# Spectroscopic Properties of Axially and Equatorially Substituted β-Trimethylstannyl Ketones and Compounds with Related Chromophores

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The synthesis of two optically active cyclohexanones, with a β-trimethylstannyl substituent, are described and their c.d. spectra are reported. Whereas the axial $SnMe_3$ group confers a dissignate (anti-octant) contribution on the $n \rightarrow \pi^*$ transition relative to the parent unsubstituted ketone, the equatorial $SnMe_3$ group contributes strongly in a consignate (octant) sense. This contrasting behaviour is rationalized in terms of a conformationally dependent through-bond coupling between the lone pair on the carbonyl oxygen atom and the electron-donating C–Sn bond which gives rise to a higher energy transition in the equatorially substituted compound. This band is assigned to the second component of the split $n \rightarrow \pi^*$ transition. The spectral properties of some βγ-unsaturated ketones, in which the p orbital on the β-carbon atom is in the same orientation with respect to the carbonyl group as the equatorial C–Sn bond, are identical. Thus the high energy band, formerly assigned to a charge transfer transition, should be reassigned as a second $n \rightarrow \pi^*$ transition.

WE have related empirically the conformational require-ments of the lone pair on a nitrogen atom in a chiral axial α-amino-ketone to the sign of the Cotton effect of

(1)

(2)
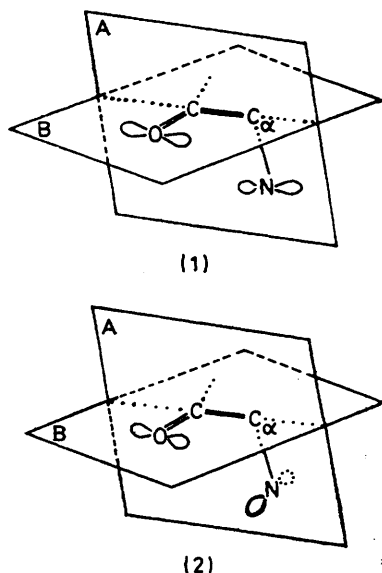
the red-shifted $n \rightarrow \pi^*$ transition.[1] The N atom induces a relatively strong consignate [2] (octant) contribution when the lone pair is *trans*-antiperiplanar to the C_α–C(=O) bond [see (1)], and a dissignate [2] (anti-octant) contribution when it is gauche to the same C–C bond [see (2)].† A new transition of opposite Cotton effect to the $n \rightarrow \pi^*$ one is observed at higher energy in the former case (1).
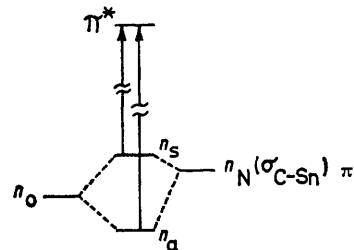
The protonation of (1) causes several changes in the c.d. spectrum: [1] (a) the consignate contribution of N to the $n-\pi^*$ transition changes to a dissignate contribution; (b) its red shift decreases; and (c) the high energy transi-

tion disappears. We have thus concluded [1] that the red shift in the $n \rightarrow \pi^*$ transition of (1) is due to a combination of two effects: (i) the coupling of the π/π^* orbitals of the C=O group with the σ/σ^* orbitals of the C–N bond [3] and (ii) the interaction of the N lone pairs with other orbitals of the C=O group. Our recent calculations [4] on various conformers and rotamers of amino-acetone show that the N and O lone pairs couple strongly *via* the intervening C_α–C(=O) bond in a conformation corresponding to (1) thus accounting for the second part of the red shift. The high energy transition is now assigned to a second $n \rightarrow \pi^*$ transition [4] (see Figure). As might be expected, the two $n \rightarrow \pi^*$ transitions should have Cotton effects of opposite sign because the two n levels have opposite symmetries.

