

Proximity Effects. XLVIII. Aprotic Decomposition of 2-Phenylcyclooctanone *p*-Toluenesulfonylhydrazone and 3-Phenylcyclooctanone *p*-Toluenesulfonylhydrazone^{1a}

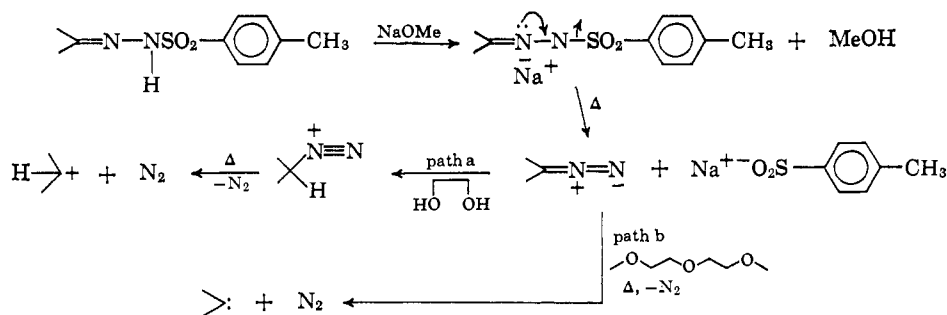
Arthur C. Cope^{1b} and Stephen S. Hecht^{1c}

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received August 11, 1967

Abstract: The aprotic decompositions of 2-phenylcyclooctanone *p*-toluenesulfonylhydrazone (tosylhydrazone) and 3-phenylcyclooctanone tosylhydrazone, promoted by sodium methoxide, were studied. Hydrocarbon products formed from 2-phenylcyclooctanone tosylhydrazone (87% yield) were 1-phenylcyclooctene (18%), 3-phenylcyclooctene (42%), *exo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (15%), *endo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (4%), 2-phenyl-*cis*-bicyclo[5.1.0]octane (3%), *exo*-8-phenyl-*cis*-bicyclo[5.1.0]octane (17%), and benzylcycloheptane (1%). The decomposition of 3-phenylcyclooctanone tosylhydrazone gave a 49% yield of hydrocarbons: 3-phenylcyclooctene (40%), 4-phenylcyclooctene (38%), 3-phenyl-*cis*-bicyclo[3.3.0]octane (17%), 1-phenyl-*cis*-bicyclo[5.1.0]octane (1%), and 3-phenyl-*cis*-bicyclo[5.1.0]octane (2%).

Transannular reactions have been the subject of considerable investigation since the observation that the major products from the solvolysis of *cis*-cyclooctene oxide resulted from hydride shifts across the eight-membered ring.² The outcome of these reactions is normally quite dependent on the relative positions of the reactive centers in space, a phenomenon which gives rise to the term "proximity effect." The intermediacy of carbonium ions, carbanions, radicals, and carbenes has been postulated.³

Scheme I



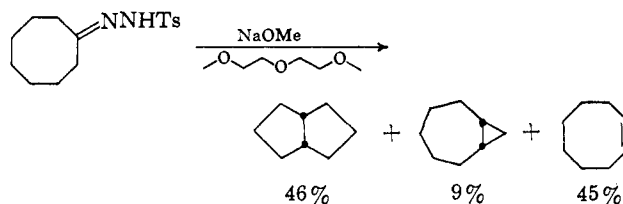
The base-promoted decomposition of *p*-toluenesulfonylhydrazones (tosylhydrazones) may proceed through a carbonium ion or a carbene intermediate, depending on the reaction conditions. In a protic solvent, such as ethylene glycol, the intermediate diazoalkane may be protonated, leading to products which typically result from the intermediacy of a carbonium ion (path a). When the reaction is carried out in aprotic solvents, such as diglyme (path b), carbene formation predominates (Scheme I).

Minor amounts of products may result from a carbonium ion pathway, since an equivalent of proton-donating methanol is formed in the reaction. The use of high temperatures, at which the decomposition

of the diazoalkane is rapid and the alcohol is quickly removed from the reaction mixture, minimizes this possibility.⁴⁻⁷

Transannular insertion reactions have been observed in aprotic decompositions of medium-ring tosylhydrazones. Cyclooctanone tosylhydrazone yields *cis*-bicyclo[3.3.0]octane and *cis*-bicyclo[5.1.0]octane in addition to cyclooctene. Cyclononanone tosylhydrazone and cyclodecanone tosylhydrazone give 76 and 80% bicyclic products, respectively.⁸

The product distribution from phenyl-substituted medium-ring tosylhydrazones indicates the relative reactivity of benzylic *vs.* nonbenzylic hydrogen in the



transannular insertion reaction. The steric relationship of the benzene ring to the bridgehead hydrogens in bicyclic products may reveal the nature of the transition state. The decompositions of 2-phenylcyclo-

(1) (a) This project was supported in part by NSF Grant No. GP-6222; (b) deceased June 4, 1966; (c) National Science Foundation Summer Fellow, 1965. National Institutes of Health Fellow, 1965-1967. To whom inquiries should be addressed at the Massachusetts Institute of Technology, Cambridge, Mass. 02139.

(2) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5884 (1952).

(3) A. C. Cope, M. A. McKervey, and M. M. Martin, *Quart. Rev.* (London), 119 (1966).

(4) L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

(5) G. H. DePuy and D. H. Froemsdorf, *ibid.*, **82**, 634 (1960).

(6) G. L. Closs, L. W. Closs, and W. A. Boll, *ibid.*, **85**, 3796 (1965).

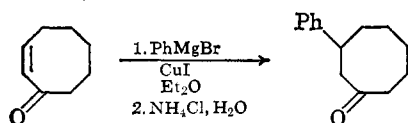
(7) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 49.

(8) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961).

octanone tosylhydrazone (1) and 3-phenylcyclooctanone tosylhydrazone (9) are reported here.

Results

2-Phenylcyclooctanone and 3-phenylcyclooctanone were prepared by published procedures.^{9,10} A convenient alternative route to 3-phenylcyclooctanone is the Cu(I)-catalyzed addition of phenylmagnesium bromide to 2-cycloocten-1-one. Conjugate addition



under the conditions used occurs to the virtual exclusion of nonconjugate addition.¹¹ The tosylhydrazones were prepared in 84–95% yield by reaction of an ethanolic solution of the ketone with *p*-toluenesulfonylhydrazide.

