is also blue-shifted by about 8 nm versus that of radialene **12**. There is little doubt, however, that in all three molecules this absorption band is due to the linearly conjugated ene–yne–yne–ene segment.

The slight bathochromic shift of the lowest energy absorption of radialene **12** relative to **13** or **15** is interesting as it could signify an increased contribution from cross- or homoconjugation to the overall electronic communication that results from the constricted interior yne–ene–yne bond angles of **12** relative to those of **15**.[15] At this point, however, it can not be ruled out that this red shift results from inductive effects or the increased planarity and/or ring strain of **12** versus **15**. However, these explanations seem less likely, given the similar absorption spectra of **13** and **15** (Figure 2). Additional model compounds are now being synthesized in an effort to resolve this question.

The synthesis and characterization of radialenes **5** and **12** provides preliminary details of the electronic properties of these cross-conjugated enyne macrocycles. The hexameric radialene **5**, with nearly optimal sp^2 interior bond angles, shows no enhanced π-electron delocalization attributable to homoconjugation, as shown by comparison with acyclic iso-PDA analogues. The absorption spectrum of hybrid radialene **12**, however, suggests that a reduction of the interior bond angles could lead to additional electronic effects in these molecules that ultimately result in a red shift of the lowest energy absorption. The syntheses of the tri-, tetra-, and pentameric members of this new class of expanded radialenes represented by hexamer **5** are currently being conducted. The more rigorously planar structure of these smaller rings and the smaller interior bond angles promise to provide a more detailed view of the π-electron delocalization in expanded radialenes.

Received: December 4, 1998 [Z12750IE]
German version: *Angew. Chem.* **1999**, *111*, 2138–2141

Keywords: conjugation · cross-coupling · enynes · macrocycles · radialenes

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[17] The trimethylsilyl group of **14** was selectively removed with methanolic K_2CO_3 to give the terminal alkyne, which was then oxidatively coupled[10] to give **13** as a colorless solid.

[18] Vinyl triflate **6** was coupled with 1,10-undecadiyne to give the tethered bis-enediyne **16**. Protodesilylation of **16** gave the terminal alkynes, which were then oxidatively coupled[10] to give **15** as a white solid.

A New Radical Vinylation Reaction of Iodides and Dithiocarbonates**

Frédérique Bertrand, Béatrice Quiclet-Sire, and
Samir Z. Zard*

Aryl and vinyl halides can be coupled to vinylic or acetylenic groups by a number of reactions mediated by transition metals, particularly palladium.[1] In contrast, the analogous direct reaction with aliphatic halides is much more limited and remains a challenge in organic synthesis.[1e] Recently, an attempt to fill this gap was reported by Bräse, Waegell, and de Meijere,[2] but the scope of their study remains limited to bromoadamantane so far. Radical arylations and vinylations are more useful,[3] especially when such groups are delivered internally. Intermolecular addition–elimination is more sensitive to competing side reactions but can

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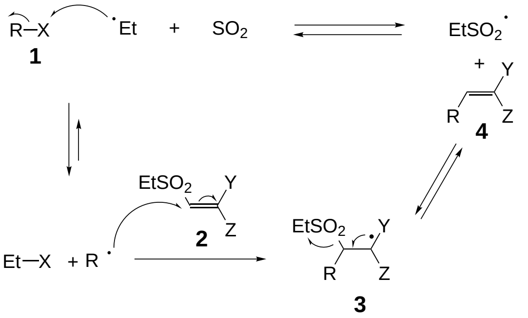
[**] We wish to thank Rhône-Poulenc for generous financial support to one of us (F.B.) and Dr. Virginie Pévère (of Rhône-Poulenc) for many friendly discussions.

be made efficient by the use of activated olefinic partners.[4] Almost all of these approaches hinge upon organotin derivatives. We now report a new method for the alkenylation and, indirectly, the alkynylation of aliphatic iodides and dithiocarbonates (xanthates) by a radical mechanism which is based on sulfone chemistry and does not involve heavy metals.

