the 0.4 g of pyridine initially introduced, was 1.1 g (71%).

Conversion of Benzylic Alcohols into Azides. General Procedure. The alcohol (10 mmol) was mixed with ethanol-free chloroform (35 mL), which was 1.7 N in hydrazoic acid (60 mmol), followed by the dropwise addition of titanium tetrachloride (5 mmol). The solution was stirred at room temperature for 2 h. Chromatography through a 4 cm by 3 cm column of alumina and removal of the solvent yielded the pure azide as a water white oil.

Benzyl azide (44) was prepared as a colorless liquid from benzyl alcohol (60%): IR (liquid film) 3090, 3065, 3030, 2960, 2870, 2110, 1495, 1455, 1270, 1215, 1090, 823, 775, 707, 690, 595 cm^{-1}; NMR ($CDCl_3$) δ 7.24 (s, 5), 4.4 (s, 2); MS, *m/e* (relative intensity) 133 (M^+, 1.8), 126 (19), 91 (100), 65 (11.3), 63 (10.6), 39 (10.8).

1-Azido-1-phenylethane (45) was prepared as a colorless liquid from 1-phenylethanol (75%; identical with **45** prepared by addition of HN_3 to 2-methylstyrene).

2-Azido-2-phenylpropane (35) was prepared as a colorless liquid from 2-phenylpropan-2-ol (76%): IR (liquid film) 3090, 3060, 3030, 2980, 2930, 2870, 2110, 1600, 1495, 1450, 1390, 1370, 1260, 1190, 1150, 1107, 1080, 1036, 773, 710, 640, 585 cm^{-1}; NMR ($CDCl_3$) δ 7.32 (m, 5), 1.53 (s, 6); MS, *m/e* (relative intensity) 161 (M^+, 5.2), 120 (9.8), 119 (100), 118 (19.3), 103 (11.4), 91 (45.3), 77 (52.4), 56 (10.5), 51 (27.2), 41 (15.5), 39 (11.1).

Azidodiphenylmethane (46) was prepared as a colorless oil from diphenylmethanol (84%): IR (liquid film) 3065, 3035, 2880, 2115, 1600, 1585, 1492, 1450, 1245, 1085, 1035, 877, 767, 752, 710, 650 cm^{-1}; NMR ($CDCl_3$) δ 7.24 (s, 10), 5.62 (s, 1); MS, *m/e* (relative intensity) 209 (M^+, 2), 181 (100), 180 (90), 104 (23), 103 (67), 85 (27), 83 (50), 78 (20), 77 (70), 76 (27), 51 (33). Identical with **45** prepared by addition of HN_3 to α-methylstyrene (75%).

1-Azido-4-*tert*-butyl-1-methylcyclohexane (19 and 20). Either the equatorial (**17**) or the axial (**18**) alcohol (1 g, 5.9 mmol) was placed in chloroform (40 mL), which was 1.7 N in hydrazoic acid (68 mmol), followed by the dropwise addition, with stirring, of titanium tetrachloride (1.1 g, 5.9 mmol). After 12 h the reaction mixture was passed down a 3 cm by 3 cm column of alumina, eluting with chloroform. The solvent was removed to yield the azide mixture as a clear oil (0.85 g, 77%, from **17** and 0.81 g, 74%, from **18**). The NMR, IR, and MS for both products are identical. Therefore, they are either the same isomer or the same mixture of isomers: IR (liquid film) 2950, 2880, 2110, 1450, 1320, 1270, 1201, 1133, 993, 942, 921, 883, 830 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (s, 3), 0.9-2.1 (m, 9), 0.87 (s, 9); MS, *m/e* (relative intensity) 153 (M - N_2, 30), 152 (5.1), 124 (8.1), 110 (7.9), 97 (33), 96 (18), 95 (16), 83 (24.8), 82 (10.2), 81 (23.8), 69 (20.6), 68 (30.5), 67 (14), 57 (100), 56 (17.5), 55 (37.7), 41 (40.7).

1-Azido-1,1-diphenylethane (47) was prepared as a colorless liquid from 1,1-diphenylethanol (68%): IR (liquid film) 3070, 3040, 2930, 2110, 1610, 1495, 1450, 1375, 1250 cm^{-1}; NMR ($CDCl_3$) δ 7.17 (s, 10), 1.9 (s, 3).

***tert*-Butyl azide (48)** was prepared as a colorless liquid from *tert*-butyl alcohol (58%): IR (liquid film) 2980, 2940, 2110, 1455, 1375, 1255 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (s, 9).

2-Azido-2-methylbutane (49) was prepared as a colorless liquid from 2-methyl-2-butanol (68%): IR (liquid film) 2970, 2930, 2110, 1460, 1380, 1260 cm^{-1}; NMR ($CDCl_3$) δ 1.53 (q, 2), 1.30 (s, 6), 0.95 (t, 3).

3-Azido-3-ethylpentane (50) was prepared as a colorless liquid from 3-ethyl-3-pentanol (65%): IR (liquid film) 2985, 2950, 2110, 1460, 1380, 1260 cm^{-1}; NMR ($CDCl_3$) δ 1.57 (q, 6), 0.95 (t, 9).

