Z)-3g, 55025-21-3; (E,E)-3g, 81981-11-5; (E,Z)-3h, 54977-81-0; (E,-E)-3h, 24738-47-4; (E,Z)-4, 70979-88-3; (E,E)-4, 33467-79-7; (E,Z)-5, 56904-85-9; (E,Z)-6, 16195-71-4; (E,Z)-7, 4313-02-4; (E,E)-7, 4313-03-5; (E,Z)-8, 25152-83-4; (E,E)-8, 25152-84-5; ethynyl bromide, 593-61-3; decanal, 112-31-2; trimethyl orthoacetate, 1445-45-0; triethyl orthoacetate, 78-39-7.

Supplementary Material Available: Tables II and III containing ^{13}C NMR data for compounds 1 and 2 (2 pages). Ordering information is given on any current masthead page.

Selectivity in the Allylic Substitutions with Organometallics through Neighboring Coordination. 2-(Allyloxy)benzothiazoles as S_N2' Electrophiles for Regio- and Stereoselective Olefin Syntheses

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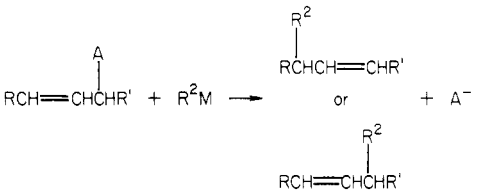
An efficient control of the regio- and stereochemistry in the allylic substitutions with organomagnesium compounds has been achieved by using 2-(allyloxy)benzothiazoles as substrates in the presence of copper bromide. The selectivity is due to the coordinative effects of the substrates toward the organometallic species.

Reacton of organomagnesium compounds with allylic ethers in the presence of a catalytic amount of copper(I) salts has been utilized as facile method for the formation of a new carbon-carbon bond.[2] But the competitive α/γ substitution by the Grignard reagent at the allylic system[3-5] has precluded a wider acceptance of the method. In fact, an extensive study[6] of a wide variety of allylic ethers revealed that the α/γ ratio was a sensitive function of stereic effects in the ether. Another severe limitation[4,6] is represented, except in a special case,[7] by the lack of stereoselectivity accompanying the S_N2' process in noncyclic allylic ethers. These drawbacks could potentially be surmounted by using an allylic substrate bearing a substituent with coordinating properties for the organometallic which could improve the positional selectivity.[8] It should also be preferable for synthetic purposes that this substituent could be lost during the C-C coupling process, as depicted in Scheme I.

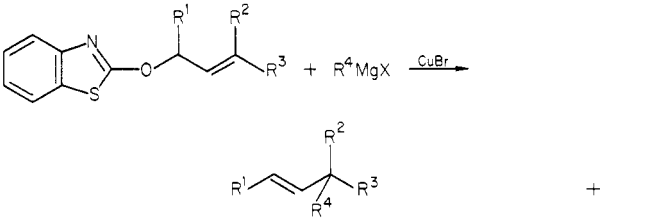
Recently we have found that some allylic ethers of benzothiazole react with carbon nucleophiles such as cuprates[9] and copper(I) acetylides[10] to give highly selective carbon-carbon coupling reactions. The surprisingly high selectivity found was tentatively explained by us as due to coordination phenomena toward the organometallic species exerted by the benzothiazole allylic ethers. In this regard, we have demonstrated that some 2-(allyloxy)-benzothiazoles behave as efficient bidentate ligands for

Scheme I[a]

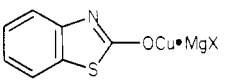


[a] A = a group with coordinating properties toward R^2M.

