After 1 h, the product was hydrolyzed (2 N H_2SO_4, 6 mL, 6 mmol). The aqueous layer was saturated with anhydrous potassium carbonate and extracted with ether (4 × 5 mL). Removal of ether produced 1.43 g of 2,2-dimethylpropanol, 81% yield: mp 52–53 °C [lit.[21] mp 52–53 °C].

The same procedure was followed for the reduction of other esters (Table IV).

Acknowledgment. We thank the U. S. Army Research Office (Durham) (Grant ARO DAAG-29-82-K-0047) for finalcial support of this study.

Registry No. $LiBH_4$, 16949-15-8; *B*-MeO-9-BBN, 38050-71-4; $B(OMe)_3$, 121-43-7; $CH_3(CH_2)_4C(O)OEt$, 123-66-0; PhC(O)OEt, 93-89-0; $(CH_3)_3CC(O)OEt$, 3938-95-2; $CH_3(CH_2)_{16}C(O)OMe$, 112-61-8; 1-AdC(O)OEt, 2094-73-7; *p*-$ClC_6H_4C(O)OEt$, 7335-27-5; $Cl(CH_2)_2C(O)OEt$, 623-71-2; *p*-$NO_2C_6H_4C(O)OEt$, 99-77-4; $CH_3(CH_2)_5OH$, 111-27-3; $CH_3(CH_2)_{17}OH$, 112-92-5; $(CH_3)_3C$-CH_2OH, 75-84-3; 1-$AdCH_2OH$, 770-71-8; $PhCH_2OH$, 100-51-6; *p*-$ClC_6H_4CH_2OH$, 873-76-7; $HO(CH_2)_3Cl$, 627-30-5; *p*-$NO_2C_6H_4CH_2OH$, 619-73-8; $CH_3(CH_2)_7CH{=}CH_2$, 872-05-9; $LiEt_3BH$, 22560-16-3; Li-9-BBNH, 76448-08-3; $LiEt_3BOMe$, 81130-65-6; $LiB(OMe)_2$-9-BBN, 81095-46-7; BF_3·OEt_2, 109-63-7; BH_3·THF, 14044-65-6; *n*-Bu_3B, 122-56-5; *n*-octB$(OMe)_2$, 81044-43-1; $(PhO)_3B$, 1095-03-0; $(n\text{-DodO})_3B$, 2467-15-4; $CH_3(CH_2)_4$-CO_2H, 142-62-1; $CH_3C(O)ONa$, 127-09-3; PhCN, 100-47-0; Ph-$C(O)NMe_2$, 611-74-5; $CH_3(CH_2)_7Br$, 111-83-1; $CH_3(CH_2)_7OTs$, 3386-35-4; Me_2S, 75-18-3; Me_2SO, 67-68-5; *n*-Bu_2SO_2, 598-04-9; ethyl cyclohexanecarboxylate, 3289-28-9; (hydroxymethyl)cyclohexane, 100-49-2; 7-oxabicyclo[4.1.0]heptane, 286-20-4.

Vinyl Sulfone Bicycloannulation of Cyclohexenones: One-Step Synthesis of Tricyclo[3.2.1.$0^{2,7}$]octan-6-ones

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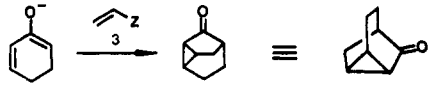
Vinyl sulfones bicycloannulate the α'-enolates of α-cyclohexenones in the presence of hexamethylphosphoramide in refluxing tetrahydrofuran to give tricyclo[3.2.1.$0^{2,7}$]octan-6-ones in a single synthetic step. In the case of β-methylcyclohexenones this method gives higher yields than vinylphosphonium bicycloannulation, but with α-methylcyclohexenones the opposite is true. The reaction is successful with both aryl vinyl sulfones and aryl isopropenyl sulfones, but the presence of electron-withdrawing para substituents on the aromatic ring was found to be disadvantageous. Based on the isolation of intermediates and side products, the mechanism of the bicycloannulation is believed to proceed via sequential conjugate addition of the enolate to the vinyl sulfone, intramolecular Michael addition, and expulsion of arene sulfinate anion with formation of the cyclopropane ring.

Efficient construction of polycyclic systems remains one of the greatest challenges of organic synthesis. As part of a program directed toward the discovery and development of new methodology for the formation of polycyclic structures in a single synthetic step from acyclic and monocyclic precursors by bicycloannulation,[1] we have reported a series of methods for the bicycloannulation of cyclohexenes[2] and cyclohexenones,[3] providing tricyclo[3.2.1.$0^{2,7}$]octanes in a one-pot operation. This tricyclic ring system (1) is a salient feature of four terpene families,

1

namely, the ishwarane[1b,4] and cycloseychellene[5] sesquiterpenes and the trachylobane[6] and helifulvane[7] diterpenes, and we have applied two of our bicycloannulation reactions to the total synthesis of ishwarane[1b,8] and trachyloban-19-oic acid.[3c,d]

Scheme I. Bicycloannulation of Cyclohexenone



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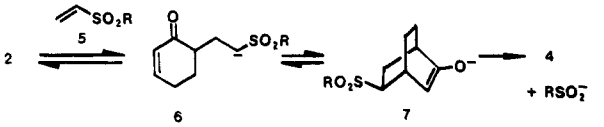
Scheme II. Vinyl Sulfone Bicycloannulation



6 7

While recent work elsewhere has focused on the construction of the tricyclooctane system of these terpenes by multistep procedures terminated by carbene insertion reactions,[9,10] our cyclohexenone bicycloannulations

(1) For the most recent previous papers in the series Bicycloannulation see: (a) Cory, R. M.; Ritchie, B. M. *J. Chem. Soc., Chem. Commun.* **1983**, 1244. (b) Cory, R. M.; Burton, L. P. J.; Chan, D. M. T.; McLaren, F. R.; Rastall, M. H.; Renneboog, R. M. *Can. J. Chem.*, in press.

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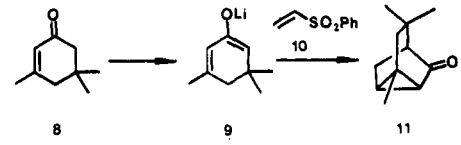
(Scheme I) follow a series of three mechanistic steps, none of which involve carbenes: (1) The α' (kinetic) enolate (2) of the enone undergoes an initial conjugate addition to an activated olefin (3) in which Z has dual character, acting here as an electron-withdrawing group and later as a leaving group. (2) The resulting stabilized carbanionic moiety undergoes an intramolecular Michael addition to the enone moiety. (3) The resulting enolate moiety displaces the leaving group (Z) to form the cyclopropane ring of the tricyclooctanone (4).[11] We have demonstrated that this type of bicycloannulation is successful with reagent 3 in the form of vinylphosphonioum salts,[3c,d,e] vinyl sulfones,[3b] and nitro olefins,[3a] and Hagiwara and co-workers have reported an analogous reaction of α-bromo acrylic esters, which they have used as the key step in a synthesis of ishwarane.[12] Vinyl sulfones, in particular, have become increasingly useful in synthesis in recent years,[13] and we present herein a full description of our own work with these versatile reagents.

