19. [2+2]-Cycloadditions to Strained Bridgehead Olefins. I. 1,1-Dichloro-2,2-difluoroethene[1])

by **Konrad B. Becker**[2]) and **Martin K. Hohermuth**

Institut für Organische Chemie der Universität Basel, St. Johanns-Ring 19, CH-4056 Basel

(19.XI.81)

Summary

The strained bridgehead olefins bicyclo[3.3.1]non-1-ene (**1**), bicyclo[4.2.1]non-1(8)-ene (**2**), and bicyclo[4.2.1]non-1-ene (**3**) react rapidly with 1,1-dichloro-2,2-difluoroethene (**5**) to yield mixtures of regioisomeric dichlorodifluorocyclobutanes **8/9**, **10/11** and **12/13**, respectively. On the contrary, the reaction of **5** with the model compound (*E*)-1-methylcyclooctene (**4**) is completely regioselective. The structure of the cycloadducts has been elucidated mainly by ^{19}F-NMR. and ^{13}C-NMR. spectroscopy.

Introduction. – The bridgehead olefins bicyclo[3.3.1]non-1-ene (**1**), bicyclo[4.2.1]non-1(8)-ene (**2**), and bicyclo[4.2.1]non-1-ene (**3**) are highly strained, but still stable at RT. These so-called *Bredt* olefins [1] formally are methylene-bridged (*E*)-cyclooctenes [2] and therefore should be comparable in strain and reactivity to the model compound (*E*)-1-methylcyclooctene (**4**). Their high reactivity has been documented by a number of additions which are not observed with unstrained alkyl-substituted olefins [3].

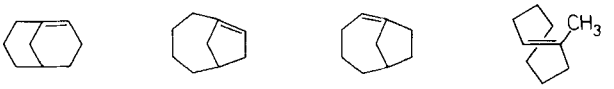
Bredt olefins belonging to the class of bridged (*E*)-cycloheptenes or (*E*)-cyclohexenes are unstable at ordinary temperatures and usually dimerize to mixtures of cyclobutanes by a [2+2]-cycloaddition [4]. It is therefore of interest to study [2+2]-cycloadditions of the stable bridged (*E*)-cyclooctenes **1**, **2**, and **3**, and compare these with more and with less strained olefins. 1,1-Dichloro-2,2-difluoroethene (**5**) was chosen as the partner, because **5** undergoes [2+2]-cycloadditions with activated olefins and because it was anticipated that the resulting isomeric dichlorodifluorocyclobutanes could be readily identified by NMR. spectroscopy. The substitution pattern of **5** may lead to two regioisomeric cyclobutanes, thereby allowing to probe the 'polarity' of the double bond of the bridgehead olefin. Mixtures of stereoisomers are formed only if isomerization at the double-bonded C-atom α to the bridgehead occurs. Reactions of **5** with conjugated dienes and with

[1]) Taken in part from the dissertation of *M. K. Hohermuth*, Basel 1980.

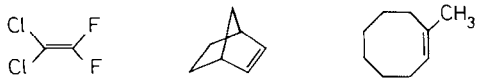
[2]) Author to whom correspondence should be addressed at *Ciba-Geigy AG*, Zentrale Forschungslaboratorien, CH-4002 Basel.

0018-019X/82/1/0229-06$01.00/0

styrenes have been studied in detail and shown to occur by a stepwise diradical mechanism [5].



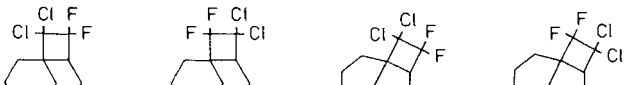
1 **2** **3** **4**



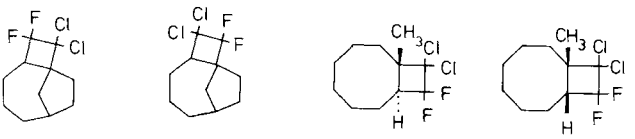
5 **6** **7**

Results. – The *Bredt* olefins **1**–**3** [6] and the comparable monocyclic (*E*)-1-methylcyclooctene (**4**) [7] react with an excess of 1,1-dichloro-2,2-difluoroethene (**5**) at 80° within 30 h. The addition of **5** to trinorbornene (**6**) required more than 3 days at 120° for completion. The reaction with the unstrained (*Z*)-1-methylcyclooctene (**7**) was even more sluggish. After 15 days at 150°, only a few percent of a cycloadduct were observed besides considerable amounts of dimeric and polymeric material originating from **5** alone.