Decomposition of the tosylhydrazones was promoted by sodium methoxide in an anhydrous system at 160° (refluxing diglyme). The composition of the hydrocarbon fractions was determined by glpc and components were identified by comparison of infrared and mass spectra and glpc retention times with those of authentic samples. Hydrocarbons were formed in 87% yield from 2-phenylcyclooctanone tosylhydrazone (1) and in 49% yield from 3-phenylcyclooctanone tosylhydrazone (9). The results of the decompositions are summarized in Scheme II.

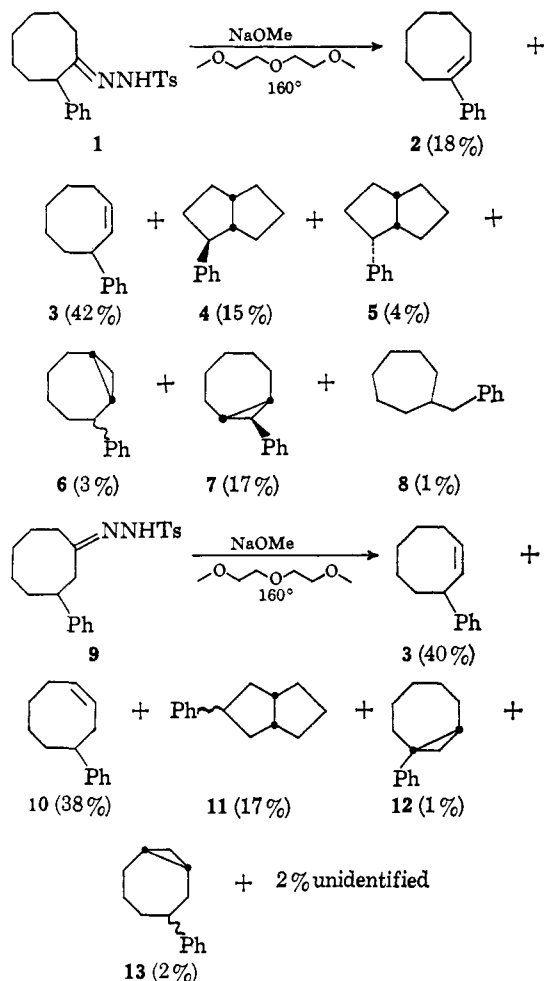
Synthesis and Stereochemistry of Products. The synthesis of compounds 4, 5, and 7 is outlined in Scheme III.

Treatment of *cis*-bicyclo[3.3.0]octan-2-one with phenylmagnesium bromide afforded the alcohol 14, which underwent hydrogenolysis to a mixture of two hydrocarbons, 4 and 5. Compound 5 may be epimerized to 4 by equilibration with potassium *t*-butoxide in dimethyl sulfoxide. Inspection of models reveals that in the hydrogenolysis reaction attack of hydrogen from the less hindered side should yield the sterically more congested and presumably the less stable of the two possible isomers. On these grounds, the 2-phenyl group is assigned the *endo* configuration in 5 and the *exo* in 4.

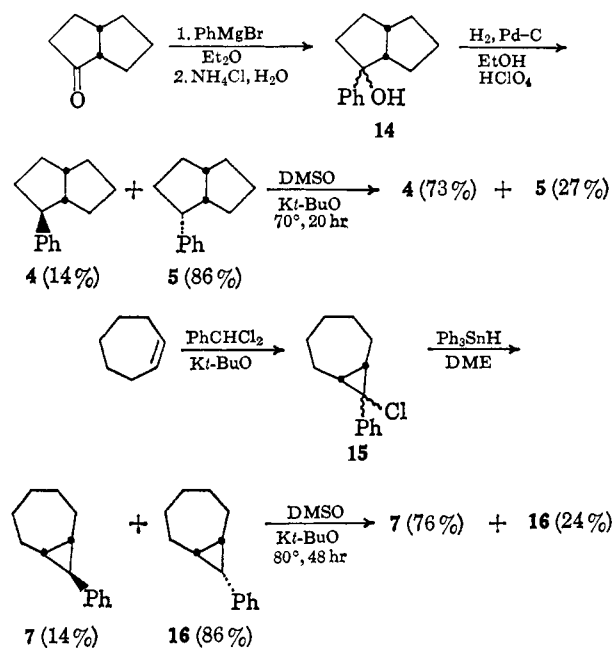
The synthesis of 8-chloro-8-phenyl-*cis*-bicyclo[5.1.0]octane (15) and its reduction with triphenyltin hydride parallels the method of Jensen and Patterson,¹² who obtained *endo*-7-phenylnorcarane in this way. The thermodynamically less stable *endo* epimer 16 may be converted into *exo*-8-phenyl-*cis*-bicyclo[5.1.0]octane (7) by treatment with potassium *t*-butoxide in dimethyl sulfoxide. The stereochemical assignment is also supported by the greater complexity of the aromatic region in the nmr spectrum of the *exo* epimer 7 compared to that of the *endo* epimer 16.¹²

The reaction of *cis*-bicyclo[3.3.0]octan-3-one with phenylmagnesium bromide afforded a crystalline alcohol, which was converted by hydrogenolysis into 3-phenyl-*cis*-bicyclo[3.3.0]octane (11). Separation of epimers was not achieved.

Scheme II



Scheme III



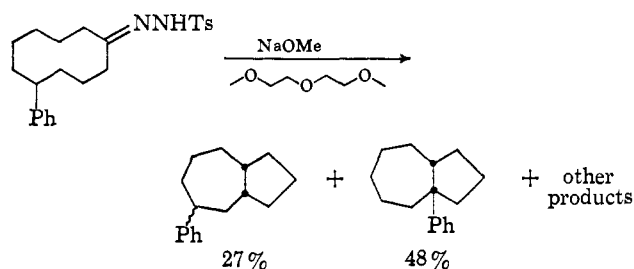
Cyclopropanes 6, 12, and 13 were prepared *via* the Simmons–Smith reaction from the corresponding olefins. The stereochemical relationship of the bridgehead hydrogens and the phenyl group in 6 and 13 was not determined. Benzyl cycloheptane (8) was obtained by a two-step reduction of α -benzylidenecycloheptanone.