The intermediate steps assumed to be operative in our bicycloannulation with vinyl sulfone (5) are shown in Scheme II, in which the initially formed sulfonyl stabilized carbanion, 6, closes to a bicyclo[2.2.2]octane system (7), which subsequently expells a sulfinate anion with the final ring closure. Conjugate addition of ketone enolates to vinyl sulfones has found recent synthetic utility,[14] and Michael addition of sulfonyl carbanions to α,β-unsaturated ketones is also becoming a productve tool.[15] In fact the combination of these two reactions as in Scheme II, leading to a bicyclic sulfonyl ketone of a type corresponding to the conjugate acid of enolate 7, has been employed in the total synthesis of an aspidofractinine derivative.[16] Although under the conditions used in the latter synthesis the sulfonyl group was not displaced, work by others has demonstrated not only the effectiveness of the intramolecular displacement of sulfinate in the formation of cyclopropane rings,[17] but also the preparative value of the combination of Michael addition and sulfonyl displacement in cyclopropanations.[18,19] Nonetheless, although the various steps in the bicycloannulation had precedent in previous studies, the combination of all *three* had not been reported prior to our investigation.

Results and Discussion

In our initial experiments the procedure previously found to be effective in bicycloannulations with vinylphosphonium salts[3c] produced no volatile products other than recovered starting material, and the remainder appeared to be polymerized vinyl sulfone. Surprisingly, however, although the addition of hexamethylphosphoramide (HMPA) had no effect on the efficiency of the phosphonium reactions, so that tetrahydrofuran (THF) alone was a perfectly effective solvent for the latter, we were gratified to discover that the bicycloannulation with vinyl sulfones was successful in many cases in the presence of HMPA.[20,21] Furthermore, since the vinyl sulfones are soluble in THF, the use of pyridine as an additional solvent, which had made addition of the vinyl phosphonium salts to the reaction mixture more convenient, was an unnecessary complication. Thus, for example, when a solution of phenyl vinyl sulfone (10, PVS) in THF was added to a solution of the lithium α' enolate (9) of isophorone (8) and 4 mol equiv of HMPA in THF at room temperature, followed by refluxing the mixture for 2 h, there was obtained a 38% (GC) yield of the desired bicycloannulation product, tricyclooctanone 11. Although



8 9 11

the use of less HMPA lowered the yield of 11, more than 4 equiv failed to increase it beyond the maximum of 38%. Furthermore, the concentration of 11 was observed by GC

(10) We have also used a carbene strategy for a total synthesis of ishwarone: Cory, R. M.; Chan, D. M. T.; McLaren, F. R.; Rasmussen, M. H.; Renneboog, R. M. *Tetrahedron Lett.* **1979**, 4133 and ref 1b. The first total synthesis of ishwarone employed a fundamentally different approach, in which the cyclopropane ring was generated by carbene addition in the *first* step of the construction of the tricyclooctane system from a cyclohexene: Piers, E.; Hall, T.-W. *Can. J. Chem.* **1980**, *58*, 2613; *J. Chem. Soc., Chem. Commun.* **1977**, 880.

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(14) (a) Hamann, P. R.; Fuchs, P. L. *J. Org. Chem.* **1983**, *48*, 914. (b) Pyne, S. G.; Spellmeyer, D. C.; Chen, S.; Fuchs, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 5729. Takaki, K.; Nakagawa, K.; Negoro, K. *J. Org. Chem.* **1980**, *45*, 4789 and references therein. For a related study see ref 22.

(15) (a) Hauser, F. M.; Mal, D. *J. Am. Chem. Soc.* **1984**, *106*, 1098. (b) Nokami, J.; Ono, T.; Kurihara, H.; Wakabayashi, S. *Chem. Lett.* **1982**, 607. (c) Hirama, M. *Tetrahedron Lett.* **1982**, *22*, 1905. (d) Kraus, G. A.; Frazier, K. *Synth. Commun.* **1978**, *8*, 483 and references therein.

(16) Ohnuma, T.; Oishi, T.; Ban, Y. *J. Chem. Soc., Chem. Commun.* **1973**, 301. For similar annulations with Michael acceptors other than vinyl sulfones see: Gibbons, E. *J. Am. Chem. Soc.* **1982**, *104*, 1767. Roberts, M. R.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 724. Narula, A. S.; Birch, A. J. *Tetrahedron Lett.* **1981**, *22*, 591. Gibbons, E. G. *J. Org. Chem.* **1980**, *45*, 1541. Weber, W.; Spitzner, D.; Kraus, W. *J. Chem. Soc., Chem. Commun.* **1980**, 1212 and references therein. An analogous annulation has been achieved by the use of vinyl sulfones as dienophiles with Danishefsky's diene: Kinney, W. A.; Crouse, G. D.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4986.

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(19) A related cyclopropanation in which vinyl sulfones are the Michael acceptors has also been reported: Agawa, T.; Yoshida, Y.; Komatsu, M.; Ohshiro, Y. *J. Chem. Soc., Perkin Trans. 1* **1981**, 751.

(20) Although a reasonable explanation for this is a facilitation of the displacement of the sulfonyl group, recent studies have shown that conjugate addition of sulfonyl carbanions to α,β-unsaturated ketones proceeds more readily, and without 1,2-addition to the carbonyl group, if HMPA is present in the reaction medium.[15b,c] Also of interest in this connection is a report that the annulation of cyclohexenone α' enolates with α-phenylthio and α-phenylsulfinyl crotonic esters does not proceed at all unless HMPA is added: Hagiwara, H.; Nakayama, K.; Uda, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3769. Further information relating to sulfonyl group displacements may be found in the papers cited in ref 23.

(21) Both the hybridization and degree of aggregation of sulfonyl carbanions are affected by variations in the nature of the solvent, including THF and HMPA: Chassaing, G.; Marquet, A. *Tetrahedron* **1978**, *34*, 1399.

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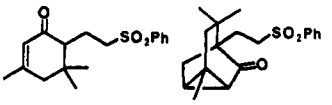
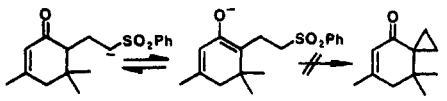
analysis to rise to a maximum during the 2 h of refluxing, and further heating served only to increase the complexity of the product mixture and decrease the yield of **11**. None of the tricyclic bicycloannulation product was formed at room temperature, before refluxing, in contrast to the corresponding vinylphosphonium reaction, in which refluxing only served to *complete* the reaction. However, in spite of the slower rate of the vinyl sulfone bicycloannulation, the yield of **11** was more than twice that (16%) for the same compound from the vinylphosphonium salt, vinyltriphenylphosphonium bromide (VTB, **3**, $Z = PPh_3Br$).

