empirical absorption corrections (Ψ scan, min. transmission 94.56%). The structure was solved by direct methods and refined with the full-matrix, least-squares method; $R_1 = 0.0398$, $wR_2 = 0.0729$ (for 4037 reflections with $I > 2\sigma(I)$), $R_1 = 0.0626$, $wR_2 = 0.0859$ (for all 5207 data); data-to-parameter ratio 15.04; residual electron density $+0.349/-0.343$ e Å^{-3}. **6**: crystals from pentane at 0 °C, $C_{32}H_{38}OPRh$ (572.50); crystal size $0.4 \times 0.3 \times 0.2$ mm; monoclinic, space group $P2_1/c$ (no. 14), $a = 9.753(3)$, $b = 13.384(4)$, $c = 20.914(6)$ Å, $\beta = 95.998(14)°$, $Z = 4$, $V = 2714.9(14)$ Å^3, $\rho_{calcd.} = 1.401$ g cm^{-3}; $T = 173(2)$ K; $2\Theta = 50°$; 3569 reflections measured, 3473 were unique ($R_{int} = 0.0328$) and 2619 observed ($I > 2\sigma(I)$); Enraf-Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated, zirconium filter (factor 16.4); Lp and empirical absorption corrections (Ψ scan, min. transmission 96.85%). The structure was solved by direct methods and refined with the full-matrix, least-squares method; $R_1 = 0.0348$, $wR_2 = 0.0604$ (for 2619 reflections with $I > 2\sigma(I)$), $R_1 = 0.0602$, $wR_2 = 0.0683$ (for all 3473 data); data-to-parameter ratio 10.24; residual electron density $+0.239/-0.240$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102818 (**5**) and CCDC-102919 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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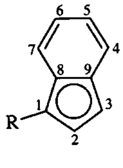
[12] Abbreviations used: vt = virtual triplet, dvt = doublet of virtual triplets, $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^1J(P,C) + {}^3J(P,C)$.

[13] For the numbering of the indenyl carbon (and corresponding hydrogen) atoms see formula **A**.



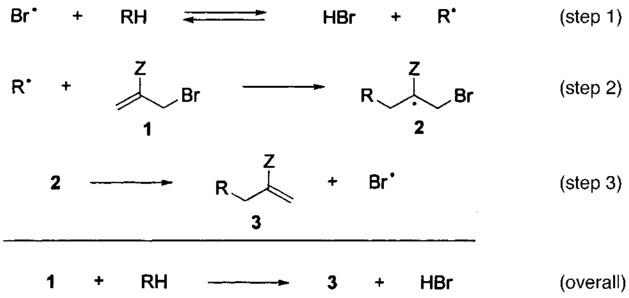
A

Functionalization of Hydrocarbons by a New Free Radical Based Condensation Reaction[**]

James. M. Tanko[*] and Mitra Sadeghipour

There is increased awareness of the need to develop new chemical reactions and processes which avoid the use or generation of toxic and/or environmentally threatening materials. Herein we report a newly developed reaction in which a C–H bond of a hydrocarbon is converted into a C–C bond by transfer of an allyl group (R–H → R–C–C=C). This process is especially attractive because (unlike other procedures which effect this conversion) the transformation is accomplished in a single step and does not require strongly acidic or basic reaction conditions, or the use of heavy metals.

The proposed mechanism of this reaction is depicted in Scheme 1. Abstraction of hydrogen from R–H (by Br$^\bullet$) yields R$^\bullet$, which subsequently adds to the C=C bond of a substituted allyl bromide (**1**). Adduct radical **2** undergoes β cleavage to yield product **3** and regenerate Br$^\bullet$. Each step depicted in Scheme 1 is well documented in the literature: A bromine atom exhibits high selectivity in hydrogen atom abstractions (step 1),[1] and is especially reactive towards benzylic hydrogen atoms (for example in the Ziegler bromination).[2] Allyl bromides have been shown to be effective chain transfer reagents in free radical polymerizations, essentially by steps identical to 2 and 3.[3]



Scheme 1. Mechanism of the proposed allyl transfer reaction.