The purpose of the present work was to isolate the role of the N lone pair (a π-donor ‡) and test experimentally its effect on the $n \rightarrow \pi^*$ transition, without the complicat-ing effect of the axial C–N bond (σ-withdrawer). In principle this can be achieved by replacing the N atom by a C atom to which is attached an atom X chosen so that the C–X bond acts as a σ-donor,‡ *i.e.* X must be less electronegative than C. We have chosen X = $SnMe_3$ for two reasons, the first being mainly synthetic and the

second theoretical. The photoelectron spectra of tin alkyl compounds [5] show that the first ionisation potential is relatively low, comparable in energy to that of the N lone pair.[6]

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† The contribution of the N atom is evaluated relative to the parent unsubstituted ketone or to a ketone in which the N atom is replaced by a C atom, using $\delta\Delta\epsilon = \Delta\epsilon$ (amino-ketone) $- \Delta\epsilon$ (parent ketone). Throughout this paper a positive $\delta\Delta\epsilon$ implies consignate contribution and negative $\delta\Delta\epsilon$ a dissignate one, the substituent being placed in a positive rear octant.

‡ The coupling of the lone pair on oxygen can take place with any filled orbital *provided* it is correctly oriented and of compar-able energy to the n_0 orbital. We distinguish its origin and describe it as a π-donor if it is derived from the n orbital of a heteroatom or a p orbital of a double bond, and a σ-donor if it is derived from a C–X σ-bond. A detailed discussion of π-/σ-donors/acceptors can be found in L. Libit and R. Hoffmann, *J. Amer. Chem. Soc.*, 1974, **96**, 1370.

[1] J. Hudec, *Chem. Comm.*, 1970, 829.
[2] W. Klyne and D. N. Kirk, *Tetrahedron Letters*, 1973, 1483.
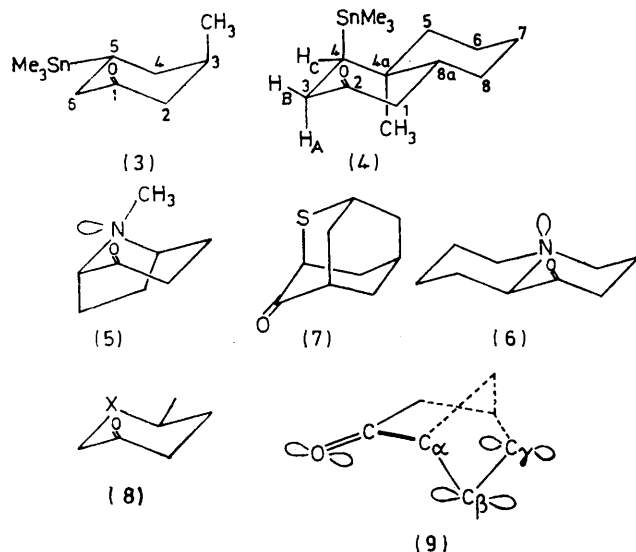[3] N. L. Allinger, J. C. Tai, and M. A. Miller, *J. Amer. Chem. Soc.*, 1966, **88**, 4495.
[4] C. C. Levin, R. Hoffmann, W. J. Hehre, and J. Hudec, *J.C.S. Perkin II*, 1973, 210.
[5] A. Schweig, V. Weidner, and G. Mannel, *J. Organometallic Chem.*, 1973, **54**, 145.
[6] S. D. Worley, *Chem. Rev.*, 1971, **71**, 295.

The required compounds (3) and (4) were made by the conjugate addition of $(Me_3Sn)_2CuLi$ to the corresponding

(3)

(4)

(5)

(7)

(6)

(8)

(9)

enones. In either case only one epimer, formed by axial 1,4-addition, could be isolated by preparative t.l.c. This parallels the reported behaviour of Me_2CuLi.[7] The structural assignments, and the conformation in case of (3), were confirmed by ^{1}H and [13]C n.m.r. spectroscopy. The axial orientation of the trimethylstannyl group in (4)

model compounds 3α- and 3β-trimethylstannylcholestane have $Sn(CH_3)_3$ resonances 9·3 and 12·1 p.p.m. upfield, respectively from Me_4Si.[8] A similar difference in chemical shift is observed for (4) ($-7\cdot5$ p.p.m.) and (3) ($-11\cdot1$ p.p.m.), indicating an axial and an equatorial Me_3Sn group. The axial orientation of the C-methyl group in (3) follows from the upfield shift of the C-5 resonance (20·1 p.p.m.) in comparison with the C-3 resonance in 3β-trimethylstannylcholestane (25·2 p.p.m.), as well as from the upfield shift of the $3-CH_3$ resonance (20·7 p.p.m.) in (3) in comparison with that in 3-methylcyclohexanone (22·9 p.p.m.) where it is oriented equatorially. These upfield chemical shifts of the terminal C atoms of a *gauche*-butane fragment relative to a *trans*-butane fragment are the result of the γ-effect,[9] a through-space interaction. If the Me_3Sn and Me groups in (3) were *cis*-diequatorial, the Me group should have the same chemical shift as in 3-methylcyclohexanone because the δ-effect of an equatorial Me_3Sn group is $\pm0\cdot0$ p.p.m.[8,10]