In addition to the desired product, 47% of the starting isophorone was recovered, and traces of the simple conjugate addition product, **12**, and its bicycloannulation product, tricyclooctanone **13**, could be isolated. The



12 **13**

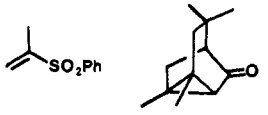
presence of the latter two side products was significant for two reasons. First, although they were formed only in trace amounts, they seem to confirm the postulated mechanism involving an initial conjugate addition of the enolate to the vinyl sulfone. Secondly, the absence of an alternative cyclopropanation product, **16**, is surprising in view of the



14 **15** **16**

success of the analogous reaction between vinyl sulfones and nitriles,[19] and in view of the fact that the formation of tricyclooctanone **13** is proof that proton transfer in the intermediate sulfonyl carbanion, **14**, occurred to some extent to give the corresponding enolate, **15**, which apparently gives rise only to **13** and, on workup, the keto form, **12**. This type of cyclopropanation (to give a product analogous to **16**) has been observed only on a single occasion in additions of simple ketone enolates to vinyl sulfones.[14a]

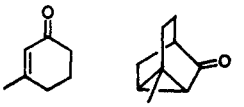
Interestingly, when enolate **9** was treated with *isopropenyl* phenyl sulfone (**17**, IPS)[24] under the same conditions as for the unsubstituted vinyl sulfone, formation of the tricyclooctanone **18** was observed at room temperature, *before* refluxing. In this case, refluxing for 2 h was



17 **18**

required to complete the reaction, giving a 21% isolated yield of **18**, in contrast to bicycloannulations with the corresponding isopropenylphosphonium salt, for which the reactions were generally complete at room temperature.[3c] The fact that the α-substituted vinyl sulfone undergoes the bicycloannulation more readily than the parent reagent[25] may be an indication that the displacement of the sulfonyl group is faster in the former case. Possible reasons for this have been suggested previously.[3c,26]

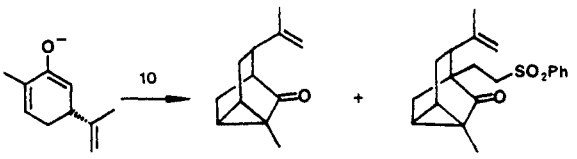
Encouraged by the 2-fold increase in the yield of tricyclooctanone **11** afforded by the use of the vinyl sulfone, PVS, relative to that from the vinylphosphonium salt, VTB, we chose to examine the bicycloannulation of another β-substituted substrate, 3-methylcyclohexenone (**19**).



19 **21**

In this case VTB had failed to provide any of the tricyclooctanone **21**,[3c] but upon treatment with *p*-chlorophenyl vinyl sulfone (**20**, CVS)[27] the corresponding enolate gave a 19% yield of **21**. Thus, when the cyclohexenone is β-substituted, the vinyl sulfone bicycloannulation method is preferred and may be the only successful procedure in some cases.

In our studies of vinylphosphonium bicycloannulation a substrate providing some of the highest yields was carvone, although these were still on the order of only 30–45%.[3c] Thus, it was of great interest to determine if the increases in yields observed for the reaction of vinyl sulfones with β-substituted cyclohexenones extended also to α-substituted cyclohexenones, in which case near quantitative yields might be expected. Unfortunately, however, when enolate **22** from *l*-carvone was treated with PVS under the standard conditions, only a 5% yield of the desired tricyclooctanone **23** was obtained. As with the



22 **23** **24**

phosphonium salt, VTB, however, the reaction was stereoselective, and none of the tricyclooctanone resulting from attack by the vinyl sulfone on the more hindered side of the enolate was identified in the product mixture.[28] Whatever the reasons for this disappointingly low yield, a small amount of the bicycloannulation product, **24**, corresponding to the 2:1 product, **13**, from isophorone was also isolated. For this reason it was felt that substitution at the α' position on the substrate cyclohexenone might increase the yield of the 1:1 bicycloannulation product by preventing the formation of enolates analogous to **15** and thus the side products resulting thereform. Carvone could readily be methylated at the α' position by treatment of its kinetic enolate, **22**, with methyl iodide, and the resulting 2,6-dimethyl-substituted cyclohexenone, **25**, as a mixture of diastereomers, could be converted without incident to its α' enolate, **26**, by reaction with LDA as usual. We were

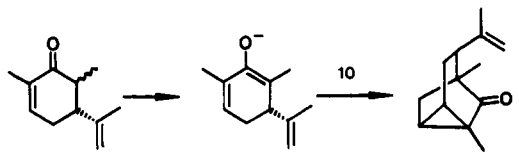
(24) This compound was prepared by a modification of the method of Ueno and (independently) of Kotake, which involves base-catalyzed reaction of β-keto sulfones with formaldehyde: Ueno, Y.; Setoi, H.; Okawara, M. *Chem. Lett.* **1979**, 47. Kotake, H.; Inomata, K.; Sumita, M. *Chem. Lett.* **1978**, 717. The required β-keto sulfone was prepared by a modification of a phase-transfer alkylation method: Samuelsson, B.; Lamm, B. *Acta Chem. Scand.* **1971**, *25*, 1555. For details see the Experimental Section.

(25) In contrast isopropenyl sulfones are orders of magnitude *less* reactive than unsubstituted vinyl sulfones with respect to conjugate addition of amines: McDowell, S. T.; Stirling, C. J. M. *J. Chem. Soc. B* **1967**, 351.

(26) See also: Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1967**, *89*, 3917. Bordwell, F. G.; Jarvis, B. B. *J. Am. Chem. Soc.* **1972**, *95*, 3585.

(27) McDowell, S. T.; Stirling, C. J. M. *J. Chem. Soc. B* **1967**, 348.

(28) The stereoselectivity was high enough for bicycloannulation of carvone with VTB that the minor isomer was difficult to isolate and identify due to the small amount obtained and the similarity of its GC retention time to that of the major isomer. In view of the very low yield of the *major* isomer from PVS, it is possible that minor amounts of the other diastereomer were obtained but not detected.