To test whether this chemistry could be coupled as shown in Scheme 1 to "invent" a viable synthetic process, we examined the reaction of several allyl bromides with toluene and cumene (Table 1). Overall, mass balances for these reactions were high, and good to excellent yields were obtained, especially when the allyl bromide possesses a radical-stabilizing substituent (e.g., Z = Ph, CO_2Et, or CN). To confirm the role of Br$^\bullet$ as the chain carrier in this reaction, a series of competition experiments were performed pitting $PhCH_3$

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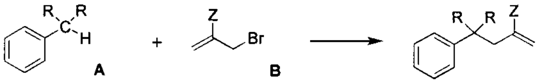
[**] Financial support from the National Science Foundation (CHE-9524986) is acknowledged and appreciated.

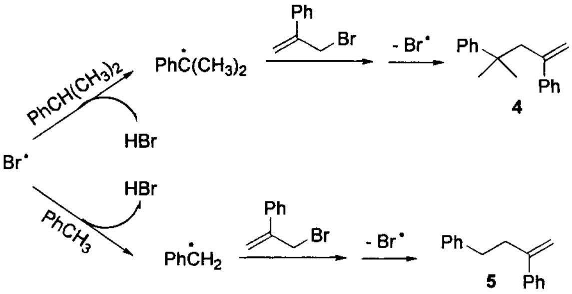
Table 1. Reactions of alkylarenes with substituted allyl bromides.



R	Z	**A**[a] [mmol]	**B** [mmol]	Initiator[b]	T [°C]	t [h]	HBr trapping reagent[c]	Yield [%]
H	H	47	0.69	DTBPO	120	94	1,2-epoxybutane	33
H	Ph	47	0.72	DTBPO	120	93	K_2CO_3	82
H	Ph	2.8[d]	0.72	DTBPO	120	93	K_2CO_3	24
CH_3	Ph	36	0.72	DTBPO	120	93	K_2CO_3	100
CH_3	Ph	1.4[d]	0.72	$(t\text{BuO})_2$	120	93	K_2CO_3	66
H	CO_2Et	47	0.77	$(PhCO_2)_2$	80	40	K_2CO_3	47
CH_3	CO_2Et	36	0.77	DTBPO	120	94	K_2CO_3	48
H	CN	38	0.77	$(PhCO_2)_2$	80	2	1,2-epoxybutane	66
CH_3	CN	29	0.77	DTBPO	120	2	1,2-epoxybutane	80

[a] Neat, when not stated otherwise. [b] 20 mol%. [c] 1.1 equiv. [d] In 5 mL of benzene.

against $PhCH(CH_3)_2$ for $Br^{\bullet}$ generated by reaction with a) α-(bromomethyl)styrene (α-BMS, Scheme 2) and b) molecular bromine.



Scheme 2. Competition experiments to establish $Br^{\bullet}$ as the chain carrier.

The results (Table 2) reveal that for reactions of α-BMS, the ratio of products formed from the tertiary and primary radicals (r(3°/1°)) decreases with increasing concentration of the HBr scavenger (1,2-epoxybutane), and levels off to a value of 25 at high concentrations. This variation in selectivity is readily explained by the fact that hydrogen abstractions by $Br^{\bullet}$ are reversible,[4] and at high scavenger concentrations the reverse reaction is effectively eliminated. The fact that r(3°/1°) observed for α-BMS is identical to that observed for the free radical bromination of these substrates with Br_2 confirms the role of $Br^{\bullet}$ as chain carrier in accordance with Scheme 1.