(9) A. C. Cope and D. S. Smith, *J. Am. Chem. Soc.*, **74**, 5136 (1952).
 (10) A. C. Cope, M. R. Kinter, and R. J. Keller, *ibid.*, **76**, 2757 (1954).
 (11) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).
 (12) F. R. Jensen and D. B. Patterson, *Tetrahedron Letters*, 3837 (1966).

Discussion

The phenyl group on the eight-membered ring does not appear to increase the lability of the benzylic hydrogen toward the insertion reaction. In the decomposition of 2-phenylcyclooctanone tosylhydrazone (1), both possible olefins, 2 and 3, were formed in amounts which indicate that the intermediate carbene lacked selectivity. The product of insertion toward the benzene ring in the decomposition of 3-phenylcyclooctanone tosylhydrazone (9), 1-phenyl-*cis*-bicyclo[5.1.0]octane (12), accounted for only 1% of the hydrocarbon fraction and, significantly, was not favored over the alternative 1-3 insertion product, 13.

A preference for 1-5 insertion toward the benzylic position was noted in the decomposition of 5-phenylcyclooctanone tosylhydrazone,¹³ where a choice between benzylic and nonbenzylic 1-5 insertion exists.



The total amount of olefin formation, 60% in the case of the 2-substituted isomer, and 78% from the 3-substituted isomer, represents a significant increase over the unsubstituted case,⁸ in which cyclooctene comprised 45% of the volatile products. This trend was also observed in the decomposition of 5-phenylcyclooctanone tosylhydrazone¹⁴ (57.5% 5-phenylcyclooctene) and may result from a slight flattening of the ring due to the presence of the phenyl group. This type of steric effect is consistent with decreased transannular insertion since the distance between the reactive centers is increased.

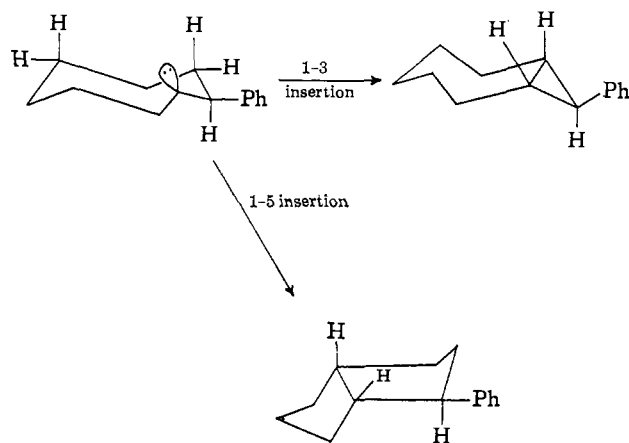
The absence of any 1-4 insertion products is in agreement with previous studies. The 1 and 4 positions are not favorably disposed sterically for a transannular reaction. Solvolysis reactions have shown minimum amounts of 1-4 hydride shifts compared to 1-2, 1-3, and 1-5 migrations.³ The unique feature of the decomposition of 2-phenylcyclooctanone tosylhydrazone (1) is the large amount of 1-3 insertion (17%) in one direction to form *exo*-8-phenyl-*cis*-bicyclo[5.1.0]octane (7); 2-phenyl-*cis*-bicyclo[5.1.0]octane (6) is observed in only 3% yield. Products resulting from 1-3 insertion when 3-phenylcyclooctanone tosylhydrazone is decomposed (12 and 13) amount to only 3% of the hydrocarbon fraction. This result is most likely due to a conformational effect which increases the proximity of the particular 1 and 3 positions which become bonded to form 7.

Only *cis*-ring junctures were observed in the bicyclic products. This is in accord with previous studies in which only *cis* junctures were found, regardless of the relative thermodynamic stability of the *cis* and *trans* bicyclic compounds. This stereospecificity is a result of concerted transfer of an axial hydrogen in the insertion reaction and is in agreement with the general

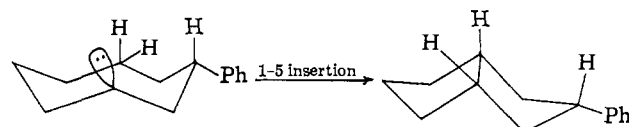
(13) R. B. Davis, Ph.D. Thesis, Massachusetts Institute of Technology, 1965.

observation that this reaction occurs with retention of configuration.^{8, 13, 14}

The major bicyclic products from the decomposition of 2-phenylcyclooctanone tosylhydrazone (1), *exo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (4), and *exo*-8-phenyl-*cis*-bicyclo[5.1.0]octane (7) reflect another mode of stereospecificity. Only 4% *endo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (5) was observed and *endo*-8-phenyl-*cis*-bicyclo[5.1.0]octane (16) was not present in the mixture. The products are not epimerized under the reaction conditions. If the cyclooctane ring exists in the crown conformation in the transition state, the phenyl group would most likely be held in a pseudo-equatorial position. Transannular insertion to the 3 or 5 position with migration of axial hydrogen then leads to the observed products. The stereochemistry



of 3-phenyl-*cis*-bicyclo[3.3.0]octane (11) was not determined. On the basis of the above arguments, the *endo* structure would be assigned to the predominant 1-5 insertion product from 3-phenylcyclooctanone tosylhydrazone (9).



Benzylcycloheptane (8), formed in the decomposition of 2-phenylcyclooctanone tosylhydrazone (1), is not an expected product. It is almost certainly not a primary product since it is difficult to imagine a process by which a nonisomeric product could be formed in the initial reaction. Small amounts of water in the system can cause hydrolysis of the tosylhydrazone to *p*-toluenesulfonylhydrazide and 2-phenylcyclooctanone (trace amounts observed). The hydrazide is a good reducing agent¹⁵ and could cause hydrogenolysis of *exo*-8-phenyl-*cis*-bicyclo[5.1.0]octane (7) resulting in formation of benzylcycloheptane (8).

Experimental Section¹⁶

2-Phenylcyclooctanone Tosylhydrazone (1). A mixture of 1.00 g (4.9 mmoles) of 2-phenylcyclooctanone,⁹ 0.92 g (5.38 mmoles) of

(14) R. B. Kinnel, Ph.D. Thesis, Massachusetts Institute of Technology, 1964.

