No reflections off the layer lines were observed. In addition, ω scans of several reflections gave sharp symmetrical peaks with no evidence of twinning.

Acknowledgment. We thank Professor Carroll W. DeKock for helpful discussions and for his assistance with the X-ray diffraction work.

Registry No. Magnesium anthracene dianion, 84559-48-8.

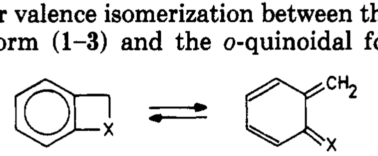
Cycloaddition Reactions of Benzothiet

Kuppusamy Kanakarajan† and Herbert Meier*

Institut für Organische Chemie der Universität Tübingen
Auf der Morgenstelle 18, D-7400 Tübingen, Germany

Received August 10, 1982

Benzo-condensed four-membered heterocyclic ring systems are of special theoretical and synthetic interest because of their valence isomerization between the strained benzenoid form (**1**–**3**) and the *o*-quinoidal form (**4**–**6**).

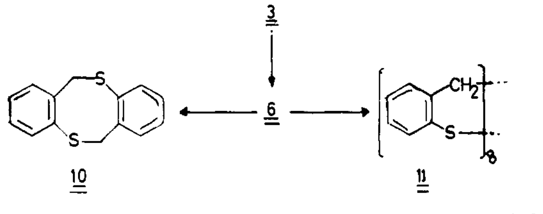


1 (X = NR) **4** (X=NR)
2 (X=O) **5** (X=O)
3 (X=S) **6** (X=S)

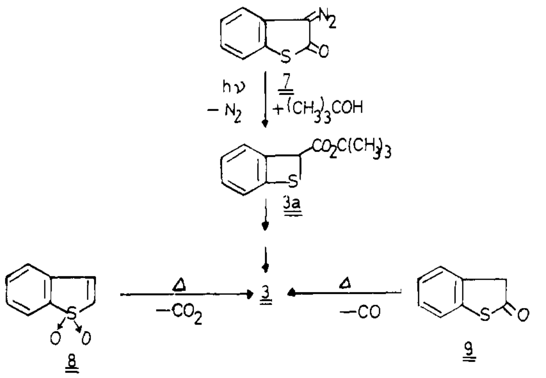
Although benzazetines **1** are well documented since the work of Burgess and McCullagh, all the published benzoxetes **2** in reality have been found to have different structures.[4-6] A few years ago we succeeded in the synthesis of the first benzothiet **3a**.[7,8] The parent compound **3** has been prepared by degradation of the ester **3a**[9] or more conveniently by flash pyrolytic methods, namely by decarboxylation of the benzothiophene dioxide **8**[10,11] or by decarbonylation of the thiolactone **9**[12] (Scheme I).

This easy access renewed the interest to continue our studies of the chemistry of **3**. Here we report the cycloaddition products from the thermal or photochemical activation of **3** in the presence of dienophiles. The aim was to find a convenient synthesis of 4*H*-1-benzothiopyrans and their 2,3-dihydroderivatives.

In boiling toluene, benzothiet (**3**) dimerizes to give 1,5-dibenzo[*b*,*f*]dithiocin (**10**),[10] whereas on being allowed to stand at room temperature in pure state for several days, **3** oligomerizes. ^{13}C and ^{1}H NMR spectra and the mass spectrum gained with the field-desorption technique reveal that the main component is the octamer **11**. Both reactions are regiospecific and presumably proceed via the intermediate formation of **6** by the opening of the four-membered ring.



Scheme I



Scheme II

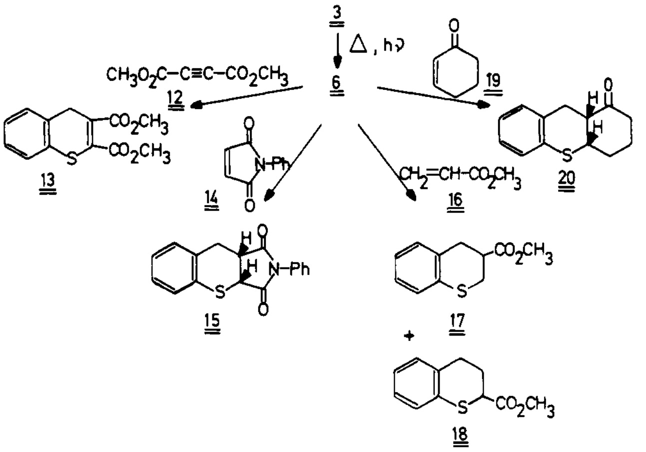


Table I. Yields of Cycloadducts 13, 15, 17, 18, and 20 and the Dimer 10

dienophile	method	cycloadduct (yield, %)	yield of dimer 10, %
12	Δ	13 (65)	20
12	hν	13 (57)	
14	Δ	15 (76)	10
14	hν	15 (66)	
16	Δ	17 (52), 18 (13)	20
19	Δ	20 (25)	55