DISCUSSION

The c.d. and u.v. data (Table) show that when the lone pair on N is replaced by an electron-donating σ bond, the expected spectral behaviour does occur, perhaps even more strongly than was anticipated. Thus (3) has two $n\rightarrow\pi^*$ bands of opposite sign of comparable $\Delta\varepsilon$, as has (5). However, a more detailed comparison between (3) and (5) is difficult on account of the conformational inversion of

Compound	C.d.		Solvent *	U.v.	
	$\lambda_{max.}/nm$	$\Delta\varepsilon$		$\lambda_{max.}/mn$	ε
$(3S,5R)$-3-Methyl-5-trimethylstannylcyclohexanone (3)	298	$+6\cdot51$	M	296·5	89
	220	$-9\cdot06$		215sh	1150
$(3R)$-3-Methylcyclohexanone	290	$+0\cdot59$	M		
$(4R,4aS,8aR)$-4a-Methyl-4-trimethylstannylperhydronaphthalen-2-one	294	$-1\cdot50$		286	33
	229	$+0\cdot55$	M	Continuously rising	
	204	$-2\cdot05$ to		end absorption	
		$-2\cdot40$			
$(4aR,8aR)$-4a-Methylperhydronaphthalen-2-one	289	$-1\cdot24$	M		
$(1R,5S)$-Tropin-2-one (5)	319	$+2\cdot4$	E	314	68
	228	$-4\cdot1$		228	500
$(1R,5R)$-Bicyclo[3.2.1]octan-2-one [a]	297	$-0\cdot84$	D	287	18
$(9aR)$-Quinolizidin-1-one (6) [b]	300	$-1\cdot42$	Io	300	37
$(4aR,8aS)$-Perhydronaphthalen-1-one [c]		$+1\cdot00$	M	280	43
3α-Trimethylstannylcholestane	203	$+1\cdot4$	E		
3β-Trimethylstannylcholestane	210	$+2\cdot2$	H †		

* M = methanol; E = ethanol; D = dioxan; Io = iso-octane; H = n-hexane.   † Insoluble in both methanol and ethanol.

[a] H. M. Walborsky, M. E. Baum, and A. A. Youssef, *J. Amer. Chem. Soc.*, 1961, **83**, 988.   [b] Ref. 13.   [c] D. N. Kirk and W. Klyne, *J.C.S. Perkin I*, 1974, 1076.

follows from the vicinal coupling constants of the ABC system. The geminal AB protons adjacent to the C=O group, J_{AB} $-14\cdot9$ Hz, δ 2·73, couple with the proton C, δ 1·72, with J_{AC} 8·0 and J_{BC} 1·9 Hz; thus proton C must be equatorial. If the Me_3Sn group were equatorial, the axial proton C should have vicinal coupling constants of *ca.* 13·5 and 6·0 Hz. Further confirmation of the axial orientation of $SnMe_3$ in (4) comes from [13]C n.m.r. The

‡ Detailed analysis of the c.d. data will be published later together with the temperature-variable [13]C n.m.r. spectra.

[7] N. L. Allinger and C. K. Riew, *Tetrahedron Letters*, 1966, 1269; J. A. Marshall and N. H. Anderson, *J. Org. Chem.*, 1967, **31**, 667.

[8] J. Hudec, unpublished work.

the N-methyl group in (5). We will therefore discuss in greater detail the spectral properties of (5).‡

Low temperature [13]C n.m.r. measurements on (5) indicate that the Me group exists *ca.* 55—70% in the axial form at room temperature. By using $\delta\Delta\varepsilon = -2\cdot4$ for the N atom with an equatorial alkyl group in (6) (which should be a maximal value on account of the solvent difference), we can calculate a $\delta\Delta\varepsilon$ range of $+7\cdot4$ to $+5\cdot3$

[9] D. M. Grant and B. W. Cheney, *J. Amer. Chem. Soc.*, 1967, **89**, 5315, 5319; H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 7445.