(15) R. S. Dewey and E. E. van Tamelen, *J. Am. Chem. Soc.*, **83**, 3729 (1961).

(16) Melting points were determined on a Kofler hot stage; boiling points are uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 237B recording spectrophotometer. Ultraviolet spectra were measured on a Cary Model 14 spectrophotometer. Nuclear

p-toluenesulfonylhydrazide, and 15 ml of ethanol was heated under reflux for 1 hr. Upon cooling, a white solid slowly precipitated. This material was collected and recrystallized from methanol, yielding 1.52 g (84.0%) of 2-phenylcyclooctanone tosylhydrazide (1) melting at 187–188°: $\nu_{\max}^{\text{CHCl}_3}$ 3252, 3200, 1165 cm^{-1} .

Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2\text{S}$: C, 68.20; H, 7.03; N, 7.58; S, 8.66. Found: C, 68.02; H, 7.20; N, 7.40; S, 8.64.

endo-2-Phenyl-*cis*-bicyclo[3.3.0]octane (5). Phenylmagnesium bromide (2.42 mmoles) was prepared in 25 ml of ether from 380 mg (2.42 mmoles) of bromobenzene and 100 mg (4.12 mg-atoms) of magnesium turnings. A solution of 232 mg (1.87 mmoles) of *cis*-bicyclo[3.3.0]octan-2-one¹⁷ in 5 ml of ether was added dropwise. The mixture was refluxed for 10 min and then decomposed with saturated aqueous NH_4Cl . The resulting two-phase system was separated and the ethereal layer was washed (saturated aqueous NaHCO_3) and dried (MgSO_4). Removal of solvent at reduced pressure yielded 385 mg of the alcohol 14, $\nu_{\max}^{\text{CCl}_4}$ 3600, 3400 cm^{-1} . This material was used without further purification. A mixture of 100 mg of 10% palladium on carbon, 380 mg of alcohol, 3 drops of 35% perchloric acid, and 10 ml of ethanol was stirred in an atmosphere of hydrogen at a pressure of 1 atm and a temperature of 20° until uptake of hydrogen was complete. The catalyst was filtered and the mixture was poured into 50 ml of water and extracted with three 25-ml portions of ether. The ether layer was washed (saturated aqueous NaHCO_3) and dried (MgSO_4). Removal of solvent at reduced pressure yielded 300 mg of crude product, which was purified by collection from glpc (8 ft \times 0.25 in., 20% SE-30, 180°). Analysis of this material on an 8 ft \times 0.25 in., 10% phenyldiethanolamine succinate column at 150° showed two peaks, 14 and 86%, corresponding to *exo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (4) and *endo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (5), respectively, and the following spectral properties of the *endo* epimer: $\nu_{\max}^{\text{CCl}_4}$ 3080, 3055, 2920, 2970, 2890, 1600, 1498, 1450, 1026, 698 cm^{-1} ; nmr (CCl_4), δ 7.09 (5 H, singlet), 2.6–1.0 (13 H, multiplet); mass spectrum, *m/e* (relative intensity), 186 (22, molecular ion), 117 (11), 104 (100), 91 (15), 67 (15).

Anal. Calcd for $\text{C}_{14}\text{H}_{18}$: C, 90.32; H, 9.68. Found: C, 90.45; H, 9.56.

exo-2-Phenyl-*cis*-bicyclo[3.3.0]octane (4). A mixture of 15.5 mg (0.083 mole) of *endo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (5), 0.60 ml of dimethyl sulfoxide, and 37 mg (0.33 mmole) of potassium *t*-butoxide was heated with stirring under a positive pressure of nitrogen at 70° for 20 hr. The resulting mixture was poured into 10 ml of water and extracted with three 50-ml portions of methylene chloride. The methylene chloride layer was washed with three 125-ml portions of water and dried (MgSO_4). Removal of solvent at reduced pressure left a residue of 29.9 mg, which was analyzed by glpc (8 ft \times 0.25 in., 20% LAC-728, 140°). The composition of the product was 27% *endo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (5) and 73% *exo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (4) having relative retention times of 1.14 and 1.00, respectively: $\nu_{\max}^{\text{CCl}_4}$ 3073, 3061, 3021, 2948, 2863, 1600, 1470, 1440, 1057, 1020, 685 cm^{-1} ; nmr (CCl_4), δ 7.09 (5 H singlet), 2.6–1.0 (13 H, multiplet); mass spectrum, *m/e* (relative intensity), 186 (19, molecular ion), 117 (9), 115 (9), 104 (100), 91 (15), 67 (9), 41 (12).

Anal. Calcd for $\text{C}_{14}\text{H}_{18}$: C, 90.32; H, 9.68. Found: C, 90.16; H, 9.84.

8-Chloro-8-phenyl-*cis*-bicyclo[5.1.0]octane (15). Benzal chloride (2.7 g, 0.017 mole) was added dropwise with stirring to a refluxing mixture of 2.0 g (0.017 mole) of potassium *t*-butoxide and 50 ml of cycloheptene. The reaction was carried out in dry equipment under a positive pressure of oxygen. After the addition was complete, the mixture was heated under reflux for 4.5 hr. The cooled mixture was poured into 100 ml of water and extracted with three 100-ml portions of ether. The ether layer was washed with 250 ml of water and dried (MgSO_4). The solvent was removed at reduced pressure; distillation yielded 950 mg (25%) of 8-chloro-8-phenyl-*cis*-bicyclo[5.1.0]octane (15); $\nu_{\max}^{\text{CCl}_4}$ 3085, 3060, 3035, 3000, 2920, 2855, 1600, 1483, 1465, 1445, 852, 685 cm^{-1} ; $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ μm (ϵ) 221 (9350), 253 (275); nmr (CCl_4), δ 7.15 (5 H, singlet), 2.50–1.20

(12 H, multiplet); mass spectrum, *m/e* (relative intensity), 220 (23, molecular ion), 138 (100), 129 (50), 128 (49), 115 (74), 91 (49).

