twice from *n*-hexane, Fisher-Johns mp 54-55° (lit.[16] mp 55.5-56.5°).

cis-2-*o*-**Tolylcyclohexanol (2).**—This alcohol was obtained by the reduction of **3** with triisobutylaluminum (K & K) in a modification of a procedure outlined by Haubenstock and Davidson[10] for the reduction of dihydroisophorone. To a stirred solution of 37.6 g of triisobutylaluminum in 200 ml of dry benzene under nitrogen a solution of 37.6 g (0.20 mole) of **3** in 120 ml of dry benzene was slowly added, maintaining the temperature below 40° by cooling in an ice bath. Stirring was continued for 15 min following the completion of the addition and then the reaction mixture was decomposed by slowly adding 100 ml of water. After acidification with hydrochloric acid, the benzene layer was separated and the aqueous layer extracted with benzene. The combined benzene solutions were washed once with 10% hydrochloric acid, then with water and dried over Drierite. Analysis of the crude reaction work-up by vpc on a Carbowax 20M column at 195° indicated three peaks in the ratio of 16:2:1, corresponding to **2**, **1**, and **3**, respectively, emerging from the column in that order. Following filtration and solvent removal, the crude product was distilled, bp 89-91° (0.35 mm). Recovery of materials was essentially quantitative (97%).

The *cis* alcohol **2** was separated from the other reaction products by column chromatography. The mixture was chromatographed over neutral alumina using benzene as the eluent; **3** and **2** eluted first. The mixtures of **3** and **2** obtained from these columns were rechromatographed over silica gel using petroleum ether (30-60°) and petroleum ether-benzene mixtures as eluents; **2** elutes first. Columns were generally prepared with 180 g of adsorbent effecting separation on 5 g of applied mixtures. Fraction analysis was carried out on a carbowax 20M column at 190°. The *cis* alcohol **2** isolated by this procedure was distilled at bp 82-84° (0.23 mm) (lit.[14] bp 76-78° (0.15-0.17 mm)).

(−)-Menthoxyacetic Acid (4) and (−)-Menthoxyacetyl Chloride (5).—The synthesis of these compounds is described.[11,17] The synthesis of **4** by a procedure slightly modified from that of Ingersoll[11] yielded a product with bp 114-116° (0.35 mm) and $[\alpha]^{25}_{\mathrm{D}}$ −92.5 (*c* 10, 95% ethanol) (lit. bp 134-137° (2 mm),[17] $[\alpha]^{25}_{\mathrm{D}}$ −91.5 (*c* 2, 95% ethanol[11])). The acid did not crystallize. The acid halide **5** was prepared using thionyl chloride as described by Ingersoll.[11] The excess thionyl chloride was removed under reduced pressure (water pump) and the product distilled *in vacuo*, bp 82-84° (0.4 mm) (lit.[11] bp 132° (10 mm)).

(±)-*trans*-2-*o*-Tolylcyclohexyl (−)-Menthoxyacetate (6 and 7).—This mixture of diastereomeric esters was prepared in 96% yield from **1** and **5** by the pyridine method as described by Ingersoll[11] for the synthesis of (±)-menthyl (−)-menthoxyacetate. The crude product was crystallized once from *n*-hexane: Fisher-Johns mp 63-66°; $[\alpha]^{26}_{\mathrm{D}}$ −50.1 (*c* 5, chloroform).

(±)-*cis*-2-*o*-Tolylcyclohexyl (−)-Menthoxyacetate (8 and 9).—This mixture of diastereomeric esters was prepared from **2** and **5** by the pyridine method as described above for the synthesis of **6** and **7**. The solvent was removed *in vacuo*, $[\alpha]^{26}_{\mathrm{D}}$ −47.5 (*c* 10, chloroform). All attempts to induce crystallization of this mixture of esters failed.

