

## HIGHLY STEREOSELECTIVE CHLOROCARBONYLATION

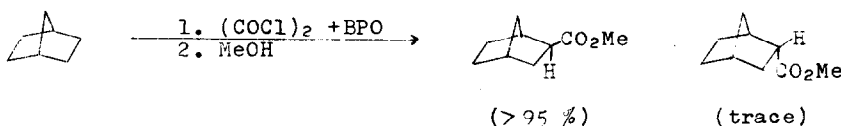
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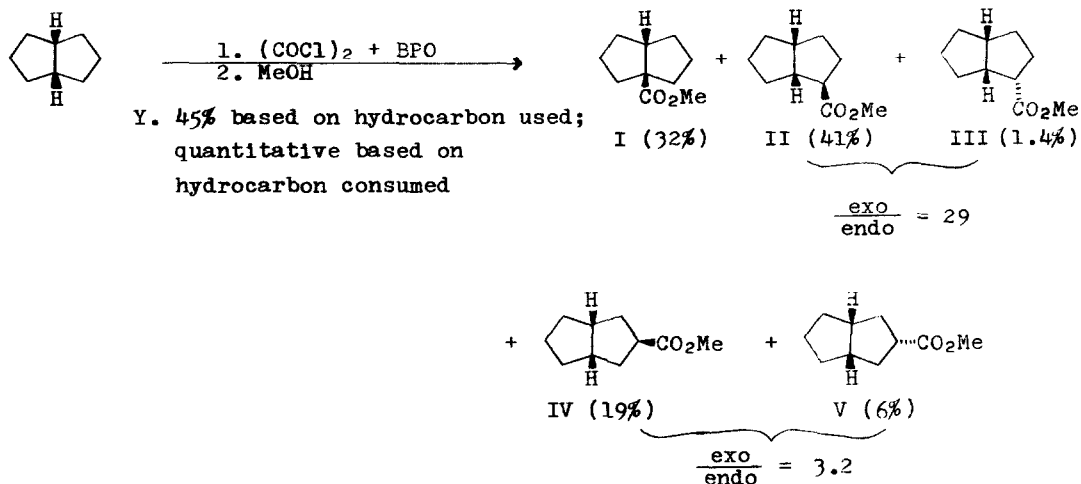
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We have reported that chlorocarbonylation afforded a convenient route to 2-adamantanecarboxylic acid from adamantane (1). Now the authors wish to report that the highly stereoselective (the exo predominated over the endo) chlorocarbonylation occurred in norbornane or cis[3,3,0]bicyclooctane.

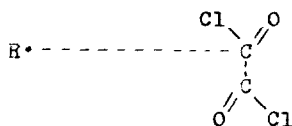
Thus, 3.45 g of oxalyl chloride and 1.30 g of benzoyl peroxide in chlorobenzene (10 ml) were added into the solution of 7.00 g of [2,2,1]bicycloheptane and 3.45 g of oxalyl chloride in 140 ml of chlorobenzene at 75-85° during 3 hours and the mixture was further heated at 85° for 15 hours. On methanolysis of the resultant acid chloride, practically sole ester was obtained which was identified as methyl exo[2,2,1]bicycloheptane-2-carboxylate (2) (15.3 % based on the hydrocarbon used but the yield was good based on the hydrocarbon consumed). The endo isomer (3) was included in only a trace amount if any. Neither the bridgehead carboxylate (4) nor the 7-carboxylate (5) was detected.



Similarly, cis[3,3,0]bicyclooctane was treated with oxalyl chloride and benzoyl peroxide in chlorobenzene. Products obtained are shown in equation (1). Determination of the products were made: for I, by IR and NMR (very characteristic) spectra; for II and III, by spectral evidence and by identification with those from relevant syntheses (6,7); for IV and V, by IR and NMR spectra and by identification with relevant syntheses from cis[3,3,0]bicyclooctan-3-one(?). Free radical substitution on the [3,3,0]bicyclooctane has never been reported.



It is noteworthy that highly stereoselective radical chlorocarbonylation occurred at the 2-position of norbornane or of the bicyclooctane. This kind of high stereoselectivity in chlorocarbonylation has not been reported. The stereoselectivity was far higher than that of equilibrated ratio of exo to endo norbornane-2-carboxylate, 2.30 at 90° (8) or than that of product ratio in the radical chlorination of norbornane, 2.8 with molecular chlorine (9). Thus a kinetic approach control in the radical transfer step seems to operate where a bulky cycloalkyl radical should approach to a crowded center of oxalyl chloride (10).



Stereoselectivity at 3-position of the [3,3,0]bicyclooctane was much lower than that of the 2-position. The finding is in accord with our previous assumption that the bicyclooctane has a "W" (probably somewhat twisted) conformation (11).