Relative rate constants k_{rel} for the addition of $PhCH_2^{\bullet}$ to several allyl bromides (Scheme 1, step 2: $R^{\bullet} = PhCH_2^{\bullet}$) were also determined from competition experiments at 80 °C: $k_{rel} = 180\ (Z = CN) > 110\ (Z = CO_2Et) > 65\ (Z = Ph) > 1.0\ (Z = H)$. The observed substituent effect is very similar to that reported by Fischer et al. for addition of $PhCH_2^{\bullet}$ to substituted alkenes.[5]

Table 2. Observed selectivity in the reaction of toluene and cumene with α-(bromomethyl)styrene (α-BMS) and Br_2.

$Br^{\bullet}$ source	1,2-epoxybutane [equiv]	r(3°/1°)[a] (80 °C)
α-BMS	0.05	50
α-BMS	0.10	48
α-BMS	0.50	34
α-BMS	1.10	25
α-BMS	2	25
Br_2	1.1	26

[a] For α-BMS: r(3°/1°) = (yield(**4**)/yield(**5**)) × 3; for Br_2: r(3°/1°) = (yield($PhCBr(CH_3)$)/yield($PhCH_2Br$)) × 3.

Although the reactivity order is the same, additions of benzyl radical to $CH_2{=}C(Z)CH_2Br$ are much less sensitive to the nature of the substituent Z. A plot of $\lg(k_{rel})$ for the addition of benzyl radical to substituted allyl bromides versus $\lg(k_{C=C})$ yields a line whose slope ($m = 0.49$) is considerably less than unity. The diminished sensitivity to the effect of substituent Z in radical additions to $CH_2{=}C(Z)CH_2Br$ may be an indication that the resulting β-bromo radical adduct is stabilized by Br, presumably by bridging.[6] Further work is needed to confirm this hypothesis.

Kinetic chain lengths (i.e., rate of product formation relative to rate of initiator dissappearance $(d[\text{product}]/dt)/(-2\,d[In_2]/dt)$)[7] were determined by monitoring product yields as a function of time. The profile for reaction of toluene (38 mmol, neat) with α-BMS (0.56 mmol) initiated by 20% di-*tert*-butyl peroxide (DTBPO) at 120 °C is depicted in Figure 1. The initial chain length for this reaction was high (400), and a

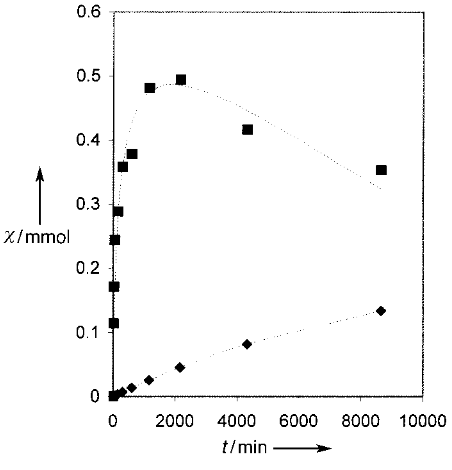
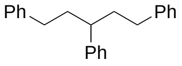


Figure 1. Amount x of product (■) and initiator radical $In^{\bullet}$ produced (◆) in the reaction of toluene (38 mmol, neat) and α-(bromomethyl)styrene (0.56 mmol) initiated by di-*tert*-butyl peroxide at 120 °C.

90 % yield of product was obtained within 24 hours (note that the half-life $t_{1/2}$ for DTBPO at 120 °C is 10^3 min). At longer reaction times, the yield of the product decreased because the C=C bond of the product is also susceptible to radical addition. At longer reaction times, **6** was detected as a byproduct by GC/MS analysis.



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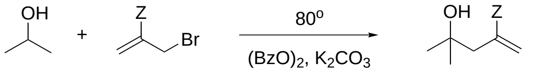
Similar results were obtained for other systems (Table 3). Generally, the effect of substituent Z on the chain length tends to parallel the reactivity of the allyl bromide towards $PhCH_2^{\bullet}$ (i.e., Z = CN ≥ CO_2Et > Ph > H), and the chain lengths for $PhCH_3$ are greater than for $PhCH(CH_3)_2$. These observations suggest that the addition of the benzylic radical to the C=C bond is likely the rate-determining step of this reaction.[8]

Table 3. Initial chain lengths for reaction of alkylarenes (neat) with allyl bromides (120 °C, $(tBuO)_2$ as initiator).

