Reactions of α-Hydroxybenzyl Free Radicals. IV. The Dicyclopropylcarbinyl Radical[1]

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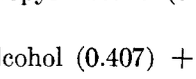
The reactions of dicyclopropylcarbinol with di-*t*-butyl peroxide and dicyclopropyl ketone with di-*t*-butyl peroxide and 2-butanol are reported. The results suggest that the α-hydroxydicyclopropylcarbinyl radical intermediate is similar to the α-hydroxycyclopropylmethylcarbinyl radical in its kinetic and ring-opening behavior. The unusual features of α-hydroxycyclopropylcarbinyl radicals are attributed to ring strain relief.

Although study of the cyclopropylcarbinyl free radical has been extensive,[1,3,4] there are few known examples of dicyclopropylcarbinyl free-radical intermediates. Since the dicyclopropylcarbinyl carbonium ion is known to be formed at an exceedingly fast rate compared to the cyclopropylcarbinyl carbonium ion,[5] a study of the α-hydroxydicyclopropylcarbinyl free radical was undertaken for comparative purposes.

In this paper we report preparation of the α-hydroxydicyclopropylcarbinyl free radical using both hydrogen atom addition to dicyclopropyl ketone and hydrogen atom abstraction from dicyclopropylcarbinol to generate the reaction intermediate. We compare the α-hydroxydicyclopropylcarbinyl radical with its α-hydroxycyclopropylmethylcarbinyl and α-hydroxycyclopropylphenylcarbinyl counterparts. Use of benzpinacol as a source of α-hydroxydiphenylmethyl free radicals is described. Hydrogen atom transfer from the α-hydroxydiphenylmethyl radical to cyclopropyl plenyl ketone but not to dicyclopropyl ketone is reported.

Results

The results of the reaction of dicyclopropylcarbinol with di-*t*-butyl peroxide and of dicyclopropyl ketone with 2-butanol and di-*t*-butyl peroxide are summarized (millimoles are given in parentheses): dicyclopropylcarbinol (0.781) + DTBT (0.321) $\xrightarrow{130°}$ cyclopropyl propyl ketone (0.356) + acetone (0.235) + *t*-butyl alcohol (0.407) + [] (0.128) + dicyclopropylcarbinol (residual, 0.081); dicyclopropyl ketone (4.75) + DTBP (3.84) + 2-butanol (23.30) $\xrightarrow{130°}$ cyclopropyl *n*-propyl ketone (0.79) + dicyclopropyl ketone (3.56) + acetone (1.22) + *t*-butyl alcohol (7.00) + 2-butanone (3.82) + 2-butanol (residual, 19.70).

The products from the thermal decomposition of benzpinacol in benzene solution under both degassed and nondegassed conditions follow (millimoles):[6] degassed using two freeze–thaw cycles, benzpinacol (0.057) $\xrightarrow{130°}$ benzophenone (0.55) + benzhydrol (0.055); sealed under air, benzpinacol (0.47) $\xrightarrow{130°}$ benzophenone (0.57) + benzhydrol (0.44). Benzpinacol provides a convenient source of α-hydroxydiphenylmethyl radicals.

When benzpinacol is decomposed in the presence of cyclopropyl phenyl ketone, hydrogen atom transfer from the α-hydroxydiphenylmethyl radical to cyclopropyl phenyl ketone occurs. Ring-opened products characteristic of the α-hydroxycyclopropylcarbinyl free-radical are observed. These results follow (millimoles): benzpinacol (0.47) + cyclopropyl phenyl ketone (3.54) $\xrightarrow{130°}$ benzophenone (0.86) + butyrophenone (0.32) + cyclopropyl phenyl ketone (residual, 3.06).

Decomposition of benzpinacol in the presence of dicyclopropyl ketone yields 1 mole of benzophenone per mole of pinacol decomposed. More significantly, we observe the distinct absence of products from the α-hydroxydicyclopropylcarbinyl free radical. These results follow (millimoles): in benzene, not degassed, benzpinacol (0.114) + dicyclopropyl ketone (3.85) $\xrightarrow{130°}$ benzophenone (0.125) + cyclopropyl *n*-propyl ketone (trace).