[10] D. Dodrell, I. Burfitt, W. Kitching, M. Bullpitt, C. H. Lee, R. J. Minott, J. L. Considine, H. G. Kuivilla, and R. H. Sarma, *J. Amer. Chem. Soc.*, 1974, **96**, 1640.

for (5) containing 55—70% of the conformer with the axial N methyl group. In comparison, $\delta\Delta\varepsilon$ for (3) is $+6\cdot5$, if we assume that the axial methyl group contributes $\delta\Delta\varepsilon$ ca. 0,[11] indicating comparable π-electron donation from the N lone pair and σ donation from the C–Sn bond. The red shift in the 290 nm band (c.d.) of (3) is $0\cdot11$ eV, whereas the value is $0\cdot39$ eV for (5) ($\lambda_{max.}$ for the parent ketone was corrected for the solvent shift dioxan→ethanol by 7 nm). A large part of this difference is due to interaction in (5) between the σ^* orbital of the C–N bond with the π^* orbital of the carbonyl group. Such interaction cannot be expected in (3).

The negative high energy Cotton effect of (5) is assigned to the $n_a{\rightarrow}\pi^*$ transition; by analogy the same assignment applies to the high energy band of (3). An alternative assignment as a $\sigma{\rightarrow}\sigma^*$ transition of Sn–C is most unlikely as it occurs at even higher energy [12] (see also c.d. of 3α- and 3β-trimethylstannylcholestane in the Table). The through-bond coupling of the nitrogen and oxygen lone pairs of (5) has a splitting of n_a and n_s levels of $1\cdot67$ eV (Figure); the corresponding splitting for (3) is $1\cdot47$ eV, resulting from the coupling of the oxygen lone pair and the C–Sn bond (Figure; n_N replaced by σ_{C-Sn}).

The comparison of (4) and (6) [13] is difficult on account of the lack of u.v. and c.d. data below 250 nm. Nevertheless, both (4) and (6) show a dissignate [2] behaviour of the $n{\rightarrow}\pi^*$ transition, $\delta\Delta\varepsilon$ $-0\cdot26$ and $-2\cdot4$ respectively. In addition, (4) has two Cotton effects at 229 and 204 nm. It is quite probable that the 229 nm band is a weak second $n{\rightarrow}\pi^*$ transition as the sign is opposite to that of the 294 nm band. Indeed, our calculations [4] predict such behaviour for α-amino-ketones such as (6). The n_o and n_N orbitals can still couple via the C_a–C(=O) bond but weakly, resulting in smaller splitting of the new n_s and n_a levels with the result that the two $n{\rightarrow}\pi^*$ transitions move closer together. Thus it is possible that (6) has a weak positive band below 250 nm—indeed, the reproduced spectra [13] indicate this. The nature of the 204 nm band of (5) is not certain; it may be a $\sigma{\rightarrow}\sigma^*$ or an $n_o{\rightarrow}\sigma^*$ transition.

The isotropic absorption of (3) and (5) parallels the c.d. both in transition probability and in $\lambda_{max.}$ for the $n_s{\rightarrow}\pi^*$ transition. The higher energy band is visible as a shoulder only for (3).

With the analogy established between a σ-donor C–X bond and a π-donor lone pair on N with respect to their effects on the spectral properties of ketones when properly oriented as in (3) and (5), it is relatively easy to generalise the concept of orbital coupling to other substituents. We predict similar spectral behaviour from other σ-donors such as SiR$_3$, GeR$_3$, HgR, and aqua- or

pyridine-bisdimethylglyoximatocobalt complexes. In case of heteroatom π-donors other than N, complex spectra explainable in terms of through-bond coupling have been observed only in the case of S,[8,14-16] one example being (7),[14] although they can be also expected with Se, P, and probably I (axial α-iodo-ketones). It appears that the main requirement, apart from the correct relative orientation of the n_o and n_X orbitals, is the n_X (or C–X) energy level which should be very close to n_o or lower.