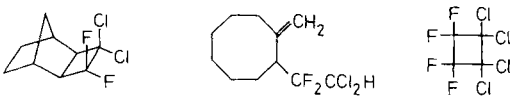
Flash distillation in a bulb tube separated the adducts **8**–**17** from excess **5**, the dimer 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (**18**), and from polymeric material. This distillate was analyzed by ^{1}H-, ^{19}F- and ^{13}C-NMR. spectroscopy. Bicyclo[3.3.1]non-1-ene (**1**) gives a 2:1 mixture of the regioisomeric dichlorodifluorocyclobutanes **8** and **9**. The regioisomer **10**, in which the chlorine-bearing C-atom is bound to the bridgehead, predominates also in the mixture of **10** and **11** (in the ratio of 3:1) found with bicyclo[4.2.1]non-1(8)-ene (**2**). The regioselectivity is reversed in the addition of **5** to bicyclo[4.2.1]non-1-ene (**3**), which yields the



8 **9** **10** **11**



12 **13** **14** **15**



16 **17** **18**

cyclobutanes **12** and **13** in the ratio of 2:7. (*E*)-1-Methylcyclooctene (**4**) and (*Z*)-1-methylcyclooctene (**7**) each produce a single (>97%) regioisomer **14** and **15**, respectively, which are stereoisomeric to each other. Trinorbornene (**6**) yields the expected *exo*-adduct **16** [8]. During the reaction of **5** with **4**, one percent of an 'ene'-adduct **17** is also formed together with the cyclobutane **14**.

The *^{1}H-NMR. spectra* of the mixtures of isomers **8/9**, **10/11** and **12/13** are not very informative, because the protons α to the CF_2- and α to the CCl_2-group overlap. However, the spectrum of the cyclobutane **14** (obtained as a single regioisomer) is analyzed readily and supports the structure shown. A one-proton *m* is found at $\delta = 2.73$ ppm with $J(H,H) = 10$ and 2.5 Hz and $J(H,F) = 20$ and 10 Hz. The absorption of the methyl group in **14** is split by $^5J(H,F) = 2.4$ Hz[3]).

More information is gained from the *^{13}C-NMR. spectra (Table 1).* Unambiguous identification of the regioisomers is possible on inspection of the C-resonances of the two C-atoms derived from the original trisubstituted double-bond. The methine C-atom (δ 46–63 ppm) shows a comparatively large $^2J(C,F)$ of 19–21 Hz in the isomers **8**, **10** and **14**, and a significantly smaller $^3J(C,F)$ of less than 10 Hz in the isomers **9** and **11**. The fully substituted C-atom (δ 45–59 ppm) appears with a coupling constant $^3J(C,F)$ of less than 12 Hz or $^2J(C,F)$ of 20–22 Hz, respectively [10]. Surprising is the fact that $^1J(C,F) = 280$–302 Hz differs for *exo*- and *endo*-fluorine[4]). For comparison the spectral data of the trinorbornene adduct **16** are also shown in *Table 1.*

The identification of the regioisomers and the determination of their relative amount in the product mixture is very simple in the *^{19}F-NMR. spectra (Table 2).* *Exo*- and *endo*-F-atoms appear as an *AB*-system at δ *ca.* 100 ppm downfield from $CFCl_3$. In the isomers **8**, **10**, **12**, **14** and **15**, $^3J(H,F) = 10$–20 Hz are observed, whereas only long-range couplings (less than 3 Hz) are found in the isomers **9**, **11** and **13**, because the nearest protons are four and more bonds away from fluorine.