Relative rates of hydrogen atom addition from α-hydroxybutyl radicals to selected ketones are reported in Table I. Although the cyclopropyl group affects the rate of hydrogen atom addition, the effect is not so marked in the case of alkyl cyclopropyl as in the case of aryl cyclopropyl ketones.

TABLE I

RELATIVE REACTIVITIES OF SELECTED KETONES TOWARD HYDROGEN ATOM ADDITION AT 130°

Ketone	k_{rel}
Phenyl cyclopropyl ketone	$\approx 1.1 \pm 0.1 \times 10^4$
Phenyl *t*-butyl ketone	33.4 ± 2.0
Dicyclopropyl ketone	1.29 ± 0.10
Cyclopropyl methyl ketone	1.22 ± 0.04
Cyclohexanone	1.00

Discussion

The reactions of dicyclopropylcarbinol with di-*t*-butyl peroxide and of dicyclopropyl ketone with 2-butanol and di-*t*-butyl peroxide produce the α-hydroxydicyclopropylcarbinyl radical intermediate. The mechanism for both reactions is analogous to that proposed for the reaction of cyclopropylphenylcarbinol with di-*t*-butyl peroxide and cyclopropyl phenyl ketone with 2-hydroxybutyl radicals in our earlier papers.[1,3,4] It is apparent that the α-hydroxydicyclopropylcarbinyl free radical (2) behaves more like the α-hydroxymethylcyclopropylcarbinyl radical (1) than the α-hydroxy-

(1) Part III: D. C. Neckers, A. P. Schaap, and J. Hardy, *J. Am. Chem. Soc.*, **88**, 1265 (1966).

(2) National Science Foundation Undergraduate Research Participant, 1965–present.

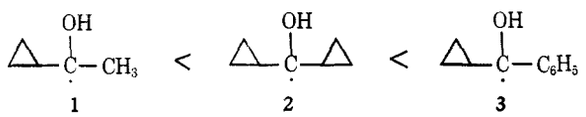
(3) D. C. Neckers, *Tetrahedron Letters*, 1889 (1965).

(4) D. C. Neckers, J. Hardy, and A. P. Schaap, *J. Org. Chem.*, **31**, 622 (1966).

(5) H. Hart and J. M. Sandri, *J. Am. Chem. Soc.*, **81**, 320 (1959).

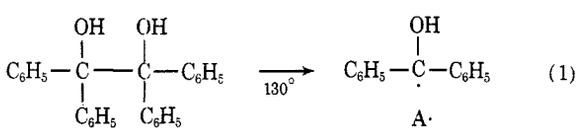
(6) The kinetics of this thermal decomposition process, as well as those of a series of other aryl pinacols, are being studied. Results of these studies will be reported at a later date.

phenylcyclopropylcarbinyl radical (**3**), although earlier relative reactivity studies suggested that cyclopropyl might be more effective in stabilizing an adjacent radical site than phenyl.[1] At the temperatures of our reaction, the α-hydroxydicyclopropylcarbinyl radical undergoes exclusive ring opening to produce, after chain transfer, cyclopropyl *n*-propyl ketone. A similar result was observed when cyclopropylmethylcarbinol was treated with di-*t*-butyl peroxide. With cyclopropylphenylcarbinol, on the other hand, a competitive oxidation of the α-hydroxyphenylcyclopropylcarbinyl species to phenyl cyclopropyl ketone was observed. We believe this result reflects the inherent stability, under our conditions, of the various cyclopropylcarbinyl species.[7]

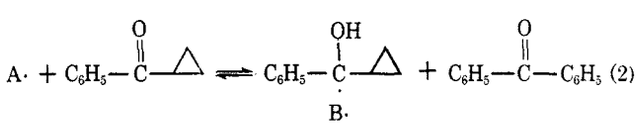


The rates of formation of the three species (Table I) indicate that formation of the α-hydroxyphenylcyclopropylcarbinyl species is at least 10^4 times faster than formation of the α-hydroxydicyclopropylcarbinyl free radical. This observation must result from the resonance interactions with the adjacent benzene ring. Contributions from the cyclopropyl group are not substantial.