Anal. Calcd for $\text{C}_{14}\text{H}_{17}$: C, 76.36; H, 7.73. Found: C, 76.10; H, 7.65.

endo-8-Phenyl-*cis*-bicyclo[5.1.0]octane (16). A mixture of 150 mg (0.68 mmole) of 8-chloro-8-phenyl-*cis*-bicyclo[5.1.0]octane (15), 77.5 mg (2.04 mmoles) of lithium aluminum hydride, and 26.2 mg (0.068 mole) of triphenyltin chloride in 5 ml of dimethoxyethane was heated under reflux for 8 hr in a nitrogen atmosphere. At the end of this time, 15 ml of cold water was added and the resulting mixture was extracted with three 25-ml portions of ether. The ether layer was washed with water and dried with magnesium sulfate. The solvent was removed at reduced pressure leaving a residue of 110 mg, which was analyzed by glpc (8 ft \times 0.25 in., 20% LAC-728, 140°). There were two peaks, 86.1 and 13.9%, having relative retention times of 1.00 and 1.34, which correspond to *endo*-8-phenyl-*cis*-bicyclo[5.1.0]octane (16) and *exo*-8-phenyl-*cis*-bicyclo[5.1.0]octane (7), respectively. Compound 16 showed the following spectral properties: $\nu_{\max}^{\text{CCl}_4}$ 3085, 3063, 3023, 3000, 2920, 2855, 1600, 1492, 1460, 1450, 1440, 1177, 1023, 720, 690 cm^{-1} ; $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ (ϵ) 218 (8910), 253 (247), 259 (247); nmr (CCl_4), δ 7.13 (5 H, broad singlet), 2.70–0.70 (13 H, multiplet); mass spectrum, *m/e* (relative intensity), 186 (62, molecular ion), 129 (43), 104 (100), 95 (80), 91 (65).

Anal. Calcd for $\text{C}_{14}\text{H}_{18}$: C, 90.32; H, 9.68. Found: C, 90.04; H, 9.95.

exo-8-Phenyl-*cis*-bicyclo[5.1.0]octane (7). A mixture of 30 mg (0.16 mmole) of *endo*-8-phenyl-*cis*-bicyclo[5.1.0]octane (16), 75 mg (0.67 mmole) of potassium *t*-butoxide, and 1.20 ml of dimethyl sulfoxide was heated to 80° for 48 hr under a positive pressure of nitrogen. The resulting mixture was poured into 10 ml of water and extracted with three 50-ml portions of methylene chloride. The methylene chloride layer was washed with three 125-ml portions of water and dried (MgSO_4). Removal of solvent at reduced pressure left a residue of 30 mg, which was analyzed by glpc (8 ft \times 0.25 in., 20% LAC-728, 140°). Two peaks, 24.3 and 75.7%, having relative retention times of 1.00 and 1.34, corresponded to the *endo* and *exo* epimers, respectively. *exo*-8-Phenyl-*cis*-bicyclo[5.1.0]octane (7) had the following spectral properties: $\nu_{\max}^{\text{CCl}_4}$ 3080, 3064, 3025, 3008, 2925, 2860, 1607, 1598, 1500, 1455, 1450, 1026, 285 cm^{-1} ; $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ μm (ϵ) 225 (12,500), 255 (638), 263 (724), 268 (758), 277 (659); nmr (CCl_4), δ 7.40–6.70 (multiplet, 5 H), 2.70–0.70 (13 H, multiplet); mass spectrum, *m/e* (relative intensity), 186 (47, molecular ion), 129 (33), 104 (100), 95 (36), 91 (42).

Anal. Calcd for $\text{C}_{14}\text{H}_{18}$: C, 90.32; H, 9.68. Found: C, 90.14; H, 9.60.

3-Phenylcycloheptene. Phenylmagnesium bromide (0.072 mole) in 50 ml of ether was prepared from bromobenzene (11.8 g, 0.075 mole) and magnesium turnings (1.75 g, 0.072 g-atom). A solution of 3-bromocycloheptene¹⁸ (4.0 g, 0.023 mole) in 15 ml of ether was added dropwise with stirring at room temperature. After stirring had been continued for 2 hr, the mixture was poured into 75 g of ice water and extracted with two 100-ml portions of ether. The ether extracts were washed (saturated aqueous NH_4Cl , 10% aqueous NH_4OH , and 10% aqueous NaOH), dried (MgSO_4), concentrated, and distilled, yielding 1.60 g (40%) of 3-phenylcycloheptene, bp 70.5–71.5° (0.4 mm). The spectral properties are as follows: $\nu_{\max}^{\text{CCl}_4}$ 3080, 3070, 3030, 2940, 2865, 1650, 1600, 1485, 1450, 1440, 685 cm^{-1} ; nmr (CCl_4), δ 7.12 (5 H, singlet), 5.92–5.68 (2 H, multiplet), 3.67–3.25 (1 H, multiplet), 2.50–1.17 (8 H, multiplet); mass spectrum, *m/e* (relative intensity), 172 (86, molecular ion), 129 (100), 115 (80), 104 (100), 91 (78).

Anal. Calcd for $\text{C}_{13}\text{H}_{16}$: C, 90.70; H, 9.30. Found: C, 90.59; H, 9.34.

2-Phenyl-*cis*-bicyclo[5.1.0]octane (6). The Simmons-Smith reagent was prepared by heating a slurry of 5.30 g of Zn–Cu couple, 5 ml of methylene iodide, a crystal of iodine, and 100 ml of ether for 1 hr at the reflux temperature. To this mixture 464 mg (2.66 moles) of 3-phenylcycloheptene was added in one portion. The mixture was heated under reflux with stirring for 69 hr. After cooling, the inorganic material was filtered and washed with five 50-ml portions of ether. The ether layer was then washed with 300 ml of 25% aqueous NH_4Cl and five 200-ml portions of water. The ether was dried (MgSO_4) and removed under reduced pressure leaving a residue of 1.96 g, which was analyzed by glpc (8 ft \times 0.25 in., 20% SE-30, 175°). The mixture contained some starting

magnetic resonance spectra were measured on a Varian Associates A-60 instrument. Peak positions are reported in parts per million using tetramethylsilane as an internal standard. Mass spectra were determined with a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Vapor phase chromatography studies were performed on a F & M Model 720 instrument with a flow rate of 1 cc of helium/sec. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Galbraith Laboratories, Inc., and Dr. S. M. Nagy and associates.

(17) R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 946 (1934).