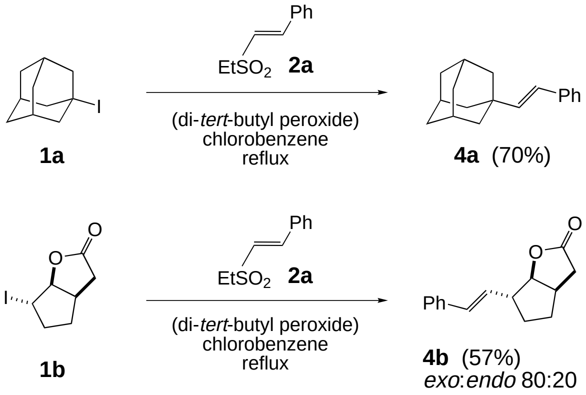
Our concept is based on the generation of radicals under conditions where the main side reactions are made either degenerate or strongly reversible. This gives the intermediate radical a sufficient lifetime to react with hindered sulfones. The system, outlined in Scheme 1, is designed in such a way that a chain reaction can nevertheless be propagated. The coproducts are sulfur dioxide and ethyl iodide or ethyl xanthate, depending on the starting material used.



Scheme 1. Radical reaction of an aliphatic iodide or xanthate **1** with an ethyl vinyl sulfone **2**, X = I, SCSOEt.

We have previously found that allyl ethyl sulfone can act by a similar mechanism as an allylating reagent for aliphatic and alicyclic iodides and xanthates;[5] however, whereas transfer of an allyl group requires an addition–fragmentation sequence on an unhindered terminal carbon, a similar introduction of a vinyl group is significantly more difficult as it implies radical addition on the same terminus of the alkene bearing the sulfone group. Additions to unsubstituted phenyl vinyl sulfone are known to occur from the least hindered and electronically more activated carbon, located β to the sulfone.[6] However, a few scattered reports suggest that if the β carbon is substituted by, for example an aryl group, then radical addition can take place at the desired α site, followed by expulsion of the sulfonyl radical. Early work by Russell et al.[7] with an organomercury derivative as the radical source was followed recently, and concurrently with our own efforts, by an elegant and more extensive study of unsaturated trifluoromethyl sulfones (triflones) by Fuchs and his collaborators.[8] The highly electron withdrawing triflone group appears to activate strongly the desired α position but, because the radical is mostly created by hydrogen abstraction by the highly electrophilic trifluoromethyl radicals, the method remains limited to relatively simple substrates (usually the solvent). The difficult problem of regioselectivity must thus be addressed if the reaction is to be applied to more complex, multifunctionalized molecules.

To establish the feasibility of the radical vinyl coupling to iodides, we prepared ethyl 2-phenylvinyl sulfone (**2a**) by radical addition of ethylsulfonyl chloride to styrene followed by elimination of HCl according to the procedure of Truce and Goralski.[9] Upon heating a chlorobenzene solution of **2a** and 1-iodoadamantane (**1a**) in the presence of di-*tert*-butyl peroxide as the initiator, a smooth reaction occurred to give the desired benzylidene derivative **4a** in 70% yield (Scheme 2). In the same way, iodolactone **1b** provided **4b** in 57% yield (72% yield based on recovered starting material) as an 80:20 mixture of *exo* and *endo* epimers.

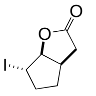
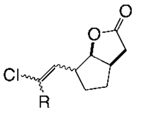
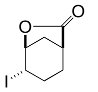
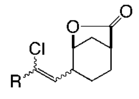
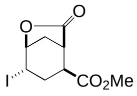
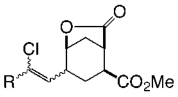
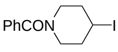
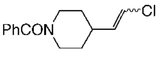
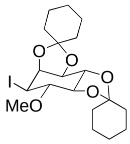
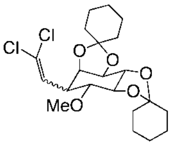
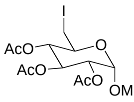
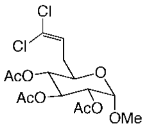


Scheme 2. Phenylvinylation of iodides with ethyl 2-phenylvinyl sulfone (**2a**).