The assignment of configuration to the adducts **14** and **15** is based on their mode of synthesis only. Spectral arguments for these assignments are weak, and

Table 1. *Selected ^{13}C-NMR. data for compounds* **8**–**11**, **14** *and* **16**[a])

	>C<		≥CH		$-CCl_2-$		$-CF_2-$	
	δ	J(C,F)	δ	J(C,F)	δ	J(C,F)	δ	J(C,F)
8	44.6	9.6/1.2	46.0	20/20	92.9	26/26	117.7	301/289
9	46.0	20/20	51.7	7.5/6	88.6	28/28	118.7	299/296
10	57.3	12/12	56.8	21/20	92.0	25/25	118.0	302/288
11	58.8	22/20	62.4	9.5/3	90.8	24/24	[b])	[b])
14	47.4	12/1.3	50.2	20/19	93.2	24/24	118.2	302/281
16	–	–	52.9	23/23	88.0	28/27	117.2	298/295
			55.3	7/7				

[a]) Solvent $CDCl_3$, δ in ppm, J in Hz. [b]) Not resolved.

[3]) For similar long-range (through-space) H,F-couplings see [9].

[4]) Although this phenomenon is readily explainable, we are not aware of any other example in the literature.

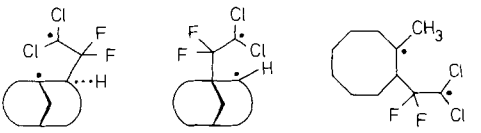
Table 2. *^{19}F-NMR. data for compounds* **8**–**16**[a])

	F_A[b])		F_B[b])		
	δ	J(H,F)	δ	J(H,F)	J(F,F)
8	110.9	12.5	93.1	12.5	183.5
9	108.6	2	106.9	2	187.5
10	109.4	12.5/5	94.1	10	183
11	110.4	2	100.2	2	184
12	116.7	16	99.1	9.5	183.5
13	109.3	<2	104.8	<2	188
14	116.9	20/2	97.6	10	185
15	107.4	20/2	94.9	4	185
16	109.2	6/3/3	88.1	13.5/5	200

[a]) Solvent CCl_4 (**12**, **13** and **16**: $CDCl_3$), δ in ppm relative to $CFCl_3$, J in Hz.
[b]) F_A = *exo*-F (*syn* to CH_3), F_b = *endo*-F for compounds **14** and **15**.

no certainty exists as to the configuration of adducts **8**–**13**. In analogy to the structure of a diphenylketene cycloadduct [11] and from consideration of strain, we believe that the cyclobutane ring is *exo*-fused to the bicyclic system.

Discussion. – The *Bredt* olefins **1**, **2** and **3** react with **5** to give mixtures of two dichlorodifluorocyclobutanes. This cycloaddition is one more example of a reaction which is not observed or is very slow with unstrained trialkyl-substituted olefins, but proceeds with reasonable yields and reaction rates with strained bridgehead olefins. Whereas the monocyclic model compound **4** yields a single regioisomer, mixtures of both possible regioisomers are found with the bridgehead olefins. *Bartlett* [5] interprets the results of the cycloaddition of **5** to butadienes and styrenes by a mechanism involving 1,4-diradicals. In the case of the addition of **5** to *Bredt* compounds and other strained alkyl-substituted olefins, the intermediate diradicals (*e.g.* **19**, **20**, **21**) lack the extra stabilization provided by a conjugated double-bond or an aromatic ring. In spite of this, there is good reason to assume that also the cycloaddition of **5** to olefins **1**–**4**, **6** and **7** follows a two-step reaction path *via* 1,4-diradicals. Because a radical center is much more stable on the Cl-substituted than on the F-substituted C-atom, only two types of diradicals, namely **19** and **20** have to be considered for additions of **5** to bridgehead olefins. Diradical **19** contains a bridgehead radical center which, although it is tertiary, is destabilized because it cannot adopt a planar conformation. The corresponding radical center in **20** is secondary, but without geometrical restrictions. Because mixtures of regioisomers are formed, both **19** and **20** must be fairly close in energy, *i.e.* there is no large energy difference between a tertiary (bridgehead) and a secondary radical in the bicyclic systems under study. For comparison, it was observed that only the



19 **20** **21**

bridgehead carbenium ion and no secondary carbenium ion is formed on protonation of the bridgehead olefins **1**, **2** and **3** [6].

Only one of the two possible stereoisomeric cyclobutanes is found. The *endo*-face of the strained double-bond in the olefins **1**, **2** and **3** is not accessible for steric reasons, and the CF_2CCl_2-group in diradical **19** must therefore be *exo*. In principle, the secondary radical center in **20** could react with the CCl_2-radical center on either side, but collapse to the *exo*-fused cyclobutane is clearly preferred for geometric reasons.