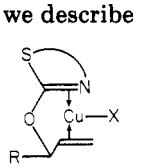
Scheme II



2a, R^1 = H; R^2 = CH_3; R^3 = $(CH_3)_2C{=}CHCH_2CH_2$
b, R^1 = C_2H_5; R^2 = R^3 = H
c, R^1 = R^2 = H; R^3 = CH_3
d, R^1 = H; R^2 = $(CH_3)_2C{=}CHCH_2CH_2$; R^3 = CH_3



copper(I) halogenides to give stable complexes in which the metal is probably inserted between the C=N of the heterocycle and C=C double bond of the allylic framework.[11] In this paper we describe the reactions of these



R = alkyl; X = Cl, Br, I

2-(allyloxy)benzothiazoles with Grignard reagents in the presence of CuBr and the consequences of the coordination phenomena toward the organometallic species on the re-

(1) Taken in part from the M.S. Thesis of A.C., University of Bari.
(2) For a recent review of these and related reactions of allylic compounds, see: Magid, R. M. *Tetrahedron* **1980**, *36*, 1901-1930.
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(7) (a) Claesson, A.; Olsson, L. I. *J. Chem. Soc., Chem. Commun.* **1978**, 621-623. (b) Gallina, C.; Ciattini, P. G. *J. Am. Chem. Soc.* **1979**, *101*, 1035-1036.
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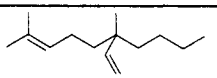
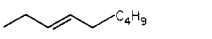
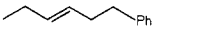
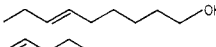
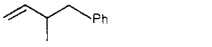
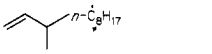
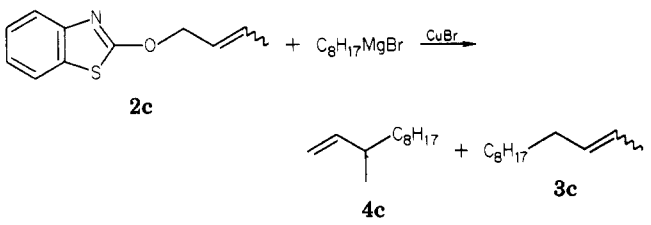
Table I. Alkylation of 2-(Allyloxy)benzothiazoles with Organomagnesium Compounds in the Presence of CuBr

entry	allylic ether	grignard reagent[a]	product	yield,[b] %
1	2a	n-C_4H_9MgBr		88
2	2b	n-C_4H_9MgBr		(85)[c]
3	2b	$PhCH_2MgCl$		73[c,d]
4	2b	$ClMgOCH_2(CH_2)_2CH_2MgBr$		90[c]
5	2c[e]	$PhCH_2MgCl$		77[d]
6	2c[e]	n-$C_8H_{17}MgBr$		87
7	2d	n-C_4H_9MgBr		80

[a] The reagents were added at once immediately after mixing 2a-d with CuBr. [b] Isolated yield; yield in parentheses was determined by GLC with an internal standard. [c] The E content was >99% (stereochemical purity tested by capillary GLC; SE-30, 50-m column). [d] Diphenylethane was a byproduct. [e] E/Z ratio of 60/40.

Scheme III



gioselectivity of these reactions.

Results

The addition of an organomagnesium compound at 0 °C to a THF solution of 2-(allyloxy)benzothiazole **2a–d** in the presence of stoichiometric amount of copper(I) bromide added immediately before the addition of the Grignard reagent afforded in high yields C–C coupling products deriving exclusively from an S_N2'-type substitution *independently of the bulkiness of substituents borne by the allylic framework* as depicted in Scheme II.

The same results are obtained if the allylic ether is added at −40 °C to a solution of alkylcopper reagent prepared by mixing in THF at −40 °C stoichiometric quantities of Grignard reagents and CuBr. The results are shown in Table I. Moreover, where possible (Table I, entries 2–4), the S_N2' process occurs under full stereochemical control, leading exclusively to (*E*)-alkenes. The reaction temperature and the copper(I) halogenide utilized show very little influence on the regioselectivity, since almost the same results are obtained by working at −30 or −60 °C or by using Cu_2Cl_2 or CuI in place of CuBr. In ethyl ether as the solvent we found the same results but slower reaction rates. Surprisingly, in the reactions of primary allylic derivatives **2a** and **2c**, we observed a variable S_N2/S_N2' ratio in the substitution, depending on the contact time between the allylic derivative and CuBr before the addition of the Grignard reagent. For example the reaction between **2c** and *n*-octylmagnesium bromide (Scheme III) led to a variable **4c**/**3c** ratio as reported in Table II. On the contrary, in the reaction of **2b** we did not observe this variation in the regioselectivity, and only S_N2' products were found. In an attempt to isolate the reaction intermediate responsible for these results, we found that on mixing CuBr with **2b** or **2c** in THF, the copper(I) salt slowly disappeared with the formation of a light gray precipitate. These solids, after filtration, proved to be identical with copper bromide–2-(allyloxy)benzothiazole π complexes synthesized as previously reported.[11] In the reaction of **2a** and **2d** with CuBr the light-colored solution turned to green, but a precipitate was not formed. The addition of n-$C_8H_{17}MgBr$ to a 1:1 mixture of **2c** and **2c**·CuBr complex in THF gave **3c** and **4c** in nearly equal amounts. Finally, both **2b** and **2b**·CuBr complex gave only the coupling product derived by an S_N2'-type substitution.