In the presence of dienophiles these processes can be largely suppressed in favor of $[_{\pi}4_s + {}_{\pi}2_s]$ or $[_{\pi}8_s + {}_{\pi}2_s]$ cycloaddition reactions; however, depending on the reactivity of the dienophile a small portion of benzothiet is converted to the dimer **10** (see Table I). In the case of unsymmetrical dienophiles a regioselectivity can be observed which corresponds to the polarity of both components; i.e., the negative sulfur adds preferentially to the

---

† Alexander von Humboldt Fellow.

(1) H. Kolshorn and H. Meier, *Z. Naturforsch., A*, **32A** 780 (1974).
(2) E. M. Burgess and L. McCullagh, *J. Am. Chem. Soc.*, **88**, 1580 (1966).
(3) For benzazets compare C. W. Rees, *Stud. Org. Chem. (Amsterdam)*, **3**, 356 (1979).
(4) H. Meier, A. Issa, and U. Merkle, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **34B**, 290 (1979).
(5) K. Kanakarajan, V. T. Ramakrishnan, and P. Shanmugam, *Synthesis* **1975**, 501.
(6) H. Meier, H.-P. Schneider, A. Rieker, and P. B. Hitchcock, *Angew. Chem.*, **90**, 128 (1978); *Angew Chem., Int. Ed. Engl.*, **17**, 121 (1978).
(7) E. Voigt and H. Meier, *Angew. Chem.*, **88**, 94 (1976); *Angew. Chem., Int. Ed. Engl.*, **15**, 117 (1976).
(8) E. Voigt and H. Meier, *Chem. Ber.*, **110**, 2242 (1977).
(9) H. Meier, E. Voigt, and U. Merkle, unpublished results. Compare Abstracts Chemiedozenten-Tagung, Marburg, Germany, 1977, p 129.
(10) W. J. M. van Tilborg and R. Plomb, *J. Chem. Soc., Chem. Commun.*, 120 (1972).
(11) W. J. M. van Tilborg and R. Plomb, *Recl. Trav. Chim. Pays-Bas*, **96**, 282 (1977).
(12) R. Schulz and A. Schweig, *Tetrahedron Lett.*, **21**, 343 (1980).

Table II. ^{13}C NMR Absorptions[a] of the Compounds 3, 10, 11, 13, 15, 17, and 20

compd	absorption[a]			
	C_{quat}	C_{arom}	CH_2	other ^{13}C nuclei
3	142.6, 139.5	128.6, 123.9, 122.6, 121.0	36.5	
10	134.1, 134.1	130.0, 128.6, 127.0, 127.0	37.9	
11	138.2, 135.7	131.9, 129.9, 127.8, 126.8	38.1	
13	137.4, 132.5, 130.5, 127.4	128.5, 127.8, 127.1, 126.3	33.7	165.1 (CO), 165.1 (CO), 53.1 (OCH_3), 52.6 (OCH_3)
15	136.6, 131.5, 130.3	129.1, 129.1, 129.1, 128.7 128.2, 128.2, 126.3	32.3	176.1 (CO), 175.0 (CO), 44.4 (CH), 44.1 (CH)
17	132.2, 132.0	130.1, 126.7, 126.4, 124.4	32.1, 28.6	173.8 (CO), 52.2 (OCH_3), 39.6 (CH)
20	131.5, 131.0	129.8, 126.3, 126.3, 124.5	40.1, 29.7, 29.5, 22.5	208.1 (CO), 48.1 (CH), 42.5 (CH)

[a] δ values; $CDCl_3$ solutions with Me_4Si as an internal standard.

carbon with the partial positive charge. Thus the considerable synthetic utility of benzothiet as a sulfur-containing diene is demonstrated here in the preparation of 4*H*-1-benzothiopyran or 2,3-dihydro-4*H*-1-benzothiopyran (thiachroman) derivatives.

