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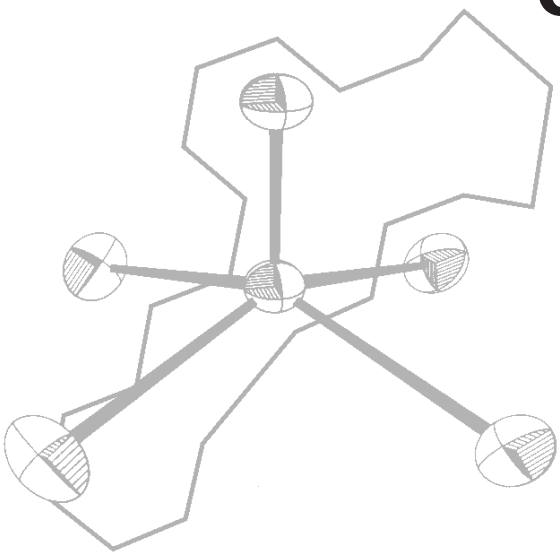

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Syntheses and *ipso*-Substitution Reactions of Some *C*-Stannylated Troponoids*

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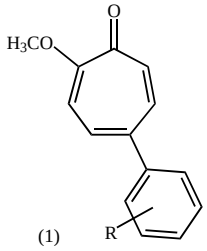
The *C*-stannylated troponoids (2)–(8) have been prepared and two of these shown to undergo palladium(0)-catalysed cross-coupling with bromobenzene to give the corresponding phenyl-substituted tropone. Compounds (3), (5) and (6)–(8) all react with electrophiles to give products of *ipso*-substitution.

Introduction

The site-selective introduction of substituents onto intact tropone (cyclohepta-2,4,6-trien-1-one) or α-tropolone (2-hydroxycyclohepta-2,4,6-trien-1-one) nuclei is often difficult to achieve. For example, treatment of troponoids and their derivatives with common electrophiles generally results in mixtures of, *inter alia*, C 3, C 5 and/or C 7 substitution products and often there are attendant problems associated with the separation of these reaction products.[1] In addition, under strongly acidic conditions tropylium ion formation can occur with the result that substitution does not take place.[1] Nucleophilic addition–elimination reactions of troponoids containing potential leaving groups are similarly complicated by lack of regiochemical control and, in certain cases, by competing ring-contraction processes.[2] In connection with efforts to overcome some of the problems associated with conventional troponoid substitution reactions, we have recently reported[3,4] that various bromotropolone derivatives undergo palladium-mediated cross-coupling with organostannanes thereby producing regiochemically pure troponoid substitution products. For example, reaction of 4-bromo-α-tropolone with trimethyl(1-methylethenyl)stannane in the presence of tetrakis(triphenylphosphine)palladium(0) has provided a direct synthesis of the monoterpene β-dolabrin [2-hydroxy-4-(1-methylethenyl)cyclohepta-2,4,6-trien-1-one] (1989 report[3]). Thus, such reactions represent a useful method for creating new carbon–carbon bonds at the intact troponoid nucleus and have enabled us to prepare (1991 paper[3]), for the purposes of structure/activity relationship studies, several bicyclic colchicine analogues of the general type (1) via Stille-type[4] cross-coupling of various readily available bromotroponoids[5] with aryl stannanes. In seeking to extend the number of compounds of the type (1) available for testing, we recognized that the tedium associated with preparing large numbers of aryl stannanes from the corresponding (and generally commercially available) aryl halides might be avoided by reversing the polarity of the cross-coupling reactions leading to the target compounds (1). Thus, coupling a *C*-stannylated troponoid with an appropriate aryl halide could provide a much more efficient entry into a



(1)

* We dedicate this paper with warm best wishes to Professor R. C. (Con) Cambie.

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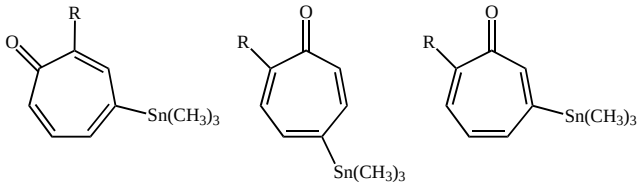
comprehensive set of AC-ring analogues (1) of the powerful antimitotic agent colchicine (1991 paper[3]). Another potentially useful feature of *C*-stannylated troponoids is that these compounds might be expected to undergo regiocontrolled *ipso*-substitution reactions with various electrophiles including carbon-centred ones.[6] Thus, a suitably located trimethylstannyl group attached to the troponoid nucleus might be used to override the normal predilection of such non-benzenoid conjugated carbocycles to react in an indiscriminate fashion with electrophiles.[1]

Despite the synthetic possibilities offered by *C*-stannylated troponoids (see above), at the time the work described here was started such compounds were not recorded in the literature.* On this basis we set out to prepare representative examples of these materials and examine their behaviour in palladium(0)-catalysed cross-coupling reactions with aryl halides as well as their reactions with simple electrophiles. We now describe the synthesis of compounds (2)–(8) and detail certain aspects of their behaviour under the reaction conditions just mentioned.

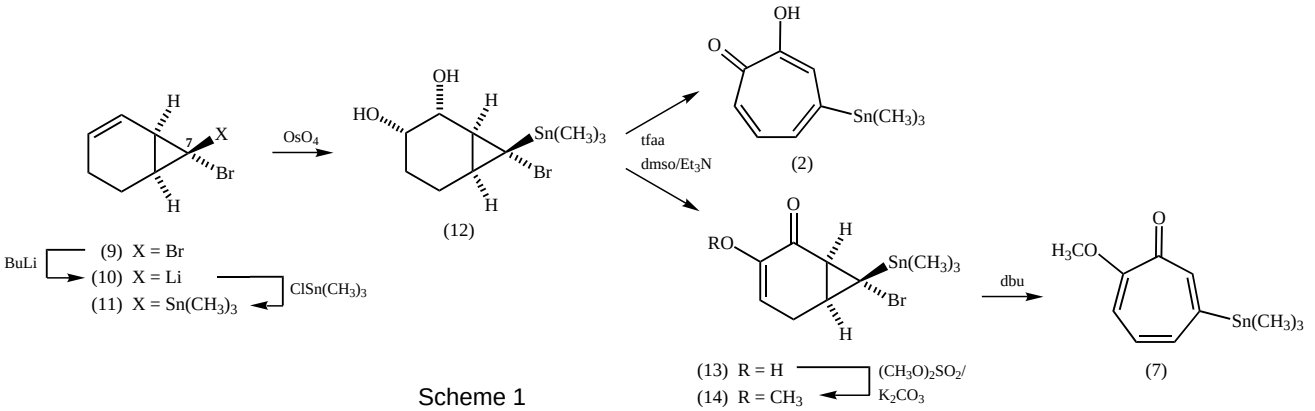


Synthesis of *C*-Stannylated Troponoids (2)–(8)

Our approach to the preparation of compounds (2)–(5) and (7), as outlined in Schemes 1 and 2, is based upon a general method for the synthesis of α-tropolones which we described some time ago (1985).[5]

Thus, treatment of the readily available[8] *gem*-dibromo-Δ^2-norcarene (9) with butyllithium at $-100°$C resulted in metal-for-halogen exchange and formation of the lithiated species (10) which could be intercepted with chlorotrimethylstannane at $-100°$C thereby providing, in a completely diastereoselective manner, the stannylated product (11) (96% yield). The $\{^1H\}^{13}C$ n.m.r. spectrum of this material showed the expected eight signals including one (at δ $-6\cdot4$) due to the three equivalent methyl carbons attached to tin. The dominant feature in the ^1H n.m.r. spectrum of this compound was a singlet at δ $0\cdot24$ and associated 'satellite doublets'† [$J(^{117,119}Sn–H)$ 52 and 54 Hz] which, when considered together, integrate to nine protons and these have been assigned to the newly introduced trimethylstannyl moiety. The stereochemistry at C 7 in compound (11) could not be readily established by spectroscopic means. However, on the basis of mechanistic considerations[9] and by analogy with related reactions for which product stereochemistry has been established by X-ray methods,[10] *endo*-stereochemistry is assigned to the newly incorporated trimethylstannyl group. It should be noted, that the relative disposition of the leaving group (Br^- in the present case) at the apex of the cyclopropane ring in such norcaranes is not important in terms of the subsequent ring-expansion step leading to the troponoid nucleus.[5] Thus, either compound (11) or its C 7 epimer would be expected to act as a precursor to the target stannanes.

Dihydroxylation of the double bond within norcarene (11), with catalytic quantities of osmium tetraoxide in conjunction with stoichiometric quantities of the reoxidant trimethylamine *N*-oxide,[11] provided a stereochemically pure diol (66%) as a crystalline solid. We have previously established (1989),[10] by X-ray methods, that *cis*-dihydroxylation of a closely related Δ^2-norcarene under very similar conditions produced the corresponding α,α-diol so we have assumed that



Scheme 1

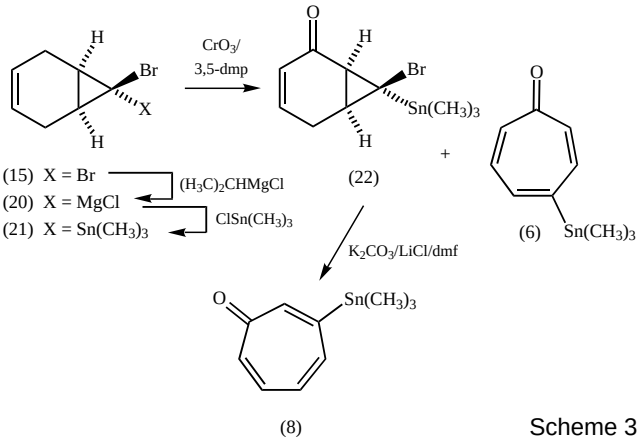
* Very recently (1996) Barbachyn *et al.* disclosed[7] preliminary details of the preparation of compounds (3), (5) and (7) as well as their use in Stille-type cross-coupling reactions with aryl iodides for the purposes of producing various potent antibacterial agents. However, the strategy employed by this group in the synthesis of *C*-stannylated troponoids is rather different from that used in the work described here. Furthermore, these workers did not describe the reaction of such compounds with electrophiles.
† Such 'satellite doublets' were observed in the ^1H n.m.r. spectra of all compounds containing the trimethylstannyl moiety.

the product diol derived from alkene (11) is represented by structure (12). Full spectroscopic data have been obtained on this diol and these confirm, *inter alia*, that the trimethylstannyl moiety has survived the *cis*-dihydroxylation process.

The next step in the projected synthesis of 4-trimethylstannyl-α-tropolone (2) called for subjection of diol (12) to a modified-Swern oxidation with trifluoroacetic anhydride (tfaa) activated dimethyl sulfoxide (dmso) at $-60°C$.[12] Interestingly, the outcome of this process was critically dependent upon the length of time the reaction mixture was left at room temperature prior to workup. Thus, when diol (12) was treated under previously (1985)[5] specified conditions at $-60°C$ and then allowed to warm to ambient temperatures and stand for 2 h, the required tropolone (2) (57%) was obtained. In contrast, subjection of the diol to the same conditions, with the exception that workup was commenced immediately the reaction mixture had warmed to room temperature, resulted in isolation of the bicyclic hydroxy enone (13) (72%). It is assumed that, during the extended reaction period employed in the former process, the initially formed α-hydroxy enone (13) undergoes ring expansion and subsequent dehydrobromination, by a pathway analogous to that proposed previously,[5] to give the α-tropolone (2). The suggested intermediacy of compound (13) in this conversion is supported by the observation that resubjection of the compound to the Swern oxidation affords tropolone (2) (85%). *O*-Methylation of α-hydroxy enone (13) with dimethyl sulfate in the presence of potassium carbonate afforded the expected product (14) (80%) which upon treatment with the weakly nucleophilic base 1,8-diazabicyclo[5.4.0]undec-5-ene (dbu) gave the tropolone *O*-methyl ether (7) (85%) as the only isolable product of reaction. In contrast, *O*-methylation of the free tropolone (2) (with dimethyl sulfate/potassium carbonate) provided a *c.* 1 : 1 mixture of troponoid (3) and regioisomer (7) which could be separated from one another by preparative t.l.c. (albeit with some difficulty).