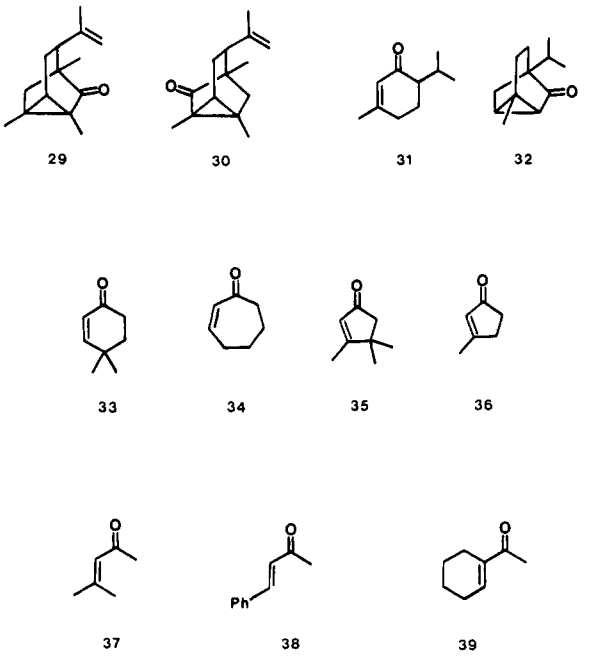
25 26 27

indeed pleased to find that reaction of this enolate with PVS under the standard conditions gave stereoselectively a 17% yield of tricyclooctanone **27**. Similarly, treatment of the same enolate with *p*-chlorophenyl isopropenyl sulfone (**28**, CIS)[24] produced a 20% yield of the tricyclooctanone having the isopropenyl and carbonyl groups syn to each other (**29**) and only 2% of the epimer, **30**, resulting from attack by CIS on the more hindered side of the enolate. Since vinylphosphonium salts had given higher yields than vinyl sulfones for carvone itself, the next logical step was to see if this held true also for its methylated derivative, and, as expected, the same enolate (**26**) with the vinylphosphonium salt, VTB, provided a 65% yield of **27**, the highest yield yet obtained in any of our bicycloannulation reactions with activated vinyl reagents.[29] It would therefore appear that in the case of α-substituted cyclohexenones the bicycloannulation method of choice is the one employing vinylphosphonium salts, so that these two methods seem to complement each other for synthetic purposes.[30]

Although the presence of an α' methyl group increases the yield of the bicycloannulation product when compared with the unmethylated substrate, a substituent larger than methyl at the α' position can have the opposite effect. Thus, when bicycloannulation of the α' enolate of piperitone (**31**) was carried out with PVS, only 1% of tricyclooctanone **32** was obtained. This near failure may be attributed to steric hindrance toward attack by PVS afforded by the bulky isopropyl group of the enolate. As was the case for the vinylphosphonium salt, VTB, bicycloannulation with PVS was unsuccessful with 4,4-dimethylcyclohexenone (**33**), and cycloheptenone (**34**) was similarly uncooperative. In spite of the successful bicycloannulation of cyclopentenone **35** with nitro olefins,[3a] this enone also provided no evidence of the desired tricyclic ketone on treatment of its enolate with PVS, and similar results were obtained for 3-methylcyclopentenone (**36**). Furthermore, attempts to extend the vinyl sulfone bicycloannulation to *acyclic* enones, including mesityl oxide (**37**) and 4-phenylbut-3-en-2-one (**38**) also met with failure, as did attempted bicycloannulation of 1-acetylcyclohexene (**39**). Thus, it would appear that vinyl sulfone bicycloannulation is limited strictly to cyclohexenones.

Although, in cases where this bicycloannulation method is successful, the yields are low to moderate, most of the product tricyclooctanones cannot be prepared by any other method, with the notable exception of vinylphosphonium and nitro olefin bicycloannulation. In all cases large amounts of polymeric material were generated, and it is apparent that anionic polymerization of the vinyl sulfones and their copolymerization with the substrates are the major nonproductive pathways involved in these experiments.[31] Nevertheless, it was hoped that one of the main advantages of the vinyl sulfone bicycloannulation method

Chart I



29 30 31 32

33 34 35 36

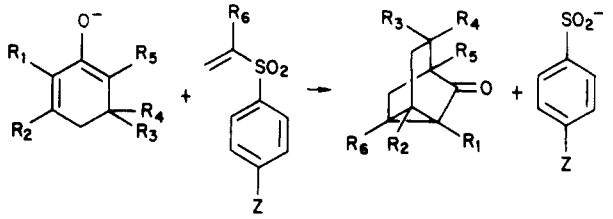
37 38 39

over the vinylphosphonium and nitro olefin procedures would be the ease of varying the reactivity of the vinyl sulfones by varying the *non*olefinic substituent bonded to the sulfonyl group. In particular, it seemed reasonable that the more electron withdrawing that substituent was, the more electron withdrawing the sulfonyl group would be, and hence the more activating it would be toward conjugate addition of the enolate to the vinyl sulfone and the better the sulfonyl group would be as a leaving group in the last step of the bicycloannulation reaction. Thus, in theory one should be able to tailor the reagent to the specific requirements of a particular substrate and increase the yield of the bicycloannulations by increasing the electron-withdrawing power of the sulfonyl group.[32]

Unfortunately, as shown by the data in the Table I, for bicycloannulation of isophorone (**8**) the presence of a *p*-chloro group on the aromatic ring of the reagent (CVS) actually *lowered* the yield, although in the case of carvone and its methylated derivative (**25**) the chloro group seemed to have virtually no effect. A similar decrease in yield was found when isopropenyl phenyl sulfone (IPS) was compared with *p*-chlorophenyl isopropenyl sulfone (CIS) in the bicycloannulation of isophorone. In spite of the fact that this is the opposite effect to that anticipated, this downward trend was continued by the observation that the corresponding *p*-nitrophenyl vinyl sulfone (NVS, **40**)[27] gave little or no tricyclooctanone. Thus, substitution of the aryl group of the aryl vinyl sulfones with electron-withdrawing groups serves no purpose and is even detrimental in most cases.[33,34]

(29) Cory, R. M.; Bailey, M. D. unpublished work in this laboratory.
(30) A comparison of the vinyl sulfone and vinylphosphonium bicycloannulations with the nitro olefin method will be presented separately, although preliminary data can be found in ref 3a.
(31) In an attempt to diminish polymerization of the vinyl sulfone, the conditions of the bicycloannulation were modified so that PVS was added *at reflux* to the enolate in THF–HMPA, but this served only to *decrease* the yield of the tricyclooctanone.
(32) The kinetics of the conjugate addition of amines to aryl vinyl sulfones have been studied as a function of substitution on the aromatic ring, and a satisfactory Hammett correlation was obtained with a ρ value of +1.59.[27] For a *p*-chlorophenyl group this meant a rate increase by approximately a factor of two over PVS, and for *p*-nitrophenyl the ratio was greater than 10:1. Although these relatively small reflects indicated that the electronic influence of the substituent groups was somewhat attenuated by the intervening sulfonyl group, the synthetic consequences were expected to be significant. Furthermore, the leaving group abilities (nucleofugalities) of a series of leaving groups in 1,3-elimination reactions of sulfones having a leaving group at the 3-position to give sulfonyl cyclopropanes were found to correlate well with the pK_a values of the conjugate acids of the leaving groups, including phenylsulfinate and *p*-tolylsulfinate, although *reliable* data for the acidities of the corresponding sulfinic acids are not available: Issari, B.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 684.