The regioselectivity of the addition of **5** to both (*E*)- and (*Z*)-1-methylcyclooctene (**4** and **7**) is in accord with the expectations. The diradical **21** with a tertiary radical center (which in this case can adopt a planar conformation) is formed in preference to the corresponding diradical with a secondary radical center. However, diradical **21** has such a short lifetime that it preserves its stereochemical integrity, *e.g.* does not undergo extensive conformational changes. Otherwise the same stereoisomer or stereoisomeric mixture of **14** and **15** would result from addition of **5** to olefins **4** and **7**. This behaviour has a precedent in the stereospecific addition of **5** to unsubstituted (*E*)- and (*Z*)-cyclooctene [12]. The formation of the 'ene'-adduct **17** from (*E*)-1-methylcyclooctene (**4**) and **5** is readily explained by a H-transfer from the methyl group to the Cl-substituted radical center in the diradical **21**.

Financial support by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and the *Ciba-Geigy AG* is gratefully acknowledged.

Experimental Part

General remarks. See [4]. ^{19}F-NMR. spectra were recorded with $CFCl_3$ as internal standard either at 94.1 MHz on a *Varian*-XL-100 by *A. Borer (Ciba-Geigy AG)* or at 188.1 MHz on a *Bruker* WP-200 SY at *Spectrospin AG*, Fällanden. Their cooperation is gratefully acknowledged.

2,2-Dichloro-3,3-difluorotricyclo[5.3.1.0^{1,4}]undecane (**8**) *and 3,3-dichloro-2,2-difluorotricyclo[5.3.1.0^{1,4}]undecane* (**9**). Bicyclo[3.3.1]non-1-ene (**1**, 180 mg, 1.47 mmol) and 1,1-dichloro-2,2-difluoroethene (**5**, 3.7 g, 27.8 mmol) were sealed in a *Pyrex* pressure tube and kept at 80° for 84 h. The volatile components were evaporated i.V. and the residue distilled in a bulb tube at 160°/12 Torr to give 207 mg (55%) of a mixture of **8** and **9** (2:1). – ^{1}H-NMR. ($CDCl_3$): 2.6 (*m*, 1H); 2.2 (*m*, 1H); 2.0 (*m*, 1H); 1.9–1.2 (*m*, 11H). – ^{13}C-NMR. ($CDCl_3$): **8**: C(1)–C(4) see *Table 1;* 32.8 (*t*, ^4J(C,F) = 2.7 and 2.6, C(10) or C(11)); 32.1 (*t*, ^4J(C,F) = 2.6 and 1.1, C(10) or C(11)); 31.1; 26.7 (*d*, C(7)); 23.9; 19.3; 14.7 (*t*, ^3J(C,F) = 5.9, C(5)). **9**: C(1)–C(4) see *Table 1;* 31.7 (*t*, C(10) or C(11)); 30.1 (*t*, C(5)); 27.5 (*t*, ^3J(C,F) = 5.5, C(10) or C(11)); 24.9 (*d*, ^4J(C,F) = 1.2, C(7)); 23.7; 18.7; 17.2. – ^{19}F-NMR. (CCl_4): see *Table 2.*

2,2-Dichloro-3,3-difluorotricyclo[4.4.1.0^{1,4}]undecane (**10**) *and 3,3-dichloro-2,2-difluorotricyclo[4.4.1.0^{1,4}]undecane* (**11**). From bicyclo[4.2.1]non-1(8)-ene (**2**, 550 mg, 4.5 mmol) and **5** (4.0 g, 30.1 mmol) as above, there was obtained 892 mg (78%) of a mixture of **10** and **11** (3:1). – ^{1}H-NMR. ($CDCl_3$): 2.8 (*m*, 1H); 2.6 (*m*, 1H); 2.3 (*m*, 1H); 2.1–1.1 (*m*, 11H). – ^{13}C-NMR. ($CDCl_3$): **10**: C(1)–C(4) see *Table 1;* 40.8 (*d*, C(6)); 37.9 (*t*, ^4J(C,F) = 2.2 and 1.5, C(10) or C(11)); 36.3 (*t*, C(7)); 33.7 (*t*, ^4J(C,F) = 2.5 and 2.5, C(10) or C(11)); 28.7 (*t*, ^3J(C,F) = 5.8, C(5)); 25.0 and 22.9 (each *t*, C(8) and C(9)). **11**: C(1)–C(4) see *Table 1;* 41.0 (*d*, ^4J(C,F) = 2.2, C(6)); 36.3 (*t*, C(7)); 35.0 (*t*, ^3J(C,F) = 1.5 and 1.5, C(10) or C(11)); 33.3 (*t*, C(5)); 30.8 (*t*, ^3J(C,F) = 6.6, C(10) or C(11)); 24.5 and 23.3 (each *t*, C(8) and C(9)). – ^{19}F-NMR. (CCl_4): see *Table 2.*