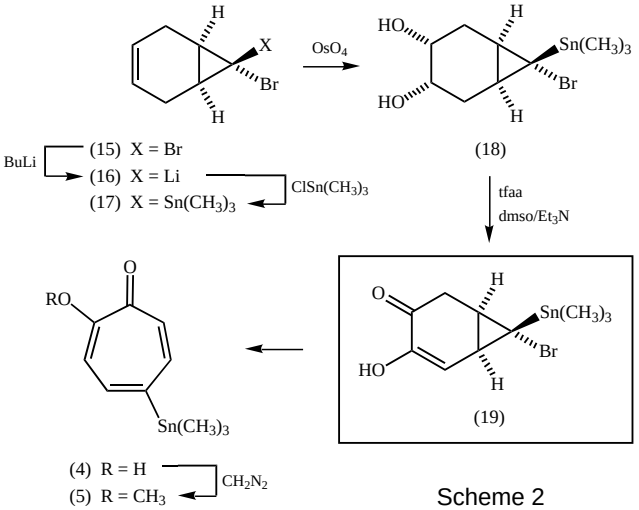
The synthesis of 5-trimethylstannyl-α-tropolone (4) and the derived *O*-methyl ether (5) involved (Scheme 2) the same strategy as described above but used the Δ^3-norcarene (15)[8] as starting material.

Interestingly, on one occasion oxidation of the intermediate diol (18), under the same modified-Swern conditions as used in the conversion (12) $\rightarrow$ (13), afforded significant quantities (71%) of the α-hydroxy enone (19)—the first example of an isolable and spectroscopically characterizable 7-halogenobicyclo[4.1.0]hept-4-en-3-one that we have encountered in our work on the synthesis of troponoid compounds. In contrast, treatment of diol (18) with a greater excess (4·5 mol. equiv.) of oxidant afforded the tropolone (4) directly and this unstable material was immediately *O*-methylated with diazomethane to give the target tropolone *O*-methyl ether (5) [55% from (18)].



Scheme 3

The preparation (Scheme 3) of 4- and 3-trimethylstannyltropone, (6) and (8) respectively, was achieved by adaptation of our previously reported (1985)[5] syntheses of 3- and 4-halogenotropones. Thus, the Δ^3-norcarene (15) was reacted with isopropylmagnesium chloride at $-100°C$ and the metallated species (20) so-formed was then intercepted with chlorotrimethylstannane to give the *exo*-trimethylstannylated product (21) in 72% yield. This last material was spectroscopically distinct from compound (17) obtained by sequential reaction of norcarene (15) with butyllithium and chlorotrimethylstannane.* Allylic oxidation of compound (21) with the chromium trioxide/3,5-dimethylpyrazole (3,5-dmp) complex (1985 communication[5]) provided a mixture of the bicyclic enone (22) (56%), tropone (6) (5%) and isomer (8) (4%). The enone (22) could be separated from troponoids (6) and (8) by preparative t.l.c. but the latter two compounds could not be separated from



Scheme 2

* At this point no particular significance should be attached to the use of Δ^3-norcarene (21), rather than epimer (17), in this reaction sequence. This situation simply reflects the non-availability of butyllithium at the time the work described here was carried out and our consequent inability to prepare compound (17).

one another by this means. Ultimately, h.p.l.c. techniques were required to separate these latter products from one another and in this manner spectroscopically pure samples of each of compounds (6) and (8) were able to be obtained. While treatment of compound (22) with dbu failed to provide any characterizable products, reaction of this substrate with potassium carbonate/lithium chloride in *N*,*N*-dimethylformamide (dmf) at room temperature resulted in dehydrobrominative ring-expansion to give tropone (8) (64% yield). This material was identical, in all respects, with the sample of compound (8) obtained directly from the allylic oxidation of alkene (21).

While the troponoids (2), (3), (5) and (7) are stable crystalline materials, compounds (4), (6) and (8) proved to be quite unstable and could not be kept for extended periods of time even when the normal precautions of excluding air, moisture and light were taken in conjunction with low-temperature storage. This situation has restricted the number of experiments that could be undertaken with the latter group of substrates.

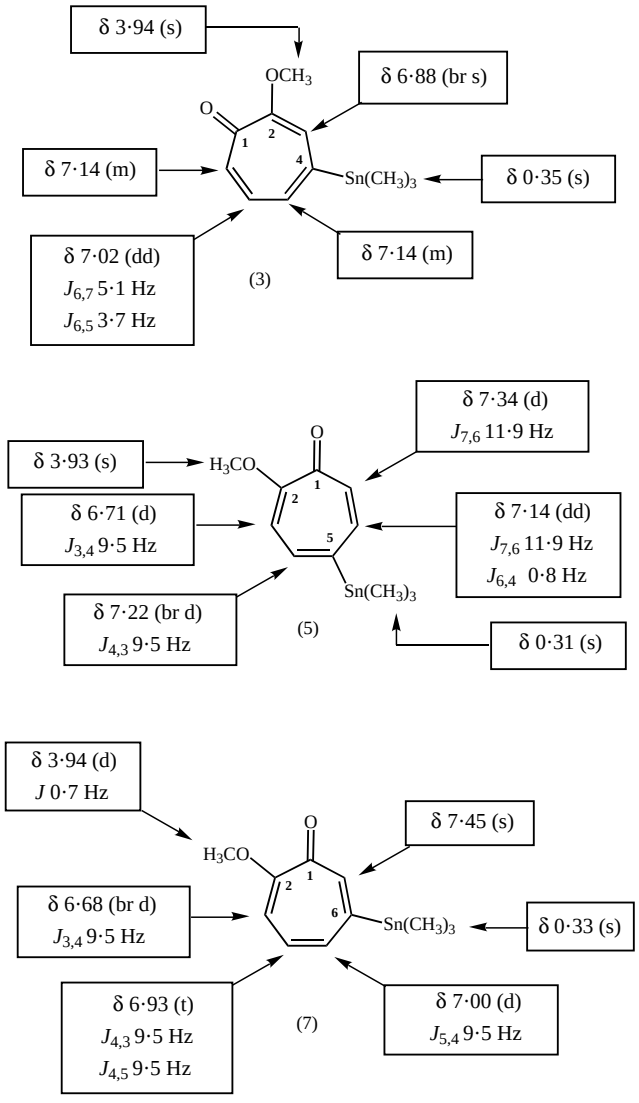


Fig. 1. ^{1}H n.m.r. spectroscopic data for troponoids (3), (5) and (7). The spectra were recorded at 400 MHz in $CDCl_3$ solution.

Spectroscopic Properties of *C*-Stannylated Troponoids (2)–(8)

The spectroscopic data obtained for the title troponoids were fully consistent with the assigned structures. Thus, the infrared spectra of these compounds each displayed diagnostic troponoid absorption maxima[1] in the range ν_{max} 1630–1540 cm^{-1} which are assigned to C=C and C=O stretching bands. In the 70 eV electron impact mass spectra of these compounds appropriate molecular ion clusters were observed in each case and these were generally accompanied by, *inter alia*, fragment ions derived from loss of carbon monoxide, a typical fragmentation pathway for troponoids.[13]

The ^{1}H n.m.r. spectroscopic data derived from the title compounds not only served to establish the presence of the trimethylstannyl group but in three instances also allowed ready confirmation of the location of this substituent on the troponoid framework. Thus, in the 400 MHz ^{1}H n.m.r. spectra of the tropolone *O*-methyl ethers (3), (5) and (7) the proton attached to C 3 (and which is, therefore, β-related to the OCH_3 moiety) always represented the most shielded of all the resonances due to the ring protons. This observation, which is in accord with expectation,[14] provided a useful 'point of entry' for assignment of all the resonances observed within the ^{1}H n.m.r. spectrum of each of these compounds (Fig. 1). The dominant feature in each of these spectra was a nine-proton 'singlet' in the range δ 0·30–0·35 which was accompanied by diagnostic 'satellite doublets' due to ^{117}Sn–H and ^{119}Sn–H couplings (these being of the order of 52 and 54 Hz, respectively).

Table 1. ^{13}C n.m.r. spectroscopic assignments of *C*-stannylated troponoid (7)

Spectrum was recorded at 100 MHz in $CDCl_3$ solution

δ_C value	Multiplicity	$^1J_{C-H}$ (Hz)	$^3J_{C-H}$ (Hz)	Assignment
179·0	d	—	$J_{1,3}$ 9·5	C 1
164·4	br m	—	—	C 2
156·7	d	—	$J_{6,4}$ 11·2	C 6
144·5	dd	159	$J_{7,5}$ 10·0	C 7
133·8	ddd	157	$J_{5,7}$ 9·5	C 5
			$J_{5,3}$ 14·4	
130·4	d	156	—	C 4
112·1	dd	152	$J_{3,5}$ 12·0	C 3
56·3	q	146	—	OCH_3
−8·8	q	130·3	—	$Sn(CH_3)_3$

Analysis of the fully coupled ^{13}C n.m.r. spectrum of compound (7) clearly indicated that, as is the case for benzenoid aromatics,[15] three bond C–H coupling is quite significant (10–14 Hz) while two-bond coupling is vanishingly small. For example, the resonance due to C 4 appears as a doublet ($^1J_{C-H}$ 156 Hz) as there is no two-bond coupling to H 3 or H 5. In contrast, the

Table 2. ^{13}C n.m.r. spectroscopic assignments for *C*-stannylated troponoids (2), (3) and (5)

δ_C values are given

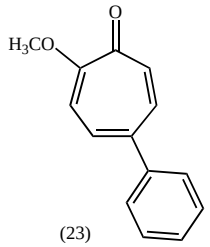
Compound	$Sn(CH_3)_3$	OCH_3	C 1	C 2	C 3	C 4	C 5	C 6	C 7
(2)[A]	−8·8	—	176·3	169·6	136·0[C]	159·6	135·3[C]	130·7	123·3
(3)[B]	−8·8	56·2	180·5	162·9	118·2	152·9	136·0	135·9	135·7
(5)[B]	−9·1	56·2	180·5	164·9	112·5	140·6	145·8[C]	135·4	142·7[C]

[A] Spectrum was recorded at 22·5 MHz in $CDCl_3$ solution.
[B] Spectra were recorded at 100 MHz in CDCl solution.
[C] This assignment may be interchanged with an equivalently marked signal from the same row.

resonance due to C 7 appears as a doublet of doublet of doublets with $^1J_{C-H}$ 159 and $^3J_{C-H}$ 10 Hz. From such observations the ^{13}C n.m.r. spectrum of compound (7) could be completely assigned (Table 1) and using such assignments in conjunction with the results of certain long-range HETCOR experiments allowed the resonances associated with the ^{13}C n.m.r. spectra of compounds (2), (3) and (5) to be almost fully assigned (Table 2).