For this approach to have some generality, groups other than aryl must be tolerated. In the first instance, we considered the introduction of a 2,2-dichlorovinyl unit with 2,2-dichlorovinyl ethyl sulfone (**2b**),[10] where the two chlorine atoms would hinder attack from the unwanted β site. We were initially dismayed to find that when **1b** was subjected to the same reaction conditions in the presence of **2b**, the desired reaction proceeded poorly and the reaction mixture darkened ominously. However, upon repeating the reaction in a refluxing heptane/chlorobenzene mixture (6/1) with lauroyl peroxide as the initiator (more suitable at this lower reaction temperature), the iodine atom was replaced by a dichlorovinyl group to give **4c** in 64% yield (76% yield based on recovered starting material) and high selectivity (*exo*:*endo* 85:15).[11] A number of other substrates were subjected to the same transformation (Table 1). We were also pleasantly surprised to find that even a chlorovinyl group can be introduced with relative ease (**4c′**, **4d′**, **4e′**, **4f**). Why, in the case of the chlorovinyl sulfone **2c**, the regioselectivity of the radical attack is still mostly on the α carbon (with respect to the sulfone) is not clear and raises the question of the extent (and mode) of activation of the α and β positions by a sulfone group. It is possible that an addition–elimination process with formation of highly reactive chlorine atoms took place on the β terminus in the case of **2c** because the reaction mixture darkened even under these milder conditions.

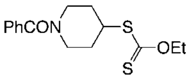
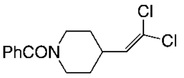
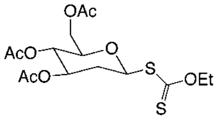
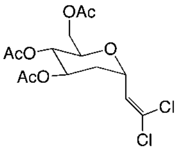
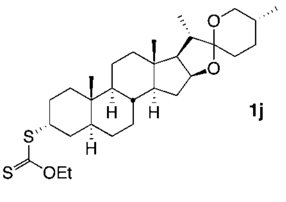
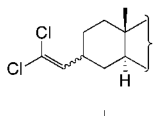
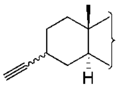
Transfer of dithiocarbonates (xanthates)[12] is akin to that of iodides, and the same vinylation reaction can be performed with such substrates (Table 2). Xanthates can be made by substitution of halides with potassium or sodium *O*-alkylxanthate or, more importantly, by a radical xanthate transfer reaction which is itself a carbon–carbon bond forming process.[12] The latter possibility is exemplified by the synthesis of **1l** from xanthate **1k** and allyl acetate; this reaction is

Table 1. Radical chlorovinylation and dichlorovinylation of iodides.

Iodide **1**	Y in vinyl sulfone **2** with Z = Cl	Product **4**	Yield [%][a] isomers
 **1b**	Cl (**2b**) H (**2c**)	 **4c**, R = Cl **4c'**, R = H	64 (76) *exo*:*endo* 85:15 75 three isomers 55:37:8
 **1c**	Cl (**2b**) H (**2c**)	 **4d**, R = Cl **4d'**, R = H	69 *exo*:*endo* 20:80 79 four isomers 35:25:25:15
 **1d**	Cl (**2b**) H (**2c**)	 **4e**, R = Cl **4e'**, R = H	88 *exo*:*endo* 30:70 67 four isomers 55:35:5:5
 **1e**	H (**2c**)	 **4f**	49 (64) *trans*:*cis* 55:45
 **1f**	Cl (**2b**)	 **4g**	39 α:β 35:65
 **1g**	Cl (**2b**)	 **4h**	19 (46)

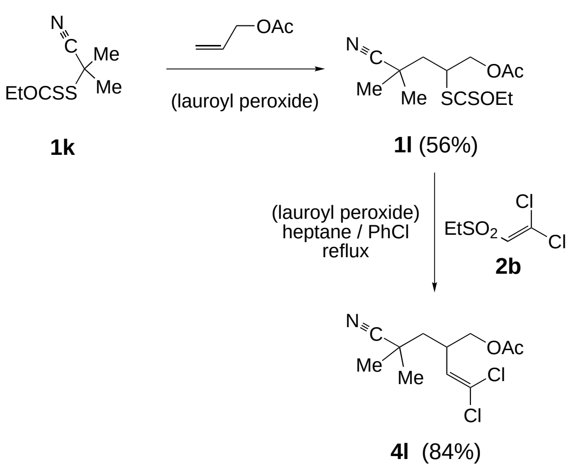
[a] The yields based on recovered starting material are given in parentheses.

Table 2. Radical dichlorovinylation of xanthates.