Table II. S_N2'/S_N2 Ratio from the Reaction between 2-[(2-Buten-1-yl)oxy]benzothiazole (2c) and n-$C_8H_{17}MgBr$ in the Presence of CuBr

time of stirring[c]	4c/3c ratio[a]	time of stirring[c]	4c/3c ratio[a]
0[b]	100/0	1 h	50/50
10 min	85/15	6 h	5/95

[a] Determined by GLC (6-ft column, SP2100 on 100–120 Supelcoport). [b] The organomagnesium was added at once immediately after the addition of **2c** to a CuBr suspension in THF. [c] Stirring time of **2c** and CuBr before the addition of n-$C_8H_{17}MgBr$.

Discussion

The isolation of the complex derived from 2-(allyloxy)benzothiazoles and CuBr[11] clearly demonstrates the ability of our reagents to behave as ligands toward copper(I) halognides. It is worth mentioning that among copper(I) π complexes with dienes, particularly stable are those formed with 1,5-dienes such as 1,5-cyclooctadiene (COD), in which the boat-shaped COD acts as a bidentate ligand.[12-14] In our reagents both C=N and C=C double bonds are in a 1,5 relationship. Therefore, it is reasonable to assume that the 2-(allyloxy)benzothiazoles, besides the copper(I) halogenides, could coordinate other Cu(I) species such as, for example, alkylcopper reagents. In light of these arguments, our results can be explained in the following manner. If the Grignard reagent is added immediately, before the coordination of CuBr by the allylic ethers could occur, the alkylcopper reagent produced from the fast reaction between CuBr and RMgX is initially coordinated by the allyl ether and subsequently reacts at the γ-position of the allylic framework to give exclusively S_N2'-type products (Scheme IV). On the other hand, if the organomagnesium compound is added later, therefore allowing CuBr coordination by the allylic ether, the regioselectivity of the RMgX reaction probably depends on the steric requirements of the preformed CuBr complex; i.e., the

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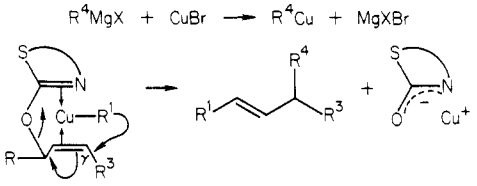
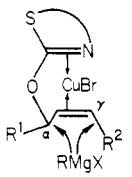
(13) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889–1897.
(14) Leyendecker, F.; Jesser, F. *Tetrahedron Lett.* **1980**, *21*, 1311–1314.

Scheme IV



nucleophilic attack by the organomagnesium compound occurs on the less hindered position, α or γ, in the allylic framework.[15] Moreover, the stereoselectivity observed in



the reactions of **2b** should be ascribed to a lack of conformational mobility in the transition state with either the **2b**·CuBr or **2b**·RCu complexes as intermediates. In fact, simple noncyclic allylic ethers with poor complexing properties toward copper(I) react with a S_N2' mechanism without stereospecficty.[4,6] It appears that simply by using allylic ethers with coordinating properties toward organometallic species, the regio- and stereoselectivity in certain allylic substitutions can be made into a synthetic method of great potential. We are actively pursuing extension of this methodology to the synthesis of natural products.