Palladium-Mediated Cross-Coupling of *C*-Stannylated Troponoids (5) and (7) with Bromobenzene

The cross-coupling of stannanes (5) and (7) with bromobenzene in the presence of dichlorobis(triphenylphosphine)palladium(II) (1991 report[3]) proceeded smoothly to give the expected products, viz. the phenyltropolone *O*-methyl ethers (23) and (24), respectively. These products were found to be identical to the phenylated compounds obtained in our earlier work.[3] However, the yields associated with the title reactions were somewhat lower than those obtained in the previously reported[3] 'normal polarity' couplings.



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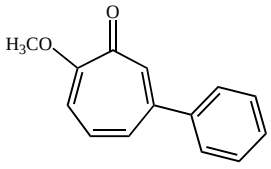

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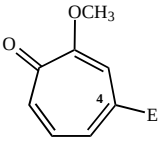
Attempts to couple either of the *C*-stannylated tropones (6) and (8) with bromobenzene under the same reaction conditions as defined above for congeners (5) and (7) failed to provide any significant quantities of the corresponding phenyltropone—only complex mixtures were obtained. We attribute these results to the instability of compounds (6) and (8) under the reaction conditions employed.

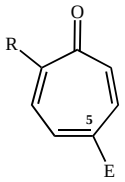
The successful Stille cross-coupling of stannanes (5) and (7) with bromobenzene prompted a brief investigation of the coupling of the same compounds with acid chlorides in the hope that *C*-acylated troponoids could be obtained. In the event, however, both compound (5) and (7) failed to deliver the desired products when treated with benzoyl or 4-methylbenzoyl chloride in the presence of various palladium-based catalysts. This outcome was despite attempts to effect the desired cross-coupling reactions under a range of different conditions including those involving use of carbon monoxide atmospheres in an effort to suppress potential competitive decarbonylation reactions.[16] Although no characterizable products could be obtained, it was apparent from analysis of the ^{1}H n.m.r. spectra of the crude reaction mixtures that the trimethylstannyl group associated with each of the starting materials was being lost under all of the various reaction conditions that were examined.

Reaction of Stannanes (3) and (5)–(8) with Electrophiles: the Formation of *ipso*-Substitution Products*

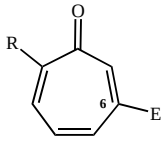
Reaction of the title stannanes with molecular bromine, DCl and/or *N*,*N*-dimethylmethyleneammonium chloride as electrophiles has also been investigated. With the exception of compound (6), each of these substrates reacted with bromine (either in the form of molecular bromine or pyridinium hydrobromide perbromide) to give the corresponding *ipso*-bromination products (25), (27), (31) and (34) in high yield (≤78%). The reason for the rather poor yield (43%) associated with the conversion (6) → (30) remains unclear at the present time. Nevertheless, these results not only establish that the directing effect of the trimethylstannyl group can override the normal predilection



(25) E = Br
(26) E = D



	R	E
(27)	OCH_3	Br
(28)	OCH_3	D
(29)	OCH_3	$CH_2N(CH_3)_2$
(30)	H	Br



	R	E
(31)	OCH_3	Br
(32)	OCH_3	D
(33)	OCH_3	$CH_2N(CH_3)_2$
(34)	H	Br

* It could be argued that the reactions of *C*-stannylated troponoids (3) and (5)–(8) with electrophiles (as described in this section) is less efficient, in terms of the total number of steps, than allowing anions (10), (16) or (20) to react with the same electrophiles then elaborating the resulting 7-substituted bicyclo[4.1.0]heptenes to the corresponding troponoids. While this latter approach is certainly useful (see the 1989 communication[10]) the capacity to effect regioselective electrophilic substitution at intact troponoid nuclei must still be considered a synthetically advantageous possibility.

Table 3. ^{13}C n.m.r. spectroscopic assignments for brominated troponoids (25), (27) and (31)

Spectra were recorded at 100 MHz in $CDCl_3$ solution. δ_C values are given

Compound	OCH_3	C 1	C 2	C 3	C 4	C 5	C 6	C 7
(25)	56·6	179·4	163·1	117·4	129·9	130·4	135·0	135·6
(27)	56·5	179·6	164·8	111·5	134·3	122·6	140·1	136·1
(31)	56·4	177·2	165·2	110·9	131·5	132·5	136·9	139·4

Table 4. ^{13}C n.m.r. spectroscopic assignments for troponoids (26), (28), (32) and (35)

δ_C values are given

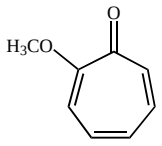
Compound	OCH_3	C 1	C 2	C 3	C 4	C 5	C 6	C 7
(26)[A]	56·3	180·6	165·5	112·3	132·4[B]	127·8	137·0	136·7
(28)[A]	56·3	180·6	165·5	112·3	132·6	127·6[B]	137·0	136·5
(32)[A]	56·3	180·6	165·5	112·4	132·7	127·8	136·3[B]	136·9
(35)[C]	56·2	180·3	165·4	112·6	136·7	127·8	136·7	132·9
(35)[D]	—	180·1	165·0	112·2	132·4	127·6	136·3	136·3

[A] Spectra were recorded at 100 MHz in $CDCl_3$ solution.
[B] Triplet due to ^{13}C–^{2}H coupling (see text).
[C] Assignments due to Bagli and St.-Jacques.[17]
[D] Assignments due to Singh *et al.*[18]

of troponoid compounds to undergo indiscriminate electrophilic substitution but, since the structures of the products are secure, they also serve to confirm the structures of the *C*-stannylated starting materials.

By using two-dimensional (^{1}H/^{1}H and ^{1}H/^{13}C) n.m.r. techniques it was possible to assign all of the resonances in the ^{13}C n.m.r. spectra of bromotroponoids (25), (27) and (31), and the results of such studies are shown in Table 3.

Treatment of stannanes (3), (5) and (7) with DCl in D_2O/CD_3OD resulted in the efficient formation (≤70%) of the 4-, 5- and 6-deuterium-substituted α-tropolone *O*-methyl ethers (26), (28) and (32), respectively. The observation of triplets, due to ^{13}C–^{2}H coupling, at δ 132·4 (J 24 Hz) 127·6 (J 27 Hz) and 136·3 (J 23 Hz) in the {^{1}H}^{13}C n.m.r. spectra of compounds (26), (28) and (32), respectively, allowed the assignment of these signals to C 4, C 5 and C 6, respectively. Taken together, these results (Table 4) support the assignments of the {^{1}H}^{13}C n.m.r. data for the undeuterated (parent) α-tropolone *O*-methyl ether (35) reported by Bagli and St.-Jacques[17] and not the partially conflicting assignments presented by Singh *et al.*[18]



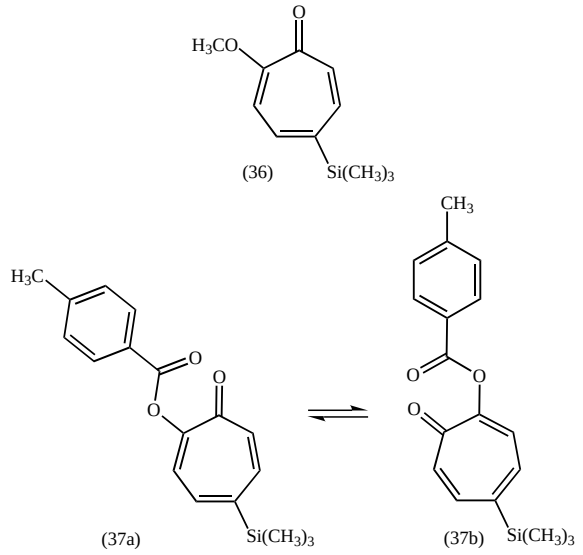
(35)

The Mannich reaction of aryltrialkylstannanes with *N*,*N*-dialkylmethyleneammonium salts to give (dialkylaminomethyl)arenes has been reported by Heaney and coworkers.[19] This report prompted an investigation of the analogous reactions of the *C*-stannylated troponoids (5) and (7). In the event, reaction of these substrates with *N*,*N*-dimethylmethyleneammonium chloride (Aldrich) in refluxing acetonitrile gave the expected products [(29) and (33), respectively] although only in modest (40–62%) yield. Compounds (29) and (33) afforded spectroscopic data in full accord with the assigned structures. Thus, in the electron impact mass spectrum of each compound molecular ions were observed at *m/z* 193 and accurate mass measurements confirmed the molecular formulae as being $C_{11}H_{15}NO_2$ in each case. The 400 MHz ^{1}H n.m.r. spectrum of the former product displayed resonances at, *inter alia*, δ 3·27 and 2·24 which integrated for two and six hydrogens, respectively, and which are assigned to the methylene and dimethylamino hydrogens, respectively, of the newly introduced ring substituent. The ^{1}H n.m.r. spectrum of the isomeric compound (33) contained analogous resonances. The ^{13}C n.m.r. spectra of compounds (29) and (33) each showed the expected 11 signals the assignments of which (see Experimental Section) were determined by using DEPT and HETCOR experiments. In particular, the signals at δ 66·9 and 45·2 [in the spectrum of (29)] and at δ 67·8 and 45·3 [in the spectrum of (33)] can be assigned to the methylene and dimethylamino carbons, respectively, of the newly introduced side chain. The formation of product (33) is of interest in that this compound bears some structural resemblance to the troponoid C-ring of the alkaloid colchicine.

Due to the relative inaccessibility and instability of (6) and (8), the Mannich reactions of the *C*-stannylated tropones (6) and (8) with *N*,*N*-dialkylmethyleneammonium salts were not investigated.

Attempts to effect *ipso*-substitution of the stannyl group in compounds (3), (5) and (7) with various other carbon-centred electrophiles (such as acylium ions generated by treatment of acid chlorides with Lewis acids) produced only complex mixtures of products. Presumably part of the problem here is that the tropolone *O*-methyl ethers are demethylated under the

reaction conditions employed and stable, chemically inert tropolone/metal complexes result.[1] Some support for such a proposal stems from the observation that 5-trimethylsilyl-α-tropolone *O*-methyl ether (36) [prepared by *O*-methylation of the previously reported (1985)[5] free tropolone] reacted with 4-methylbenzoyl chloride in the presence of aluminium trichloride to give the ester (37) (44% at 70% conversion).*



Conclusion

The *C*-stannylated troponoids described herein behave in the expected manner (viz. undergo *ipso*-substitution of the trimethylstannyl group) when subjected to reaction with simple electrophiles or with bromobenzene in the presence of palladium(0). However, the somewhat sensitive nature of these compounds makes them difficult to handle and detracts from their broader application in the synthesis of other troponoids. The procedures detailed here for the preparation of the title compounds are probably inferior to the syntheses recently disclosed by the Pharmacia and Upjohn group.[7]

Experimental

Infrared spectra were recorded on a Perkin Elmer 397, Shimadzu IR27G or Perkin–Elmer 938G instrument. ^{1}H n.m.r. spectra were recorded on either a Varian EM 360L or JEOL GX-400 spectrometer while ^{13}C n.m.r. spectra were obtained on a JEOL GX-400, JEOL JNM-FX 60 or JEOL FX-200 instrument. N.m.r. spectra were recorded in (D)chloroform solution unless otherwise specified. Positive-ion electron impact mass spectra were measured on a VG Micromass 7070F, Varian MAT CH7 or JEOL AX-505H mass spectrometer while high-resolution mass spectra were run on a VG Micromass 7070F, JEOL AX-505H, GEG–AEI MS 902 or AEI MS30 instrument. In the low-resolution mass spectra of stannylated compounds only the three most intense peaks (due to the presence of ^{120}Sn, ^{118}Sn and ^{116}Sn) associated with tin-containing ions have been listed. Unless otherwise specified all mass spectra were recorded at 70 eV. Electronic spectra were recorded in the specified solvent on a Varian u.v. DMS, Varian Carey 219 or Varian Superscan-3 u.v.–visible spectrometer. H.p.l.c. runs were carried out on one of two modular units: (i) that consisting of a Waters Associates u.v. 440 detector, U6K injector and 6000A pump attached to a Waters Associates semipreparative μ-Porasil column (Part No. 84175) or (ii) that consisting of an ISCO 2350 pump, ERMA ERC-7512 ultra high-sensitivity refractive index detector and a Spectra Physics SP4270 reporting integrator attached to a Waters Associates semipreparative μ-Porasil column (Part No. 84175). Gas liquid chromatographic (g.l.c.) analyses were carried out on a Perkin–Elmer Sigma 3B gas chromatograph with a 2 m by 2 mm (i.d.) glass column containing 3% Dexsil on Chromosorb WHP 100/120 and with a nitrogen carrier gas flow rate of 16·1 ml/min. A standard temperature program was used, viz., 70°C (5 min)/heat 10°C min^{-1}/300°C (10 min). Other general experimental procedures have been reported previously (1991 paper[3]).

