TABLE I (*Continued*)

[a] C = chromatography, R = recrystallization of the reaction mixture. [b] Compounds in italics were obtained by hydrolysis of the corresponding 21-acetates. [c] Yields of recrystallized material based on enol ether, except where not isolated, otherwise on Δ^4-3-one. [d] Solvent: C = chloroform, P = pyridine. [e] Calcd. for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.67; H, 9.76. [f] Ref. 2, m.p. 211–212°, $[\alpha]_D$ +27°, λ_{max} 236 mμ (log ε 4.14). [g] Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.55; H, 9.02. [h] C. Amendolla, G. Rosenkranz, and F. Sondheimer, *J. Chem. Soc.*, 1226 (1954), m.p. 217–218°, $[\alpha]^{20}_D$ +34°, λ_{max} 236 mμ (ε 13,800). [i] Calcd. for $C_{19}H_{28}O_3 \cdot {}^1/_2C_3H_6O$: C, 73.91; H, 9.53. Found: C, 73.91; H, 9.30. [j] Calcd. for $C_{22}H_{30}O_3$: C, 77.15; H, 8.83. Found: C, 77.02; H, 8.97. [k] Calcd. for $C_{21}H_{28}O_4$: C, 73.22; H, 8.19. Found: C, 72.63, 72.31; H, 8.26, 8.47. [l] D. H. Peterson and H. C. Murray, *J. Am. Chem. Soc.*, **74**, 1871 (1952), m.p. 245–248°, $[\alpha]^{24}_D$ +144°. [m] B. Camerino, C. G. Alberti, A. Vercellone, and F. Ammannati, *Gazz. chim. ital.*, **84**, 301 (1954), m.p. 260–262°, $[\alpha]_D$ +164°, λ_{max} 240 mμ (ε 12,220). [n] J. Fried, R. W. Thoma, D. Perlman, J. E. Herz, and A. Borman, *Recent Progr. Hormone Res.*, **11**, 149 (1949), m.p. 230–232°, $[\alpha]_D$ +75°. [o] Calcd. for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87. Found: C, 74.23; H, 9.14. [p] S. H. Eppstein, P. D. Meister, D. H. Peterson, H. C. Murray, H. M. Leigh, D. A. Lyttle, L. M. Reineke, and A. Weintraub, *J. Am. Chem. Soc.*, **75**, 408 (1953), m.p. 196–198°, $[\alpha]_D$ +113°, λ_{max} 237 mμ (ε 13,900). [q] Ref. *p*, m.p. 198–202°, $[\alpha]^{23}_D$ +101°. [r] Calcd. for $C_{24}H_{34}O_5$: C, 71.61; H, 8.51. Found: C, 71.84; H, 8.79. [s] Calcd. for $C_{23}H_{32}O_6$: C, 68.29; H, 7.97. Found: C, 68.05; H, 8.26. [t] R. Neher and A. Wettstein, *Helv. Chim. Acta*, **29**, 2062 (1956), m.p. 225–227°, $[\alpha]^{21}_D$ +118°, λ_{max} 237 mμ (log ε 4.13). [u] Calcd. for $C_{24}H_{34}O_5$: C, 71.61; H, 8.51. Found: C, 71.48; H, 8.70. [v] Calcd. for $C_{23}H_{32}O_6$: C, 68.29; H, 7.97. Found: C, 68.08; H, 8.14, ref. *p*, m.p. 258–260°, $[\alpha]^{23}_D$ +74°, λ_{max} 237 mμ (ε 14,100). [w] K. Florey and M. Ehrenstein, *J. Org. Chem.*, **19**, 1331 (1954), m.p. 229–230°, $[\alpha]_D$ +43.7°, λ_{max} 235 mμ (ε 13,100). [x] A. Ercoli, U. S. Patent 3,009,858, November 21, 1961, m.p. 189–192°, $[\alpha]_D$ +20.5°. [y] Ref. 3, m.p. 246–248°. [z] Ref. *y*, m.p. 236–238°, $[\alpha]_D$ +117°, λ_{max} 232 mμ (log ε 4.14). [aa] S. Bernstein and R. Littell, *J. Org. Chem.*, **27**, 2544 (1962), m.p. 208–210°, $[\alpha]^{25}_D$ +107°, λ_{max} 236 mμ (ε 13,400). [bb] S. Bernstein and R. Littell, *ibid.*, **25**, 313 (1960), m.p. 241–243°, $[\alpha]_D$ +90°, λ_{max} 234–235 mμ (ε 12,000). [cc] Calcd. for $C_{23}H_{32}O_7$: C, 65.69; H, 7.67. Found: C, 65.07; H, 7.76. [dd] Ref. *bb*, m.p. 220–222°. [ee] Calcd. for $C_{23}H_{30}O_6$: C, 68.63; H, 7.51. Found: C, 68.91; H, 7.87. [ff] Calcd. for $C_{21}H_{28}O_5$: C, 69.97; H, 7.83. Found: C, 69.56; H, 7.78.