In the presence of α-hydroxydiphenylmethyl radicals generated by the thermal decomposition of benzpinacol,[8] although hydrogen atom transfer to cyclopropyl phenyl ketone occurs (eq 1–4) there is no tendency for a similar hydrogen atom transfer to dicyclopropyl ketone (eq 5).



(1)



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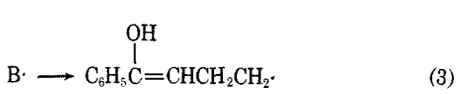

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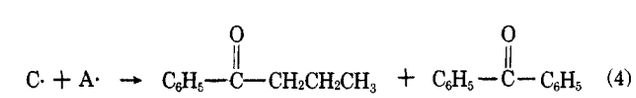
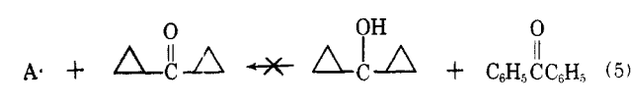


(4)



(5)

If resonance contributions from the cyclopropyl group were important then dicyclopropyl ketone should also react with α-hydroxydiphenylmethyl free radicals.[5] No hydrogen transfer is observed because no *n*-propyl cyclopropyl ketone results from the reaction of benzpinacol with dicyclopropyl ketone. Also the amount of benzophenone produced from the decomposition is essentially 1 mole per mole of pinacol. We feel that these results indicate that effects of a cyclopropyl group adjacent to radical sites are the manifestation of the ring strain only. The cyclopropylcarbinyl radical, although often strange in its behavior, is analogous to almost any other alkyl carbinyl radical.

The thermal decomposition of benzpinacol is, in itself, interesting. The disproportionation of the α-hydroxydiphenylmethyl radicals is quantitative in the absence of oxygen such that equimolar quantities of benzophenone and benzhydrol are produced from the reaction. In the presence of oxygen however, the α-hydroxydiphenylmethyl radical is oxidized to benzophenone.[9]

Experimental Section[10]

Materials.—Dicyclopropyl ketone, cyclopropyl phenyl ketone, and di-*t*-butyl peroxide were commercially available materials shown to be greater than 99.5% pure before use. Benzpinacol, mp 186° (lit.[11] mp 186–187°), was prepared by the photoreduction of benzophenone. Dicyclopropylcarbinol was prepared by sodium borohydride reduction of dicyclopropyl ketone, phenyl-*t*-butyl ketone, bp 69° (0.5 mm) [lit.[12] bp 110° (18 mm)], from benzene and pivaloyl chloride by Friedel–Crafts procedures.

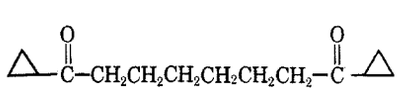
Decomposition of Benzpinacol (Degassed).—Aliquots (2 ml) of a stock benzene solution of benzpinacol (1.43 mmole/cc) were added to several tubes, degassed by two successive freeze–thaw cycles, sealed, and placed in an oil bath thermostated at 130 ± 2°. After several days, the tubes were removed and analyzed for benzophenone and benzhydrol by infrared analysis. The benzophenone analysis was verified by vapor phase chromatography using a 1.5-ft 5% GE-SE-30 column on Chromosorb W at 155–165° against ethyl cinnamate as the internal standard.

Decomposition of Benzpinacol in the Presence of Air.—A procedure exactly analogous to the above was used with the exception that the tubes were sealed without degassing.