Brief examination of the photochemistry of 3 revealed that the same cycloaddition reactions can also be initiated by irradiation. However, in this process, only a small amount of polymeric material and not the dithiocin 10 was observed as a byproduct.

Structure elucidations have been performed on the basis of careful analytical investigations. The ^{13}C chemical shifts are listed in Table II. 15 is identical with the compound obtained in the photolysis of 3*H*-1,2-benzodithiole 2,2-dioxide[13] or of 1-thia-2-indanone (9)[14] in the presence of *N*-phenylmaleimide (14, Scheme II).

Experimental Section

Melting points were taken in a Büchi melting point apparatus and are not corrected. ^{1}H and ^{13}C NMR spectra were run on Bruker WH-90 and WP-80 instruments. The IR spectra were recorded on a Perkin-Elmer 21 spectrometer. Mass experiments were performed on a Varian MAT 711 A instrument.

Benzothiet 3 by Flash Pyrolysis of 9.[15] 1-Thia-2-indanone (9, 1 g) is slowly vaporized over a period of 4 h through a quartz tube (40 × 4 cm) filled with quartz chips held at 1200 °C under 0.1 mm pressure. The pyrolysate is condensed in a cold trap using liquid nitrogen. TLC of the pyrolysate shows the presence of only one product besides a trace of starting material. It is filtered through a short column (1.5 × 10 cm) of silica gel with petroleum ether (bp 30–50 °C) as the eluant to give 730 mg (90%) of benzothiet (3) as a colorless foul-smelling liquid.

1,5-Dibenzo[*b*,*f*]dithiocin (10). Benzothiet (3; 61 mg, 0.5 mmol) in 3 mL of dry toluene is heated to reflux for 3 h, the solvent evaporated, and the residue filtered through a short column (1.5 × 10 cm) of silica gel with petroleum ether (bp 30–60 °C) as the eluant. Recrystallization from petroleum ether gave colorless crystals: 45 mg (75%); mp 170 °C (lit.[16] mp 170–173 °C); ^{1}H NMR ($CDCl_3$) δ 6.81–7.24 (m, 8 H, Ar H), 4.36 (br s, 4 H, CH_2). At lower temperatures a splitting of this singlet into two AB systems corresponding to a boat and a chair conformation (ratio 76:24) is in accordance with the literature.[17]

Octamer 11. Benzothiet (3, 250 mg) on standing at room temperature for 30 days becomes viscous. When it is dissolved in 1 mL of dichloromethane and diluted with petroleum ether (bp 30–60 °C), 50 mg (20%) of a colorless solid, 11, can be isolated. Unchanged 3 (80%) remains in solution. 11 gives no sharp melting point: ^{1}H NMR ($CDCl_3$) δ 7.02–7.34 (m, 32 H, Ar H), 4.12 (s, 16 H, CH_2); IR ($CHCl_3$) 3060, 3000, 2930, 2860, 1587, 1465, 1448, 1060, 1040 cm^{-1}; MS (FD) *m/e* 976 ($M^{+}\cdot$). Anal. Calcd for $C_{56}H_{48}S_8$: C, 68.88; H, 4.91; S, 26.23. Found: C, 68.01; H, 4.71; S, 25.50.

General Procedure for the Cycloaddition Reaction of Benzothiet 3 with Dienophiles. Dimethyl 4*H*-1-Benzothiopyran-2,3-dicarboxylate (13). A solution of benzothiet (3; 61 mg, 0.5 mmol) and dimethyl acetylenedicarboxylate (12; 100 mg, 1.4 equiv) in dry toluene (3 mL) is refluxed for 3 h, the solvent evaporated, and the residue chromatographed over a short column (10 × 1.5 cm) of silica gel with petroleum ether (bp 30–50 °C)/dichloromethane (9:1) as the eluant. The fast-moving dithiocin 10 is isolated, followed by 13 as viscous liquid. 10: yield 12 mg (20%). 13: yield 86 mg (65%); ^{1}H NMR ($CDCl_3$) δ 7.20–7.40 (m, 4 H, Ar H), 3.86 (s, 3 H, CH_3), 3.81 (s, 3 H, CH_3), 3.67 (s, 2 H, CH_2); IR (CCl_4) 3085, 3000, 2950, 2840, 1740, 1720 (C=O), 1610, 1570, 1435, 1270, 1260, 1240, 1195, 1130, 1040 cm^{-1}; mass spectrum, *m/e* (relative intensity) 264 ($M^{+}\cdot$; 24), 233 (27), 232 (65), 217 (9), 205 (50), 174 (32), 163 (10), 146 (100), 134 (11), 102 (14), 84 (32). Anal. Calcd for $C_{13}H_{12}O_4S$: C, 59.09; H, 4.55; S, 12,12. Found: C, 59.21; H, 4.39; S, 12.00.