2,2-Dichloro-3,3-difluorotricyclo[6.2.1.0^{1,4}]undecane (**12**) *and 3,3-dichloro-2,2-difluorotricyclo[6.2.1.0^{1,4}]undecane* (**13**). From bicyclo[4.2.1]non-1(2)-ene (**3**, 60 mg, 0.5 mmol) and **5** (6 g, 45 mmol)

as above, there was obtained 30 mg (24%) of a mixture of **12** and **13** (2:7). – ^{13}C-NMR. ($CDCl_3$): **12**: not observed. **13**: C(2) and C(3) not resolved; 59.3 (*d*, ^3J(C,F) = 9.6, C(4)); 56.3 (*s*, ^{2}J(C,F) = 20.6 and 20.6, C(1)); 38.2; 37.8 (*d*, C(8)); 35.3; 34.7 (*t*, ^3J(C,F) = 2.9, C(10) or C(11)); 25.1; 24.9; 22.0. – ^{19}F-NMR. ($CDCl_3$): see *Table 2*.

10,10-Dichloro-9,9-difluoro-1-methyl-trans-*bicyclo[6.2.0]decane* (**14**) *and 2-(2,2-dichloro-1,1-difluoroethyl)-1-methylidenecyclooctane* (**17**). From (*E*)-1-methylcyclooctene (**4**, 450 mg, 3.6 mmol) and **5** (2.4 g, 18.0 mmol) as above, there was obtained 220 mg (24%) of a mixture of **14** and **17** (20:1); b.p. 150°/60 Torr; GC. (OV 17, 180°) showed that the sample contained less than 1% *cis*-isomer **15**. – ^{1}H-NMR. ($CDCl_3$): **14**: 2.73 (*m*, J(H,F) = 20 and 10, J(H,H) = 10 and 2.5, H–C(8)); 2.1–1.0 (*m*, 12 H, CH_2); 1.26 (*d*, J(H,F) = 2.4, CH_3–C(1)). **17**: 5.91 (*d*×*d*, J(H,F) = 16 and 2, H–C(2')); 5.16 (br. *s*, 2 H, H_2C=C(1)). – ^{13}C-NMR. ($CDCl_3$): **14**: C(1), C(8)–C(10) see *Table 1;* 38.7 (*t*, ^4J(C,F) = 3.7 and 2.4, C(2)); 29.6; 29.1; 28.2; 26.0; 21.8 (*t*, ^3J(C,F) = 3.1 and 0.7, C(7)); 19.1 (*qa*, ^4J(C,F) = 4.4 and 1.6, CH_3–C(1)). **17**: not observed. – ^{19}F-NMR. (CCl_4): **14**: see *Table 2*. **17**: 116.6 (*m*, J(F,F) = 245, J(H,F) = 16 and 8); 110.6 (*m*, J(F,F) = 245; J(H,F) = 25).

10,10-Dichloro-9,9-difluoro-1-methyl-cis-*bicyclo[6.2.0]decane* (**15**). From (Z)-1-methylcyclooctene (**7**, 1.0 g, 8.1 mmol) and **5** (6 g, 45 mmol) at 150° for 15 days, 50 mg (2.4%) of an impure distillate containing **15**; b.p. 160°/12 Torr; GC. (OV 17, 180°) showed that the ratio of **15**:**14** (*cis/trans*) was at least 97:3. – ^{19}F-NMR. (CCl_4): see *Table 2*.