Experimental Section

General Methods. The stereochemical purity of the reaction products was tested by capillary GLC performed on a Hewlett-Packard Model 5780 (SE-30, 50 m). The proton magnetic resonance (^{1}H NMR) spectra were determined on Varian A-60A and HA-100 spectrometers. The boiling points of the products were measured with a Kugelrohr distillation apparatus. Geraniol, nerol, 1-penten-3-ol, crotyl alcohol, and 2-chlorobenzothiazole were purchased from Aldrich.

General Procedure for the Synthesis of the 2-(Allyloxy)benzothiazoles 2a–d. To the allylic alcohol (0.12 mol) dissolved in 50 mL of ether is added at 0 °C potassium (0.04 mol) in small pieces with stirring. After the reaction of the metal, 2-chlorobenzothiazole (Aldrich, 0.04 mol) dissoved in 20 mL of ether is added and reaction mixture is left at room temperature until the complete disappearance (TLC, hexane/ethyl acetate, 20:1 v/v) of the halo compound (12–24 h). The reaction mixture is then washed with water, dried, and evaporated, and the oily residue was chromatographed (silica gel, eluant hexane/ethyl acetate, 20:1 v/v) to give the products as colorless oils, yield 75–90%. Attempted vacuum distillation of these ethers results in a partial O → N Claisen rearrangement to give *N*-allylbenzothiazol-2-one.[16]

(2*E*)-2-[(3,7-Dimethyl-2,6-octadien-1-yl)oxy]benzothiazole (2a). This ether is obtained in 75% yield on starting from geraniol: ^{1}H NMR (CCl_4) δ 1.60 (d, 6), 1.78 (s, 3), 2.05 (s, 4), 4.97 (m, 3), 5.48 (t, 1), 7.98–8.26 (m, 2), 8.44–8.60 (m, 2). Anal. Calcd for $C_{17}H_{21}NOS$: C, 71.04; H, 7.37; N, 4.87. Found: C, 69.90; H, 7.43, N, 4.78.

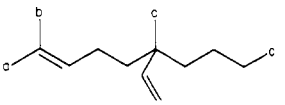
2-[(1-Penten-3-yl)oxy]benzothiazole (2b) was synthesized as previously reported.[9]

2-[(2-Buten-1-yl)oxy]benzothiazole (2c). This ether was obtained in 90% yield by starting from crotyl alcohol: ^{1}H NMR (CCl_4) δ 1.70–1.85 (m, 3), 4.90–5.05 (m, 2), 5.75–5.90 (m, 2), 7.15–7.80 (m, 4). Anal. Calcd for $C_{11}H_{11}NOS$: C, 64.36; H, 5.40; N, 6.82. Found: C, 64.20; H, 5.45; N, 6.80. This product proved to be a 60/40 mixture of *E* and *Z* isomers.

(2*Z*)-2-[(3,7-Dimethyl-2,6-octadien-1-yl)oxy]benzothiazole (2d). This product was obtained by starting from nerol: yield 80%; ^{1}H NMR (CCl_4) δ 1.58 (s, 3), 1.76 (d, 6), 2.10 (s, 4), 4.97 (m, 3), 5.48 (t, 1), 7.98–8.26 (m, 2), 8.44–8.60 (m, 2). Anal. Calcd for $C_{17}H_{21}NOS$: C, 71.04; H, 7.37; N, 4.87. Found: C, 70.20; H, 7.20; N, 4.80.

General Method for Reaction of 2-(Allyloxy)benzothiazoles with Grignard Reagents. CuBr (0.01 mol) was added to 0.01 mol of the allyl ether dissolved in 20 mL of dry THF under N_2 at 0 °C without stirring. To this suspension was added at once the organomagnesium reagent under stirring. The resulting black solution was stirred another 30 min, evaporated to a small volume, and chromatographed (silica gel, eluant hexane or hexane/ether, 5:1 v/v), depending on the polarity of the reaction product, to give pure alkene in 73–90% yield. Alternatively, the evaporated suspension is acidified with dilute hydrochloric acid and extracted with ether. This solution is washed four times with 5% sodium hydroxide solution to remove 2-hydroxybenzothiazole and once with water, dried, and evaporated to give almost pure alkene. According to the above procedure the following compounds were prepared (yields are in Table I).