Stereochemistry of Reactions of the Norbornyl Grignard Reagent

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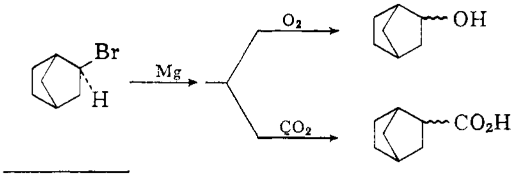
The stereochemistry of reactions of 2-bicycloheptyl Grignard reagents has not been thoroughly investigated. Interpretation of much of the earlier literature on reactions of bornyl Grignard reagents is complicated by the lack of adequate data on the structure and purity of some of the products involved.[2] More recently, Koch and Haaf[3] carbonated the Grignard reagent of norbornyl bromide and apparently obtained mainly *endo*-2-norbornanecarboxylic acid.

We undertook a more systematic study of reactions of the norbornyl Grignard reagent to evaluate the synthetic utility of this reagent. In particular, we studied the oxidation and carbonation reactions at two different temperatures (equation 1). The alcohols and acids (after conversion to methyl esters) were analyzed by gas-liquid chromatography. Table I summarizes the results.



(1)

TABLE I

exo–endo RATIOS OF PRODUCTS FROM REACTIONS OF NORBORNYL GRIGNARD REAGENT

	Reaction	
Temp.	Carbonation	Oxygenation
−78°	90:10	80:20
25°	70:30	79:21

The change in the *exo–endo* ratio of acids with temperature is of some interest. Since the yields at the lower temperature were lower, the possibility exists that carbonation was incomplete and that the *exo* Grignard reagent carbonated faster than the *endo* isomer.[4] A control experiment in which the length of the carbonation period at −78° was doubled led to the same ratio of acids in slightly higher yield. An attractive alternate rationale is that the *exo* and *endo* forms of the Grignard reagent exist in mobile equilibrium. The preponderance of *exo* acid in the product would be due to the fact that the transition state leading to it is of lower energy. Raising the temperature would be expected to shift the equilibrium toward *endo* Grignard as well as decrease the difference in transition state energies, thus leading to a smaller *exo–endo* ratio.

If the above explanation for carbonation is correct, it may be necessary to assume a different type of mechanism for oxidation, since the ratio of *exo–endo* alcohols did not change with temperature. Any possible explanation is complicated by the fact that there are two steps in which carbon–metal

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(1) Abstracted from the Bachelor's thesis of G.T.K. (1962).

(2) For a summary and further references see C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, **77**, 6039 (1955).

(3) H. Koch and W. Haaf, *Ann.*, **638**, 111 (1960).

(4) It is assumed that carbonation is stereospecific with retention of configuration; *cf.* H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **83**, 2595 (1961).

bonds are broken: formation of the hydroperoxide salt and reduction of the salt.[5] The stereochemistry of the two steps apparently is the same, however.[2] The insensitivity of the product ratio to temperature is suggestive of a free-radical process for these steps. Kooyman and Vegter,[6] for example, obtained the same ratio of *exo–endo* norbornyl chlorides at both 42° and 150° in an investigation of radical-catalyzed chlorination of norbornane.

Experimental

Chromosorb P (35/80) was the solid phase used in the gas chromatographic work. The columns were $^1/_4$-in. o.d. copper tubing of the indicated lengths. Boiling points are uncorrected.

exo-**Norbornyl bromide** was prepared by addition of hydrobromic acid to norbornene[7] and had b.p. 78–80° (19 mm.) (lit.[7] b.p. 82°/29 mm.).

Preparation of the Grignard Reagent of Norbornyl Bromide.—The reagent was prepared in dried apparatus under nitrogen by addition of 5.0 g. (0.029 mole) of the bromide in 20 ml. of dry ether to 1.0 g. (0.041 g.-atom) of magnesium under 15 ml. of ether containing a crystal of iodine. The mixture was refluxed for 1 hr.