Table I. Effects of Para Substitution on Bicycloannulation Yields



entry	substrate	R_1	R_2	R_3	R_4	R_5	reagent	R_6	Z	yield, %
1	**9**	H	CH_3	CH_3	CH_3	H	**10**	H	H	38
2	**9**	H	CH_3	CH_3	CH_3	H	**20**	H	Cl	7
3	**9**	H	CH_3	CH_3	CH_3	H	**40**	H	NO_2	0
4	**9**	H	CH_3	CH_3	CH_3	H	**17**	CH_3	H	21
5	**9**	H	CH_3	CH_3	CH_3	H	**28**	CH_3	Cl	2
6	**26**	CH_3	H	H	C_3H_5	CH_3	**10**	H	H	17
7	**26**	CH_3	H	H	C_3H_5	CH_3	**20**	H	Cl	20
8	**26**	CH_3	H	H	C_3H_5	CH_3	**40**	H	NO_2	1
9	**26**	CH_3	H	H	C_3H_5	CH_3	**28**	CH_3	Cl	2

In summary, the use of vinyl and isopropenyl sulfones in the bicycloannulation of cyclohexenones is advantageous only when the enone has a substituent at the β position. In such cases vinylphosphonium bicycloannulation gives lower yields or none of the tricyclooctanone, but with α-substituted cyclohexenones just the opposite is true, and the phosphonium reagents are the ones of choice for the latter substrates. Thus, these two bicycloannulation methods complement each other, and the availability of both of these synthetic tools greatly expands the pool of tricyclo[3.2.1.$0^{2,7}$]octan-6-ones within our reach. These tricyclooctanones have found wide application in a variety of synthetic contexts,[3,9,11,12] and with the additional proven utility of nitro olefin bicycloannulation,[3a] we are now in a position to prepare almost any one we wish. Furthermore, aside from the fact that these reactions make possible the preparation of tricyclooctanones not available by any other method, even when multistep alternatives *are* known, the overall yields of the latter are usually inferior to those of our bicycloannulation procedures, which have the additional advantage of convenience and provide a tremendous savings in time and expense.

Experimental Section

All reactions were conducted under a positive pressure of argon. Ether (when used as a reaction solvent) and THF were freshly distilled from sodium benzophenone ketyl, diisopropylamine was distilled from CaH and stored over 4-A molecular sieves, and HMPA was distilled from 13X molecular sieves. Butyllithium (in hexane) was obtained from Ventron and was titrated[35] with 2-butanol in xylene (bipyridyl indicator) before use.

Preparative TLC was performed on precoated E. Merck silica gel GF (2 mm) on glass plates. Ethyl acetate was used to extract the separated components from the silica gel. GC was carried out on 10% SILAR-5CP (Applied Science silicone ASI 50 phenyl/50 cyanopropyl) on GAS-CHROM Q (100/120 mesh) in a 0.2 in. × 6 ft stainless-steel column with a helium flow rate of 60 mL/min unless otherwise noted.

NMR spectra were recorded on a Varian Model XL-100 spectrometer, and ^1H and ^{13}C chemical shifts are reported in ppm (δ) downfield from internal Me_4Si. IR spectra were obtained on a Beckman Model 4250 spectrophotometer, and mass spectra were determined by electron impact on a Varian MAT Model 311A spectrometer employing an ionizing voltage of 70 eV. Melting and boiling points are uncorrected.

α-(Phenylsulfonyl)propiophenone. To a solution of 3.07 g (77 mmol) of NaOH and 0.22 g of benzyltriethylammonium chloride in 50 mL of water was added a solution of 4.8 mL (10.94 g, 77 mmol) of CH_3I and 10 g (38 mmol) of α-(phenylsulfonyl)-acetophenone in 50 mL of CH_2Cl_2. The mixture was stirred rapidly for 1 h, after which the organic layer was washed with 5% aqueous HBr and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was recrystallized from 95% ethanol to give the β-keto sulfone: 6.65 g (63%); colorless needles; mp 88–90 °C; IR (CCl_4) 1681, 1328, 1141 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36–8.10 (m, 10 H), 5.20 (q, 1 H, J = 7.5 Hz), 1.59 (d, 3 H, J = 7.5 Hz); mass spectrum, m/z (relative intensity) 274 (M^+, 10), 210 (16), 106 (10), 105 (100), 77 (3); high-resolution mass spectrum, m/z calcd for $C_{15}H_{14}O_3S$ 274.0664, found 274.0658.

α-[(*p*-Chlorophenyl)sulfonyl]propiophenone. To a solution of 2.70 g (68 mmol) of NaOH and 0.23 g of benzyltriethylammonium chloride in 50 mL of water was added a solution of 4.2 mL (9.57 g, 68 mmol) of CH_3I and 10 g (34 mmol) of α-[(*p*-chlorophenyl)sulfonyl]acetophenone in 50 mL of CH_2Cl_2. The mixture was stirred rapidly for 3 h, after which the organic layer was washed with water and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was recrystallized from 95% ethanol to give the β-keto sulfone: 8.72 g (83%); biege plates; mp 125 °C; IR ($CHCl_3$) 1680, 1324, 1139 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–8.10 (m, 9 H), 5.22 (q, 1 H, J = 7 Hz), 1.56 (d, 3 H, J = 7 Hz); mass spectrum, m/z (relative intensity) 308 (M^+, 3), 244 (10), 105 (100), 77 (34); high-resolution mass spectrum, m/z calcd for $C_{15}H_{13}O_3SCl$ 308.0274, found 308.0272.

Isopropenyl Phenyl Sulfone (17). To a suspension of 0.84 g (35 mmol) of NaH (prepared by washing 1.67 g of a 50% dispersion of NaH in mineral oil with THF) in 180 mL of THF was added dropwise, with stirring, 6.65 g (24 mmol) of α-(phenylsulfonyl)propiophenone in 60 mL of THF over 30 min. After the mixture had been allowed to stir for an additional 30 min, 4.34

(33) Similar behavior was observed by Posner and Brunelle for conjugate addition of organocopper reagents to *p*-chlorophenyl and *p*-fluorophenyl vinyl sulfones: Posner, G. H.; Brunelle, D. J. *J. Org. Chem.* **1973**, *38*, 2747.

(34) Although the reasons for these effects are unknown, they were sufficiently discouraging that further investigation of the possibility of improving the yields of the bicycloannulations by varying the nonolefinic group of the vinyl sulfone was abandoned. It is conceivable that the introduction of *p*-chloro and *p*-nitro groups on the aromatic ring leads to other side reactions such as nucleophilic aromatic substitution under the conditions of the bicycloannulation (see, for example: Colter, A. K.; Miller, R. E. *J. Org. Chem.* **1971**, *36*, 1898), and that other types of substituents would indeed increase the yields. One such group, trifluoromethyl, which in the form of triflones is relatively expensive and in our hands proved to be difficult to obtain, has been exploited successfully by Hendrickson and co-workers in enhancing the reactivity of vinyl sulfones toward conjugate addition and displacement of the sulfonyl group: Hendrickson, J. B.; Sternbach, D. D.; Bair, K. W. *Acc. Chem. Res.* **1977**, *10*, 306. Hendrickson, J. B.; Bair, K. W.; Bergeron, R.; Giga, A.; Skipper, P. L.; Sternbach, D. D.; Wareing, J. A. *Org. Prep. Proc.* **1977**, *9*, 173. Hendrickson, J. B.; Skipper, P. L. *Tetrahedron* **1976**, *32*, 1627 and references therein.