Cinnamyl azide (51) was prepared as a colorless liquid from cinnamyl alcohol (84%): IR (liquid film) 3060, 3030, 2920, 2110, 1950, 1880, 1800, 1665, 1450, 1250 cm^{-1}; NMR ($CDCl_3$) δ 7.22 (x, 5), 6.20 (m, 2), 3.80 (d, 2).

Acknowledgment. This research was supported by DHEW Grant CA-19203 from the National Cancer Institute, NIH.

Registry No. **4**, 100-42-5; **5**, 32366-25-9; **6**, 591-49-1; **8**, 22530-83-2; **9a**, 91633-37-3; **9b**, 91633-38-4; **9c**, 91633-39-5; **10a**, 91633-22-6; **10b**, 91633-40-8; **17**, 16980-56-6; **18**, 16980-55-5; **19**, 91633-34-0; **20**, 91633-35-1; **21**, 83386-09-8; **22**, 22293-23-8; **23**, 66021-71-4; **24**, 66021-70-3; **25**, 91633-20-4; **26**, 91633-21-5; **27**, 32872-42-7; **29**, 91633-23-7; **30**, 71879-79-3; **31**, 91633-25-9; **32**, 91633-26-0; **33a**, 65501-08-8; **34**, 91633-27-1; **35**, 32366-26-0; **36**, 69664-68-2; **37**, 91633-28-2; **38**, 91633-29-3; **39**, 65501-11-3; **40**, 91633-30-6; **41**, 91633-31-7; **42**, 91633-32-8; **43**, 91633-33-9; **44**, 622-79-7; **46**, 6926-47-2; **48**, 13686-33-4; **50**, 91633-36-2; **51**, 57294-86-7; $TiCl_4$, 7550-45-0; $AlCl_3$, 7446-70-0; BF_3-OEt_2, 109-63-7; $SnCl_4$, 7646-78-8; $SbCl_5$, 7647-18-9; $PdCl_2$, 7647-10-1; HOAc, 64-19-7; $AgClO_4$, 7783-93-9; $Ti(O\text{-}i\text{-}Pr)_4$, 546-68-9; $PhCH{=}C(CH_3)_2$, 768-49-0; $Ph_2C{=}CH_2$, 530-48-3; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; $CH_3CH_2CH{=}C(CH_3)_2$, 625-27-4; $CH_3CH{=}C(CH_3)_2$, 513-35-9; $PhC(CH_3){=}CH_2$, 98-83-9; $HOCH_2C(CH_3){=}CH_2$, 513-42-8; $Ph_2C{=}C(CH_3)OSi(CH_3)_3$, 51425-63-9; $PhCH{=}C(CH_3)OSi(CH_3)_3$, 43108-63-0; $CH_2{=}C(OSi(CH_3)_3)C(CH_3)_3$, 17510-46-2; $PhC(CH_3){=}CHOSi(CH_3)_3$, 51075-23-1; $CH_3CH{=}C(Ph)OSi(CH_3)_3$, 37471-46-8; $CH_3CH{=}C(CH_2CH_3)OSi(CH_3)_3$, 17510-47-3; $(CH_3)_2CHCH_2OCH{=}CH_2$, 109-53-5; $PhC(OCH_3){=}CH_2$, 4747-13-1; $PhCH_2OH$, 100-51-6; $PhCH(CH_3)OH$, 98-85-1; $PhC(CH_3)_2OH$, 617-94-7; Ph_2CHOH, 91-01-0; $Ph_2C(CH_3)OH$, 599-67-7; $(CH_3)_3COH$, 75-65-0; $EtC(CH_3)_2OH$, 75-85-4; Et_3COH, 597-49-9; $PhCH{=}CHCH_2OH$, 104-54-1; $p\text{-}CH_3OC_6H_4CH{=}CH_2$, 637-69-4; $p\text{-}CH_3C_6H_4CH{=}CH_2$, 622-97-9; $p\text{-}ClC_6H_4CH{=}CH_2$, 1073-67-2; $p\text{-}NO_2C_6H_4CH{=}CH_2$, 100-13-0; HN_3, 7782-79-8; $Ph_2CHCOCH_3$, 781-35-1; Ph_2CO, 119-61-9; $Ph_2CHC(CH_3)(N_3)OSi(CH_3)_3$, 91633-24-8; $PhCH_2COCH_3$, 103-79-7; $PhCH(CH_3)CHO$, 93-53-8; $PhCOCH_2CH_3$, 93-55-0; 1-phenylcyclohexene, 771-98-2; 1-phenylcyclopentene, 825-54-7; 5-cholestene, 570-74-1; methylenecyclohexane, 1192-37-6; 2-isopropenyl-5-methylcyclohexanol, 7786-67-6; 1-[(trimethylsilyl)oxy]cyclohexene, 6651-36-1; 1-chloro-1-methylcyclohexane, 931-78-2.