(18) M. Mennrath and M. Gauducheau, *Compt. Rend.*, **252**, 1622 (1961).

material in addition to 2-phenyl-*cis*-bicyclo[5.1.0]octane (6). There was no indication of any separation of epimers under the conditions used. The major components could therefore be either the *endo* or *exo* epimer, or a mixture of both. The spectral properties are as follows: $\nu_{\text{max}}^{\text{CCl}_4}$ 3083, 3063, 3018, 2993, 2918, 2858, 1600, 1490, 1450, 1440, 1022, 695 cm^{-1} ; nmr (CCl_4), δ 7.20–6.60 (5 H, singlet with shoulder), 2.70–0.30 (13 H, multiplet); mass spectrum, *m/e* (relative intensity), 186 (17, molecular ion), 117 (11), 104 (100), 91 (18), 67 (11).

Anal. Calcd for $\text{C}_{14}\text{H}_{18}$: C, 90.32; H, 9.68. Found: C, 90.12; H, 9.68.

Benzylcycloheptane (8). A mixture of 3.0 g (0.015 mole) of α -benzylidenecycloheptanone,¹⁹ 50 ml of absolute ethanol, and 0.5 g of 10% palladium-on-charcoal catalyst was agitated in an atmosphere of hydrogen at a pressure of 1 atm and a temperature of 20° until the theoretical amount of hydrogen (360 ml) was taken up. The catalyst was filtered and the ethanol was evaporated, leaving a residue of 3.0 g (99%) of α -benzylcycloheptanone showing $\nu_{\text{max}}^{\text{CCl}_4}$ 1700 cm^{-1} .

A mixture of 2.0 g (0.0099 mole) of α -benzylcycloheptanone, 4.0 g (0.125 mole) of 100% hydrazine, and 10 ml of ethanol was heated under reflux for 2 hr. Most of the ethanol was removed under reduced pressure and the residue was extracted with three 25-ml portions of ether. The ether solution was dried (MgSO_4) and concentrated, yielding an oil whose infrared spectrum exhibited N–H bands and showed no carbonyl absorption. This material was mixed, without further purification, with 800 mg (0.014 mole) of powdered potassium hydroxide and heated to 150° for 1 hr, after which 25 ml of water was added. The mixture was extracted with three 25-ml portions of ether and the ether solution dried (MgSO_4). The ether was removed at reduced pressure leaving 1.50 g (80%) of benzylcycloheptane (8) which was homogeneous by glpc (8 ft \times 0.25 in., 20% SE-30, 170°); $\nu_{\text{max}}^{\text{CCl}_4}$ 3080, 3052, 3025, 2925, 2850, 1600, 1488, 1444, 1019, 708, 688 cm^{-1} ; nmr (CCl_4), δ 7.10 (5 H, singlet), 2.49 (2 H, doublet), 1.9–1.0 (13 H, multiplet); mass spectrum, *m/e* (relative intensity), 188 (33, molecular ion), 97 (62), 96 (44), 92 (86), 91 (55), 55 (100).

Anal. Calcd for $\text{C}_{14}\text{H}_{20}$: C, 89.36; H, 10.64. Found: C, 89.39; H, 10.70.

Anhydrous Decomposition of 2-Phenylcyclooctanone Tosylhydrazone (1). All equipment was flamed dry under vacuum. Diglyme (40 ml) was distilled from lithium aluminum hydride into a mixture of 151 mg (2.80 mmoles) of sodium methoxide and 970 mg (2.62 mmoles) of 2-phenylcyclooctanone tosylhydrazone (1). The resulting mixture was immersed in an oil bath which had been preheated to 180°. Refluxing was continued for 2 hr under a positive pressure of N_2 . The mixture was cooled and the precipitated sodium toluenesulfinate was filtered. The resulting solution was diluted with 100 ml of ether and 100 ml of water. The layers were separated and the ether layers were washed with 25 40-ml portions of water. The ether was dried (MgSO_4) and removed under reduced pressure, yielding 460 mg of crude product. This material was distilled in a Hickman still at a pot temperature of 120–140° and a pressure of 1 mm. The resulting hydrocarbon mixture (422 mg, 87%) was analyzed by glpc (8 ft \times 0.25 in., 20% LAC-728, 140°) to give the following compounds (the relative retention times are in parentheses): benzylcycloheptane (8) (0.62), *exo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (4) (0.69), *endo*-2-phenyl-*cis*-bicyclo[3.3.0]octane (5) (0.79), 2-phenyl-*cis*-bicyclo[5.1.0]octane (6) (0.86), 3-phenylcyclooctene (3) (1.00), *exo*-8-phenyl-*cis*-bicyclo[5.1.0]octane (7) (1.06), 1-phenylcyclooctene (2) (1.11). The composition of the mixture was determined by measuring peak areas with a planimeter and the reported percentages represent the average of three decompositions. For spectral data, samples were obtained by collecting on a 2 ft \times 0.25 in., 20% SE-30 column at 180°.

3-Phenylcyclooctanone. Phenylmagnesium bromide (0.16 mole) was prepared in 400 ml of ether from 25.0 g (0.16 mole) of bromobenzene and 4.0 g (0.17 g-atom) of magnesium turnings. Cuprous iodide (15.2 g, 0.08 mole) was added in one portion. A solution of 10.0 g (0.08 mole) of 2-cycloocten-1-one¹⁰ in 100 ml of ether was added dropwise with stirring. After the addition was complete, the mixture was heated under reflux for 15 min and decomposed by dropwise addition of 500 ml of saturated aqueous NH_4Cl . After dilution with 1000 ml of water and 500 ml of ether, the layers were separated and the organic phase was washed (500 ml of saturated aqueous NaHCO_3) and dried (MgSO_4). Removal of solvent at reduced pressure followed by distillation yielded 6.0 g

(37%) of 3-phenylcyclooctanone, bp 118–120° (0.5 mm). The ketone solidified rapidly and was recrystallized from a 5:1 methanol-water mixture to a melting point of 61–62° (lit.¹⁰ mp 61–62.5°).

3-Phenylcyclooctanone Tosylhydrazone (9). A mixture of 2.00 g (9.8 mmoles) of 3-phenylcyclooctanone, 1.84 g (10.8 mmoles) of *p*-toluenesulfonylhydrazide, and 25 ml of ethanol was heated under reflux for 1 hr. A white solid precipitated when the mixture was cooled. This material was collected and recrystallized from ethanol, yielding 3.40 g (95%) of 3-phenylcyclooctanone tosylhydrazone (9) at 151–153°; $\nu_{\text{max}}^{\text{CCl}_4}$ 3250, 3200, 1165 cm^{-1} .

Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2\text{S}$: C, 68.20; H, 7.03; N, 7.58; S, 8.66. Found: C, 67.91; H, 7.10; N, 7.48; S, 8.76.

1-Phenyl-*cis*-bicyclo[5.1.0]octane (12). The Simmons–Smith reagent was prepared by heating a slurry of 4.71 g of Zn–Cu couple, 5.0 ml of methylene iodide, a crystal of iodine, and 100 ml of ether for 1 hr under reflux. 1-Phenylcycloheptene²⁰ (435 mg, 2.50 mmoles) was added in one portion. The mixture was heated under reflux with stirring for 64 hr. After cooling, the inorganic material was filtered and washed with five 50-ml portions of ether. The ether layer was then washed with 300 ml of 25% aqueous NH_4Cl and five 200-ml portions of water. The ether was dried (MgSO_4) and removed under reduced pressure leaving a residue of 1.70 g, which was analyzed by glpc (8 ft \times 0.25 in., 20% SE-30, 175°). The mixture contained only one high-boiling component, which had retention time different from that of 1-phenylcycloheptene. This material was identified as 1-phenyl-*cis*-bicyclo[5.1.0]octane (12) of by its spectral properties: $\nu_{\text{max}}^{\text{CCl}_4}$ 3076, 3066, 3018, 2996, 1600, 1490, 1462, 1445, 1025, 695 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ μm (ϵ) 215 (7170), 253 (430), 260 (430); nmr (CCl_4), δ 7.13 (5 H, singlet), 2.70–0.50 (13 H, multiplet); mass spectrum, *m/e* (relative intensity), 186 (100, molecular ion), 158 (51), 129 (70), 118 (60), 104 (63), 91 (50).

Anal. Calcd for $\text{C}_{14}\text{H}_{18}$: C, 90.32; H, 9.68. Found: C, 90.28; H, 9.61.

3-Phenyl-*cis*-bicyclo[3.3.0]octane (11). Phenylmagnesium bromide (4.80 mmoles) was prepared in 50 ml of ether from bromobenzene (760 mg, 4.80 mmoles) and magnesium turnings (200 mg, 8.24 mg-atoms). A solution of *cis*-bicyclo[3.3.0]octan-3-one²¹ (460 mg, 3.70 mmoles) in 10 ml of ether was added dropwise. The mixture was heated under reflux for 10 min and decomposed with saturated aqueous NH_4Cl . The resulting two-phase system was separated and the organic layer was washed (saturated aqueous NaHCO_3) and dried (MgSO_4). Concentration at reduced pressure yielded a residue of 551 mg, which rapidly solidified. The alcohol, mp 74–75° after recrystallization from hexane, $\nu_{\text{max}}^{\text{CHCl}_3}$ 3600, 3400 cm^{-1} , was used without further purification. A mixture of 227 mg of the alcohol, 75 mg of 10% palladium on carbon, 3 drops of 35% aqueous perchloric acid, and 10 ml of absolute ethanol was stirred in an atmosphere of hydrogen at 20° and a pressure of 1 atm until uptake of hydrogen was complete. The catalyst was filtered and the mixture was poured into 50 ml of water and extracted with three 25-ml portions of ether. The organic phase was washed (saturated aqueous NaHCO_3) and dried (MgSO_4). Removal of solvent at reduced pressure yielded 200 mg of crude hydrocarbon, which was purified by collection by glpc (8 ft \times 0.25 in., 20% LAC-728, 140°) and recollection (2 ft \times 0.25 in., 20% SE-30, 180°). There was no evidence of separation of epimers. The stereochemistry of the product, 3-phenyl-*cis*-bicyclo[3.3.0]octane (11), may therefore be either *endo*, *exo*, or a mixture of both. The spectral properties are as follows: $\nu_{\text{max}}^{\text{CCl}_4}$ 3070, 3059, 3020, 2950, 2860, 1600, 1495, 1470, 1462, 1449, 1026, 695 cm^{-1} ; nmr (CCl_4), δ 7.10 (5 H, singlet), 2.70–1.30 (13 H, multiplet); mass spectrum, *m/e* (relative intensity), 186 (79, molecular ion), 104 (100), 91 (32), 89 (31), 67 (23).

Anal. Calcd for $\text{C}_{14}\text{H}_{18}$: C, 90.32; H, 9.68. Found: C, 90.17; H, 9.89.

3-Phenylcycloheptanone. Phenylmagnesium bromide (0.13 mole) was prepared in 400 ml of ether from bromobenzene (22.0 g, 0.13 mole) and magnesium turnings (3.4 g, 0.14 g-atom). Cuprous iodide (12.2 g, 0.064 mole) was added in one portion. A solution of 2-cyclohepten-1-one²² (7.0 g, 0.064 mole) in 100 ml of ether was added dropwise with stirring. After the addition was complete, the mixture was heated under reflux for 15 min and decomposed by dropwise addition of 500 ml of saturated aqueous NH_4Cl . Following dilution with 1000 ml of water and 500 ml of ether, the two-phase system was separated and the ether layer was washed (500

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ml of saturated aqueous NaHCO_3) and dried (MgSO_4). Concentration at reduced pressure followed by distillation yielded 4.0 g (33%) of 3-phenylcycloheptanone, bp 105° (0.5 mm). The semicarbazone melted at $219\text{--}220^\circ$ (lit.²² mp $220\text{--}221^\circ$).

3-Phenylcycloheptanol. A solution of 3-phenylcycloheptanone (3.50 g, 18.5 mmoles) in 45 ml of ether was added dropwise with stirring to a slurry of lithium aluminum hydride (500 mg, 13.2 mmoles) in 50 ml of ether at room temperature. Stirring was continued for 1 hr and the mixture was decomposed by dropwise addition of water. The ether layer was separated, washed (H_2O), dried (MgSO_4), and concentrated at reduced pressure yielding 3.50 g (99%) of 3-phenylcycloheptanol. Analysis by glpc (8 ft \times 0.25 in., Carbowax, 240°) indicated a 50:50 mixture of *cis* and *trans* isomers with the following spectral properties: $\nu_{\text{max}}^{\text{CCl}_4}$ 3600, 3400, 3080, 3055, 3025, 2930, 2855, 1500, 1490, 1450, 1025, 695 cm^{-1} ; nmr (CCl_4), δ 7.09 (5 H, singlet), 3.84 (1 H, multiplet), 3.09–1.00 (11 H, multiplet); mass spectrum; *m/e* (relative intensity), 190 (12, molecular ion), 117 (43), 104 (100), 91 (69), 41 (46).

Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.10; H, 9.47. Found: C, 81.85; H, 9.45.

Dehydration of 3-Phenylcycloheptanol. Phosphorus oxychloride (3.0 ml) was added dropwise with stirring to a solution of 3-phenylcycloheptanol (1.80 g, 9.5 mmoles) in 50 ml of pyridine at room temperature. The mixture was heated at 100° for 1 hr and, after cooling, was diluted with 200 ml of water and extracted with two 100-ml portions of ether. The ether extracts were washed (6 *N* HCl) and dried (MgSO_4). Concentration yielded 1.65 g of a mixture of olefins which was analyzed by glpc (8 ft \times 0.25 in., 10% phenyldiethanolamine succinate, 140°). The mixture was separated into two components, in the ratio of 44 to 56%, having relative retention times of 1.00 and 1.10, respectively. No isomerization to 1-phenylcycloheptene was observed. The first component was identified as 3-phenylcycloheptene by comparison of its infrared spectrum and retention time to those of an authentic sample. The spectral properties of the second component established its structure as 4-phenylcycloheptene: $\nu_{\text{max}}^{\text{CCl}_4}$ 3080, 3070, 3030, 2930, 2850, 1650, 1600, 1475, 1450, 1435, 685 cm^{-1} ; nmr (CCl_4), δ 7.08 (5 H singlet), 5.87–5.62 (2 H, multiplet), 2.68–1.18 (9 H, multiplet); mass spectrum, *m/e* (relative intensity), 172 (56, molecular ion), 117 (92), 104 (100), 91 (81), 39 (56).

Anal. Calcd for $\text{C}_{13}\text{H}_{16}$: C, 90.70; H, 9.30. Found: C, 90.85; H, 9.26.

3-Phenyl-*cis*-bicyclo[5.1.0]octane (13). A slurry of Zn–Cu couple (1.04 g), 1.1 ml of methylene iodide, and a crystal of iodine in 25 ml of ether was heated under reflux for 1 hr. 4-Phenylcycloheptene (95.0 mg, 0.55 mmoles) was added in one portion. The mixture was stirred and refluxed for 60 hr. The inorganic material was filtered, and the ether solution was washed (saturated aqueous NH_4Cl and H_2O), dried (MgSO_4), and concentrated at reduced pressure yielding a residue of 176 mg, which was analyzed by glpc (8 ft \times 0.25 in., LAC-728, 140°). There was one high-boiling component with retention time different from 4-phenylcycloheptene. This was identified as 3-phenyl-*cis*-bicyclo[5.1.0]octane (13) by comparison of spectral and chromatographic properties with those of an authentic sample.¹⁴ There was no evidence for separation of epimers under any conditions tried. The stereochemistry of the product may therefore be either *endo* or *exo* or a mixture of both with a mass spectrum; *m/e* (relative intensity), 186 (73, molecular ion), 129 (31), 117 (48), 104 (100), 91 (67).

Aprotic Decomposition of 3-Phenylcyclooctanone Tosylhydrazone (9). The procedure was identical with that used in the aprotic decomposition of 2-phenylcyclooctanone tosylhydrazone (1). In a typical run, the decomposition of 700 mg (1.89 mmoles) of 3-phenylcyclooctanone tosylhydrazone (9) was promoted by 109 mg (2.02 mmoles) of sodium methoxide. This yielded a mixture of hydrocarbons (119 mg, 49%) which was analyzed by glpc (8 ft \times 0.25 in., 20% LAC-728, 140°) to give the following compounds (the relative retention times are given in parentheses): 1-phenyl-*cis*-bicyclo[5.1.0]octane (12) (0.71), 3-phenyl-*cis*-bicyclo[3.3.0]octane (11) (0.80), 3-phenyl-*cis*-bicyclo[5.1.0]octane (13) (0.96), 3-phenylcyclooctene (3) (1.00), 4-phenylcyclooctene (10) (1.05), unidentified (1.15). The composition of the mixture was determined by measuring peak areas with a planimeter and the reported percentages represent the average of three decompositions. Spectral data were obtained by recollecting from a 2 ft \times 0.25 in., 20% SE-30 column at 180° .

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Effect of Preceding Mer Units on Stereospecific Polymerization Found in Oligomers of Isopropyl Acrylate

Tsuneo Yoshino, Jiro Komiyama, and Hikaru Iwanaga

Contribution from the Basic Research Laboratories, Toyo Rayon Company, Kamakura, Kanagawa, Japan. Received February 16, 1967

Abstract: A series of oligomers was prepared by adding heavy water to a solution of isopropyl acrylate- $\alpha,\beta\text{-d}_2$, which was polymerizing by an anionic mechanism under conditions which give, without hydrolysis, a highly diisotactic polymer through *trans* opening of the double bond. Nmr analysis of the products showed that the oligomers comprised a homologous series, all mer units of which had isotactic α -methine configurations. The first and second units of each oligomer, however, had β -methylene carbons of nearly random configuration and all units added later had isotactic β configurations corresponding to *trans* opening of the double bond like the high polymers produced in this system. Apparently regular isotactic placement of the terminal α -methine carbon of a growing anion does not require the prior occurrence of an isotactic placement and is independent of the mode of incorporation of the β carbon of the terminal unit into the growing chain. Mer units other than the last two of a growing anion are not required to direct the mode of approach of another monomer into a transition state.

The effect of preceding mer units on the placement of the terminal unit of a growing chain can be derived from the intensities of the nmr signals characteristic of dyads, triads, tetrads, etc., of mer units of the polymer obtained. It has been found¹ from the inten-

sities of the dyad and triad signals that anionic polymerizations of methyl methacrylate usually cannot be explained by a *single Bernoullian* process. In any non-Bernoullian as, for example, multistate² polymerization, the intensities of the signals of tetrads and higher

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