3-Butyl-3,7-dimethyl-1,6-octadiene (Table I, entries 1 and 7): bp 60 °C (0.01 mm);



^{1}H NMR (CCl_4) δ 0.95 (CH_3(c) s, 6 H), 1.56 (CH_3(a), s, 3 H), 1.64 (CH_3(b), s, 3 H), 4.82 (CH_2=CH and $(CH_3)_2C$=CH, m, 3 H), 5.56 (CH_2=CH, m, 1 H); IR (CCl_4) 3080, 1645, 985, 905 cm^{-1} (CH_2=CH). Anal. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48. Found: C, 86.45; H, 13.40.

***trans*-3-Nonene**, bp 149 °C [lit.[17] bp 147 °C (750 mm)].

***trans*-1-Phenyl-3-hexene**, bp 100 °C (15 mm) [lit.[18] bp 102 °C (15 mm)].

trans-6-Nonen-1-ol, bp 80 °C (0.2 mm) [lit.[19] 76 °C (0.2 mm)].

4-Phenyl-3-methyl-1-butene: bp 51 °C (4 mm); ^{1}H NMR (CCl_4) δ 4.84, (m, 2 H), 5.80 (m, 1 H), 7.0 (m, 5 H). Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.10; H, 9.90.

3-Methyl-1-undecene: bp 84 °C (20 mm); ^{1}H NMR (CCl_4) δ 5.00 (m, 2 H), 5.85 (m, 1 H); IR (neat) 3080, 1640, 990, 910 cm^{-1}.

2-[(2-Buten-1-yl)oxy]benzothiazole–copper bromide complex (mp 123 °C dec) and 2-[(1-penten-3-yl)oxy]benzothiazole–copper bromide complex (mp 122 °C dec) were synthesized as previously reported.[11]

Reaction of 2c·CuBr Complex in the Presence of 2c and CuBr with Octylmagnesium Bromide. To 3.5 g (0.01 mol) of the complex suspended in 30 mL of THF were added 1.43 g (0.01 mol) of CuBr and 2.05 g (0.01 mol) of 2-[(2-buten-1-yl)oxy]-benzothiazole (**2c**), followed by at once addition with a syringe of 0.02 mol of *n*-octylmagnesium bromide dissolved in 20 mL of THF at 0 °C under stirring. Product isolation as described above and GLC analysis (SP 2100 on 100/120 Supelcoport, 6-ft column) showed two peaks in the ratio 55:45. The first peak was identified as 3-methyl-1-undecene and the second as 2-dodecene by comparison with authentic samples. A GLC analysis with a capillary column (SE-30, 50-m, on 100/120 Supelcoport) of the dodecene showed two peaks in a ratio 60/40 corresponding to *trans*- and *cis*-2-dodecene, respectively.

Alkylation of (2*E*)-2-[(3,7-Dimethyl-2,6-octadien-1-yl)-oxy]benzothiazole (2a) with Butylmagnesium Bromide in the Presence of CuBr. The allyl ether **2a** (2.87 g, 0.01 mol) dissolved in 30 mL of THF was stirred for 1 h with 1.43 g of CuBr (0.01 mol) at room temperature. The colorless solution turn to dark green, and *n*-butylmagnesium bromide in THF (10 mL of a 1.8 M solution) was added dropwise under stirring at 0 °C. After 30 min GLC analysis (SP 2100 on 100/120 Supelcoport, 6-ft

(15) Mukaiyama et al. have found that 2-(allyloxy)piridine reacted with RMgBr and that the regioselectivity was also a sensitive function of steric effects in the ether: Mukaiyama, T.; Yamaguchi, M.; Narasaka, K. *Chem. Lett.* **1978**, 689.

(16) Elwood, J. K.; Gates, J. W., Jr. *J. Org. Chem.* **1967**, *32*, 2956–2959.