Xanthate **1**	Product **4**	Yield [%] isomers
 **1h**	 **4i**	76
 **1i**	 **4j**	68 < 5% β-Isomer
 **1j**	 **4k**	57 α:β 2:1
	1) BuLi 2) NH$_4$Cl  **5**	100 α:β 2:1

followed by the efficient (84%) exchange of the xanthate group by a dichlorovinyl group (Scheme 3).

The possibility of introducing a monochloro, dichloro-, and other substituted vinyl unit into aliphatic or alicyclic iodides or xanthates with cheap, readily available ethyl vinyl sulfone reagents opens up tremen-



Scheme 3. Xanthate transfer followed by radical dichlorovinylation.

dous opportunities for synthetic planning. The reaction works well with secondary and tertiary derivatives, but is less efficient with primary substrates (for example, **1g**) because the corresponding primary radical has a similar stability to the ethyl radical used to generate it. Both the monochloro and dichlorovinyl groups are immediate precursors of an acetylide anion by exposure to a simple base or butyllithium, respectively, in the Corey–Fuchs reaction.[13] This is illustrated by the quantitative conversion of **4k** into alkyne **5** (Table 2). The dichlorovinyl motif also serves as a source of chloroalkynes by exposure to base.[14] Chloroalkynes and both the monochloro- and dichlorovinyl derivatives are substrates for various transition metal induced couplings.[1] Moreover, ongoing preliminary studies seem to indicate that the vinyl sulfone reagent can be substituted in various other ways to provide a convergent, flexible strategy for the rapid assembly of complex structures.

Experimental Section

Typical procedures are as follows:

Procedure A: A solution of iodide **1a**, **b** (1 mmol) and ethyl vinyl sulfone **2a** (3 mmol) in degassed chlorobenzene (2 mL) was heated under reflux and treated portionwise with di-*tert*-butyl peroxide (3 to 4 drops) over 12–16 h. The solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography on silica gel to furnish the desired products **4a**, **b**.

Procedure B: A solution of iodide or xanthate **1b–j** (1 mmol) and ethyl vinyl sulfone **2b**, **c** (3 mmol) in degassed heptane/chlorobenzene (6/1, 2 mL) was heated under reflux and treated portionwise by lauroyl peroxide (0.12–0.3 mmol) over 5–12 h. The solvent was evaporated under reduced pressure, and the crude residue was purified by column chromatography on silica gel to give the desired products **4c–k**. With **2b** as sulfone, prior treatment for a few minutes with aqueous ammonia (to destroy excess sulfone) can sometimes simplify purification.

Received: December 21, 1998 [Z12810IE]
German version: *Angew. Chem.* **1999**, *111*, 2135–2138

Keywords: alkenes · allylation · C–C coupling · radical reactions · vinyl sulfones

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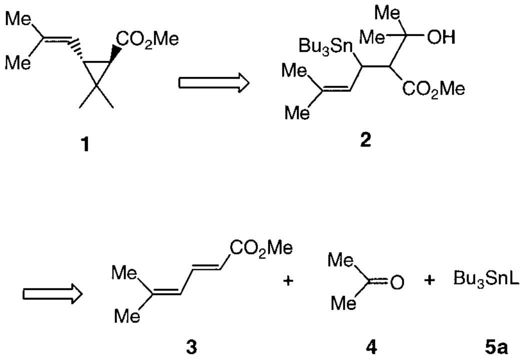
Metal-Mediated, Completely Diastereofacial Conjugate Addition of Trialkylstannylmetal Reagents to γ-Alkoxy-α,β-Unsaturated Esters[**]

Alain Krief,[*] Laurent Provins, and Willy Dumont

Dedicated to Professor L. Ghosez
on the occasion of his 65th birthday

A few years ago, we disclosed an efficient "three-component" synthesis of *trans*-methyl chrysanthemate **1** which allows the construction of the cyclopropane ring by insertion of the isopropylidene moiety arising from acetone **4** (Scheme 1).[1] We wanted to extend this strategy to the



Scheme 1. Synthesis of (1*R*)-*trans*-methyl chrysanthemate from a dienoic ester, acetone, and tributylstannyllithium.

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[**] F.R.I.A. (Fonds pour la Formation à la Recherche dans l'Industrie et dans l'Agriculture) is greatly acknowledged for financial support of this work (fellowship to L.P.).

1433-7851/99/3813-1946 $ 17.50+.50/0