Cyclizations of ω-Alkynyl Halides by Cr(II) Reduction[1]

Jack. K. Crandall* and W. J. Michaely

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

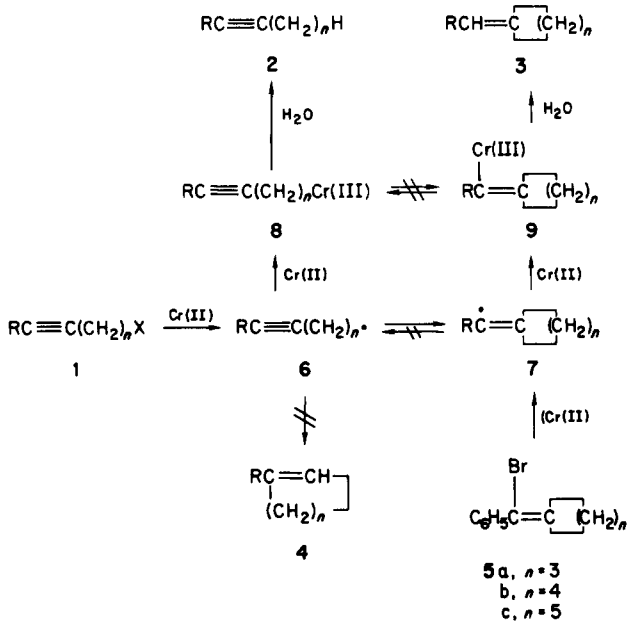
Received May 16, 1984

Reduction of halides of the types $RC{\equiv}C(CH_2)_nX$ with Cr(II) in aqueous DMF containing ethylenediamine proceeds by way of the intermediate radicals which cyclize regioselectively in the $n = 4$ and $n = 5$ cases to give substituted methylenecycloalkanes. Experimental conditions which favor longer lifetimes for the intermediate radicals (low concentrations, slow addition times, and an inverse-addition mode) result in increased cyclization. The iodides curiously give more cyclic product than the corresponding bromides. These results are discussed.

Cyclizations of free radicals possessing remote unsaturation have been studied in some detail, particularly in the olefinic series where a good understanding of the potential and limitations of these reactions has been achieved, in-

0022-3263/84/1949-4244$01.50/0

Scheme I



cluding an appreciation of regiochemical and stereochemical selectivities.[2] More recently such transformations have been incorporated into synthetic approaches to complex target molecules, where the compatibility of a variety of other functional groups to the required reaction conditions proves to be a useful feature.[3] Although the acetylenic analogues have received much less attention, the intramolecular additions of the corresponding radicals have been implicated in a number of instances, including the reaction of substituted ethyl cyanoacetates with benzoyl peroxide,[4] the reaction of alkyl halides with *n*-butyllithium,[5] tin hydrides,[6,7] magnesium,[8] and electrolytically,[9] and in several other transformations.[10] Synthetic applications have begun to appear where the residual double bond in the cyclic products is clearly an important asset.[11]

Table I. Cr(II) Reductions of 1 and 5

	R	*n*	X	method[a]	% 3[d]
1a	*n*-C_4H_9	3	Br	A, B	0
1b	*n*-C_4H_9	3	I	A, B	0
1c	C_6H_5	3	Br	A, B	0
1d	*n*-C_4H_9	4	Br	A	1
				C[b]	53
1e	*n*-C_4H_9	4	I	A	1
				B	67
				C	72
				C[b]	85
1f	C_6H_5	4	Br	A	7
				B	92
				C	95
1g	C_6H_5	4	I	A	9
				B[c]	92
				B	96
				C	96.5
1h	*n*-C_4H_9	5	Br	A	0
				B	7
1i	*n*-C_4H_9	5	I	A	0
				B	9
				C	12
1j	C_6H_5	5	Br	A	3
				B	74
				C	79
1k	C_6H_5	5	I	A	5
				B	81
				C	85
1l	C_6H_5	6	I	A, B	0
1m	*p*-FC_6H_4	4	Br	A	5
				B	93
1n	*p*-$CH_3C_6H_4$	4	Br	A	5
				B	93
1o	*p*-$CH_3OC_6H_4$	4	Br	A	5
				B	93
5a	C_6H_5	3	Br	A, B	100
5b	C_6H_5	4	Br	A, B	100
5c	C_6H_5	5	Br	A, B	97[e]

[a] Method A, direct addition; method B, inverse addition, 0.1 M RX, 1 h; method C, inverse addition, 0.05 M RX, 1 h. [b] 2-h addition time. [c] 0.25-h addition time. [d] The relative percentage of **3** present in the product mixture. The remainder was acyclic hydrocarbon **2** except for trace components. [e] Two unidentified products accounted for 3%. No **2** was present.

In the present study, we elaborate on our earlier work concerning the reduction of acetylenic halides by Bu_3SnH[6] with an exploration of Cr(II) as a reagent for the reductive cyclization of these compounds.[12]

The reaction of Cr(II) complexes, such as that formed between $Cr(ClO_4)_2$ and ethylenediamine, with alkyl halides is generally considered to proceed by the following mechanism:[13]

$$R\text{–}X + Cr(II) \rightarrow R\cdot + XCr(III)$$

$$R\cdot + Cr(II) \rightarrow RCr(III)$$

$$RCr(III) + H_2O \rightarrow RH + Cr(III)$$

If the intermediate radical R· has a facile isomerization pathway available, structurally rearranged products can be obtained according to the following scheme:

$$R\cdot \rightarrow R'\cdot \xrightarrow{Cr(II)} R'Cr(III) \xrightarrow{H_2O} R'H$$

However, any rearrangement process must be very rapid in order to compete with radical scavenging by Cr(II), which has been estimated to have a bimolecular rate constant on the order of 10^7 M^{-1} s^{-1}.[13] The product ratio

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administrated by the American Chemical Society, for partial support of this research.