1,3-Dioxo-2-phenyl-1,3,3a,9a-tetrahydro-2*H*-pyrrolo[2,3-*c*]benzothiopyran (15). Benzothiet (3; 61 mg, 0.5 mmol) and *N*-phenylmaleimide (14; 95 mg, 1.1 equiv) were used as above to yield 15: 112 mg (76%); mp 167–168 °C (lit.[14] mp 167–168 °C). All spectral and analytical data are identical with the reported values.

Methyl 2,3-Dihydro-4*H*-1-benzothiopyran-3-carboxylate (17) and Methyl 2,3-Dihydro-4*H*-1-benzothiopyran-2-carboxylate (18). Benzothiet (3; 61 mg, 0.5 mmol) and methyl acrylate (16; 129 mg, 1.5 equiv) were used as above to give yields of 17 and 18 of 94 mg (65%). Glass capillary chromatographic analysis shows a product ratio of 79:21: ^{1}H NMR ($CDCl_3$) δ 7.00–7.25 (m, 4 H, Ar H) 2.76–3.21 (m, 5 H, aliphatic protons); two separate signals are observed for the methyl protons, 17 at δ 3.74 (s, 3 H, CH_3) and 18 at δ 3.76 (s, 3 H, CH_3); IR (CCl_4) 3060, 3000, 2950, 1740 (C=O), 1480, 1435, 1360, 1308, 1255, 1170, 1190 cm^{-1}; GC/MS, *m/e* (relative intensity) for 17 208 ($M^{+}\cdot$, 80), 177 (2), 149 (46), 148 (100), 147 (85), 134 (30), 116 (37), 115 (29), 103 (5), 77 (14); for 18 208 ($M^{+}\cdot$, 38), 178 (1), 149 (100), 148 (14), 147 (19), 134 (20), 116 (33), 105 (3). Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.46; H, 5.77; S, 5.77; S, 15.39. Found: C, 63.20; H, 5.51; S, 14.68.

1-Oxo-1,2,3,4,4e,9e-hexahydrothioxanthene (20). Benzothiet (3; 61 mg, 0.5 mmol) and 2-cyclohexenone (19; 72 mg, 1.5 equiv) were used as above to give 20: yield 28 mg (25%); mp 134–135 °C (colorless crystals from petroleum ether (bp 30–50 °C); ^{1}H NMR ($CDCl_3$) δ 6.92–7.18 (m, 4 H, Ar H), 3.93 (m, 1 H, HC-9a), 3.02 (9, 1 H, HC-4a), 3.32 and 2.73 (AB part, 2 H, H_2C-9, $^2J_{AB}$ = 15.5 Hz). IR (KBr) 3070, 3000, 2940, 2870, 1700 (C=O), 1565, 1480, 1435, 1420, 735 cm^{-1}; mass spectrum, *m/e* (relative intensity) 218 ($M^{+}\cdot$, 100), 185 (8), 173 (16), 161 (20), 147 (89), 135 (38), 134 (90), 115 (12), 91 (15), 84 (20). Anal. Calcd for $C_{13}H_{14}OS$: C, 71.55; H, 6.42; S, 14.68. Found: C, 72.06; H, 6.84; S, 14.48.

Photolysis. A solution of 61 mg of benzothiet (3) and 95 mg of *N*-phenylmaleimide (14) in 140 mL of dry cyclohexane is irradiated by using a 450-W Hanovia mercury medium-pressure lamp (with Pyrex filter, λ ≥ 280 nm). The temperature of the

---

[13] A. G. Hortmann, A. J. Aron, and A. K. Bhattacharya, *J. Org. Chem.*, 43, 3374 (1978).

[14] G. Jacquin, J. Nasielski, G. Billy, and M. Remy, *Tetrahedron Lett.*, 3655 (1973).

[15] The reaction conditions of ref 12 have been slightly modified.

[16] W. D. Ollis, J. S. Stephanatou, J. F. Stoddart, and M. Nogradi, *J. Chem. Soc., Perkin Trans. 1*, 1421 (1978).