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(18) Ansell, M. F.; Selleck, M. E. *J. Chem. Soc.* **1956**, 1238–1242.

(19) Jacobson, M.; Keiser, I.; Chambers, D. L.; Miyashita, D. H.; Harding, C. *J. Med. Chem.* **1971**, *14*, 236–239.

column) showed two peaks in the ratio 80:20. This mixture was separated by preparative TLC (silica gel, hexane) to give 3-butyl-3,7-dimethyl-1,6-octadiene as the major product and (6*E*)-2,6-dimethyl-2,6-dodecadiene. The latter product [bp 65 °C (0.1 mm)] had IR and H^1NMR data identical with those reported by Normant.[6]

Acknowledgment. This research was supported by grants from the Ministry of Education, and National Research Council of Italy.

Registry No. 2a, 73969-14-9; **2b**, 72737-52-1; **2b**·CuBr, 82434-18-2; (*E*)-**2c**, 82679-45-6; (*Z*)-**2c**, 82679-48-9; (*Z*)-**2c**·CuBr, 82434-17-1; **2d**, 82679-46-7; *n*-C_4H_9MgBr, 693-03-8; $PhCH_2MgCl$, 6921-34-2; $ClMgOCH_2(CH_2)_2CH_2MgBr$, 82679-47-8; *n*-$C_8H_{17}MgBr$, 17049-49-9; CuBr, 7787-70-4; 3-butyl-3,7-dimethyl-1,6-octadiene, 69747-29-1; *trans*-3-nonene, 20063-92-7; *trans*-1-phenyl-3-hexene, 60669-38-7; *trans*-6-nonen-1-ol, 31502-19-9; 4-phenyl-3-methyl-1-butene, 1647-06-9; 3-methyl-1-undecene, 18435-37-5.

Favorsky Rearrangements of α-Halogenated Acetylcycloalkanes.[1-3] 3

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The rearrangement of 21-bromopregnenolone acetate with sodium methoxide in dimethoxyethane leads to an epimeric mixture of 17-methylated etio esters in which the 17α-methyl derivative prevails, in contradistinction to the rearrangement under identical conditions of 17-bromopregnenolone acetate which affords predominantly the 17β-methyl 17α-etio ester. This excludes the possibility that in *every* cyclopropanonic Favorsky rearrangement a dipolar species is formed as the primary *intermediate* from the originally produced enolate ion. All the results of cyclopropanonic Favorsky rearrangements may be explained by the assumption of a competition between a concerted and a nonconcerted cyclopropanone formation, the protic and polar character of the medium exerting an important influence on the concertedness and the nonconcertedness of the mechanism. As a possible alternative, a gradient of mechanisms could be considered. The competition between reactions leading to rearrangement and substitution products and the dependence of their relative importance on the medium are also discussed.

Some years ago we suggested [1,6,7] that the complex stereochemical results of Favorsky rearrangements of α-halogenated acetylcycloalkanes, in particular of α-halogenated 20-keto steroids, in which cyclopropanones are considered to be intermediates, can be explained by the assumption that two mechanistic pathways may be operative, in some cases simultaneously: one, corresponding to a "Loftfield-type" mechanism,[8] in which the initially formed enolate is converted directly, concertedly, and stereospecifically to a cyclopropanone which is then opened to rearrangement products with a unique stereochemistry at the originally halogenated carbon atom (cf. pathway *a* in Scheme I) and another one, corresponding to a "Dewar-type" mechanism,[9] in which the enolate is first transformed into a dipolar intermediate which may lead to two epimeric cyclopropanones which are opened to epimeric rearrangement products (pathway b in Scheme I).[10] We further suggested that a polar and protic medium would favor the formation of a dipolar intermediate (cf. **3**) and a nonprotic and mildly polar medium a "concerted" ring closure[11] and that, in the case of the nonconcerted pathway, steric factors could result in a marked stereoselectivity of the conversion of the dipolar intermediate to one of the epimeric cyclopropanones and thus result in a stereoselective formation of rearrangement products with one of the two possible configurations.[15]