Synthesis of Stannylated Troponoids (2)–(8)

(1α,6α,7β)-7-Bromo-7-trimethylstannylbicyclo[4.1.0]hept-2-ene (11)

A solution of (1α,6α)-7,7-dibromobicyclo[4.1.0]hept-2-ene[8] (5·00 g 19·8 mmol) in thf (50 ml) maintained under an atmosphere of nitrogen at −100°C was treated in a dropwise fashion with BuLi (13·2 ml of a 1·5 M solution in hexane, 19·8 mmol). The resulting pale-yellow solution was stirred at −100°C for 2 h, after which time a solution of chlorotrimethylstannane (4·50 g, 22·5 mmol) in thf (15 ml) was added dropwise and stirring was continued at −100°C for a further 1·5 h. The reaction mixture was then allowed to warm to −30°C and quenched with 1:1 thf/water (10 ml). The resulting mixture was poured into water (50 ml) and extracted with Et_2O (3×50 ml). The combined organic phases were then dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the *title compound (11)* (6·38 g, 96%) as a yellow oil which was used without further purification in the next step of the reaction sequence. A portion of this oil was subjected to vacuum distillation thereby providing a spectroscopically pure sample of compound (11) as a clear colourless oil, b.p. 110°C/0·1 mmHg (Found: $M^{+\bullet}$, 335·9535. $C_{10}H_{17}{}^{79}Br^{120}Sn$ requires $M^{+\bullet}$, 335·9536). ν_{max} (NaCl) 2981, 2923, 2860, 1448, 1066, 773, 714, 665 cm^{-1}. ^{1}H n.m.r. (90 MHz) δ 6·20–5·50, m, 2H, H2, H3; 2·20–1·50, m, 6H, H1, H4, H5, H6; 0·24, s, 9H, $Sn(CH_3)_3$. ^{13}C n.m.r. (22·5 MHz) δ 129·6, 126·0, 36·3, 26·7, 25·3, 22·3, 20·9, −6·4. Mass spectrum *m/z* (15 eV) 338 (1%) 336 (1, M); 231 (24) 229 (35) 227 (26, C_2H_6BrSn); 165 (44) 163 (35) 161 [21, $(H_3C)_3Sn$]; 91 (100, C_7H_7).

(1α,2α,3α,6α,7β)-7-Bromo-7-trimethylstannylbicyclo-[4.1.0]heptane-2,3-diol (12)

A mixture of compound (11) (9·25 g, 27·5 mmol), t-butyl alcohol (105 ml), water (33 ml), pyridine (5·3 ml) and trimethylamine *N*-oxide dihydrate (6·67 g, 60 mmol) was treated in one portion with osmium tetraoxide (2·3 ml of a 2·5 wt % solution in t-butyl alcohol, 0·23 mmol). The resulting brown solution was heated at reflux under an atmosphere of nitrogen for 30 h, then cooled to room temperature and treated with sodium metabisulfite (50 ml of a 20% wt solution). The volume of the resulting solution was reduced to *c.* 50 ml by

* At 20°C compound (37) exists as a rapidly interconverting mixture of isomers (37a) and (37b) with the result that only nine resonances are observed in the $\{^1H\}^{13}C$ n.m.r. spectrum of this material. However, at −40°C this interconversion is slow on the n.m.r. scale and the expected 14 resonances are observed at this temperature. This type of isomerization has been observed previously in α-tropolone acetates.[20]

rotary evaporation and the dark-brown residue obtained in this manner was extracted with Et_2O (5×50 ml); the solution was dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford a brown oil (7·21 g). Subjection of this material to flash chromatography[21] (silica gel, Et_2O elution) afforded, after concentration of the appropriate fractions (R_F 0·6), the *title compound (12)* (6·70 g, 66%) as a white solid. A sample of this material was recrystallized (benzene) to give spectroscopically pure diol (12) as fine white needles, m.p. 64–65°C (Found: C, 33·1; H, 5·1; Br, 21·5. $C_{10}H_{19}BrO_2Sn$ requires C, 32·5; H, 5·2; Br, 21·6%). ν_{max} (KBr) 3359, 2913, 1442, 1352, 1095, 1066, 1019, 975, 774, 528, 510 cm^{-1}. ^1H n.m.r. (400 MHz) δ 3·85, dd, $J_{2,3}$ 3·4, $J_{2,1}$ 2·2 Hz, 1H, H 2; 3·57, ddd, $J_{3,4a}$ 7·6, $J_{3,4b}$ 3·3, $J_{3,2}$ 3·4 Hz, 1H, H 3; 2·11, m, 1H; 1·85, m, 1H; 1·78, dd, J 2·1, J 10·3 Hz, 1H; 1·65, m, 1H; 1·55, m, 1H; 1·20, m, 1H; 0·35, s, 9H, $Sn(CH_3)_3$ (hydroxy group protons were not observed). ^{13}C n.m.r. (100 MHz) δ 68·2, 67·5, 33·4, 30·7, 26·2, 24·8, 19·3, −5·6. Mass spectrum *m/z* 339 (1%) 337 (2) 335 (2, M − CH_3 − H_2O); 231 (31) 229 (46) 227 [36, $(H_3C)_2SnBr$]; 165 (100) 163 (75) 161 [43, (H_3C_3Sn)].

2-Hydroxy-4-trimethylstannylcyclohepta-2,4,6-trien-1-one (2)

A magnetically stirred solution of dmso (3·70 ml, 52·3 mmol) in CH_2Cl_2 (200 ml) maintained at −60°C under an atmosphere of nitrogen was treated in a dropwise fashion with tfaa (6·67 ml, 47·26 mmol). The resulting colourless solution was stirred at −60°C for 15 min after which time a solution of diol (12) (5·00 g, 13·4 mmol) dissolved in a minimum volume of 1:1 CH_2Cl_2/dmso was added in a dropwise fashion. The resulting solution was stirred at −60°C for 1·5 h and then treated with Et_3N (15·2 ml, 109·0 mmol). Stirring was continued at −60°C for 1·5 h and then the reaction mixture was allowed to warm to room temperature and stirring continued for a further 2 h. The resulting bright-yellow solution was poured into HCl (200 ml of a 2 M aqueous solution) and extracted with CH_2Cl_2 (3×100 ml). The combined organic phases were then dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford a brown solid (4·28 g). Recrystallization (Et_2O/hexane) of this material afforded the *title compound (2)* (2·20 g, 57%) as yellow needles, m.p. 68·5–69·5°C (Found: C, 42·5; H, 4·9%; $M^{+\bullet}$, 286·0016. $C_{10}H_{14}O_2{}^{120}Sn$ requires C, 42·2; H, 5·0%; $M^{+\bullet}$, 286·0016). ν_{max} (KBr) 3198, 1600, 1542, 1454, 1255, 774 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·58, br s, 1H, OH; 7·30–7·18, m, 4H, H 3, H 5, H 6, H 7; 0·37, s, 9H, $Sn(CH_3)_3$. ^{13}C n.m.r. (22·5 MHz) δ 171·3, 169·6, 159·6, 136·0, 135·3, 130·7, 123·3, −8·8. Mass spectrum *m/z* (70 eV) 286 (64%) 284 (45) 282 (24, M); 271 (98) 269 (69) 267 (40, M − CH_3); 165 (100) 163 (75) 161 [45, $(H_3C)_3Sn$].

(1α,6α,7β)-7-Bromo-3-hydroxy-7-trimethylstannylbicyclo-[4.1.0]hept-3-en-2-one (13)

A magnetically stirred solution of dmso (1·00 ml, 14·2 mmol) in CH_2Cl_2 (60 ml) maintained at −60°C under an atmosphere of nitrogen was treated in a dropwise fashion with tfaa (1·62 ml, 11·70 mmol). The resulting colourless solution was stirred at −60°C for 15 min after which time a solution of the diol (12) (1·50 g, 4·07 mmol) dissolved in a minimum volume of 1:1 CH_2Cl_2/dmso was added in a dropwise fashion. The colourless solution so formed was stirred at −60°C for 1·5 h and then treated with Et_3N (3·34 ml, 27·1 mmol). The resulting yellow solution was stirred for a further 1·5 h at −60°C and then warmed to room temperature and immediately poured into HCl (100 ml of a 2 M aqueous solution). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3×100 ml). The combined organic phases were washed with water (2×100 ml) then dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford an off-white solid. This material was recrystallized (Et_2O/petroleum spirits) to give the *title compound (13)* (1·06 g, 72%) as colourless prisms, m.p. 113–113·5°C (Found: C, 33·0; H, 4·1; Br, 22·2. $C_{10}H_{15}BrO_2Sn$ requires C, 32·8; H, 4·1; Br, 21·8%). ν_{max} (KBr) 3413, 1654, 1638, 1407, 1228, 1214, 1172, 779 cm^{-1}. ^1H n.m.r. (90 MHz) δ 6·16, br s, 1H, OH; 6·15, br t, J 4·4 Hz, 1H, H 4; 3·35–3·10, complex m, 2H; 3·05–2·89, complex m, 2H; 0·73, s, 9H, $Sn(CH_3)_3$. ^{13}C n.m.r. (100 MHz) δ 190·0, 145·2, 113·8, 37·4, 30·9, 28·2, 23·8, −5·9. Mass spectrum *m/z* 353 (23%) 351 (36) 349 (24, M − CH_3); 271 (19) 269 (34) 267 (45, M − CH_3, − HBr); 231 (58) 229 (90) 227 [62, $(H_3C)_2SnBr$]; 165 (100) 163 (75) 161 [45, $(H_3C)_3Sn$]. λ_{max} ($CHCl_3$) 274 nm (log ϵ 3·73).