(2) (a) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (b) Beckwith, A. L. J.; Ingold, K. U.; "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press; New York, 1980; Vol. I., p 161. (c) Surzur, J.-M. "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum; New York, 1982; Vol. 2, p 121.

(3) Hart, D. J. *Science (Washington , D.C.)* **1984**, *223*, 883.

(4) Julia, M.; James, C. *C. R. Hebd. Seances Acad. Sci., Ser. B* **1962**, *255*, 959.

(5) Ward, H. *J. Am. Chem. Soc.* **1967**, *89*, 5517.

(6) Crandall, J. K.; Keyton, D. J. *Tetrahedron Lett.* **1969**, 1653.

(7) (a) Ohnuki, T.; Yoshida, M.; Simamura, O. *Chem. Lett.* **1972**, 797. (b) Ohnuki, T.; Yoshida, M.; Simamura, O.; Fukayawa, M. *Chem. Lett.* **1972**, 999. (c) Dodson, S. A.; Stipanovic, R. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 410. (d) Ueno, Y.; Khare, R. K.; Okawara, M. *J. Chem. Soc., Perkins Trans. 1* **1983**, 2637.

(8) Crandall, J. K.; Michaely, W. J., unpublished observations.

(9) (a) Moore, W. M.; Salajegheh, A.; Peters, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 4954. (b) Willett, B. C.; Moore, W. M.; Salajegheh, A.; Peters, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 1162.

(10) (a) Corey, E. J.; Pyne, S. G. *Tetrahedron Lett.* **1983**, *24*, 2821. (b) Clive, D. L. J.; Beaulieu, P. L.; Set, L. *J. Org. Chem.* **1984**, *49*, 1314. (c) Pradhan, S, K.; Kadam, S. R.; Kolhe, J. N.; Radhakrishnan, T. V.; Sohani, S. V.; Thaker, V. B. *J. Org. Chem.* **1981**, *46*, 2622. (d) Kuehne, M. E.; Parsons, W. H. *J. Org. Chem.* **1977**, *42*, 3408. (e) Pradhan, S. K.; Kolhe, J. N.; Mistry, J. S. *Tetrahedron Lett.* **1982**, *43*, 4481.

(11) (a) Buchi, G.; Wuest, H. *J. Org. Chem.* **1979**, *44*, 546. (b) Stork, G.; Malhotra, S.; Thompson, H.; Uchibayashi, M. *J. Am. Chem. Soc.* **1965**, *87*, 1148. (c) Okabe, M.; Abe, M.; Tada, M. *J. Org. Chem.* **1982**, *47*, 1775. (d) Stork, G.; Mook, R. *J. Am. Chem. Soc.* **1983**, *105*, 3720. (e) Pattenden, G.; Teague, S. J. *Tetrahedron Lett.* **1982**, *23*, 5471. (f) Okabe, M.; Tada, M.; *J. Org. Chem.* **1982**, *47*, 5382. (g) Choi, J.-K.; Hart, D. J.; Tsai, Y.-M.; *Tetrahedron Lett.* **1982**, *23*, 4765. (h) Bachi, M. D.; Frolow, F.; Hoornaert, C. *J. Org. Chem.* **1983**, *48*, 1841.

(12) Hanson, J. R. *Synthesis* **1972**, 1. Ho, T.-L. *Synthesis* **1979**, 1.

(13) Kochi, J. K.; Powers, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 137.

R'H:RH can be manipulated somewhat by varying the concentration of Cr(II), provided that the isomerization is not reversible under the reaction conditions. The hydrolysis of the RCr(III) complexes is presumably a heterolytic process,[13] and it appears that rearrangement of the alkyl substituent is not normally a complication during this relatively slow reaction of the substitution-inert RCr(III) species.

Results

In the present study, reductions were performed by using the ethylenediamine complex of Cr(II) in aqueous dimethylformamide (DMF) solutions at room temperature under an argon atmosphere. In direct-addition reactions 1 equiv of the organic halide was added rapidly to 2.5 equiv of 0.25 M Cr(II). Inverse-addition experiments involved the slow addition of 2.5 equiv of the 0.25 M Cr(II) reagent to a 0.1 M solution of the halide in DMF. Iodides reacted instantaneously; bromides required several minutes. The reactions were stirred for 1 h after the additions were complete, hydrolyzed with 3 N HCl, and processed for analysis by GC. Major products were characterized by spectroscopic comparison with authentic samples, while minor components were identified by GC comparisons. The acetylenic halides **1a–o** were examined under various conditions. The observed products were the acyclic acetylenes **2** and the substituted methylenecycloalkanes **3**. The results are assembled in Table I.

No cyclization was found for the $n = 3$ systems **1a**, **1b**, and **1c** under any of the reaction conditions tried. The corresponding acetylenes **2** ($n = 3$, R = C_4H_9 or C_6H_5) were the only products observed.

The $n = 4$ series was examined in some detail. The alkyl-substituted compounds **1d** and **1e** gave only a trace of cyclic product **3** ($n = 4$, R = C_4H_9) upon direct addition to the Cr(II) reagent, but this was dramatically increased in inverse-addition experiments. Both using a more dilute solution of **1e** in DMF and increasing the addition time for the Cr(II) reagent aided cyclization. Interestingly, the iodide **1e** gives significantly more cyclic product than bromide **1d**. Under the most favorable conditions utilized, 85% of the product was cyclic.