Decomposition of Benzpinacol in the Presence of Cyclopropyl Phenyl Ketone.—Aliquots (2 ml) of a stock benzpinacol solution in benzene (2.00 *M*) were added to tubes containing ≈3.75 mmoles of cyclopropyl phenyl ketone, and the tubes were degassed, sealed, and placed in a thermostated oil bath (T = 130°). After several days the tubes were removed and the contents were analyzed for benzophenone, residual cyclopropyl phenyl ketone, and butyrophenone using conditions similar to those previously reported.[1]

Decomposition of Benzpinacol in the Presence of Dicyclopropyl Ketone.—A procedure similar to that above was employed. Residual dicyclopropyl ketone and cyclopropyl *n*-propyl ketone were analyzed using a 15-ft 5% Carbowax column at 100°, 15 psi of helium.

Decomposition of DTBP in Presence of Dicyclopropylcarbinol.—A procedure similar to that employed for cyclopropylphenylcarbinol was used.[1] Cyclopropyl *n*-propyl ketone, dicyclopropyl ketone, and residual dicyclopropylcarbinol were analyzed using the procedure described above with cyclohexanone as the internal standard. A dimeric material with major infrared absorption at 3010, 2950, 1790, 1380, 1160, and 1020 cm^{-1} and assigned the structure



(7) The degree of ring opening is a function of temperature. At lower temperatures, both cyclopropyl methyl and dicyclopropyl ketone are observed among the reaction products resulting from the α-hydroxycyclopropylmethylcarbinyl and α-hydroxydicyclopropylcarbinyl radical intermediates.

(8) E. G. Janzen, private communication.

(9) With radicals of the α-hydroxydiphenylmethyl type, total reduction even in the presence of the partner radical, can be accomplished using facile chain-transfer agents.

(10) Melting points are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained using a Beckman IR-8, vpc analyses were performed using a Wilkens Model Hi-Fi or A-90-P-3.

(11) G. Ciamician and P. Silber, *Ber.*, **30**, 2911 (1900).

(12) K. Von Auwers, *ibid.*, **45**, 2772 (1912).

was also obtained by preparative chromatography on the 1.5-ft 5% GE-SE 30 column at 150°, 15 psi of helium.

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.46; H, 9.86.

Reactions of Dicyclopropyl Ketone and Cyclopropyl Methyl Ketone with 2-Butanol and DTBP at 130°.—A procedure similar to that used for cyclopropyl phenyl ketone was employed. Analysis was accomplished by the methods described earlier.[1]

Relative Reactivities of Ketones with DTBP and 2-Butanol.—A procedure like that employed earlier was employed.[1] Vpc analysis for residual ketone against an appropriate standard was employed.

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Reactive Intermediates in the Bicyclo[3.1.0]hexyl and Bicyclo[3.1.0]hexylidene Systems. III. The Addition of Hydrogen Chloride and Deuterium Chloride to Bicyclo[3.1.0]hexene-2[1,2]

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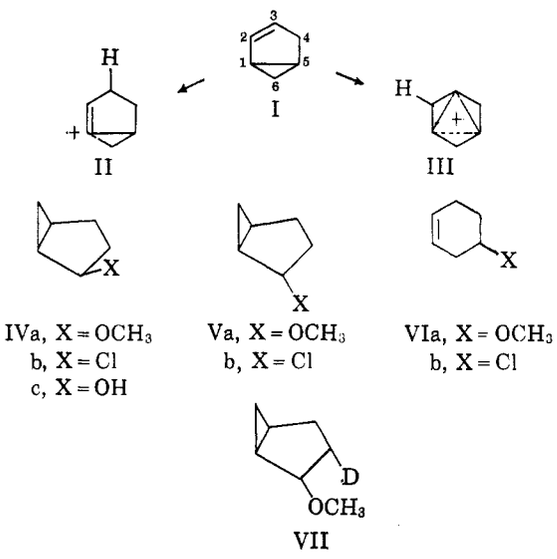
The addition of hydrogen chloride to bicyclo[3.1.0]hexene-2 results in *cis*-2-chlorobicyclo[3.1.0.]hexane and *trans*-2-chlorobicyclo[3.1.0]hexane, as the major products, accompanied by a small amount of 4-chlorocyclohexene. The addition of deuterium chloride to bicyclo[3.1.0]hexene-2 produces *cis*-2-chloro-*cis*-3-deuteriobicyclo[3.1.0]hexane and *trans*-2-chloro-*trans*-3-deuteriobicyclo[3.1.0]hexane, with a minor amount of deuterated 4-chlorocyclohexene.