Positional selectivity (relative reactivity of bridgehead H/bridge H) for chlorocarbonylation was in the order: adamantane (1), 3.7; [3,3,0]bicyclooctane, 2-H, 1.5-3.0; 3-H, 1.3-2.6; norbornane, very small. The positional selectivity may be interpreted by local symmetry of a radical to be formed (12, 13).

## REFERENCES

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See also references therein. Recently, similar radical acetylation of hydrocarbons with diacetyl was reported: W.G. Bentrude and K.R. Darnall, *J. Am. Chem. Soc.*, 90, 3538 (1968).
- . The exo ester was prepared by "iodolactone procedure" followed by hydrogenation on Raney Ni. E.E. van Tamelen and M. Shamma, *J. Am. Chem. Soc.*, 76, 2315 (1954) and C.S. Rondestvedt, Jr. and C.D. Ver Nooy, *J. Am. Chem. Soc.*, 77, 4878 (1955).
- . The endo ester was obtained as the major product from Diels-Alder reaction of cyclopentadiene with methyl acrylate at room temperature followed by hydrogenation.
- . Relevant synthesis from 2,2-dichloronorbornane; R.L. Bixler and C. Niemann, *J. Org. Chem.*, 23, 742 (1958).
- . Relevant synthesis from 2,7-dibromonorbornane; H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, 76, 4072 (1954).
- . a) See I. Tabushi, K. Fujita and R. Oda, *Tetrahedron Letters*, 3815 (1968).  
b) The exo carboxylic acid was reported by; R. Dowbenko, *Tetrahedron*, 20, 1343 (1964).  
c) The endo carboxylic acid was reported by; A.C. Cope and W. Brown, *J. Am. Chem. Soc.*, 80, 2859 (1958).
- . Separation and quantitative determination of the exo and the endo isomers were performed very successfully after converting them into the corresponding methylols (6a).
- .  $K(\frac{exo}{endo})$  was found to be 2.30 at 90.0°C for the methyl esters; A.C. Cope, E. Ciganek and N.A. LeBel, *J. Am. Chem. Soc.*, 81, 2799 (1959).
- . The ratio of exo to endo chloride was found to be 2.8 in the chlorination with molecular chlorine; E.C. Kooyman and G.C. Vegter, *Tetrahedron*, 4, 382 (1958).
- . Stereoselective chlorination of norbornane with bulky sulfonyl chloride or phosphorous pentachloride was reported (9).

- 11). The assumption was based on NMR shielding effect on  $\alpha$ -proton of exo- and endo-[3,3,0]bicyclooct-3-yl alcohols: I.Tabushi, K.Fujita and R.Oda to be published.
- 12). Classically, nonplanar radical is considered to be unstable and not to be formed. But adamantyl-1 radical was formed "normally" in spite of its nonplanarity (See a) I.Tabushi, J.Hamuro and R.Oda, J. Am. Chem. Soc., 89, 7127 (1967) and references therein. See also; b) J.P.Lorand, S.D.Chodroff and R.W.Wallace, J. Am. Chem. Soc., 90, 5266 (1968) and c) R.C.Fort, Jr., R.E.Franklin, J. Am. Chem. Soc., 90, 5267 (1968)). Further, a highly strained [1,1,1]bicyclopentane readily gave the corresponding bridgehead radical; d) K.B.Wiberg and D.S.Connor, J. Am. Chem. Soc., 88, 4437 (1966) and e) K.B.Wiberg and V.Z.Williams, Jr., J. Am. Chem. Soc., 89, 3373 (1967).
- 13). Our conclusion on adamantyl radicals are: in the radical formation step, both of 1- and 2-radicals behave "normally" (a transition state leading to 1-radical is more stable than that to 2-radical), which is compatible with the results of decomposition of peresters (13b, 13c). The "normal" behavior suggests that both radicals are formed in nonplanar forms (discussion on the subject was given in I.Tabushi, J.Hamuro and R.Oda, J. Chem. Soc. Japan, 89, 789 (1968)). Nonplanar radical formation is well demonstrated for decalyl (P.D.Bartlett, P.E.Pincock, J.H.Rolston, W.G.Schindel and L.A.Singer, J. Am. Chem. Soc., 87, 2590 (1965); F.D.Greene and N.N.Lowry, J. Org. Chem., 32, 875 (1967)) or cyclopropyl (H.M.Walborsky and C.Chen, J. Am. Chem. Soc., 89, 5499 (1967)). But in the radical transfer step, 1-radical is less selective than 2-radical so that 2-radical may gain further stabilization.