The phenyl-substituted acetylenes **1f** and **1g** yielded cyclic product **3** ($n = 4$, R = C_6H_5) more readily than their alkyl-substituted counterparts. Direct addition gave appreciable amounts of cyclic product, whereas up to 95% cyclization was achieved by inverse-addition methods. In inverse additions, dilution increased cyclization marginally, whereas a faster addition time decreased this product slightly. The iodide again gave more cyclization than the bromide. In this case it was unambiguously demonstrated that 1-phenylcyclohexene (**4**; $n = 4$, R = C_6H_5) was not present in detectable amounts (<1%).

Some cyclization to **3** was also observed with the $n = 5$ series. The alkyl-substituted compounds **1h** and **1i** gave no cyclization using direct addition and only minor amounts of **3** ($n = 5$, R = C_4H_9) under the most favorable inverse-addition conditions. The phenyl-substituted analogues **1j** and **1k** cyclized more easily. Although only small amounts of cyclic product **3** ($n = 5$, R = C_6H_5) were formed upon direct addition, inverse-addition procedures gave on the order of 80% cyclization. Concentration and halogen effects were similar to those observed in the other series. 1-Phenylcycloheptene (**4**; $n = 5$, R = C_6H_5) was not present in detectable amounts in the product mixtures from **1j** and **1k**.

The $n = 6$, phenyl-substituted acetylene **1l** gave only acetylene **2** ($n = 6$, R = C_6H_5). Thus, the upper limit for competitive cyclization appears to be the $n = 5$ compounds.

The reversibility of the cyclizations under the reaction conditions was checked by reducing the cyclic vinyl bromides **5a–c** under both direct- and inverse-addition conditions. The corresponding cyclic olefin **3** was obtained as the predominant product in each instance. Although about 3% of minor products was observed from **5c**, GC comparisons demonstrated that neither the alkynes **2** nor isomeric olefins **4** were formed in detectable quantities in any of these reactions.

In order to probe the electronic demands of the cyclization process, the *p*-F (**1m**), *p*-CH_3 (**1n**), and *p*-OCH_3 (**1o**) phenyl derivatives in the $n = 4$ series were prepared and subjected to reduction by the Cr(II) reagent. Under the standard reaction conditions, the cyclizations of these compounds were not significantly different from those of the phenyl compound **1f**. Consequently, mixtures of these compounds were reacted with Cr(II) under conditions where approximately equal amounts of acyclic and cyclic products were formed. Under these competitive conditions the formation of the acyclic radicals and their trapping by Cr(II) is not expected to be influenced to any appreciable extent by the remote substituent. Consequently the relative rates of cyclization are given simply by the ratio of cyclic to acyclic products. In this fashion the relative rates were determined to be *p*-CH_3O, 1.000; *p*-CH_3, 1.108; H, 1.275; and *p*-F, 1.345. A Hammett plot of these data against σ[14] gives a ρ of $+0.38 \pm 0.01$ ($r = 0.9988$). This small positive value of ρ is consistent with the assumed radical-addition mechanism.[15]

A brief study of the relative ease of cyclization of key acetylenic compounds under free-radical conditions was performed by using the more commonly employed tin hydride methodology.[16] Thus halides **1e**, **1f**, and **1k** were each reduced with Bu_3SnH in refluxing benzene under identical conditions. Making the reasonable assumption that the rates of formation and trapping of the acyclic radical intermediates are essentially independent of the position and substitution of the remote acetylenic group,[17] the relative rates of cyclization can be estimated from the ratios of cyclic product **3** to acetylene **2** observed for the different acetylenic halides. In this fashion it can be shown that the $n = 4$, R = C_6H_5, radical **6** cyclizes about 19 times faster than its $n = 5$, R = C_6H_5 homologue.[18] Likewise, in the $n = 4$ series the R = C_6H_5 radical **6** cyclizes 39 times faster than the R = C_4H_9 species.

Discussion

The results of this study are fully consistent with prior work on the cyclizations of radicals of general type **6**. The use of Cr(II) for radical generation gives results comparable to those obtained with tin hydride.[6,7] Thus, highly regioselective cyclizations of **6** occur in the exo sense[19] to give **7** for the $n = 4$ and $n = 5$ species. The $n = 4$ radicals cyclize more efficiently than their $n = 5$ homologues and R = C_6H_5 promotes cyclization relative to R = C_4H_9. Experimental conditions favorable for cyclization of the $n = 3$ or $n = 6$ radicals of type **6** were not achieved. The behavior of radical **6** as a function of n parallels the effect of this variable on cyclizations in the olefinic series and is similarly explained.[2a] The beneficial influence of the R = C_6H_5 substituent is attributable to stabilization of the

(14) Wells, P. R. *Chem. Rev.* **1963**, *63*, 171.
(15) Afanas'ev, I. B. *Russ. Chem. Rev.* **1971**, *40*, 216.
(16) Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47. Kuivila, H. G. *Synthesis* **1970**, 499.
(17) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.
(18) These results agree with unpublished data on the relative rates of cyclization of ω-alkynyl radicals.[2a]
(19) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