Our recent investigation[4] of the reaction alternatives for electrophilic addition to bicyclo[3.1.0]hexene-2 utilized the acid-catalyzed additions of methanol and methanol-*d*. Using mild reaction conditions, the addition of methanol resulted in *cis*-2-methoxy- and *trans*-2-methoxybicyclo[3.1.0]hexane (IVa and Va) and small amounts of 4-methoxycyclohexene (VIa). Since no 3-methoxybicyclo[3.1.0]hexanes were detected using reaction conditions under which the 3 ethers would have survived if formed, it was concluded that the trishomocyclopropenyl carbonium ion (III) (or a classical relative) was not a product-determining intermediate. Formation of IVa, Va, and VIa can be accounted for as a result of generation of a 2-bicyclo[3.1.0]hexyl carbonium ion (II). The addition of methanol-*d* leading to *trans*-2 ether was investigated and found to be completely *cis*, producing *trans*-2-methoxy-*trans*-3-deuteriobicyclo[3.1.0]hexane (VII). (See Scheme I.)

SCHEME I



Interpretation of the *cis* polar addition of the elements of CH_3OD to I is complicated by the unknown degree to which the stereochemistry is controlled by the position of the cyclopropane methylene. Similar difficulties are encountered in interpreting the *cis* addition of methanol-*d* to *endo*-trimethylenenorbornene,[5] *cis* polar addition of deuterium bromide to norbornene,[6] *cis* oxymercuration of norbornadiene, norbornene, and norbornene derivatives,[7-10] *cis* oxythallation of norbornadiene and norbornene,[7,11] and *cis* addition of nitrosyl chloride and bromide to norbornadiene, norbornene, and norbornene derivatives.[12] In these cases one can argue that *cis* addition is not the result of the intrinsic requirements of the double bond but is the result of effective steric shielding by methano, ethano, or etheno bridge elements.[13] Clarification of the importance of such steric shielding

(1) Part II: P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, **30**, 1047 (1965).

(2) Presented at the Northwest Regional Meeting of the American Chemical Society, Corvallis, Ore., June 1965, Abstracts, p 40.

(3) National Defense Education Act Fellow, 1961–1964.

(4) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).

(5) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, **No. 4**, 185 (1963).

(6) H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964).

(7) K. C. Pande and S. Winstein, *Tetrahedron Letters*, **No. 46**, 3393 (1964).

(8) J. K. Stille and S. C. Stinson, *Tetrahedron*, **20**, 1387 (1964).

(9) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963); T. G. Traylor and A. W. Baker, *Tetrahedron Letters*, **No. 19**, 14 (1959).

(10) M. M. Anderson and P. M. Henry, *Chem. Ind.* (London), 2053 (1961).

(11) F. A. L. Anet, *Tetrahedron Letters*, **No. 46**, 3399 (1964).

(12) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **86**, 4074 (1964).

(13) When both faces of the double bond are sterically shielded to the same degree, as in bicyclo[2.2.2]octene, oxymercuration in aqueous acetone yields both *cis* and *trans* addition products: T. G. Traylor, *ibid.*, **86**, 244 (1964). In comparing oxymercuration of norbornene and bicyclo[2.2.2]-octene, Professor Traylor emphasizes the importance of the rigidity of the starting olefin. The greater flexibility of the bicyclo[2.2.2]octene mercurinium ion complex would permit backside attack with less torsional strain than in the corresponding process with the norbornene complex.