(1α,6α,7β)-7-Bromo-3-methoxy-7-trimethylstannylbicyclo-[4.1.0]hept-3-en-2-one (14)

A magnetically stirred solution of α-hydroxy enone (13) (1·00 g, 2·8 mmol) in acetone (75 ml) was treated with K_2CO_3 (11·30 g, 80 mmol) and dimethyl sulfate (12·2 ml, 127 mmol). The resulting mixture was stirred at room temperature for 14 h then a pH 8 buffer solution (70 ml) was added and the mixture stirred at ambient temperatures for a further 9 h. The reaction mixture was extracted with Et_2O (3×50 ml) then dried, filtered and concentrated under reduced pressure to afford the *title compound (14)* (820 mg, 80%) as an off-white solid. A sample of this material was recrystallized (Et_2O/CH_2Cl_2) to afford spectroscopically pure enone (14) as colourless needles, m.p. 141–142°C (Found: C, 34·9; H, 4·4; Br, 20·9. $C_{11}H_{17}BrO_2Sn$ requires C, 34·8; H, 4·5; Br, 21·0%). ν_{max} (KBr) 1667, 1625, 1209, 1172 cm^{-1}. ^1H n.m.r. (400 MHz) δ 5·34, m, 1H, H 4; 3·54, s, 3H, OCH_3; 2·90–2·70, m, 2H, H 5α, H 5β; 2·55, br d, J 8·5 Hz, 1H, H 1; 2·37, br t, J 7·5 Hz, 1H, H 6; 0·22, d, J 0·5 Hz, 9H, $Sn(CH_3)_3$. ^{13}C n.m.r. (100 MHz) δ 188·8, 149·4, 111·2, 54·6, 39·7, 30·5, 28·0, 24·2, −5·8. Mass spectrum *m/z* 367 (29%) 365 (44) 363 (12) 361 (3, M − CH_3); 231 (64) 229 (100) 227 [68, $(CH_3)_2SnBr$].

2-Methoxy-6-trimethylstannylcyclohepta-2,4,6-trien-1-one (7)

A magnetically stirred solution of α-methoxy enone (14) (1·50 g, 3·9 mmol) in dry benzene (100 ml) was treated with dbu (6·3 ml, 39 mmol). The resulting mixture was stirred at room temperature for 2 h at which point t.l.c. analysis (silica gel, 1:9 Et_2O/CH_2Cl_2 elution) showed complete consumption of starting material (R_F 0·7) and the appearance of another chromophoric spot (R_F 0·1). The mixture was then poured into HCl (100 ml of a 2 M aqueous solution) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3×50 ml) and the combined organic phases were washed with water (2×50 ml) then dried, filtered and concentrated under reduced pressure to afford a yellow solid (1·10 g). Recrystallization (Et_2O) of this material afforded compound (7)[7] (1·00 g, 85%) as off-white needles, m.p. 85·5–86·5°C (Found: C, 44·3; H, 5·2%; $M^{+\bullet}$, 300·0169. Calc. for $C_{11}H_{16}O_2{}^{120}Sn$: C, 44·2; H, 5·4%; $M^{+\bullet}$, 300·0172). ν_{max} (KBr) 1603, 1587, 1556, 1227 cm^{-1}. ^1H n.m.r. (400 MHz) see Fig. 1. ^{13}C n.m.r. (100 MHz) see Table 1. Mass spectrum *m/z* 300 (54%) 298 (43) 296 (22, M); 285 (34) 283 (26) 281 (15, M − CH_3); 257 (29) 255 (40) 253 (28, M − CH_3 − CO); 165 (100) 163 (75) 161 [45, $(H_3C)_3Sn$]. λ_{max} ($CHCl_3$) 367sh, 353sh, 340sh, 327sh, 248 nm (log ϵ 3·62, 3·86, 3·92, 3·97, 4·41).

O-*Methylation of 2-Hydroxy-4-trimethylstannylcyclohepta-2,4,6-trien-1-one (2): Formation of 2-Methoxy-4-trimethylstannylcyclohepta-2,4,6-trien-1-one (3) and 2-Methoxy-6-trimethylstannylcyclohepta-2,4,6-trien-1-one (7)*

A solution of α-tropolone (2) (390 mg, 1·30 mmol) in acetone (40 ml) was treated with dimethyl sulfate (7·5 ml,

78 mmol) and K_2CO_3 (7·5 g). The resulting pale-yellow suspension was stirred at ambient temperatures for 2 h then a pH 8 buffer solution was added and the ensuing mixture stirred at ambient temperatures for 24 h. After this time the reaction mixture was poured into CH_2Cl_2 (50 ml) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (2×50 ml), and the combined organic extracts were dried, filtered and concentrated under reduced pressure to give a brown oil. Subjection of this material to preparative t.l.c. (silica gel, ethyl acetate elution, three sweeps) afforded a single major and chromophoric band (R_F 0·9–0·8).

Extraction of the top third of this band afforded a white solid which was recrystallized (Et_2O) to give compound (3)[7] (120 mg, 39%) as colourless needles, m.p. 123–123·5°C (Found: C, 44·4; H, 5·4%; $M^{+\bullet}$, 300·0172. Calc. for $C_{11}H_{16}O_2{}^{120}Sn$: C, 44·2; H, 5·4%; $M^{+\bullet}$, 300·0172). ν_{max} (KBr) 2907, 1602, 1572, 1250, 1224 cm^{-1}. ^1H n.m.r. (400 MHz) see Fig. 1. ^{13}C n.m.r. (100 MHz) see Table 2. Mass spectrum *m/z* 300 (70%) 298 (53) 296 (30, M); 285 (89) 283 (67) 281 (40, M − CH_3); 257 (97) 255 (86) 253 (54, M − CH_3 − CO); 165 (100) 163 (75) 161 [45, $(H_3C)_3Sn$]. λ_{max} ($CHCl_3$) 368sh, 355, 340sh, 329, 250 nm (log ϵ 3·60, 3·84, 3·88, 3·88, 4·38).

Extraction of the lower third of the above-mentioned chromophoric band gave compound (7) (140 mg, 45%) which was identical, in all respects, with the material prepared earlier.

Extraction of the middle of the above-mentioned chromophoric band afforded a *c.* 1:1 mixture of compounds (3) and (7) (40 mg, 13%)

(1α,6α,7β)-7-Bromo-7-trimethylstannylbicyclo[4.1.0]hept-3-ene (17)

A solution of (1α,6α)-7,7-dibromobicyclo[4.1.0]hept-3-ene[8] (15) (7·00 g, 25·8 mmol) in thf (80 ml) maintained under an atmosphere of nitrogen at −100°C was treated in a dropwise fashion with BuLi (16·0 ml of a 1·63 M solution in hexane, 26·1 mmol). The resulting pale-yellow solution was stirred at −100°C for 2 h, after which time a solution of chlorotrimethylstannane (6·16 g, 30·9 mmol) in thf (5 ml) was added dropwise and stirring was continued at −100°C for a further 1·5 h. The reaction mixture was allowed to warm to −30°C and then treated with thf/water (10 ml of a 1:1 mixture). The resulting solution was poured into water (50 ml) and extracted with Et_2O (3×50 ml). The combined organic phases were dried ($MgSO_4$), filtered and then concentrated under reduced pressure to afford the title compound (17) [9·78 g, 86% compound (17) by g.l.c., 94%] as a yellow oil. ^1H n.m.r. (90 MHz) δ 5·48, s, 2H, H 3, H 4; 2·35, br s, 4H, H 2, H 5; 1·75, m, 2H, H 1, H 6; 0·20, s, 9H, $Sn(CH_3)_3$. ^{13}C n.m.r. (22·5 MHz) δ 124·1 (CH), 32·0 (C), 25·5 (CH), 23·3 (CH_2), −6·1 (CH_3). R_t 1016 s.

(1α,3α,4α,6α,7β)-7-Bromo-7-trimethylstannylbicyclo-[4.1.0]heptane-3,4-diol (18)

A mixture of alkene (17) (8·41 g, 25·0 mmol), t-butyl alcohol (115 ml), water (34 ml), pyridine (5·5 ml) and trimethylamine *N*-oxide dihydrate (6·96 g, 62·5 mmol) was treated in one portion with osmium tetraoxide (2·40 ml of a 2·5 wt % solution in t-butyl alcohol 0·24 mmol). The resulting brown solution was heated at reflux under an atmosphere of nitrogen for 60 h. The cooled reaction mixture was then treated with sodium metabisulfite (50 ml of a 20% w/v solution) and the volume of the resulting solution reduced to *c.* 50 ml by rotary evaporation. The dark brown residue obtained in this manner was extracted with Et_2O (5×50 ml) then dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford a brown solid (8·1 g). Recrystallization (benzene) of this material afforded the *title compound (18)* (5·70 g, 62%) as white needles, m.p. 118–119°C (Found: C, 32·6; H, 5·4; Br, 21·7. $C_{10}H_{19}BrO_2Sn$ requires C, 32·5; H, 5·2; Br, 21·6%). ν_{max} (KBr) 3380, 2907, 1065, 880, 774, 533, 516 cm^{-1}. ^1H n.m.r. (400 MHz) δ 3·52, m, 2H, H 3, H 4; 2·15, m, 2H, H 1, H 6; 1·87–1·75, complex m, 4H; 0·33, s, 9H, $Sn(CH_3)_3$. ^{13}C n.m.r. (100 MHz) δ 68·0 (CH), 34·3 (C), 28·8 (CH_2), 24·9 (CH), −6·0 (CH_3). Mass spectrum *m/z* (70 eV) 357 (4%) 355 (5) 353 (3, M − CH_3); 79 (100).

(1α,6α,7β)-7-Bromo-4-hydroxy-7-trimethylstannylbicyclo-[4.1.0]hept-4-en-3-one (19)

A magnetically stirred solution of dmso (390 μl, 1·57 mmol) in CH_2Cl_2 (30 ml) maintained at −60°C was treated in a dropwise manner with tfaa (618 μl, 5·0 mmol). The resulting mixture was stirred at −60°C for 10 min, after which time a solution of diol (18) (580 mg, 1·57 mmol) dissolved in a minimum volume of 1:1 CH_2Cl_2/dmso was slowly added. The resulting colourless solution was stirred at −60°C for 1·5 h then Et_3N (1·30 ml, 9·3 mmol) was added and the by now yellow solution stirred at −60°C for a further 1 h then poured into water (50 ml). The resulting mixture was extracted with CH_2Cl_2 (3×50 ml) and the combined organic extracts were washed with water (1×100 ml) then dried, filtered and concentrated under reduced pressure to afford a yellow oil which crystallized on standing. Recrystallization ($CHCl_3$/hexane) of this material afforded the title compound (19) (410 mg, 71%) as pale-yellow needles.* ^1H n.m.r. (400 MHz) δ 6·42, m, 1H, H 5; 6·09, s, 1H, OH; 2·95, m, 2H, H 2; 2·22, m, 2H, H 1, H 6; 0·21, s, 9H, $Sn(CH_3)_3$. ^{13}C n.m.r. (100 MHz) δ 190·6 (C 3), 146·2 (C 4), 119·0 (C 5), 35·7 (C 7), 34·6, 27·2, 26·4, −6·9. Mass spectrum *m/z* (70 eV) 351 (0·3%, M − CH_3); 165 (100) 163 (75) 161 [45, $(H_3C)_3Sn$].