The recent work [16] on the c.d. of 1-methyl- and 1-ethyl-6-methylpiperidin-3-one (8; X = NMe or NEt) and 6-methyltetrahydrothiopyran-3-one (8; X = S) requires some comment in the light of the above conclusions. The reported $\lambda_{max.}$ (MeOH) 296 nm for (8; X = NEt) compares well with the $\lambda_{max.}$ value of (6) and thus the lone-pair on N in (8; X = NEt) must be axial, resulting in a dissignate contribution of the nitrogen atom. It is difficult at present to rationalise the difference between the magnitudes of the dissignate $\delta\Delta\varepsilon$ contributions in (6) ($\delta\Delta\varepsilon$ $2\cdot4$) and (8; X = NEt) ($0\cdot8$); it may be due to the difference in pattern of substitution on the C atoms attached to the N atom [8] (C-6 and C-2). Similar comment applies also to the large difference in the consignate contributions of S in (7) [14] ($\delta\Delta\varepsilon$ $+21\cdot8$) and (8; X = S) ($+1\cdot75$); it is probably amplified further by a distortion of the tetrahydrothiopyranone ring in (8; X = S) which cannot take place in (7). Compounds (7) and (8; X = S) have a second band of opposite chirality to the one at ca. 315 nm, at 257 and 250 nm, respectively. This band has been assigned in the latter case to the $n{\rightarrow}\sigma^*$ transition of S.[16] Our work [8] on thioketones of the type (7) or (8; X = S) shows that this band should be assigned to the second $n{\rightarrow}\pi^*$ transition, $n_a{\rightarrow}\pi^*$.

The last and probably most extensively studied substituents that fall into this category are the double bond in a $\beta\gamma$-unsaturated ketone [17,18] and the phenyl group of an α-axial phenyl ketone.[18,19] These chromophores, when the relative orientation of the double bond and the carbonyl group is as in (9), give rise to a red-shifted and greatly enhanced $n{\rightarrow}\pi^*$ transition with positive Cotton effect as well as a high energy band of opposite sign. The latter transition was at first assigned to a charge transfer transition [19] and later to a $\pi{\rightarrow}\pi^*$ transition.[17b] Comparison of (1) and (9) shows that the p orbital on C_β has the same orientation as the lone pair on N and is thus ideally disposed for a through-bond coupling with n_o. It is thus possible to reassign the high-energy transition of (9) to a second $n_a{\rightarrow}\pi^*$ transition. The $\beta\gamma$-unsaturated ketone (9), a homoconjugated π-system, has been classified as an inherently disymmetric chromophore [18]

[11] G. Snatzke, B. Ehrig, and J. Klein, *Tetrahedron*, 1969, **25**, 5601.

[12] C. W. N. Cumper, A. Melinkoff, and A. I. Vogel, *J. Chem. Soc. (A)*, 1966, 242; P. P. Shorygin, V. A. Petukov, O. M. Nefedov, S. P. Kolesnikov, and V. I. Shiryaer, *Teor. eksp. Khim.*, 1966, **2**, 190.

[13] S. Yamada and T. Kunieda, *Chem. and Pharm. Bull. (Japan)*, 1967, **15**, 490; S. F. Mason, K. Schofield, and R. J. Wells, *J. Chem. Soc. (C)*, 1967, 626.

[14] G. Snatzke and B. Wolfram, *Tetrahedron*, 1972, **28**, 655.

[15] C. H. Robinson, L. Milewich, G. Snatzke, W. Klyne, and S. R. Wallis, *J. Chem. Soc. (C)*, 1968, 1245.

[16] M. M. Cook and C. Djerassi, *J. Amer. Chem. Soc.*, 1973, **95**, 3678.

[17] (a) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 1956, 2302; (b) D. E. Bays and R. C. Cookson, *J. Chem. Soc. (B)*, 1967, 226.

[18] K. Mislow, M. A. W. Glass, A. Moskowitz, and C. Djerassi, *J. Amer. Chem. Soc.*, 1961, **83**, 2771; 1962, **84**, 1945.