Separation of (+)-*trans*-2-*o*-Tolylcyclohexyl (−)-Menthoxyacetate (6).—Following the method of semisystematic recrystallization outlined by Ingersoll[11] for the resolution of (±)-menthyl (−)-menthoxyacetate, the separation of **6** was accomplished. The most suitable solvent was acetonitrile; differential solubility of the isomers in petroleum ether, *n*-hexane, carbon tetrachloride, chloroform, and dioxane was insufficient to produce significant separation. Progress of the separation was followed by melting point determination and nmr spectroscopy. After several recrystallizations, a few milligrams of seed crystals were obtained. The following is a typical separation. Approximately a 10% solution of the 50:50 mixture of esters in hot acetonitrile was allowed to cool to room temperature and seeded, and after several hours a first crop of crystals was collected by filtration and washed with cold acetonitrile. The filtrate, now somewhat diluted, was cooled to 10° and a second crop obtained. Under these conditions approximately 10% of the mixture was recovered as essentially pure **6**; the melting point was generally in the vicinity of 92-96°. Further attempts to secure more of this isomer in a relatively pure state by chilling the mother liquors proved fruitless. The solvent was removed and the residues saved for the elution chromatography procedure described below.

Recrystallization of the ester, mp 92-95°, twice from acetonitrile and once from *n*-hexane produced no change in melting point or specific rotation over the latter two recrystallizations: Kofler mp 95.2-96.4°; $[\alpha]^{27}_{\mathrm{D}}$ −32.5 (*c* 10, chloroform). The nmr spectrum indicated only a single isomer.

Anal. Calcd for $C_{25}H_{38}O_3$: C, 77.68; H, 9.91. Found: C, 77.48; H, 9.93.

Separation of (−)-*trans*-2-*o*-Tolylcyclohexyl (−)-Menthoxyacetate (7).—The separation of **7** was accomplished by column chromatography over neutral alumina of the residues from the above recrystallization process, using petroleum ether and petroleum ether-benzene mixtures 95:5. From 5 g of applied mixture to 180 g of adsorbent approximately 600-800 mg of essentially pure **7** was obtained. Analysis of fraction composition was by nmr spectroscopy. When contamination with the other ester **6** occurred, the column was immediately stripped (benzene and ethanol). The residues from the stripping of several columns were combined and the cycle of separation repeated starting with fractional recrystallization from acetonitrile.

The essentially pure **7** obtained by this process was recrystallized successively from acetonitrile, *n*-hexane, and acetonitrile with no change in melting point or specific rotation from the last two recrystallizations Kofler mp 79.0-80.0°; $[\alpha]^{28}_{\mathrm{D}}$ −67.9 (*c* 10, chloroform). The nmr spectrum indicated a single isomer present.

Anal. Calcd for $C_{25}H_{38}O_3$: C, 77.68; H, 9.91. Found: C, 77.35; H, 9.65.

Separation of (±)-*cis*-2-*o*-Tolylcyclohexyl (−)-Menthoxyacetate (8 and 9).—The separation of this mixture of esters was accomplished by column chromatography over neutral alumina as described for the isolation of **7**. In this case, however, the elution process was extended until the separation of both isomers was evident. The (−)-*cis* ester **9** elutes first. Fractions were analyzed by nmr spectroscopy.

Isolation of (−)-*cis*-2-*o*-Tolylcyclohexyl (−)-Menthoxyacetate (9).—This ester, which eluted first from the columns, was obtained in larger quantities and in purer state than its diastereomer **8**. The purest sample of **9** isolated was a viscous liquid, judged from its nmr spectrum to be at least 95% pure, $[\alpha]^{28}_{\mathrm{D}}$ −143.5 (*c* 10, chloroform). The presence of **8** in the nmr spectrum of this sample was undiscernible.

Isolation of (+)-*cis*-2-*o*-Tolycyclohexyl (−)-Menthoxyacetate (8).—This ester was never isolated in pure state. The purest sample isolated, estimated from its nmr spectrum and specific rotation to be about 75% **8**, was a viscous liquid, $[\alpha]^{28}_{\mathrm{D}}$ +3.22 (*c* 10, chloroform).

The hydrolysis of the separated esters is reported in another publication.[8] Hydrolysis of **6** gave (+)-*trans*-2-*o*-tolylcyclohexanol, $[\alpha]^{25}_{\mathrm{D}}$ +70.6° (*c* 10, chloroform) and hydrolysis of **7** gave the levo enantiomer, $[\alpha]^{25}_{\mathrm{D}}$ −70.6 (*c* 10, chloroform). Hydrolysis of a sample of **9** considered to be about 85% pure gave (−)-*cis*-2-*o*-tolylcyclohexanol, $[\alpha]^{25}_{\mathrm{D}}$ −102° (*c* 0.128, methanol).[8] Ester **8** was not hydrolyzed.