2-Methoxy-5-trimethylstannylcyclohepta-2,4,6-trien-1-one (5)

A magnetically stirred solution of dmso (750 μl, 8·73 mmol) in CH_2Cl_2 (45 ml) maintained at −60°C under an atmosphere of nitrogen was treated in a dropwise fashion with tfaa (1·35 ml, 4·3 mmol). The ensuing colourless solution was stirred at −60°C for 15 min after which time a solution of diol (18) (1·00 g, 2·7 mmol) dissolved in a minimum volume of 1:1 CH_2Cl_2/dmso was added in a dropwise fashion. The resulting solution was stirred at −60°C for 1·5 h and then treated with Et_3N (3·15 ml, 42·9 mmol). Stirring was continued at −60°C for 1·5 h and then the solution was allowed to warm to *c.* 5°C. The now bright-yellow solution was poured into water (50 ml) and extracted with CH_2Cl_2 (3×50 ml). The combined organic extracts were dried ($MgSO_4$) then filtered and concentrated under reduced pressure to afford a yellow oil. The residue was dissolved in thf (20 ml) and the yellow solution so formed cooled to 0°C and treated with a sixfold excess of ethereal diazomethane. The reaction mixture was allowed to stand at room temperature for 1·5 h then concentrated under reduced pressure to afford a yellow oil which was purified by flash chromatography[21] (1:1 CH_2Cl_2/Et_2O elution). Concentration of the appropriate fractions (R_F 0·6) gave the title compound (5)[7] (0·45 g, 55%) as a light-yellow solid. A portion of this material was recrystallized (Et_2O) to give a spectroscopically pure sample of (5) as yellow needles, m.p. 63–64°C (Found: C, 44·2; H, 5·5%; $M^{+\bullet}$, 300·0169; Calc. for $C_{11}H_{16}O_2{}^{120}Sn$: C, 44·2; H, 5·4%; $M^{+\bullet}$, 300·0172). ν_{max} (KBr) 2971, 1613, 1597, 1583, 1566, 1480, 1447, 1368, 1276, 1250, 829 cm^{-1}. ^1H n.m.r. (400 MHz) see Fig. 1. ^{13}C n.m.r. (100 MHz) see Table 2. Mass spectrum *m/z* 300 (44%) 298 (36) 296 (20, M); 285 (100) 283 (75) 281 (24, M − CH_3); 257 (69) 255 (60) 253 (37, M − CH_3 − CO). λ_{max} ($CHCl_3$) 370, 353, 327, 317, 242 nm (log ϵ 3·51, 3·82, 4·08, 4·04, 4·39).

* This compound decomposed on heating above *c.* 70°C so a melting point could not be determined.

(1α,6α,7α)-7-Bromo-7-trimethylstannylbicyclo[4.1.0]hept-3-ene (21)

The title compound was prepared essentially according to the method employed by Seyferth *et al.*[22] for the synthesis of the corresponding saturated analogue. Thus, freshly distilled isopropyl chloride (2·60 ml, 28·4 mmol) was added to a flame-dried, three-necked flask containing magnesium turnings (0·445 g, 18·3 mmol) and thf (20 ml) maintained under a nitrogen atmosphere. The mixture was stirred mechanically while being heated at reflux for 2·5 h. After this time all of the magnesium had been consumed. The reaction mixture was then cooled to −100°C (Et_2O/dry-ice bath) and compound (15) (4·01 g, 15·8 mmol) in thf (5·0 ml) was added in a dropwise fashion. The reaction mixture was stirred at −78°C for 6 h (acetone/dry-ice bath) and the by now cloudy solution was recooled to −100°C and chlorotrimethylstannane (2·20 g, 11·1 mmol) in thf (5·0 ml) was added in a dropwise fashion. The reaction vessel was maintained at −100°C for 11 h, by which time a cream-coloured slurry had formed. At this point the mixture was warmed to ambient temperature and quenched with ammonium chloride (10 ml of a saturated aqueous solution). The phases were separated and the aqueous phase was extracted with pentane (3×20 ml). The combined organic phases were then dried (Na_2SO_4), filtered, and concentrated under reduced pressure to yield a pale-yellow oil. This material was subjected to Kugelrohr distillation and the *title compound (21)* (2·70 g, 72% based on chlorotrimethylstannane used) was obtained as a colourless oil, b.p. 70°C/0·15 mmHg [Found: $(M-CH_3^{\bullet})^+$, 320·9297. $C_{10}H_{17}{}^{79}Br^{120}Sn$ requires $(M-CH_3^{\bullet})^+$, 320·9301]. ν_{max} (neat film on NaCl plates) 3050, 3000, 2910, 2850, 1680, 1435, 780, 660 cm^{-1}. ^1H n.m.r. (60 MHz) δ 5·58, br s, 2H, H 3, H 4; 2·85–1·68, complex m, 4H, H 2, H 5; 1·18, br m, 2H, H 1, H 6; 0·20, 9H, $Sn(CH_3)_3$. ^{13}C n.m.r. (15 MHz) δ 123·9 (C 3, C 4); 35·0 (C 7); 21·7 (C 1, C 6); 14·2 (C 2, C 5); −9·8 [$Sn(CH_3)_3$]. Mass spectrum *m/z* 338 (0·5%) 336 (0·8) 334 (0·5, M); 323 (18) 321 (27) 319 (18, $M-CH_3$); 231 (42) 229 (60) 227 [44, $(H_3C)_2BrSn$]; 165 (27) 163 (22) 161 [13, $(H_3C)_3Sn$]; 91 (100, C_7H_7).

Allylic Oxidation of Alkene (21): Formation of (1α,6α,7α)-7-Bromo-7-trimethylstannylbicyclo[4.1.0]hept-3-en-2-one (22), 4-Trimethylstannylcyclohepta-2,4,6-trien-1-one (6) and 3-Trimethylstannylcyclohepta-2,4,6-trien-1-one (8)

Anhydrous chromium trioxide (9·63 g, 96·3 mmol) was added to a flame-dried, three-necked flask containing CH_2Cl_2 (8 ml) which was maintained at −20°C under a nitrogen atmosphere. 3,5-Dimethylpyrazole (9·26 g, 96·3 mmol) was then added, in one portion, to the reaction mixture and the resulting brick-red solution was stirred at −20°C for 15 min. The temperature of the reaction mixture was permitted to rise to −10°C and a solution of alkene (21) (2·60 g, 7·7 mmol) in CH_2Cl_2 (5 ml) was added in one portion. The reaction mixture was then stirred at −15 to −10°C for 4 h at which time sodium hydroxide (13 ml of a 0·5 M aqueous solution) and Et_2O (26 ml) were added. Stirring was continued for 1 h while the mixture was maintained at *c.* 0°C. The resulting mixture was then filtered through a 5 cm deep pad of Celite™ and the phases associated with the filtrate were separated. The aqueous phase was extracted with Et_2O (2×25 ml) and the combined organic phases were washed with HCl (2×50 ml of a 2 M aqueous solution), water (2×50 ml) then brine (1×50 ml). The organic phase was then dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a brown-red oil. This material was subjected to column chromatography (Riedel–de Häen silicagel-S, CH_2Cl_2 elution) and, in this manner, two fractions were obtained.

Concentration of the more mobile fraction afforded *compound (22)* (1·50 g, 56%) as pale-yellow crystals, m.p. 63–67°C [Found: $(M-CH_3^{\bullet})^+$, 330·9095. $C_{10}H_{15}{}^{79}BrO^{116}Sn$ requires $(M-CH_3^{\bullet})^+$, 330·9089]. ν_{max} ($CHCl_3$ solution) 3040, 2950, 2840, 1670, 1640, 1425, 1410, 850, 545 cm^{-1}. ^1H n.m.r. (60 MHz) δ 6·77, dt, $J_{3,4}$ 10, $J_{4,5}$ 3·0 Hz, 1H, H 4; 6·03, dt, $J_{3,4}$ 10, $J_{3,5}$ 2·0 Hz, 1H, H 3; 3·03–2·63, br m, 2H, H 5; 2·33–1·60, br m, 2H, H 1, H 6; 0·35, s, 9H, $Sn(CH_3)_3$. ^{13}C n.m.r. (15 MHz) δ 193·5 (C 2), 147·3 (C 4), 129·0 (C 3), 29·6, 25·0, 22·1, −9·3 [$Sn(CH_3)_3$] (one signal was not observed). Mass spectrum *m/z* 352 (0·4%) 350 (0·6) 348 (0·4, M); 165 (70) 163 (50) 161 [30, $(H_3C)_3Sn$]; 121 (100, C_8H_9O). λ_{max} (hexane) 250 sh, 228 nm ($\log\epsilon$ 3·64, 3·66).

Concentration of the less mobile fraction afforded a yellow oil (238 mg) which was subjected to h.p.l.c. (95 : 5 CH_2Cl_2/CH_3CN elution; flow rate 8·0 ml/min; sample concentration 100 mg/1·5 ml; sample volume 0·1 ml).

Concentration of those fractions containing the more mobile component (R_t 630 s) afforded *compound (8)* (77 mg, 4%) as a near colourless oil (Found: $M^{+\bullet}$, 266·0069. $C_{10}H_{14}O^{116}Sn$ requires $M^{+\bullet}$, 266·0062). ν_{max} ($CHCl_3$ solution) 3000, 2925, 1630, 1590, 1570, 920, 840, 580, 540 cm^{-1}. ^1H n.m.r. (60 MHz) δ 7·30, d, *J* 2·0 Hz, 1H, H 2; 7·07, br m, 4H, H 4, H 5, H 6, H 7; 0·35, s, 9H, $Sn(CH_3)_3$.^{13}C n.m.r. (15 MHz) δ 186·9 (C 1), 156·3 (C 3), 149·9, 140·8, 140·5, 135·9, 132·6 (C 2, C 4, C 5, C 6, C 7), −8·9 [$Sn(CH_3)_3$]. Mass spectrum *m/z* 270 (73%) 268 (52) 266 (31, M); 255 (51) 253 (36) 251 (23, $M-CH_3$); 227 (54) 225 (49) 223 (31, $M-CH_3-CO$); 165 (100) 163 (71) 161 [43, $(H_3C)_3Sn$]. λ_{max} (hexane) 312, 301, 253 nm ($\log\epsilon$ 3·49, 3·53, 4·16).

Concentration of the fractions containing the less mobile component (R_t 890 s) afforded *compound (6)* (78 mg, 5%) as a pale-yellow oil (Found: $M^{+\bullet}$, 266·0061. $C_{10}H_{14}O^{116}Sn$ requires $M^{+\bullet}$, 266·0062). ν_{max} ($CHCl_3$ solution) 3000, 2925, 1625, 1585, 1560, 1230, 920, 540 cm^{-1}. ^1H n.m.r. (60 MHz) δ 7·40–6·73, complex m, 5H, H 2, H 3, H 5, H 6, H 7; 0·33, s, 9H, $Sn(CH_3)_3$. ^{13}C n.m.r. (15 MHz) δ 188·4 (C 1), 155·7 (C 4), 142·9, 141·9, 141·1, 140·1, 135·5, −9·0 [$Sn(CH_3)_3$]. Mass spectrum *m/z* 270 (69%) 268 (49) 266 (30, M); 255 (83) 253 (62) 251 (38, $M-CH_3$); 227 (100) 225 (71) 223 (43, $M-CH_3-CO$); 165 (83) 163 (59) 161 [38, $(H_3C)_3Sn$]. λ_{max} (hexane) 313, 300, 279, 254 nm ($\log\epsilon$ 3·08, 3·15, 3·22, 3·56).

Reaction of Compound (22) with Potassium Carbonate/Lithium Chloride: Formation of 3-Trimethylstannylcyclohepta-2,4,6-trien-1-one (8)

Anhydrous potassium carbonate (47 mg, 0·34 mmol) and anhydrous lithium chloride (15 mg, 0·34 mmol) were added to a magnetically stirred solution of enone (22) (60 mg, 0·2 mmol) in dmf (2·0 ml). The resulting mixture was maintained at 50°C under a nitrogen atmosphere for 12 h then cooled to *c.* 0°C and filtered through a 2 cm deep Celite™ pad. The filtrate was concentrated under reduced pressure and the residue subjected to preparative t.l.c. (silica gel, 9 : 1 CH_2Cl_2/Et_2O elution). The single major and chromophoric band (R_F 0·45) thereby obtained was extracted (2 : 1 CH_2Cl_2/Et_2O) to give the title tropone (8) (30 mg, 64%) as a pale-yellow oil. This material was identical, in all respects, with that obtained directly from the CrO_3/3,5-dimethylpyrazole-mediated oxidation of compound (21).