Table II. Synthesis and Properties of $RC{\equiv}C(CH_2)_nX$ (1)[a]

	yield, %	bp, °C (torr)	NMR
1a	35	90–94 (9)	3.48 (t, 2), 2.5–1.7 (m, 6), 1.5–1.1 (m, 4), 0.92 (t, 3)
1b	71	110–112 (4)	3.19 (t, 2), 2.4–1.1 (m, 10), 0.91 (t, 3)
1c[10b]	55	112–115 (1)	7.4–7.0 (m, 5), 3.43 (t, 2), 2.48 (t, 2), 1.98 (p, 2)
1d	75	113–115 (7)	3.40 (t, 2), 2.4–1.1 (m, 12), 0.91 (t, 3)
1e	72	105–106 (2)	3.19 (t, 2), 2.3–1.5 (m, 12), 0.91 (t, 3)
1f	77	115–117 (0.8)	7.4–7.0 (m, 5), 3.30 (t, 2), 2.32 (t, 2), 2.1–1.4 (m, 4)
1g	82	135–140 (0.2)	7.5–7.1 (m, 5), 3.1 (t, 2), 2.33 (t, 2), 2.1–1.3 (m, 4)
1h	68	104–106 (3)	3.37 (t, 2), 2.4–1.1 (m, 14), 0.93 (t, 3)
1i	73	84–87 (0.25)	3.18 (t, 2), 2.4–1.1 (m, 14), 0.92 (t, 3)
1j	74	138–140 (0.5)	7.5–7.1 (m, 5), 3.28 (t, 2), 2.33 (t, 2), 2.1–1.2 (m, 6)
1k	74	135–137 (0.15)	7.4–7.1 (m, 5), 3.08 (t, 2), 2.32 (t, 2), 2.0–1.2 (m, 6)
1l	62	140–144 (0.1)	7.4–7.1 (m, 5), 3.08 (t, 2), 2.33 (t, 2), 2.0–1.1 (m, 8)
1m	71	95–100 (0.15)	7.5–6.8 (m, 4), 3.39 (t, 2), 2.37 (t, 2), 2.1–1.4 (m, 4)
1n	84	111–119 (0.6)	7.05 (m, 4), 3.33 (t, 2), 2.34 (t, 2), 2.26 (s, 3), 2.1–1.5 (m, 4)
1o	72	150–155 (0.4)	7.4–6.6 (m, 4), 3.65 (s, 3), 3.35 (t, 2), 2.35 (t, 2), 2.2–1.4 (m, 4)

[a] Elemental analyses were within experimental error.

developing vinyl radical in the transition state for the **6** → **7** transformation. Under the experimental conditions used, the cyclizations appear to be essentially irreversible as judged by the lack of ring-opened products in the Cr(II) reductions of the cyclic vinyl bromides **5**. This is true even with the strained $n = 3$ system, where no **6** → **7** cyclization is observed.

Interestingly the $n = 5$ radical **6** does not show the preference for endo cyclization predicted by vector analysis.[19] The endo mode has, however, been observed in more complicated systems where substituents modify the relative stabilities of the radical intermediates.[2c,4,11g,h] Consequently, some control over the regiochemistry of these radical cyclizations can apparently be exercised in favorable cases by an appropriate choice of substituents.

A puzzling aspect of the reactions of halides **1** with Cr(II) is the more efficient cyclization of the iodides. This observation, of course, does not follow from the mechanistic schemes considered above. We attribute this unexpected result to the very rapid reaction of the reagent with alkyl iodides which results in a local depletion of Cr(II) when the reagent is added to a solution of an iodide. Consequently, radicals **6** have a longer effective lifetime and give more cyclic product. This feature is not important with the less reactive bromides.[13,20] Alternate explanations, such as halide ligand effects on the reactivity of the Cr(II) species, cannot be excluded at this time.

Finally, the possibility of interconversion of organochromium species **8** and **9** can be ruled out as a significant process in the present study. Thus, in direct-addition experiments **1** → **2** and **5** → **3** via **8** and **9**, respectively, without appreciable crossover.

Experimental Section

General Methods. Nuclear magnetic resonance (NMR) spectra were recorded on CCl_4 solutions using Varian A-60, HR-100, and HA-220 spectrometers. Mass spectra were obtained with AEI MS-9 and Varian MAT CH-7 spectrometers. Infrared (IR) spectra were recorded on a Model 137 Perkin-Elmer Infracord. Gas chromatography (GC) was performed on Varian Model 1200 (analytical, flame-ionization detector) and A600 (preparative, thermal-conductivity detector) instruments. Peak areas were measured with a disk integrator. Analytical columns were 10 ft × 0.125 in. of 15% Carbowax 20M, 15 ft × 0.125 in. of 15% Ucon-2000 polar, and 20 ft × 0.125 in. of 30% SE-30, all on 60-80 Chromosorb W. Preparative columns were 5 ft × 0.375 in. of 15% Ucon-2000 polar, 5 ft × 0.375 in. of 20% SE-30, and 10 ft × 0.375 in. of 20% Carbowax 20M, all on 60-80 Chromosorb W. Microanalyses were performed by Midwest Microlabs, Inc.

