), U.S. Patent 4,140,724, **1979**; b) W. D. Emmons, K. Nyi, (Rohm & Haas Co.), U.S. Patent Appl. 4,097,677; *Chem. Abst.* **1978**; 616935.

[15] a) T. Akima, A. Kobayashi, S. Akihiro, T. Saito T. Fujita, (Hitachi Chemical Co.), Japanese Patent 02101044; *Chem. Abst.* **1990**; 554770; b) T. Aoki, Y. Namatame, (Hitachi Chemical Co.), Japanese Patent 08193108; *Chem. Abst.* **1996**; 618138; c) K. Tanaka, Y. Namatane, T. Aoki, (Hitachi Chemical Co.), Japanese Patent 08193109, *Chem. Abst.* **1996**; 595817; d) Y. Okamoto, (Sanyo-Kokusaku Pulp Co.), Japanese Patent 62081378, *Chem. Abst.* **1988**; 132450.

[16] Hitachi Chemical Co. , Japanese Patent 57200331; *Chem. Abst.* **1983**; 422009.

[17] a) R. W. Marshmann, *Aldrichimica Acta* **1995**, *28*, 77; b) S. Kobayashi, M. Sugiura, H. Kitagawa, W. W.-L. Lam, *Chem. Rev.* **2002**, *102*, 2227; c) M. Shibasaki, N. Yoshikawa, *Chem. Rev.* **2002**, *102*, 2187, and references cited therein.

[18] The formation of the ether product of HEMA was independently confirmed from an authentic sample. The formation of DCPD oligomers was supported by GLC-MS analysis of a reaction mixture of DCPD and TfOH treated at 80 °C for 2 h. In addition to these two main side-products, minor amounts of transesterification and/or hydrolysis products of HEMA, that is, methacrylic acid, ethylene glycol, as well as the addition product of ethylene glycol across DCPD, were also detected.

[19] T. C. Wabnitz, J.-Q. Yu, J. B. Spencer, *Chem. - Eur. J.* **2004**, *10*, 484.

[20] J. Nie, H. Kobayashi, T Sonada, *Catal. Today* **1997**, 36, 81.

[21] For the use of $Co(N(Tf)_2)_2$-$HNTf_2$ in Friedel–Crafts acylation reactions, see: M. J. Earle, U. Hakala, B. J. McAuley, M. Nieuwenhuyzen, A. Ramani, K. R. Seddon, *Chem. Commun.* **2004**, 1368.

[22] I. A. Koppel, R. W. Taft, F. Anvia, S.-Z. Zhu, L.-Q. Hu, K.-S. Sung, D. D.; DesMarteau, L. M. Yagupolskii, Y. L. Yagupolskii, N. V. Ignat′ev, N. V. Kondratenko, A. Y. Volkonskii, *J. Am. Chem. Soc.* **1994**, 116, 3047.

[23] T. C. Wabnitz, J. B. Spencer, *Org. Lett.* **2003**, *5*, 2141.

[24] a) J.-S. Wang, K. Matyjaszewski, *Macromolecules* **1995**, *28*, 7572, and references cited therein; b) D. M. Haddleton, A. J. Clark, M. C. Crossman, D. J. Duncalf, A. M. Heming, S. R. Morsley, A. J. Shooter, *Chem. Commun.* **1997**, 1173.

[25] H. C. Brown, B. Kanner, *J. Am. Chem. Soc.* **1966**, *88*, 986.

[26] K. E. Nosova, E. V. Tretyakov, G. V. Romanenko, V. I. Ovcharenko, *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 2231.

[27] a) S. K. Ginotra, V. K. Singh, *Tetrahedron* **2006**, *62*, 3573; b) V. D. M. Hoang, P. A. N. Reddy, T.-J. Kim, *Organometallics* **2008**, 27, 1026; c) M. B. Andrus, X. Chen, *Tetrahedron* **1997**, *53*, 16229.

[28] a) A. N. Vedernikov, K. G. Caulton, *Chem. Commun.* **2004**, 162; b) K. Sreenath, C. V. Suneesh, V. K. Ratheesh Kumar, K. R. Gopidas, *J. Org. Chem.* **2008**, 73, 3245.

[29] A similar resonance, slightly shifted due to the absence of paramagnetic Cu(II), is observed on mixing TfOH and DCPD at room temperature.

[30] GLC-MS analyses of this mixture and attempts at isolating organic products from larger scale reactions failed also.

[31] J.-F. Croisy, P. Grosius, (Norsolor SA), European. Patent 0360628, **1990**.

[32] Considering the large (1000-fold) excess of reagents with catalyst loadings as low as 0.1 mol%, the presence of *ca.* 250 ppm of stabilizers in such reagents provides amounts of phenolic derivatives theoretically sufficient to generate TfOH from $Cu(OTf)_2$.