We have already presented arguments[1] against suggestions[16,17] that in *all* cyclopropanonic Favorsky rearrangements the cyclopropanones had to be formed in a concerted fashion. Certain authors, in particular Bordwell and his collaborators,[18] suggested for *all* cyclopropanonic Favorsky rearrangements a nonconcerted pathway, implying the formation, prior to the cyclopropanone cyclization, of a dipolar intermediate or, at least, a dipolar ion-like transition state.[18a,c,19,20] We relate here the results of the rearrangement of 21-bromopregnenolone acetate (**10a**) with

(1) Part 2: Engel, Ch. R.; Roy, S. K.; Capitaine, J.; Bilodeau, J.; McPherson-Foucar, C.; Lachance, P. *Can. J. Chem.* **1970**, *48*, 361.

(2) This publication represents paper 49 in our series on "Steroids and Related Products". Paper 48: Engel, Ch. R.; Lourdusamy, M. M.; Mukherjee, D.; Le-Van, Chau, *Pol. J. Chem.*, in press.

(3) Reported in part at the 46th Congress of the French-Canadian Association for the Advancement of Sciences (ACFAS), Ottawa, May 1978, and contained in part in a paper presented to the 28th Congress of the International Union of Pure and Applied Chemistry, Vancouver, Aug 1981.

(4) Abbreviated from part of the doctoral thesis of Y.M., Université Laval, Quebec, Canada, 1976.

(5) Abbreviated in part from the M.Sc. thesis of J. C., Université Laval, Quebec, Quebec, Canada, 1973.

(6) Engel, Ch. R.; Roy, S. K.; Bilodeau, J.; Lachance, P. "Abstracts of Papers", 19th International Congress of Pure and Applied Chemistry, London, 1963; Section A, pp 53–54.

(7) Engel, Ch. R. *Chimia*, **1965**, *19*, 507.

(8) Loftfield, R. B. *J. Am. Chem. Soc.* **1951**, *73*, 4707.

(9) Burr, J. C.; Dewar, M. J. S. *J. Chem. Soc.* **1954**, 1201.

(10) For reasons of simplicity, we have depicted in Scheme I only rearrangement products arising from the principal mode of opening of the cyclopropanone rings.

(11) Similar suggestions have been made by House and Gilmore[12] and, subsequently to our preliminary reports,[6,7] by Tchoubar and co-workers.[13,14]

(12) House, H. O.; Gilmore, F. *J. Am. Chem. Soc.* **1961**, *83*, 3980.

(13) Gaudemar, A.; Parello, J.; Skrobek, A.; Tchoubar, B. *Bull. Soc. Chim. Fr.* **1965**, 2405.

(14) Skrobek, A.; Tchoubar, B. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1966**, *263*, 80.

(15) For an added verification of this hypothesis, cf. a subsequent paper of this series.

(16) Smissman, E. E.; Lemke, T. L.; Kristiansen, O. *J. Am. Chem. Soc.* **1966**, *88*, 334.

(17) House, H. O.; Frank, G. A. *J. Org. Chem.* **1965**, *30*, 2948.

(18) (a) Bordwell, F. G.; Scamehorn, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 3410. (b) Bordwell, F. G.; Strong, J. C. *J. Org. Chem.* **1973**, *38*, 579. (c) Cf. also: Bordwell, F. G.; Carlson, M. W. *J. Am. Chem. Soc.* **1970**, *92*, 3370.

(19) (a) Bordwell, F. G.; Scamehorn, R. G. *ibid.* **1968**, *90*, 6751. (b) Bordwell, F. G.; Scamehorn, R. G.; Springer, W. R. *ibid.* **1969**, *91*, 2087. (c) Cf. also: Bordwell, F. G.; Frame, R. R.; Scamehorn, R. G.; Strong, J. C.; Meyerson, S. *Ibid.* **1967**, *89*, 6704. (d) Bordwell, F. G.; Almy, J. *J. Org. Chem.* **1973**, *38*, 575.

(20) Cf. also: Hunter, D. H.; Stothers, J. B.; Warnhoff, E. W. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, pp 391 ff.

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