Palladium-Mediated Cross-Coupling Reactions of Stannylated Troponoids (5) and (7) with Bromobenzene

2-Methoxy-5-phenylcyclohepta-2,4,6-trien-1-one (23)

The *C*-stannylated troponoid (5) was added to a solution of bromobenzene (53 μl, 0·5 mmol) and dichlorobis(triphenylphosphine)palladium(II)* (23 mg, 0·33 mmol) in

* Banwell *et al.* (1991).[3]

1,4-dioxan (5·0 ml) and the resulting solution was heated at reflux for 20 h. The cooled reaction mixture was then poured into water (10 ml) and CH_2Cl_2 (10 ml) added. The phases were separated and the aqueous phases extracted with CH_2Cl_2 (3×10 ml). The combined organic phases were then washed with water (2×20 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a yellow oil which was subjected to preparative t.l.c. (silica gel, 1 : 1 CH_2Cl_2/Et_2O elution). The single major and chromophoric band (R_F 0·4) was extracted (CH_2Cl_2/Et_2O) to give the title compound (23) (51 mg, 72%) as light-yellow microcrystals, m.p. 140–141°C [lit. (1991)[3] 140–141·5°C] (Found: $M^{+\bullet}$, 212·0837. Calc. for $C_{14}H_{12}O_2$: $M^{+\bullet}$, 212·0837). ν_{max} (KBr) 1620, 1573, 1556, 1282, 1256, 1116, 779 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·54, dd, $J_{6,7}$ 12·7, $J_{6,4}$ 2·0 Hz, 1H, H 6; 7·49–7·36, complex m, 5H, aromatic hydrogens; 7·33, d, $J_{7,6}$ 12·7 Hz, 1H, H 7; 7·27, dd, $J_{4,3}$ 10·3, $J_{4,6}$ 2·0 Hz, 1H, H 4; 6·86, d, $J_{3,4}$ 10·3 Hz, 1H, H 3; 4·00, s, 3H, OCH_3. ^{13}C n.m.r. (100 MHz) δ 179·8, 164·2, 142·1, 141·6, 138·0, 137·0, 131·2, 128·9, 128·0, 127·3, 112·8, 56·3. Mass spectrum *m/z* 212 (100%, M); 184 (25, M − CO); 183 (53, M − H − CO); 181 (34, M − OCH_3); 141 (45); 115 (45). λ_{max} ($CHCl_3$) 337, 245 nm (log ϵ 4·25, 4·33).

2-Methoxy-6-phenylcyclohepta-2,4,6-trien-1-one (24)

The *C*-stannylated troponoid (7) (100 mg, 0·33 mmol) was cross-coupled with bromobenzene in the same manner as described immediately above for the conversion (5) → (23). Workup provided a yellow oil which was subjected to semipreparative h.p.l.c. (ethyl acetate elution; flow rate 2·0 ml/min) and concentration of the single major fraction (R_t 625 s) gave the title compound (24) (40 mg, 56%) as light-yellow microcrystals, m.p. 114–115°C (lit.[23] 115°C) (Found: $M^{+\bullet}$, 212·0837. Calc. for $C_{14}H_{12}O_2$: $M^{+\bullet}$, 212·0837). ν_{max} (KBr) 1619, 1592, 1579, 1566, 1470, 1231, 760 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·54–7·38, complex m, 6H; 7·14–7·06, complex m, 2H; 6·72, dd, *J* 8·0, *J* 2·7 Hz, 1H, H 3; 3·96, s, 3H, OCH_3. ^{13}C n.m.r. (100 MHz) δ 179·6, 165·2, 149·9, 142·4, 136·2, 131·9, 129·8, 128·7(8), 128·7(6), 127·7, 111·5, 56·3. Mass spectrum *m/z* 212 (100%, M); 184 (44, M − CO); 183 (35, M − H − CO); 181 (30, M − CH_3O); 154 (33); 141 (39). λ_{max} ($CHCl_3$) 370sh, 356sh, 277 nm (log ϵ 3·57, 3·75, 4·42).

Reactions of Stannylated Troponoids (2)–(8) with Electrophiles

Generalized Procedure for the Reaction of Stannylated Troponoids (3), (5) and (7) with Pyridinium Hydrobromide Perbromide. Formation of Compounds (25), (27) and (31)

Pyridinium hydrobromide perbromide (53 mg, 0·17 mmol) was added to a magnetically stirred solution of the appropriate stannane (50 mg, 0·17 mmol) in CH_2Cl_2 (3 ml) maintained under a nitrogen atmosphere. The ensuing yellow solution was stirred at 0°C for 30 min and then at room temperature for 16 h. The resulting pale-yellow reaction mixture was then poured into water (15 ml) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (2×15 ml) and the combined organic phases were washed with HCl (2×20 ml of a 2 M aqueous solution) then water (2×20 ml) before being dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the appropriate brominated troponoid.

4-Bromo-2-methoxycyclohepta-2,4,6-trien-1-one (25)

Reaction of compound (3) with pyridinium hydrobromide perbromide according to the generalized procedure afforded the title compound (25) (28 mg, 78%) as a pale-yellow solid, m.p. 116–118°C (lit.[24] m.p. 117–118°C) (Found: $M^{+\bullet}$, 213·9629. Calc. for $C_8H_7{}^{79}BrO_2$: $M^{+\bullet}$, 213·9629). ν_{max} (KBr) 1624, 1573, 1251, 1221, 1174, 884, 824 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·21, ddd, *J* 9·1, 1·5, 0·7 Hz, 1H, H 5; 7·10, dd, *J* 11·9, 0·7 Hz, 1H, H 7; 6·93, dd, *J* 11·9, 9·1 Hz, 1H, H 6; 6·92, m, 1H, H 3; 3·93, d, *J* 0·6 Hz, 3H, OCH_3. ^{13}C n.m.r. (100 MHz) see Table 3. Mass spectrum *m/z* 216 (65%) 214 (68, M); 185 (89) 183 (57); 107 (71) 105 (61); 77 (100, C_6H_5). λ_{max} ($CHCl_3$) 369sh, 356sh, 340, 255 nm (log ϵ 3·58, 3·84, 3·91, 4·44).

5-Bromo-2-methoxycyclohepta-2,4,6-trien-1-one (27)

Reaction of compound (5) under the conditions specified above afforded the title compound (27) (36 mg, 100%) as a pale-yellow solid, m.p. 134–137°C [lit. (1988)[5] 135–137°C] (Found: $M^{+\bullet}$, 213·9630. Calc. for $C_8H_7{}^{79}BrO_2$: $M^{+\bullet}$, 213·9629). ν_{max} (KBr) 1607, 1591, 1568, 1496, 1276, 1253 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·43, dd, $J_{6,7}$ 13·1, $J_{6,4}$ 2·1 Hz, 1H, H 6; 7·41, dd, $J_{4,3}$ 10·7, $J_{4,6}$ 2·0 Hz, 1H, H 4; 7·00, d, $J_{7,6}$ 13·1 Hz, 1H, H 7; 6·48, d, $J_{3,4}$ 10·7 Hz, 1H, H 3; 3·92, s, 3H, OCH_3. ^{13}C n.m.r. (100 MHz) see Table 3. Mass spectrum *m/z* 216 (71%) 214 (73, M); 185 (100) 183 (61, M − CH_3O); 135 (34, M − Br); 107 (35, M − CO − Br). λ_{max} ($CHCl_3$) 379sh, 362, 329, 308sh, 256, 247 nm (log ϵ 3·51, 3·75, 4·02, 3·98, 4·07, 4·19).

6-Bromo-2-methoxycyclohepta-2,4,6-trien-1-one (31)

Reaction of compound (7) under the conditions specified above afforded the title compound (31) (33 mg, 92%) as a pale-yellow solid, m.p. 129–131°C (lit.[24] 129·5–131·5°C) (Found: $M^{+\bullet}$, 213·9630. Calc. for $C_8H_7{}^{79}BrO_2$: $M^{+\bullet}$, 213·9629). ν_{max} (KBr) 1605, 1589, 1573, 1496, 1443, 1281, 1227 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·68, d, $J_{7,5}$ 2·0 Hz, 1H, H 7; 7·09, ddd, $J_{5,4}$ 11·2, $J_{5,7}$ 2·0, $J_{5,3}$ 0·5 Hz, 1H, H 5; 6·81, dd, $J_{4,3}$ 10·3, $J_{4,5}$ 11·1 Hz, 1H, H 4; 6·61, br d, $J_{3,4}$ 10·0 Hz, 1H, H 3; 3·93, d, *J* 0·7 Hz, 3H, OCH_3. ^{13}C n.m.r. (100 MHz) see Table 3. Mass spectrum *m/z* 216 (59%) 214 (59, M); 185 (74) 183 (50, M − OCH_3); 92 (44); 77 (100) (C_6H_5). λ_{max} ($CHCl_3$) 367sh, 353, 340sh, 326sh, 314sh, 254sh, 250 nm (log ϵ 3·48, 3·73, 3·80, 3·84, 3·78, 4·36, 4·38).

Generalized Procedure for the Reaction of Stannylated Troponoids (3), (5) and (7) with Deuterium Chloride. Formation of Compounds (26), (28) and (32)

A magnetically stirred solution of the appropriate troponoid (50 mg, 0·17 mmol) in CD_3OD (0·5 ml) was treated with DCl (33 μl of a 20% wt solution in D_2O, 0·20 mmol) and the resulting mixture was stirred at room temperature for 16 h. The reaction mixture was then poured into water (10 ml) and extracted with CH_2Cl_2 (3×15 ml). The combined organic phases were washed with water (2×10 ml) then dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was subjected to preparative t.l.c. (1 : 1 CH_2Cl_2/Et_2O elution) and the major chromophoric band (R_F 0·4) was extracted (1 : 1 CH_2Cl_2/Et_2O) to give the appropriate deuterated troponoid.

2-Methoxy(4-^{2}H)cyclohepta-2,4,6-trien-1-one (26)

Treatment of compound (3) with DCl under the conditions defined above afforded a white solid which was recrystallized (Et_2O) to give the *title compound (26)* (15 mg, 65%) as a crystalline solid, m.p. 35–37°C (Found: $M^{+\bullet}$, 137·0587. $C_8{}^1H_7{}^2HO_2$ requires: $M^{+\bullet}$, 137·0587). ν_{max} (KBr) 2920, 1619, 1589, 1561, 1555, 1463, 1280, 1219 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·28, m, 2H; 6·90, m, 1H; 6·76, br s, 1H, H 3; 3·97, d, *J* 0·7 Hz, 3H, OCH_3. ^{13}C n.m.r. (100 MHz) see Table 4. Mass spectrum *m/z* 137 (72%, M); 108 (48, M − H − CO); 106 (100, M − CH_3O). λ_{max} ($CHCl_3$) 352sh, 344sh, 332sh, 321sh, 310sh, 246 nm (log ϵ 3·32, 3·64, 3·72, 3·78, 3·73, 3·98).

2-Methoxy(5-^{2}H)cyclohepta-2,4,6-trien-1-one (28)

Treatment of compound (5) with DCl under the conditions defined above afforded a white solid which was recrystallized (Et_2O) to give the *title compound (28)* (16 mg, 70%) as a crystalline solid, m.p. 38–39°C (Found: $M^{+\bullet}$, 137·0583.