Registry No.—**1**, 6125-71-9; **2**, 15315-32-9; **6**, 15315-33-0; **7**, 15315-34-1; **8**, 15352-72-4; **9**, 15315-35-2.

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[16] A. C. Huitric and W. D. Kumler, *J. Am. Chem. Soc.*, **78**, 614 (1956).

[17] M. T. Leffler and A. E. Calkins, *Org. Syn.*, **23**, 52 (1943).

The Palladium-Catalyzed Decarbonylation of β-Phenylisovaleraldehyde. A Notable Diminution of the Neophyl Rearrangement

JAMES W. WILT AND VICTOR P. ABEGG

Department of Chemistry, Loyola University,
Chicago, Illinois 60626

Received October 2, 1967

Recently Newman and Gill[1] described the preparation of neopentylbenzene by the decarbonylation of 3,3-dimethyl-4-phenylbutanal (1) (eq 1). They used a method earlier employed by Newman and Zahm[2]

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[1] M. S. Newman and N. Gill, *J. Org. Chem.*, **31**, 3860 (1966).

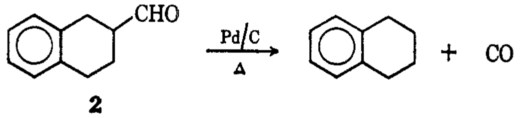
[2] M. S. Newman and H. V. Zahm, *J. Am. Chem. Soc.*, **65**, 1097 (1943).

whereby the neat aldehyde was heated with palladium on charcoal to effect decarbonylation. We have for some time been interested in the decarbonylation of

$$\underset{\mathbf{1}}{C_6H_5CH_2C(CH_3)_2CH_2CHO} \xrightarrow[\Delta]{Pd/C} C_6H_5CH_2C(CH_3)_3 + CO \quad (1)$$

aldehydes[3] and, in fact, had occasion to employ this same method ourselves.

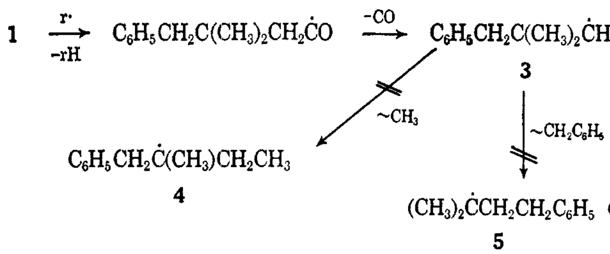
In particular, we were concerned with testing the possibility of carbon skeletal rearrangement in the metal-catalyzed process. No such rearrangement had occurred with **1**, nor had rearrangement accompanied the analogous decarbonylation of tetralin-2-carboxaldehyde (**2**) (eq 2) earlier detailed by Newman and Zahm.



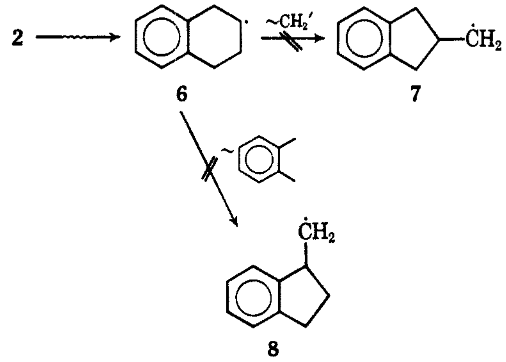
2 (2)

In fact, both these and the several studies of other such aldehyde decarbonylations reported by others[4] indicated the reaction to be remarkably rearrangement free, with only occasional *cis*, *trans* or positional olefin isomerization,[4d] dehydrogenation,[4c] and polymerization[4c] occurring as side reactions.