[17] R. Crossley, A. P. Downing, M. Nogradi, A. Braga de Oliveira, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 205 (1973).

reaction vessel is maintained below 20 °C by cold water circulation. After 3 h, the solvent is evaporated under vacuo, and the product is isolated by using a silica gel column (1.5 × 10 cm): yield of **15**, 97 mg (66%); recovered benzothiet, 6 mg (10%).

A similar experiment with dimethyl acetylenedicarboxylate (**12**) gave **13** in 57% yield. The recovery of benzothiet was 22%.

Acknowledgment. Financial support to this work was provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank the Alexander von Humboldt Foundation for the award of a Fellowship to K.K.

Registry No. **3**, 63559-01-3; **6**, 59130-11-9; **9**, 496-31-1; **10**, 263-06-9; **11**, 84559-50-2; **12**, 762-42-5; **13**, 84559-51-3; **14**, 941-69-5; **15**, 66303-97-7; **16**, 96-33-3; **17**, 84559-52-4; **18**, 84559-53-5; **19**, 930-68-7; **20**, 84582-82-1.

Vicinal ^{13}C–^{13}C Coupling Constants as a Configurational Probe: Stereochemistry of the Base-Catalyzed Double Bond Shift in Proacacipetalin

Jerzy W. Jaroszewski*

Department of Chemistry BC, Royal Danish School of Pharmacy, DK-2100 Copenhagen, Denmark

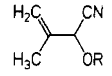
Martin G. Ettlinger

Chemical Laboratory II, University of Copenhagen, DK-2100 Copenhagen, Denmark

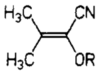
Received July 7, 1982

In recent years a considerable amount of information about ^{13}C–^{13}C spin–spin coupling constants has become available,[1] confirming their potential utility for solving stereochemical problems. Although observation of ^{13}C–^{13}C couplings usually requires ^{13}C-enriched materials, which prevents them from being routinely accessible at present,[2] the usefulness or even uniqueness of the stereochemical information provided by ^{13}C–^{13}C coupling constants may sometimes make their use attractive, especially when introduction of the necessary label is straightforward. We report a case belonging to this category.

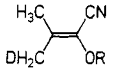
Proacacipetalin (**1a**),[3] a natural glucoside occurring in *Acacia* species, undergoes isomerization in base to the conjugated isomer **2a**, acacipetalin.[3] The stereospecific nature of the isomerization became apparent when the reaction was carried out in deuterium oxide, which resulted[3] in incorporation of one deuterium atom per molecule of product exclusively into the more shielded (^{1}H and ^{13}C NMR spectra) of the two methyl groups of **2a**.[3] Similarly, **1b**, a synthetic analogue of proacacipetalin, is converted by base to **2b**, and isomerization in methanol-*d* yields a product containing one deuterium atom in the more shielded methyl group. However, unambiguous assignment of the methyl resonances in ^{1}H and ^{13}C NMR spectra of **2a** and **2b**, and thus a decision as to whether the deuterated products are the *Z* isomers **3a** and **3b** or the *E* isomers **4a** and **4b**, cannot be made immediately.



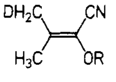
1



2



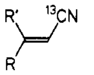
3



4

a R = β-D-glucopyranosyl
b R = 2-tetrahydropyranyl

Earlier studies on α,β-unsaturated carboxylic acids and esters indicated that vicinal ^{13}C–^{13}C coupling constants across a double bond may be suitable for differentiation between *E* and *Z* configurations.[4-6] That the relationship $^3J_{\text{cis}} < {}^3J_{\text{trans}}$, familiar for ^{1}H–^{1}H and also established for ^{13}C–^{1}H coupling constants,[7-9] is likewise valid for vicinal ^{13}C–^{13}C couplings to the nitrile group in α,β-unsaturated nitriles is now demonstrated by measurement of ^{13}C NMR spectra of **5–7** (Table I). The ratio $^3J_{\text{cis}}/^3J_{\text{trans}}$ for couplings either within the same molecule (**7**) or in an *E,Z* isomeric pair (**5** and **6**) is 0.5–0.6 and overlaps the range of 0.55–0.7 already established[10] for ^{1}HC=CX (X = ^{1}H, ^{13}C) couplings in ethene and propene and their monocyano derivatives. For ^{1}HC=CX couplings in monomethoxy and monoacetoxy derivatives of ethene and propene both $^3J_{\text{cis}}$ and $^3J_{\text{trans}}$ are substantially reduced, and their ratio appears to be slightly lower (0.4–0.5).[10] Synthesis of **2b** enriched with ^{13}C in the nitrile group and measurement of three-bond ^{13}C–^{13}C coupling constants to the methyl groups (Table I) show that the constants are reduced as expected compared with those of **7** by attachment of an oxygen atom to the double bond, for $^3J_{\text{cis}}$ is still clearly lower than $^3J_{\text{trans}}$, their experimental ratio being 0.6 rather than its reciprocal. Thus the high-field methyl resonance of **2b** (and consequently also that of **2a**) must be assigned to the methyl group trans to the nitrile group, and the deuterated