3,3-Dichloro-4,4-difluorotricyclo[4.2.1.0^{2,5}]nonane (**16**) [8]. From trinorbornene (**6**, 1.5 g, 15.9 mmol) and **5** (5.0 g, 37.6 mmol) at 120° for 3 days, 280 mg (9%); b.p. 160°/12 Torr. – ^{1}H-NMR. ($CDCl_3$): 2.89 (*d*×*d*×*d*, J(H,F) = 14 and 7, J(H,H) = 6, H–C(5)); 2.70 (br. *d*, *J ca.* 5, H–C(2)); 2.58 (br. *s*, 1 H); 2.49 (br. *s*, 1 H); 2.05 (*d*×*d*, J = 9 and 2, 1 H); 1.57 (*m*, 2 H); 1.34 (*s*, 1 H); 1.19 (*d*, J = 5, 1 H); 1.10 (*d*, J = 5, 1 H). – ^{13}C-NMR. ($CDCl_3$): C(2)–C(5) see *Table 1;* 38.7 (*d*, C(1)); 34.9 (*t*, C(9)); 34.6 (*d*, C(6)); 27.6 and 27.1 (each *t*, C(7) and C(8)). – ^{19}F-NMR. ($CDCl_3$): see *Table 2*.

1,1,2,2-Tetrachloro-3,3,4,4-tetrafluorocyclobutane (**18**) [13]. Pyrolysis of **5** alone at 180° for 14 days gave **18**. – ^{13}C-NMR. ($CDCl_3$): 113.8 (^1J(C,F) = 300, ^2J(C,F) = 27, CF_2); 89.2 (*m*, CCl_2). – ^{19}F-NMR. ($CDCl_3$): 113.8 (*s*).

REFERENCES

[1] *G. Köbrich*, Angew. Chem. *85*, 494 (1973), ibid. Int. Ed. *12*, 464 (1973); *G.L. Buchanan*, Chem. Soc. Rev. *3*, 41 (1974); *R. Keese*, Angew. Chem. *87*, 568 (1975), ibid. Int. Ed. *14*, 528 (1975); *K.J. Shea*, Tetrahedron *36*, 1683 (1980).

[2] *J.R. Wiseman*, J. Am. Chem. Soc. *89*, 5966 (1967).

[3] *J.A. Marshall & H. Faubl*, J. Am. Chem. Soc. *92*, 948 (1970); *J.R. Wiseman & W.A. Pletcher*, ibid. *92*, 956 (1970); *K.B. Becker*, Helv. Chim. Acta *60*, 94 (1977); *K.B. Becker & M.K. Hohermuth*, ibid. *62*, 2025 (1979).

[4] *K.B. Becker & J.L. Chappuis*, Helv. Chim. Acta *63*, 1812 (1980).

[5] *J.D. Roberts & C.M. Sharts*, Org. Reactions *12*, 1 (1962); *P.D. Bartlett, L.K. Montgomery & B. Seidel*, J. Am. Chem. Soc. *86*, 616 (1964); *L.K. Montgomery, K. Schueller & P.D. Bartlett*, ibid. *86*, 622 (1964); *P.D. Bartlett, G.H. Wallbillich, A.S. Wingrove, J.S. Swenton, L.K. Montgomery & B.D. Kramer*, ibid. *90*, 2049 (1968); *P.D. Bartlett*, Science *159*, 833 (1968); *P.D. Bartlett, C.J. Dempster, L.K. Montgomery, K.E. Schueller & G.E.H. Wallbillich*, J. Am. Chem. Soc. *91*, 405 (1969); *P.D. Bartlett*, Quart. Rev. *24*, 473 (1970).

[6] *K.B. Becker*, Helv. Chim. Acta *60*, 81 (1977).

[7] *A.J. Bridges & G.H. Whitham*, Chem. Commun. *1974*, 142.

[8] *P.D. Bartlett, G.E.H. Wallbillich & L.K. Montgomery*, J. Org. Chem. *32*, 1290 (1967).

[9] *M. Takahashi, D.R. Davis & J.D. Roberts*, J. Am. Chem. Soc. *84*, 2935 (1962).

[10] *E.W. Della, E. Cotsaris & P.T. Hine*, J. Am. Chem. Soc. *103*, 4131 (1981) and ref. therein.

[11] *K.B. Becker, M.K. Hohermuth & G. Rihs*, Helv. Chim. Acta *65*, 235 (1982).

[12] *R. Wheland & P.D. Bartlett*, J. Am. Chem. Soc. *95*, 4003 (1973).

[13] *A.L. Henne & R.P. Ruh*, J. Am. Chem. Soc. *69*, 279 (1947).