However, no earlier study had tested a skeletal system prone to radical rearrangement. Thus, no carbon skeleton rearrangement would be anticipated for radical **3**, derivable from **1** (see eq 3) because 1,2 methyl shifts (**3** → **4**) are unknown in radicals,[5] and the *a priori* more plausible 1,2 benzyl shift (**3** → **5**) has in fact been shown *not* to occur in the analogous 2,2-dibenzylethyl radical.[6] Nor would radical **6**, a possible intermediate from **2**, be likely to rearrange (eq 4).

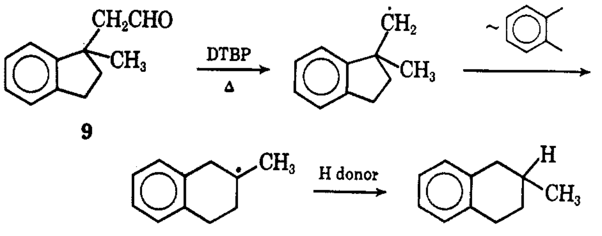


(3)



(4)

Ring contraction by methylene migration (**6** → **7**) was not found for the cyclohexyl radical in a radical decarbonylation study,[7] and the conversion **6** → **8** is the near *reverse* of what actually was observed[8] in the radical decarbonylation of (1-methylindanyl)acetaldehyde (**9**) (eq 5).



(5)

Similar arguments can be made to show that no case of decarbonylation by palladium yet reported allowed a decision about the reliability of the process in systems prone to radical rearrangement.

It is well-known that β-phenylisovaleraldehyde (**10**) rearranges when subjected to radical decarbonylation induced by di-*t*-butyl peroxide (DTBP) (eq 6); this is the classical neophyl rearrangement.[9] Depending on

$$\underset{\mathbf{10}}{C_6H_5C(CH_3)_2CH_2CHO} \xrightarrow[\Delta]{DTBP}$$
$$\underset{\mathbf{11}}{(CH_3)_2CHCH_2C_6H_5} + \underset{\mathbf{12}}{C_6H_5C(CH_3)_3} +$$
$$\underset{\mathbf{13}}{C_6H_5CH_2C(CH_3){=}CH_2} + \underset{\mathbf{14}}{C_6H_5CH{=}C(CH_3)_2} + CO \quad (6)$$

conditions, rearrangement to **11** and the related olefins **13** and **14** can reach *ca.* 90%.[10] Palladium-catalyzed decarbonylation of **10**, then, should provide a test of the type we desired. Should significant amounts of **11** or its related olefins **13** and **14** be formed from **10** a mechanism analogous to that for the DTBP-promoted reaction would be implicated in the palladium-catalyzed process. However, the exclusive formation of unrearranged *t*-butylbenzene (**12**), particularly if under dilute conditions where rearrangement is favored,[10] would tend to eliminate such a free-radical mechanism.

In fact, neither situation seemed to apply. The decarbonylation of **10**, neat in the presence of palladium on charcoal at *ca.* 190°, proceeded nearly quantitatively and led to carbon monoxide and *t*-butylbenzene (**12**), largely *but not entirely* free of contaminants, in yields of over 80% isolated material. The contaminants were

$$\mathbf{10} \xrightarrow[190^\circ]{Pd/C} \underset{\mathbf{12}\left\{\begin{array}{l}>80\%\text{ yield}\\ 94\text{–}99\%\text{ pure}\end{array}\right.}{C_6H_5C(CH_3)_3} + CO + \underbrace{\mathbf{11} + \mathbf{13} + \mathbf{14}?}_{\text{trace–}6\%} \quad (7)$$

shown to be **11**, **13**, and perhaps **14** by comparison with a known mixture of these in **12** (eq 7). Infrared, nmr, and gas chromatographic analyses indicated the contaminant level in **12** to be variable over several runs, ranging from a trace to about 6%. A small, complex residue was also obtained, which contained unchanged

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[3] *Cf.* J. W. Wilt, L. L. Maravetz, and J. F. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966).