Preparation of Acetylenic Halides 1. To 0.10 mol of 1.5 M *n*-butyllithium in hexane was added 0.12 mol of a terminal alkyne in 40 mL of THF. The solution was heated to reflux until gas evolution ceased (2–4 h). The appropriate dihalide (0.14 mol) was added and the reaction mixture was heated to reflux overnight. After cooling, 2 mL of water was added carefully and the solution was dried ($MgSO_4$) and concentrated. Vacuum distillation of the residual oil gave the desired product. Table II collects the data pertaining to the acetylenic halides prepared in this fashion.

Chromous Reductions of 1 and 5. All operations were performed under an argon atmosphere. Solutions of 0.25 M Cr(II) reagent were prepared by syringe transfer of one part of aqueous 1.0 M chromous perchlorate to three parts of 1.0 M ethylenediamine in degassed reagent-grade DMF.[21,22] In direct-addition experiments 2 mmol of **1** or **5** was injected directly into 20 mL of the Cr(II) reagent. Inverse-addition experiments were conducted by adding dropwise 20 mL of the Cr(II) reagent to 2 mmol of halide in either 20 or 40 mL of DMF over the indicated period of time. After the addition was completed, the solution was stirred for 1 h and added to 3 N HCl solution. The aqueous solution was extracted several times with pentane, and the combined extracts were washed with water, dried ($MgSO_4$), and concentrated. Analysis of the residual oil by GC provided the results given Table I. Major products were isolated by preparative GC and identified by spectroscopic comparison with authentic samples.[6,8] Minor components were generally assigned by GC or GC–mass spectrometric comparison.

The relative rate studies on the para-substituted phenyl compounds were performed in a similar manner, except that mixtures of **1f**, **1m**, **1n**, and **1o** were used with the inverse-addition method and addition time of about 5 min. The relative rates of cyclization obtained by measuring the ratios of **3**:**2** in a given experiment and normalizing to **1o** as 1.000 were **1f**, 1.275; **1m**, 1.345; **1n**, 1.108.

Bu_3SnH Reductions of 1e, 1f, and 1k. Solutions of 0.2 M **1**, 0.2 M Bu_3SnH,[23] and 0.01 M azobis(isobutyronitrile) initiator in benzene were heated to reflux for 24 h before analysis by GC. The following ratios of **3**:**2** were observed: **1c**, 0.29; **1f**, 11.1; **1k**, 0.59.

Cycloalkylidenephenylmethyl Bromides (5). To 4.3 g of benzylidenecyclobutane[24] in 50 mL of CCl_4 at 0 °C was added 5.0 g of bromine. After stirring for 1 h, the solvent was removed by flash evaporation. The crude dibromide (8 g) was added to a solution of potassium *tert*-butoxide prepared by dissolving 3.0 g of potassium in 100 mL of *tert*-butyl alcohol. After stirring the reaction mixture at room temperature for 1 h, ether was added, and the solution was washed several times with water. After drying ($MgSO_4$) and concentration, vacuum distillation gave 5.0 g (75%) of **5a**: bp 99–103 °C (0.2 torr); NMR (220 MHz) δ 1.85 (p, 2, $J = 8$ Hz), 2.71 (t, 4, $J = 8$ Hz) 7.0–7.4 (m, 5); exact mass calcd for $C_{11}H_{11}Br$ 222.0044, found 222.004.

In a similar fashion benzylidenecyclopentane[6] was converted into **5b** in 72% yield: bp 107–109 °C (0.1 torr); NMR δ 1.4–1.8

(20) Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343.

(21) Lux, H.; Illman, G. *Chem. Ber.* **1958**, *91*, 2143.
(22) House, H. O.; Kinloch, E. F. *J. Org. Chem.* **1974**, *39*, 1173.
(23) Kuivila, H. G.; Buemel, O. F. *J. Am. Chem. Soc.* **1961**, *83*, 1246.
(24) Bestmann, H. J.; Kranz, E. *Chem. Ber.* **1969**, *102*, 1802.

(m, 4), 2.1–2.7 (m, 4), 7.0–7.4 (m, 5); exact mass calcd for $C_{12}H_{13}Br$ 236.0201, found 236.021.

Likewise, benzylidenecyclohexane[25] was converted in 84% yield into **5c**: bp 135–137 °C (0.2 torr); NMR δ 1.47 (m, 6), 2.08 (m, 2), 2.52 (m, 2), 7.0–7.3 (m, 5); exact mass calcd for $C_{13}H_{15}Br$ 250.0357, found 250.038.

(25) Seyferth, D.; Hughes, W. B.; Heeren, J. K. *J. Am. Chem. Soc.* **1965**, *84*, 2847.

Registry No. **1a**, 68275-02-5; **1b**, 3416-75-9; **1c**, 57718-13-5; **1d**, 35843-78-8; **1e**, 42049-41-2; **1f**, 16664-48-5; **1g**, 57718-12-4; **1h**, 92078-64-3; **1i**, 42049-47-8; **1j**, 92078-65-4; **1k**, 57718-14-6; **1l**, 57718-15-7; **1m**, 92078-66-5; **1n**, 92078-67-6; **1o**, 92078-68-7; **3** (R = n-C_4H_9, n = 4), 53366-55-5; **3** (R = C_6H_5, n = 4), 4410-77-9; **3** (R = C_6H_5, n = 5), 1608-31-7; **3** (R = p-FC_6H_4, n = 4), 92078-69-8; **3** (R = p-$CH_3C_6H_4$, n = 4), 92078-70-1; **3** (R = p-$CH_3OC_6H_4$, n = 4), 20758-63-8; **3** (R = C_6H_5, n = 3), 5244-75-7; **5a**, 82833-97-4; **5b**, 57718-23-7; **5c**, 92078-71-2; $Cr(ClO_4)_2$, 13931-95-8; Bu_3SnH, 688-73-3.