(35) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

g (0.146 mol as CH_2O) of paraformaldehyde was added in small portions, and the resulting mixture was stirred for 5 h. The thick gel thus produced was thinned with THF and filtered, and the filtrate was concentrated on the steam bath. The residual brown oil was subjected to open column liquid chromatography on neutral alumina ($CHCl_3$ eluent), giving isopropenyl phenyl sulfone (**17**): 2.38 g (34%); colorless, light-sensitive oil; IR 1682, 1307, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2–7.9 (m, 5 H), 6.19 (s, 1 H), 5.65 (q, 1 H, J = 1.5 Hz), 1.96 (d, 3 H, J = 1.5 Hz).[36]

***p*-Chlorophenyl Isopropenyl Sulfone (28).** To a suspension of 0.67 g (28 mmol) of NaH (prepared by washing 1.34 g of a 50% dispersion of NaH in mineral oil with THF) in 180 mL of THF was added dropwise, with stirring, 8.75 g (28 mmol) of α-[(*p*-chlorophenyl)sulfonyl]propiophenone in 60 mL of THF over 30 min. After the mixture had been allowed to stir for an additional 30 min, 5.04 g (0.168 mol as CH_2O) of paraformaldehyde was added in small portions, and the resulting mixture was stirred for 5 h. The thick gel thus produced was thinned with THF and filtered, and the filtrate was concentrated on the steam bath. The residual yellow oil was subjected to open column liquid chromatography on neutral alumina ($CHCl_3$ eluent), giving sulfone **28**: 3.54 g (58%); light yellow, light-sensitive oil; IR 1686, 1311, 1147 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.61 (d, 2 H, J = 9 Hz), 7.32 (d, 2 H, J = 9 Hz), 6.10 (s, 1 H), 5.63 (q, 1 J = 1.5 Hz), 1.92 (d, 3 H, J = 1.5 Hz); mass spectrum, m/z (relative intensity) 216 (M^+, 31), 176 (9), 159 (100), 134 (24), 113 (46), 106 (100), 78 (61), 51 (26), 43 (19); high-resolution mass spectrum, m/z calcd for $C_9H_9O_2ClS$ 216.0012, found 216.0015.

(5*R*)-2,6-Dimethyl-5-isopropenylcyclohex-2-en-1-one (25). To a solution of 4.96 mL (3.58 g, 35 mmol) of diisopropylamine and 5 mg of 2,2′-bipyridyl in 25 mL of THF at 0 °C was added dropwise, with stirring, 23.0 mL (37 mmol) of 1.6 M *n*-butyllithium over 1 h. After the resulting crimson solution had been stirred at 0 °C for 15 min, a solution of 5.00 mL (4.80 g, 32 mmol) of *l*-carvone in 45 mL of THF was added dropwise, with stirring, over 2.5 h. After the solution had been allowed to stir at 0 °C for an additional 15 min, 10.0 mL (22.8 g, 0.157 mol) of CH_3I was added rapidly, and stirring was continued for 5 min more. The mixture was poured into 50 mL of saturated aqueous $NaHCO_3$, and the aqueous phase was extracted with petroleum ether (boiling range 30–60 °C). The combined extracts were washed with 5% aqueous HBr, water, and brine and dried over Na_2SO_4. The solvent was distilled on a steam bath, and the residual brown oil was subjected to shortpath distillation to give methylated carvone **25**: 3.92 g (75%); colorless oil; bp 136–170 °C (35 mm); IR 1668 cm^{-1}; ^1H NMR ($CDCl_3$) (mixture of two diastereomers, epimeric at C-6) δ 6.70 (m, 1 H), 4.82 (m, 2 H), 2.10–2.85 (m, 8 H), 1.78 and 1.73 (broad singlets, 6 H), 1.04 and 0.92 (doublets, 3 H, J = 6 and 7 Hz); mass spectrum, m/z (relative intensity) 164 (M^+, 6), 149 (4), 136 (2), 106 (3), 94 (15), 83 (100), 67 (13); high-resolution mass spectrum, m/z calcd for $C_{11}H_{16}O$ 164.1201, found 164.1198.

Bicycloannulation Procedure. 1,2,4,4-Tetramethyltricyclo[3.2.1.0^{2,7}]octan-6-one (18). To a solution of 0.77 mL (0.55 g, 5.4 mmol) of diisopropylamine and 3 mg of 2,2′-bipyridyl in 4 mL of THF at 0 °C was added dropwise, with stirring, 3.9 mL (5.1 mmol) of 1.3 M *n*-butyllithium over 10 min. To the resulting crimson solution at 0 °C was added dropwise, with stirring, a solution of 0.47 mL (0.50 g, 3.6 mmol) of isophorone (**8**) in 4 mL of THF over 1 h. After the solution had been allowed to stir at 0 °C for an additional 15 min, 2.5 mL of HMPA was added, and the mixture was allowed to warm to room temperature. To the resulting deep purple solution was added dropwise, with stirring, a solution of 0.76 g (4.2 mmol) of isopropenyl phenyl sulfone (**17**) in 10 mL of THF over 1 h. The mixture was then heated and refluxed for 2 h, after which it was partitioned between saturated aqueous $NaHCO_3$ and petroleum ether (boiling range 30–60 °C). The aqueous phase was extracted with petroleum ether, and the combined extracts were washed with water, aqueous $CuSO_4$ (saturated solution diluted with an equal portion of water), and brine and dried over Na_2SO_4. The solvent was distilled through a Vigreux column on a steam bath, and the residual oil was subjected to preparative GC (200 °C) to give tricyclooctanone **18**: 0.132 g (21%); colorless oil; IR 1721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47–2.07 (m, 5 H), 1.31 (s, 3 H), 1.27 (m, 1 H), 1.11 (s, 3 H), 1.02 (s, 3 H), 0.91 (s, 3 H); mass spectrum, m/z (relative intensity) 178 (M^+, 12), 150 (18), 135 (55), 119 (11), 107 (100), 91 (33), 79 (35); high-resolution mass spectrum, m/z calcd for $C_{12}H_{18}O$ 178.1358, found 178.1358.

Similarly, 0.25 g (1.8 mmol) of isophorone (**8**) and 0.43 g (2.0 mmol) of *p*-chlorophenyl isopropenyl sulfone (**28**) gave 7 mg (2%) of the same tricyclic ketone (**18**).