[4] In addition to **1** and **2**, the process has been reported on (a) benzaldehyde, furfural, and terpene aldehydes by H. E. Eschinazi [*Bull. Soc. Chim. France*, 967 (1952)]; (b) myrtenal by H. E. Eschinazi and H. Pines [*J. Org. Chem.*, **24**, 1369 (1959)]; (c) a number of aromatic aldehydes and *n*-heptaldehyde by J. O. Hawthorne and M. H. Wilt [*ibid.*, **25**, 2215 (1960)]; and (d) various *trans*-α-substituted cinnamaldehydes by N. E. Hoffman, A. T. Kanakkanatt, and R. F. Schneider [*ibid.*, **27**, 2687 (1962)].

[5] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 273.

[6] L. H. Slaugh, E. F. Magoon, and V. P. Guinn, *J. Org. Chem.*, **28**, 2643 (1963).

[7] F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **76**, 3732 (1954).

[8] J. W. Wilt and C. A. Schneider, *J. Org. Chem.*, **26**, 4196 (1961). Because the case of **9** is not exactly comparable to that of **2**, one might still envision a rearrangement of radical **6**, particularly *via* an aromatic shift to **8**, because under certain conditions the related β-phenylethyl radical has been observed to rearrange slightly (2–5%): L. H. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959). However, the present study is considered a better test in any case, because a more sensitive skeletal system has been used.

[9] Reference 5, p 266 ff.

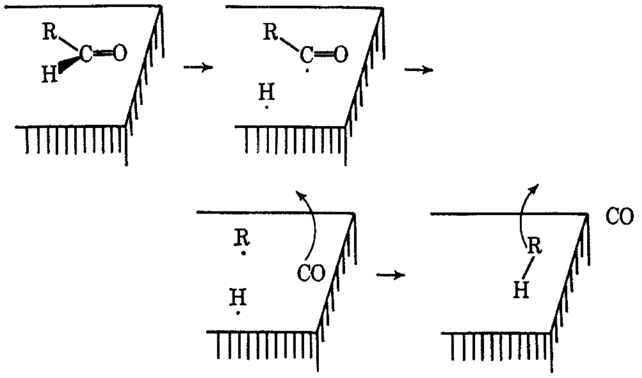
[10] C. Rüchardt, *Chem. Ber.*, **94**, 2599 (1961).

10 and a small amount of β-phenylisovaleric acid together with an undefined carbonyl compound(s).

Since it is known[11] that conversion of neophyl chloride to its Grignard reagent can produce small amounts (1–6%) of **11**, **13**, and **14** and because the starting aldehyde **10** was prepared from this Grignard reagent, **10** was carefully purified *via* its bisulfite adduct. Its spectra showed ~99% purity with a trace of neophyl chloride only. As a further precaution, **12** itself was treated with the catalyst under reaction conditions and found to be unaffected. So it is probable that these contaminants are true decarbonylation products.

Similar results were obtained when a 1 *M* solution of **10** in biphenyl was decarbonylated with palladium on charcoal. Here the reaction was slower, 220° being required for brisk carbon monoxide evolution. But again essentially only **12** was formed.

It seems clear that the process, if radical, proceeds in a fashion where the neophyl radical does not in the main become free enough to rearrange, perhaps as shown [R = $C_6H_5C(CH_3)_2CH_2$-]



where the radicals formed would be chemisorbed to the metal surface and not free to any great extent. Our results, however, do not warrant undue speculation about the detailed mechanism.

In any case, the present results add to the structural reliability of this kind of decarbonylation in degradative or synthetic studies. One can now also understand why this process is effective with compounds that fail to undergo clean peroxide-promoted decarbonylation, such as aromatic[12] and unsaturated[13] aldehydes. The radical (peroxide) path would require formation of highly reative free aromatic radicals from the former and allow acyl radical addition to the double bond of the latter. Neither trouble exists in the palladium-catalyzed process.