Z	R	Initial chain length	Z	R	Initial chain length
H	H	10			
Ph	H	400	Ph	CH_3	60
CO_2Et	H	800	CO_2Et	CH_3	60
CN	H	700	CN	CH_3	400

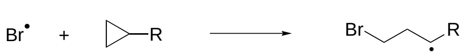
This reaction was extended to other substrates possessing reactive C–H bonds (e.g., secondary alcohols).[9] Reaction of *i*PrOH (1.56 M) with α-BMS (0.14 M) in benzene produces the tertiary alcohol **7a** in 60 % yield [Eq. (1)]. A similar reaction of *i*PrOH (2.0 M) with α-bromoacrylonitrile (0.2 M) results in a 54 % yield of **7b**.



(1)

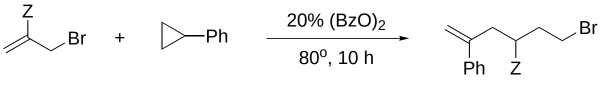
7a: Z = Ph (60%)
7b: Z = CN (54%)

Finally, $Br^{\bullet}$ is also known to be reactive towards cyclopropanes, yielding ring-opened products by an S_H2 process: $Br^{\bullet}$ attack occurs at the least-hindered carbon atom of the cyclopropane (with inversion of configuration) to provide the most stable radical [Eq. (2)].[10]



(2)

Reaction of phenylcyclopropane (32 mmol, neat) with α-BMS (0.56 mmol) results in a 57 % yield of 6-bromo-2,4-diphenylhex-1-ene [**8a**, Eq. (3)], with 43 % of the starting material remaining unchanged. In benzene (0.72 mmol of α-BMS and 7.2 mmol of C_6H_5-*c*-C_3H_5 in 4 mL of solvent), the yield decreases to 42 % (44 % unchanged starting material). Similar reaction of phenylcyclopropane (32 mmol, neat) with α-bromoacrylonitrile (0.77 mmol) produces **8b** in quantitative yield. In benzene (1 mmol of α-bromoacrylonitrile and 10 mmol of phenylcyclopropane in 3.7 mL of benzene), the yield decreased to 85 %). This reaction of an allyl bromide with a cyclopropane is especially attractive in that it provides a simple one-step synthesis of Δ^5-hexenyl bromides, which are excellent precursors for the formation of five- and six-membered rings by radical reactions with R_3MH (M = Ge, Sn, Si).[11]



(3)

8a: Z = Ph (57%)
8b: Z = CN (100%)

In summary, a new reaction has been developed for the allylation of a hydrocarbon (and other substrates) by a free radical chain process involving a bromine atom. This reaction is unique in that it accomplishes this transformation in a single step in an environmentally benign manner, thereby demonstrating that "green chemistry" does not necessarily mean that high reaction yields and selectivites have to be compromised.

Experimental Section

In a typical procedure, the hydrocarbon, allyl bromide, the initiator, the solvent (if used), and an HBr scavenger (e.g., K_2CO_3 or epoxide) were combined in a 30-mL pressure tube. The resulting mixture was deoxygenated (three cycles of freeze-pump-thaw) and placed in a heated oil bath. Afterward, the reaction mixture was filtered, washed with saturated $NaHCO_3$, and concentrated. The crude product was further purified by either preparative TLC or HPLC. All products were fully characterized by IR, UV, ^1H NMR, and ^{13}C NMR spectroscopy, mass spectrometry, and either elemental analysis or high-resolution mass spectrometry. Typical reaction conditions and quantities of materials are summarized in Table 1.

Received: July 9, 1998 [Z 12122 IE]
German version: *Angew. Chem.* **1999**, *111*, 219–222

Keywords: bromine · C–C coupling · radical reactions · radicals · reaction mechanisms

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