[19] R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 1962, 429; R. C. Cookson and S. Mackenzie, *Proc. Chem. Soc.*, 1961, 423.

on account of its very high $\delta\Delta\varepsilon$ values relative to the saturated ketone or to an axial α-halogeno-ketone, which are classed as asymmetrically perturbed symmetric chromophores.[18] Although this distinction was valuable originally, we consider that its retention is no longer necessary.[20]

EXPERIMENTAL

¹H N.m.r. spectra were measured for solutions in CDCl₃ with a Varian HR-100 and ¹³C n.m.r. spectra with a Bruker FT 20 instrument. ¹³C Assignments were made by comparison of fully decoupled and off-resonance spectra. A benzene lock was used for ¹H n.m.r. and Me₄Si was employed as internal reference for ¹³C n.m.r. The low-temperature ¹³C runs were carried out in CD₂Cl₂–CS₂ (4 : 6) down to 153 K. Chemical shifts are quoted in p.p.m. downfield from Me₄Si. C.d. spectra were run on a JASCO UV-CD-5 instrument modified with an SS-20 attachment.

The starting $\alpha\beta$-unsaturated ketones were synthesized in the following manner. Bromination of (3R)-3-methylcyclohexanone gave (2R,5R)-2-bromo-5-methylcyclohexanone,[21] m.p. 81—82°, which was dehydrobrominated in refluxing collidine to give (5R)-5-methylcyclohex-2-enone, b.p. 164—170°. 4a,5,6,7,8,8a-Hexahydro-4a-methylnaphthalen-2(1H)-one was prepared as described [22] from the antipodal bicyclic intermediate [23] used for the total synthesis of steroids.

General Method for Trimethylstannylation of $\alpha\beta$-Unsaturated Ketones.—Hexamethyldistannane (1·8 g, 5 mmol) was added to dry tetrahydrofuran (15 ml) in which were suspended freshly cut lithium wire pieces (*ca.* 100 mg). The mixture was stirred under a stream of dry nitrogen for 3—4 h at room temperature. The black solution of trimethylstannyl-lithium was transferred (syringe) into another flask containing copper(I) iodide (60 mg) under dry nitrogen. The mixture was stirred for 1 h, and the $\alpha\beta$-unsaturated ketone (7—8 mmol) was then added. Stirring at room temperature was continued for another 2 h, then the tetrahydrofuran was slowly distilled off (steam-bath) to one quarter of the original volume in 30—45 min. The mixture was diluted with water and filtered through Celite. The residue was well washed with ether, which was used for extraction of the filtrate. The extract was washed 5 times with water, dried (Na₂SO₄), filtered, and evaporated. The residue was chromatographed on silica gel plates (0·8 mm thick) with 10% ether in n-pentane as the eluant.

(3S,5R)-3-Methyl-5-trimethylstannylcyclohexanone (3) had b.p. *ca.* 80° at 0·1 mmHg, δ_H −0·04 (MeSn, $J_{Sn.H}$ 51 and 53 Hz) and 0·87 (Me, J 7·0 Hz); δ_C −11·1 (Me₃Sn), 20·1 (C-5), 20·7 (Me), 34·2 (C-3), 37·2 (C-4), 45·2 (C-6), 49·1 (C-2), and 211·7 (C-1); ν_{max} (neat) 1705 and 865 cm⁻¹.

(4R,4aS,8aR)-4a-Methyl-4-trimethylstannylperhydro-naphthalen-2-one (4) had m.p. 58—60°; δ_H 0·17 (Me₃Sn, J 51 and 53 Hz), 1·18 (Me), 1·72 (H_O, J 8·0 and 1·9 Hz), 2·47 (H_B, J 14·9 and 1·9 Hz), and 3·00 (H_A, J 14·9 and 8·0 Hz); δ_C −7·5 (Me₃Sn), 17·6 (Me), 22·1 (C-6), 26·0 (C-7), 29·6 (C-8), 37·5 (C-4a), 41·7 (C-4), 42·4 (C-3), 44·1 (C-8a), 45·3 (C-1), and 211·1 (C-2); ν_{max} (Nujol) 1705 and 875 cm⁻¹.

[20] *Cf.* K. N. Houk, K. J. Northington, and R. E. Dude, *J. Amer. Chem. Soc.*, 1972, **94**, 6233.

[21] C. Djerassi, L. E. Geller, and E. J. Eisenbraun, *J. Org. Chem.*, 1960, **25**, 1.

[22] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223.

[23] A. J. Speciale, J. A. Stephens, and Q. E. Thompson, *J. Amer. Chem. Soc.*, 1954, **76**, 5011.