Carbonations were carried out by bubbling carbon dioxide from Dry Ice through concentrated sulfuric acid, a calcium chloride drying tower, and into the reaction flask held at 25° or −78°. The mixture was decomposed with 2 *N* hydrochloric acid and extracted with ether. The acidic products were removed by washing with potassium carbonate solution. The yields of acidic and neutral products formed at the two temperatures were as follows: 25°, 1.4 g. (35%) and 1.7 g. −78°, 0.9 g. (22%) and 2.3 g. (1 hr. carbonation); 1.0 g. (25%) and 2.3 g. (2 hr. carbonation).

Analyses of the acids were effected by conversion to methyl esters using boron trifluoride–methanol reagent[8] followed by gas chromatography. The best separation was acheived on a 10 ft. castorwax column (25%) at 142°. The curves were matched with known mixtures of the esters prepared by weighing pure samples. No noticeable epimerization took place during the esterification since the standard samples were also made with the boron trifluoride reagent. The analyses are probably accurate to ±3%. At 25° the *exo:endo* ratio was 70:30; at −78° the ratio was 90:10 in both cases.

Oxygenations were carried out in a similar manner using air in place of carbon dioxide. The reaction mixtures were decomposed with dilute sulfuric acid and extracted with ether. The alcohols were separated from the other neutral products by chromatography on "activated" alumina. Hexane was used to elute everything but the alcohols and methanol was used to remove the alcohols. The analyses were carried out by gas chromatography on an 8 ft. column of carbowax 20M (15%) at 102°. At 25° the yield of mixed norbornanols was 1.8 g. (56%) and 2.4 g. of other neutral products were obtained; the ratio of *exo* to *endo* alcohol was 79:21. At −78° there was obtained 1.9 g. (59%) of alcohols and 2.4 g. of other products; the ratio of *exo* to *endo* a lcohols was 80:20. Ratios of peak areas were used to determine these percentages. It was shown that the alumina did not isomerize *exo*-norbornanol.

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(5) C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, **77**, 6032 (1955).

(6) E. Kooyman and G. Vegter, *Tetrahedron*, **4**, 382 (1958).

(7) J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(8) Applied Science Laboratories, Inc., State College, Pennsylvania. See L. D. Matcalfe and A. A. Schmitz, *Anal. Chem.*, **33**, 363 (1961), for procedure.

The Synthesis of Bridged Ferrocene Derivatives with Functional Groups on the β-Carbon of the Bridge[1]

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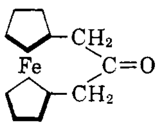
For future mechanistic studies it was desirable to have bridged ferrocene derivatives with functional groups on the β-carbon of the bridge. To this end, the dimethyl ester of ferrocene-1,1′-diacetic acid,[2] was treated with sodium triphenylmethyl in anhydrous ether. The red color of the triphenylmethyl anion soon disappeared and after work-up and chromatography there was obtained in 85% yield 1,1′-(α-carbomethoxy β-ketotrimethylene)ferrocene which was directly hydrolyzed and decarboxylated in glacial acetic acid with hydrochloric acid to 1,1′-(α-ketotrimethylene)ferrocene (I). Reduction of the ketone with sodium borohydride led to 1,1′-(β-hydroxy-trimethylene)ferrocene. The structure of the ketone was proved by desulfurization of its dimethylthioketal derivative with Raney nickel which produced the known 1,1′-trimethyleneferrocene.[3]



I

A principal point of interest in the synthesis is the ease of effecting the Dieckmann cyclization which may suggest that two of the bridging atoms can be planar with considerable double bond character between them. This is further borne out by the smooth preparation of an enol acetate derivative of 1,1′-(α-carbomethoxy-β-ketotrimethylene)ferrocene which possesses a double bond between the α- and β-carbons of the bridge. This is the first reported case of a ferrocene derivative bridged by a three-carbon chain containing a double bond.

NOTE ADDED IN PROOF: Rosenblum[4] has also recently reported bridged ferrocene derivatives with double bonds in the bridge.

A second point of interest is the carbonyl stretching frequency of 1,1′-(β-ketotrimethylene)ferrocene which occurs at 1703 cm.$^{-1}$ in carbon tetrachloride solution. This shift to lower frequencies (*cf.*

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(1) Supported in part by a grant from the NSF and from the Paint Research Institute.

(2) K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, *J. Am. Chem. Soc.*, **79**, 3420 (1957).

(3) K. Schlögl and H. Seiler, *Monatsh.*, **91**, 79 (1960).

(4) M. Rosenblum, A. K. Banerjee, N. Danieli, and R. W. Fish, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–14, 1962, p. 2-Q.