2,4,4-Trimethyltricyclo[3.2.1.0^{2,7}]octan-6-one (11). By the standard bicycloannulation procedure, 0.50 g (3.6 mmol) of isophorone (**8**) and 0.73 g (4.3 mmol) of phenyl vinyl sulfone (**10**) gave **11**: 38% (GC, triphenylmethane internal standard); colorless oil; IR, NMR, and mass spectrum identical with those of an authentic sample.[3c] In addition, 47% of the starting isophorone was recovered, as determined by GC, and open column liquid chromatography on silica gel eluting with 2:3 ethyl acetate–cyclohexane gave the following three side products: (a) 3,5,5-Trimethyl-6-[2-(phenylsulfonyl)ethyl]cyclohex-2-ene-1-one (**12**): 4 mg (0.4%); light yellow syrup; IR 1660, 1308, 1147 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–8.0 (m, 5 H), 5.81 (s, 1 H), 3.10 (t, 2 H, J = 8 Hz), 1.8–2.4 (m, 6 H), 1.43 (s, 3 H), 1.02 (s, 6 H); mass spectrum, m/z (relative intensity) 306 (M^+, 20), 291 (75), 183 (16), 164 (100), 141 (4), 121 (49), 108 (34), 93 (8), 79 (33), 68 (15); high-resolution mass spectrum, m/z calcd for $C_{17}H_{22}O_3S$ 306.1290, found 306.1287. (b) 3,5,5-Trimethyl-2-[2-(phenylsulfonyl)ethyl]cyclohex-2-en-1-one: 8 mg (0.8%); light yellow syrup; IR 1658, 1310, 1152 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–8.0 (m, 5 H), 3.20 (t, 2 H, J = 7.5 Hz), 2.68 (t, 2 H, J = 7.5 Hz), 2.20 (s, 2 H), 2.14 (s, 2 H), 1.94 (s, 3 H), 0.96 (s, 6 H); mass spectrum, m/z (relative intensity) 306 (M^+, 35), 291 (12), 165 (100), 149 (52), 121 (6), 109 (53), 93 (5), 81 (38); high-resolution mass spectrum, m/z calcd for $C_{17}H_{22}O_3S$ 306.1290, found 306.1287. (c) 2,4,4-Trimethyl-5-[2-(phenylsulfonyl)-ethyl]tricyclo[3.2.1.0^{2,7}]octan-6-one (**13**): light yellow syrup; IR 1710, 1304, 1143 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–8.0 (m, 5 H), 3.48 (t, 2 H, J = 8 Hz), 1.25 (s, 6 H), 0.94 (s, 3 H); mass spectrum, m/z (relative intensity) 332 (M^+, 10), 317 (4), 306 (8), 196 (4), 190 (100), 147 (56), 134 (80), 119 (62), 78 (12); high-resolution mass spectrum, m/z calcd for $C_{19}H_{24}O_3S$ 332.1446, found 332.1445.

Similarly, 0.50 g (3.6 mmol) of isophorone (**8**) and 0.87 g (4.3 mmol) of *p*-chlorophenyl vinyl sulfone (**20**) gave a 7% (GC) yield of the tricyclic ketone **11**, a 24% recovery of isophorone, and 5-[2-[(*p*-chlorophenyl)sulfonyl]ethyl]-2,4,4-trimethyltricyclo-[3.2.1.0^{2,7}]octan-6-one, which crystallized out on concentration of the petroleum ether extracts: 49 mg (4%); biege powder; mp 175–176 °C; IR ($CDCl_3$) 1710, 1320, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.73 (d, 2 H, J = 8 Hz), 7.43 (d, 2 H, J = 8 Hz), 3.1 (m, 2 H), 2.2–1.3 (m, 8 H), 1.11 (s, 3 H), 1.00 (s, 3 H), 0.88 (s, 3 H); mass spectrum, m/z (relative intensity) 366 (M^+, 17), 190 (90), 175 (6), 162 (21), 147 (68), 133 (100), 119 (95), 105 (26), 91 (32), 83 (15), 79 (15), 54 (20); high-resolution mass spectrum, m/z calcd for $C_{19}H_{23}O_3ClS$ 366.1056, found 366.1059.

2-Methyltricyclo[3.2.1.0^{2,7}]octan-6-one (21). By the standard bicycloannulation procedure, 0.50 g (4.6 mmol) of 3-methylcyclohex-2-en-1-one (**19**) and 1.11 g (5.5 mmol) of *p*-chlorophenyl vinyl sulfone (**20**) gave (GC 170 °C) tricyclooctanone **21**: 0.119 g (19%); colorless oil; IR 1726 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35–1.61 (m, 9 H), 1.59 (dd, 2 H, J = 10, 1 Hz), 1.11 (s, 3 H); mass spectrum, m/z (relative intensity) 136 (M^+, 9), 108 (56), 93 (100), 79 (56), 67 (48), 56 (28); high-resolution mass spectrum, m/z calcd for $C_9H_{12}O$ 136.0888, found 136.0887.

4-Isopropenyl-7-methyltricyclo[3.2.1.0^{2,7}]octan-6-one (23). By the standard bicycloannulation procedure, 0.51 g (3.4 mmol) of *l*-carvone and 0.63 g (3.8 mmol) of phenyl vinyl sulfone (**10**) gave tricyclooctanone **23**: 5% (GC); colorless oil; IR, NMR, and mass spectra identical with those of an authentic sample of the enantiomer.[3c] In addition, 5% of the starting carvone was recovered, and TLC (elution with 2:3 ethyl acetate–cyclohexane) gave a small amount of 4-isopropenyl-7-methyl-5-[2-(phenylsulfonyl)ethyl]tricyclo[3.2.1.0^{2,7}]octan-6-one (**24**): IR 1720, 1644, 1304, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.02–7.44 (m, 5 H), 4.75 (s, 2 H), 3.19 (m, 2 H), 2.8–1.5 (m, 9 H), 1.65 (s, 3 H), 1.10 (s, 3 H); mass spectrum, m/z (relative intensity) 344 (M^+, 11), 329 (2), 316 (4), 261 (5), 202 (27), 187 (19), 175 (44), 159 (28), 147 (41), 134 (100), 119 (33), 105 (32), 91 (25), 79 (17), 69 (18), 54 (7); high-

(36) For further characterization of this compound see: Kul'bovskaya, N. K.; Gracheva, E. P.; Shostakovskii, M. F. *J. Org. Chem. USSR* **1960**, *30*, 84. Coover, H. W.; Hill, H. M. U.S. Patent 2 843 570, 1958; *Chem. Abstr.* **1958**, *52*, 17797c.

resolution mass spectrum, m/z calcd for $C_{20}H_{24}O_3S$ 344.1446, found 344.1435.

Similarly, 0.50 g (3.4 mmol) of *l*-carvone and 0.94 g (4.6 mmol) of *p*-chlorophenyl vinyl sulfone (**20**) gave a 4% (GC) yield of the tricyclic ketone **23** and a 20% recovery of carvone.