5 R=CH$_3$, R'=H
6 R=H, R'=CH$_3$
7 R=R'=CH$_3$

---

[1] Hansen, P. E. *Org. Magn. Reson.* **1978**, *11*, 215. Wray, V. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 177. Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1981**, *11A*, 65. Wray, V.; Hansen, P. E. *Ibid.* **1981**, *11A*, 99.

[2] See, however: Bax, A.; Freeman, R.; Kempsell, S. P. *J. Am. Chem. Soc.* **1980**, *102*, 4849; *J. Magn. Reson.* **1980**, *41*, 349. Bax, A.; Freeman, R. *Ibid.* **1980**, *41*, 507. Sørensen, O. W.; Freeman, R.; Frenkiel, T.; Mareci, T. H.; Schuck, R. *Ibid.* **1982**, *46*, 180. Cf. also: Pinto, A. C.; Goncalves, M. L. A.; Filho, R. B.; Neszmelyi, A.; Lukacs, G. *J. Chem. Soc., Chem. Commun.* **1982**, 293.

[3] Ettlinger, M. G.; Jaroszewski, J. W.; Jensen, S. R.; Nielsen, B. J.; Nartey, F. *J. Chem. Soc., Chem. Commun.* **1977**, 952.

[4] Marshall, J. L.; Faehl, L. G.; Kattner, R.; Hansen, P. E. *Org. Magn. Reson.* **1979**, *12*, 169.

[5] Chaloner, P. A. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1028.

[6] Hansen, P. E.; Berg, A. to be published. We thank Dr. P. E. Hansen, Roskilde University Center, for making the manuscript available to us prior to publication.

[7] For a useful compilation of interproton three-bond coupling constants across a double bond, see: Martin, G. J.; Martin, M. L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1972**, *8*, 163.

[8] For a recent review of ^{13}C–^{1}H coupling constants, see: Hansen, P. E. *Prog. Nucl. Magn. Reson. Spectrosc.* **1981**, *14*, 175.

[9] See also: Kowalewski, J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 1.

[10] (a) $^3J_{\text{HH}}$ coupling constants: Reddy, G. S.; Goldstein, J. H.; Mandell, L. *J. Am. Chem. Soc.* **1961**, *83*, 1300. Graham, D. M.; Holloway, C. E. *Can. J. Chem.* **1963**, *41*, 2114. Hobgood, R. T., Jr.; Mayo, R. E.; Goldstein, J. H. *J. Chem. Phys.* **1963**, *39*, 2501. Freeman, R. *Ibid.* **1964**, *40*, 3571. Wuolijoki, E. *Suom. Kemistil. B* **1966**, *B39*, 36. Feeney, J; Sutcliffe, L. H. *Spectrochim. Acta, Part A* **1968**, *24A*, 1135. Lequan, R.-M.; Simonnin, M.-P. *Bull. Soc. Chim. Fr.* **1970**, 4419. Williams, L. F.; Bothner-By, A. A. *J. Magn. Reson.* **1973**, *11*, 314. Rummens, F. H. A.; Simon, C.; Coupry, C.; Lumbroso-Bader, N. *Org. Magn. Reson.* **1980**, *13*, 33. (b) $^3J_{\text{CH}}$ coupling constants: Vogeli, U.; von Philipsborn, W. *Org. Magn. Reson.* **1975**, *7*, 617. Douglas, A. W. *Ibid.* **1977**, *9*, 69. Äyräs, P. *Ibid.* **1977**, *9*, 663. Dubs, R. V.; von Philipsborn, W. *Ibid.* **1979**, *12*, 326.[8]

0022-3263/83/1948-0883$01.50/0