$C_8{}^1H_7{}^2HO_2$ requires $M^{+\bullet}$, 137·0587). ν_{max} (KBr) 1613, 1589, 1556, 1249 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·24, m, 2H, H 6, H 7; 7·08, br d, $J_{4,3}$ 9·8 Hz, 1H, H 4; 6·74, dd, $J_{3,4}$ 9·8, J_{3,OCH_3} 0·6 Hz, 1H, H 3; 3·95, d, $J_{OCH_3,3}$ 0·5 Hz, 3H, OCH_3. ^{13}C n.m.r. (100 MHz) see Table 4. Mass spectrum *m/z* 137 (73%, M); 109 (29, M − CO); 108 (65, M − H − CO); 106 (100, M − CH_3O); 66 (54). λ_{max} ($CHCl_3$) 366sh, 350, 335sh, 324, 310sh, 249, 247sh nm (log ϵ 3·55, 3·80, 3·87, 3·93, 3·87, 4·22, 4·21).

2-Methoxy(6-^{2}H)cyclohepta-2,4,6-trien-1-one (32)

Treatment of compound (7) with DCl under the conditions defined above afforded *compound (32)* (19 mg, 86%) as yellow crystals, m.p. 35–37°C (Found: $M^{+\bullet}$, 137·0586. $C_8{}^1H_7{}^2HO_2$ requires $M^{+\bullet}$, 137·0587). ν_{max} (KBr) 1619, 1589, 1556, 1220 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·24, br s, 1H, H 7; 7·10, t, $J_{4,3}$ 10·3, $J_{4,5}$ 10·3 Hz, 1H, H 4; 6·87, br d, $J_{5,4}$ 10·3 Hz, 1H, H 5; 6·74, br d, $J_{3,4}$ 10·3 Hz, 1H, H 3; 3·95, d, *J* 0·5 Hz, 3H, OCH_3. ^{13}C n.m.r. (100 MHz) see Table 4. Mass spectrum, *m/z* 137 (93%, M); 109 (26, M − CO); 108 (69, M − H − CO); 106 (100, M − CH_3O); 79 (41); 78 (37); 66 (60). λ_{max} ($CHCl_3$) 366sh, 350sh, 336sh, 323, 313sh, 248sh, 239 nm (log ϵ 3·41, 3·69, 3·76, 3·85, 3·78, 4·17, 4·25).

Generalized Procedure for the Reaction of Stannylated Troponoids (5) and (7) with N,N*-Dimethylmethyleneammonium Chloride. Formation of Compounds (29) and (33)*

N,N-Dimethylmethyleneammonium chloride (29 mg, 0·312 mmol) was added to a solution of the appropriate stannylated troponoid (60 mg, 0·208 mmol) in dry CH_3CN (2 ml) and the resulting mixture heated at reflux under an atmosphere of nitrogen for 16 h. The cooled reaction mixture was then treated with water (3 ml) and the resulting solution concentrated under reduced pressure. The residue was acidified with HCl (2 M aqueous solution) and washed with CH_2Cl_2 (3×10 ml). The aqueous phase was basified with NaOH (1 M aqueous solution) and extracted with CH_2Cl_2 (3×10 ml). The combined organic extracts were then dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford a yellow oil which was subjected to preparative t.l.c. (silica gel, 99 : 1 $CHCl_3/CH_3OH$ elution). Extraction of the major chromophoric band (R_F 0·1–0·15) afforded the appropriate dimethylaminomethyl product.

5-(Dimethylaminomethyl)-2-methoxycyclohepta-2,4,6-trien-1-one (29)

Reaction of troponoid (5) under the conditions specified above afforded the *title compound (29)* (28 mg, 62%) as a yellow solid, m.p. 71–74°C (Found: $M^{+\bullet}$, 193·1102. $C_{11}H_{15}NO_2$ requires $M^{+\bullet}$, 193·1103). ν_{max} (KBr) 1626, 1573, 1455, 1249 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·35, dd, $J_{6,7}$ 12·5, $J_{6,4}$ 1·8 Hz, 1H, H 6; 7·22, d, $J_{7,6}$ 12·5 Hz, 1H, H 7; 6·99, br d, $J_{4,3}$ 10·0 Hz, 1H, H 4; 6·67, d, $J_{3,4}$ 10·0 Hz, 1H, H 3; 3·92, s, 3H, OCH_3; 3·27, s, 2H, CH_2; 2·24, s, 6H, $N(CH_3)_2$. ^{13}C n.m.r (100 MHz) δ 180·3 (C 1), 164·5 (C 2), 139·0 (C 5), 138·7 (C 7), 136·7 (C 6), 131·7 (C 4), 112·2 (C 3), 66·9 (CH_2), 56·2 (OCH_3), 45·2 [$N(CH_3)_2$]. Mass spectrum *m/z* 193 (21%, M); 150 (22, M − CH_3 − CO); 121 (70, $C_8H_{11}N$); 58 [100, $H_2C{=}N(CH_3)_2{}^+$]. λ_{max} ($CHCl_3$) 362sh, 325, 243, 238 (log ϵ 3·53, 3·92, 4·16, 4·25).

6-(Dimethylaminomethyl)-2-methoxycyclohepta-2,4,6-trien-1-one (33)

Reaction of troponoid (7) under the conditions specified above afforded the *title compound (33)* (16 mg, 40%) as a yellow oil (Found: $M^{+\bullet}$, 193·1104. $C_{11}H_{15}NO_2$ requires $M^{+\bullet}$, 193·1103). ν_{max} (NaCl) 1632, 1592, 1547, 1475, 1228 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·23, m, 1H, H 7; 7·03, m, 2H, H 4, H5; 6·67, dd, $J_{3,4}$ 8·2, $J_{3,5}$ 4·6 Hz, 1H, H 3; 3·94, s, 3H, OCH_3; 3·30, s, 2H, CH_2; 2·26, s, 6H, $N(CH_3)_2$. ^{13}C n.m.r. (100 MHz) δ 179·9 (C 1), 164·7 (C 2), 148·3 (C 6), 136·7 (C 7), 131·5 (C 4), 129·8 (C 5), 112·0 (C 3), 67·8 (CH_2), 56·2 (OCH_3), 45·3 [$N(CH_3)_2$]. Mass spectrum *m/z* 193 (4%, M); 150 (20, M − CH_3 − CO); 58 [100, $H_2C{=}N(CH_3)_2{}^+$]. λ_{max} ($CHCl_3$) 361sh, 345sh, 326, 252 nm (log ϵ 3·49, 3·72, 3·82, 3·86).

2-Methoxy-5-trimethylsilylcyclohepta-2,4,6-trien-1-one (36)

A solution of 2-hydroxy-5-trimethylsilylcyclohepta-2,4,6-trien-1-one* (132 mg, 0·681 mmol) in acetone (15 ml) was treated with dimethyl sulfate (3·0 ml, mmol) and K_2CO_3 (2·63 g, mmol). The resulting mixture was stirred at room temperature for 14 h after which time water (20 ml) was added and stirring was continued for an additional 16 h. The reaction mixture was then partitioned between CH_2Cl_2 (20 ml) and water (20 ml). The aqueous phase was extracted with further CH_2Cl_2 (2×20 ml) and the combined organic phases were then dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a yellow oil which was subjected to preparative t.l.c. (silica gel, 1 : 1 Et_2O/CH_2Cl_2 elution). Extraction (1 : 1 Et_2O/CH_2Cl_2) of the major and chromophoric band (R_F 0·5) afforded a pale-yellow solid which was recrystallized (Et_2O/hexane) to give the *title compound (36)* (76 mg, 54%) as fine yellow needles, m.p. 79–80°C (Found: C, 63·5; H, 7·7; Si, 13·6%; $M^{+\bullet}$, 208·0919. $C_{11}H_{16}O_2{}^{28}Si$ requires C, 63·4; H, 7·7; Si, 13·5%; $M^{+\bullet}$, 208·0919). ν_{max} (KBr) 1612, 1582, 1280, 1251 cm^{-1}. ^1H n.m.r. (400 MHz) δ 7·35, dd, $J_{6,7}$ 12·1, $J_{6,4}$ 1·1 Hz, 1H, H 6; 7·28, d, $J_{4,3}$ 9·8 Hz, 1H, H 4; 7·21, d, $J_{7,6}$ 12·0 Hz, 1H, H 7; 6·76, br d, $J_{3,4}$ 9·8 Hz, 1H, H 3; 3·95, d, *J* 0·5 Hz, 3H, OCH_3; 0·27, s, 9H, $Si(CH_3)_3$. ^{13}C n.m.r. (100 MHz) δ 180·5 (C 1), 165·3 (C 2), 142·0 (C 5), 140·2 (C 7), 138·6 (C 4), 136·0 (C 6), 112·7 (C 3), 56·2 (OCH_3), −1·35 [$Si(CH_3)_3$]. Mass spectrum *m/z* 208 (74%, M); 193 (32, M − CH_3); 165 (100, M − CH_3 − CO); 73 (72). λ_{max} ($CHCl_3$) 370sh, 353sh, 327, 244 nm (log ϵ 3·29, 3·52, 3·73, 4·02).

7-Oxo-4-trimethylsilylcyclohepta-1,3,5-trien-1-yl 4-Methylbenzoate (37)

4-Methylbenzoyl chloride (44 mg, 39 ml, 0·29 mmol) was added to a magnetically stirred slurry of $AlCl_3$ (32 mg, 0·240 mmol) in CH_2Cl_2 (1·5 ml) maintained at 0°C under an atmosphere of nitrogen. A solution of compound (36) (32·5 mg, 0·16 mmol) in CH_2Cl_2 (0·5 ml) was added and the resulting mixture stirred at 0°C for 1 h and then at 40°C for a further 2 h. After this time the cooled reaction mixture was poured into ice/water (15 ml) and HCl (15 ml of a 2 M aqueous solution) was added. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2×20 ml). The combined organic extracts were washed with KOH (2×60 ml of a 1 M aqueous solution) then dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting brown oil was subjected to preparative t.l.c. (silica gel, CH_2Cl_2 elution) and two major and chromophoric bands were observed.

Extraction (CH_2Cl_2) of the more mobile band (R_F 0·6) afforded the *title compound (37)* (15 mg, 44% at 70% conversion) as a light yellow oil (Found: $M^{+\bullet}$, 312·1181. $C_{18}H_{20}O_3{}^{28}Si$ requires $M^{+\bullet}$, 312·1182). ν_{max} (NaCl) 2957, 1736, 1620, 1556, 1260, 1163, 1071 cm^{-1}. ^1H n.m.r. (400 MHz) δ 8·09, d, *J* 8·3 Hz, 2H; 7·31, m, 6H; 2·45, s, 3H, CH_3; 0·31, s, 9H, $Si(CH_3)_3$. ^{13}C n.m.r. (100 MHz, −40°C) δ 179·2, 164·1, 158·1, 149·9, 144·8, 140·3, 138·9, 137·5, 130·4, 129·2, 128·1, 125·3, 21·9, −1·6. Mass spectrum *m/z* 312 (2%, M); 297 (0·5, M − CH_3); 119 (100, *p*-$H_3CC_6H_4CO^+$). λ_{max} ($CHCl_3$) 316, 244 nm (log ϵ 3·96, 4·55).

* Banwell and Onrust (1985).[5]

Elution (1 : 1 CH_2Cl_2/Et_2O) of the less mobile band (R_F 0·0) provided a chromophoric band (R_F 0·5) which was extracted to afford the starting material (36) (9·7 mg, 30% recovery) identical, in all respects, with an authentic sample.

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