4-Isopropenyl-5,7-dimethyltricyclo[3.2.1.0^{2,7}]octan-6-one (27). By the standard bicycloannulation procedure, 0.51 g (3.1 mmol) of (5*R*)-2,6-dimethyl-5-isopropenylcyclohex-2-en-1-one (**25**) and 0.73 g (4.3 mmol) of phenyl vinyl sulfone (**10**) gave (GC 170 °C) a 15% recovery of the starting cyclohexenone (partially deconjugated) and the tricyclooctanone **27**: 0.101 g (17%); colorless oil; IR 1726, 1646 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ [relative LIS with added Eu(fod)$_3$ in brackets] 4.69 [0.4] (m, 1 H), 4.62 [0.75] (m, 1 H), 2.61 [1.0] (dd, 1 H, J = 10, 6 Hz), 2.49-1.60 (m, 6 H), 1.53 [1.2] (bs, 3 H), 1.24 [1.0] (s, 3 H), 0.87 [1.5] (s, 3 H); ^{13}C NMR (25.2 MHz, $CDCl_3$) δ 215.5 (s), 146.4 (s), 113.6 (t), 57.1 (d), 44.7 (s), 37.8 (t), 34.4 (s), 34.0 (d), 30.7 (d), 24.1 (t), 19.0 (q), 17.2 (q), 12.9 (q);[37] mass spectrum, m/z (relative intensity) 190 (M$^+$, 25), 175 (24), 161 (8), 148 (11), 136 (100), 122 (21), 119 (20), 105 (33), 95 (37), 91 (35), 79 (45), 67 (48), 54 (7); high-resolution mass spectrum, m/z calcd for $C_{13}H_{18}O$ 190.1358, found 190.1355.

Similarly, 0.51 g (3.1 mmol) of (5*R*)-2,6-dimethyl-5-isopropenylcyclohex-2-en-1-one (**25**) and 0.89 g (4.4 mmol) of *p*-chlorophenyl vinyl sulfone (**20**) gave a 21% recovery of the starting cyclohexenone (partially deconjugated) and 0.120 g (20%) of the same tricyclic ketone, **27**. Reaction of 0.25 g (1.5 mmol) of **25** with 0.39 g (1.8 mmol) of *p*-nitrophenyl vinyl sulfone (**40**) under the same conditions gave only 3 mg (1%) of **27** and 17 mg (7%) of recovered **25**.

***syn*- and *anti*-4-Isopropenyl-1,5,7-trimethyltricyclo[3.2.1.0^{2,7}]octan-6-one (29 and 30).** By the standard bicycloannulation procedure, 0.50 g (3.1 mmol) of (5*R*)-2,6-dimethyl-5-isopropenylcyclohex-2-en-1-one (**25**) and 0.81 g (3.7 mmol) of *p*-chlorophenyl isopropenyl sulfone (**28**) gave (preparative GC on OV-225 at 175 °C) a 3% recovery of the starting cyclohexenone and the two diastereomeric tricyclooctanones: **29**: 0.126 g (20%); colorless oil; IR 1715, 1642 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.53 (m, 2 H), 2.70–1.73 (m, 5 H), 1.50 (bs, 3 H), 1.26 (s, 3 H), 1.18 (s, 3 H), 0.90 (s, 3 H); mass spectrum, m/z (relative intensity) 204 (M$^+$, 78), 189 (57), 176 (62), 161 (41), 149 (54), 136 (100), 121 (100), 109 (100), 96 (100), 94 (100), 82 (56), 68 (36), 51 (78); high-resolution mass spectrum, m/z calcd for $C_{14}H_{20}O$ 204.1514, found 204.1508. **30**: 13 mg (2%); colorless oil; IR 1720, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.60 (m, 2 H), 2.7–1.0 (m, 15 H), 0.89 (s, 3 H); mass spectrum, m/z (relative intensity) 204 (M$^+$, 43), 190 (57), 176 (32), 162 (39), 147 (38), 136 (100), 121 (70), 109 (91), 106 (50), 96 (100), 92 (67), 80 (55), 70 (42), 55 (40), 41 (75); high-resolution mass spectrum, m/z calcd for $C_{14}H_{20}O$ 204.1514, found 204.1510.

5-Isopropyl-2-methyltricyclo[3.2.1.0^{2,7}]octan-6-one (32). By the standard bicycloannulation procedure, 0.50 g (3.3 mmol) of piperitone (**31**) and 0.67 g (4.0 mmol) of phenyl vinyl sulfone (**10**) gave (GC 190 °C) tricyclooctanone **32**: 6 mg (1%); colorless oil; IR 1723 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.70–1.15 (m, 9 H), 1.10 (s, 3 H), 0.85 (d, 3 H, J = 7 Hz), 0.78 (d, 3 H, J = 7 Hz); mass spectrum, m/z (relative intensity) 178 (M$^+$, 43), 163 (11), 150 (40), 135 (43), 108 (100), 96 (63), 85 (83), 68 (43), 49 (83), 41 (49).

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Registry No. **8**, 78-59-1; **10**, 5535-48-8; **11**, 58738-47-9; **12**, 91781-44-1; **13**, 91781-45-2; **17**, 76380-14-8; **18**, 76380-15-9; **19**, 1193-18-6; **20**, 5535-51-3; **21**, 82667-39-8; **23**, 91840-33-4; **24**, 91840-34-5; **25** (isomer 1), 91781-46-3; **25** (isomer 2), 91840-35-6; **27**, 91840-36-7; **28**, 91781-47-4; **29**, 91781-48-5; **30**, 91840-37-8; **31**, 89-81-6; **32**, 91781-49-6; **40**, 5535-55-7; $PhC(O)CH_2SO_2Ph$, 3406-03-9; $PhC(O)CH_2SO_2$-*p*-C_6H_4Cl, 36603-45-9; $PhC(O)CH(CH_3)SO_2Ph$, 27839-91-4; $PhC(O)CH(CH_3)SO_2$-*p*-C_6H_4Cl, 91781-50-9; *l*-carvone, 6485-40-1; 3,5,5-trimethyl-2-[2-(phenylsulfonyl)ethyl]cyclohex-2-en-1-one, 91781-51-0; 5-[2-[(*p*-chlorophenyl)sulfonyl]ethyl]-2,4,4-trimethyltricyclo[3.2.1.0^{2,7}]octan-6-one, 91781-52-1.

(37) For a comprehensive study of the ^{13}C NMR properties of tricyclo[3.2.1.0^{2,7}]octan-6-ones and the corresponding tricyclooctanes see: Cory, R. M.; Stothers, J. B. *Org. Magn. Reson.* **1978**, *11*, 252.

Carbon–Carbon Bond-Forming Reactions Using Cerium Metal or Organocerium(III) Reagents

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Carbon–carbon bond-forming reactions using cerium metal or organocerium(III) reagents have been investigated. Cerium amalgam is an effective reagent for the chemoselective preparation of homoallylic alcohols from allyl halides and carbonyl compounds. The same reagent can also be satisfactorily employed for the Reformatsky-type reaction of α-halo esters with carbonyl compounds. It has been shown that organocerium(III) reagents are conveniently generated by the reaction of organolithiums with cerium(III) iodide or cerium(III) chloride. The reagents are less basic than organolithiums and Grignard reagents, and they react cleanly at −78 to −65 °C with various carbonyl compounds to afford the addition products in high yields, even though the substrates are susceptible to enolization or metal–halogen exchange with simple organolithiums. The same reagents react also with α,β-unsaturated carbonyl compounds to yield 1,2-addition products in high selectivity.

The elements of the rare earth series having f orbitals exhibit unique electronic and stereochemical properties, and they possess intriguing potential as reagents and catalysts.[1-4] Recently, considerable efforts have been made on the utilization of these elements in organic reactions, and many interesting synthetic procedures have been developed.[5,6] However, relatively few reports may

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