1,4-Addition to Tetracyclone. Kinetic vs. Thermodynamic Product Distribution

Robert L. Eagan[1] and Michael A. Ogliaruso*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Byron H. Arison and James P. Springer

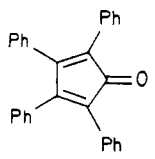
Merck, Sharp and Dohme Research Laboratories, Rahway, New Jersey 07065

Received March 28, 1984

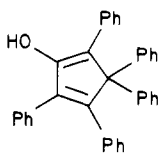
The Michael addition of cyanide ion to tetracyclone produces an enolate (**4a**) which, when protonated, affords a diastereomeric mixture of *cis*- (**5a**) and *trans*-4-cyano-2,3,4,5-tetraphenyl-2-cyclopenten-1-one (**6a**) in varying ratios depending upon the conditions employed. Quenching the enolate at low temperatures affords mainly the cis isomer, the kinetic product, while high temperature quench favors the trans isomer, the thermodynamic product. Base, acid, and heat were used to interconvert the cis and the trans isomers into a thermodynamic equilibrium ratio of products. Protonation of the enolate (**4b**) of 4-methoxy-2,3,4,5-tetraphenyl-2-cyclopenten-1-one gave similar results. Methylation of both enolates **4a** and **4b** is also reported as well as the structure elucidation of the isomers obtained from the above reactions.

Introduction

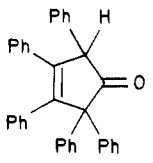
Reports in the literature concerning 1,4-addition to tetracyclone (**1**) are rare. In 1943, Allen and VanAllan[2] reported that the Michael addition of phenylmagnesium bromide to tetracyclone afforded 2,3,3,4,5-pentaphenyl-1,4-cyclopentadien-1-ol (**2**). However, reinvestigation of



1



2

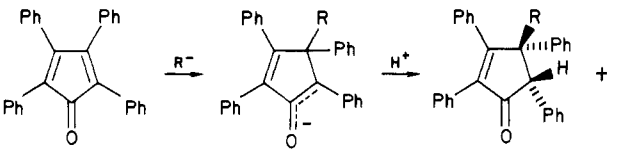


3

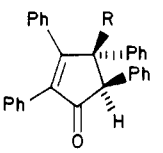
this reaction in our laboratories[3] in 1972 demonstrated that this reaction actually proceeded by a 1,2-addition of phenylmagnesium bromide followed by a thermally allowed [1,5]-sigmatropic rearrangement affording 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (**3**). 1,4-Addition has also been reported[4] in the reaction of tetracyclone with 1-indenyl- and 9-fluorenyllithium, and these results are currently under reinvestigation in our laboratories.

In 1971, Gallagher and Jenkins[5] described the Michael addition of selected organophosphorus compounds to tetracyclone and since then, several other papers[6-8] have appeared describing similar additions. However, due to the contradictory nature of these papers, it appears that the true nature of these reactions is still not completely understood.

Scheme I



1 → **4a**, R=CN; **b**, R=OMe → **5a**, R=CN; **b**, R=OMe



6a, R=CN; **b**, R=OMe

The only unquestioned report of Michael addition to tetracyclone was published in 1975 by Muckenstrum,[9] who studied the addition of various bases to tetracyclone. In this paper, we wish to extend the series of nucleophiles

(1) Presented at the 35th Southeastern Regional Meeting of the American Chemical Society, Charlotte, NC, Nov 10, 1983.
(2) Allen, C. F. H.; VanAllan, J. A. *J. Am. Chem. Soc.* **1943**, *65*, 1384.
(3) Youssef, A. K.; Ogliaruso, M. A. *J. Org. Chem.* **1972**, *37*, 2601.
(4) Bergman, E. D.; Berthier, G.; Ginsburg, D.; Hirshberg, Y.; Lavie, D.; Pinchas, S.; Pullman, B.; Pullman, A. *Bull. Soc. Chim. Fr.* **1951**, *18*, 661.
(5) Gallagher, M. J.; Jenkins, I. D. *J. Chem. Soc. C* **1971**, 210.
(6) Miller, J. A.; Stevenson, G. M.; Williams, B. C. *J. Chem. Soc. C* **1971**, 2714.
(7) Arbuzov, B. A.; Fuzhenkova, A. V.; Galyautdinov, N. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 440; *Chem. Abstr.* **1978**, *89*, 6366h.
(8) Fuzhenkova, A. V.; Galyautdinov, N. I.; Arbuzov, B. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1132; *Chem. Abstr.* **1978**, *89*, 109762p.
(9) Muckenstrum, B. *Tetrahedron* **1975**, *31*, 1933.

0022-3263/84/1949-4248$01.50/0