Experimental Section

Melting points were taken on a calibrated Fisher-Johns block but are otherwise uncorrected, as are the boiling points. For comparison purposes, hydrocarbons **11** and **12** were obtained commercially and shown to be >99% pure by glpc and spectral analysis. Spectral and glpc data for the other hydrocarbons (**13** and **14**) were available from earlier work in this laboratory on the peroxide-promoted decarbonylation of **10**.[14]

β-Phenylisovaleraldehyde (10) was prepared from neophyl chloride according to the procedure given by Rüchardt.[10] Neophylmagnesium chloride was treated with ethyl orthoformate and processed *via* the bisulfite adduct to afford **10** as a colorless, grassy-smelling oil in 22% yield: bp 76–79° (0.2 mm) in a short path unit; $n^{20}\text{D}$ 1.5148 (lit.[10] bp 79° (0.6 mm), $n^{20}\text{D}$ 1.5142); λ^{neat} 3.7, 5.83 μ (–CHO); $\delta^{\text{neat}}_{\text{TMS}}$ 9.46 t (–CHO, J = 3 cps), 7.10–7.45 m (ArH), 2.51 d (CH_2), 1.31 s (C–CH_3). Spectral data showed no impurities other than a trace of neophyl chloride.

The 2,4-dinitrophenylhydrazone was readily prepared and had mp 115–116°, from ethanol (lit.[10] mp 116–117°).

Decarbonylation Studies.—In a representative run, aldehyde **10** (1 g), was placed into a small flask together with 0.15 g of palladium on charcoal (10%). Upon heating, gas was evolved slowly at *ca.* 140° (bath) and briskly at *ca.* 190°, essentially stopping after 30 min. Collection of the gas over water indicated over 95% decarbonylation. The volatile product was distilled as formed from the reaction vessel to give an 80% yield and was shown to be nearly pure *t*-butylbenzene (**12**) by comparison with an authentic sample: bp 170–171° (atm); λ^{neat} 7.2, 7.34 (*t*-butyl), 13.13, 14.3, and a trace absorption at 13.6 μ (*i*-butylbenzene, **11**, <2%); $\delta^{\text{CCl}_4}_{\text{TMS}}$ 7.3–7.8 m (ArH), 1.30 s (CH_3); trace resonances appeared at 4.77 s, 2.5–2.3 m, 0.87 d (J = 6 cps) due to **11**, **13**, and (perhaps) **14**. Integration indicated in some samples as much as 6% of these last products, but in other cases only traces. Gas chromatographic analysis [SE-30, 170°, He carrier gas] showed *t*-butylbenzene, on occasion with a very small after-peak superimposed on some tailing from **12**.

A similar decomposition was performed on a solution of **10** 1 *M* in molten biphenyl, using 1 g of the aldehyde. The distillate from the reaction contained some biphenyl, but again it was essentially pure **12**.

The small amount of residue from these reactions was extracted with ether and filtered free from catalyst. Upon removal of the ether a semisolid material remained. Both infrared and nmr spectral analysis indicated the presence of starting **10** and β-phenylisovaleric acid by comparison with knowns, though neither of these was a major constituent. The base-washed material did not give a strong hydroxamic acid test for esters, but a 5.87-μ absorption did characterize the material as a carbonyl substance(s). Although investigated further, this part of the residue was not structurally defined.

Control Study on 12.[14]—There was no change in the nmr spectrum of pure *t*-butylbenzene (1 g) after it was heated under reflux with the catalyst (0.1 g) for 80 min.

Registry No.—**10**, 6325-41-3; **12**, 98-06-6.

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[11] C. Rüchardt and H. Trautwein, *Chem. Ber.*, **95**, 1197 (1962).

[12] F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughn, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

[13] M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949); J. W. Wilt and A. A. Levin, *ibid.*, **27**, 2319 (1962).

[14] We thank Mr. J. F. Kraemer for this data.

Stereochemistry of Thermal Reactions. III. Stereochemistry of the Thermal Rearrangement of Allylic Acetoacetates[1,2]

RICHARD K. HILL AND MARTIN E. SYNERHOLM

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Received July 5, 1967

Thermal additions and rearrangements which proceed by a cyclic electron reorganization process generally demand a transition state of stringent geometric requirements. A readily apparent consequence of this requirement is a high degree of stereospecificity, both in the geometry of the double bonds involved and in the transfer of asymmetry from an asymmetric center being destroyed to one being simultaneously created. In the Claisen rearrangement (I → II), this specificity has been observed both in formation of predominantly *trans*

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[1] This study was supported by a research grant, GP-3811, from the National Science Foundation, to whom we express our thanks.

[2] For paper II in this series, see R. K. Hill and A. G. Edwards, *Tetrahedron Letters*, 3239 (1964).