species CuA^+ and B^-. It can be formed by a combination of $Cu(l\text{-Asp})^+$ and $d\text{-Asp}^-$ or from $Cu(d\text{-Asp})^+$ and $l\text{-Asp}^-$. Statistical arguments give

$$K_3 = \frac{[Cu(l\text{-Asp})(d\text{-Asp})]}{[Cu(l\text{-Asp})^+][d\text{-Asp}^-]} = \frac{1}{2}\frac{[Cu(l\text{-Asp})(d\text{-Asp})]}{[CuA^+][B^-]} \quad (5)$$

(1), (4) and (5) give

$$K_2 = \frac{1}{2}K_1 + \frac{1}{2}K_3 \text{ or } K_3 = 2\left(K_2 - \frac{1}{2}K_1\right) \quad (6)$$

We have found K_1 and K_2 to be 2.82×10^6 and 1.74×10^6, respectively. Equation (6) thus gives a value of 7×10^5 for K_3, which is the formation constant of the mixed complex. The non-mixed complex is thus favored as compared to the mixed one.

Equation (6) further indicates that if the mixed complex did not form at all the value of K_2 would be one-half of K_1. Also, if no preferential formation of non-mixed complexes existed K_2 would equal K_1. And, finally, in the case that the mixed complexes were favored K_2 would be greater than K_1.

The experimental details of this and the results of further experiments will be reported in a later publication.

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RECEIVED NOVEMBER 1, 1958

A STEREOSPECIFIC CIS HYDRATION OF THE DOUBLE BOND IN CYCLIC DERIVATIVES

Sir:

The hydroboration of olefins, followed by oxidation of the product with hydrogen peroxide, provides a highly convenient procedure for the anti-Markownikoff hydration of double bonds.[1,2] In applying this reaction to cyclic olefins we have observed that the reaction proceeds stereospecifically to add the elements of water, hydrogen and hydroxyl, in a *cis* configuration to the double bond.

In this way 1-methylcyclopentene has been converted in a yield of 85% to *trans*-2-methylcyclopentanol, b.p. 152–153° at 745 mm., n^{20}D 1.4488, m.p. of 3,5-dinitrobenzoate, 86–87°.[3] Similarly, 1-methylcyclohexene has been converted in a yield of 90% to *trans*-2-methylcyclohexanol, b.p. 166.5° at 745 mm., n^{20}D 1.4614, m.p. of 3,5-dinitrobenzoate, 113–115°.[4,5]

In these cases the *cis* hydration results in the formation of the thermodynamically more stable isomer Consequently, the hydroboration of 1,2-dimethylcyclopentene and 1,2-dimethylcyclohexene was examined. In these cases, *cis* hydration would form the less stable isomers. 1,2-Dimethylcyclopentene yielded *cis*-1,2-dimethylcyclopentanol, b.p. 66–68° at 21 mm., m.p. 23–24°.[6] Similarly, 1,2-dimethylcyclohexene was converted into 1,2-dimethylcyclohexanol, b.p. 94° at 40 mm., n^{20}D 1.4639, m.p. 24–25°.[7]

In each case the reaction products were examined by gas chromatography (glycerol column for 2-methylcyclohexanol, Carbowax column for others). In each of the four cases, the crude reaction product was shown to contain at least 97–98% of the isomer indicated, with a maximum of 2–3% of the other isomer present.

Not only does this hydration occur *cis*, but it takes place predominantly from the less hindered side of a double bond. Thus, norbornene is converted to *exo*-norborneol, m.p. 125–126°, 3,5-dinitrobenzoate, m.p. 104–105°.[8]

α-Pinene yields an alcohol, m.p. 35–38°. On basis of proposed rules, this should be isopinocamphenol.[9] Examination is continuing.

The following procedure is typical. Excess diborane (from 3.8 g. of sodium borohydride in diglyme and boron trifluoride etherate[10] was passed into 16.4 g., 0.2 mole, of 1-methylcyclopentene, b.p. 74–75° at 744 mm., n^{20}D 1.4313, in 60 ml. of tetrahydrofuran at 0° over a period of two hours. After 1 hour at room temperature, several small pieces of ice were added to hydrolyze the excess diborane. The reaction mixture was immersed in an ice-bath, 45 ml. of 3 *M* sodium hydroxide was added, and then 25 ml. of 30% hydrogen peroxide, over a period of 1 hour. After 1 hour at room temperature, the upper layer was separated, the aqueous phase was extracted with ether, and the combined extracts were dried. Gas chromatographic examination of the organic phase showed the presence of 98% *trans*-1-methylcyclopentanol, with a small neighboring peak of 2% which may be the *cis* derivative. The product was isolated by fractionation in an efficient column.

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(1) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 5694 (1956).

(2) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1135 (1957).

(3) W. Hückel and H. D. Sauerland, *Ber.*, **87**, 1003 (1954), report b.p. 149–151.2° at 735 mm., n^{20}D 1.4501, m.p. of 3,5-dinitrobenzoate, 88°.

(4) M. G. Vavon, A. Perlin and M. A. Horeau, *Bull. Soc. chim. France*, **51**, 644 (1932), report b.p. 165° at 750 mm.

(5) L. M. Jackman, A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 1717 (1949), report n^{20}D 1.4616, m.p. of 3,5-dinitrobenzoate, 117°.

(6) L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949), report *cis*-1,2-dimethylcyclopentanol, b.p. 62° at 17 mm., m.p. 24–26°; *trans*-, b.p. 51° at 17 mm., m.p. 24–25°.

(7) G. Chiurdoglu, *Bull. Soc. chim. Belg.*, **47**, 241 (1938), reports *cis*-1,2-dimethylcyclohexanol, b.p. 82.8° at 25 mm., n^{20}He 1.4649, m.p. 23.2°; *trans*-, b.p. 74° at 25 mm., n^{20}He 1.4614, m.p. 13.2°.

(8) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939), report *exo*-norborneol m.p. 128–129°, 3,5-dinitrobenzoate, m.p. 105°; *endo*-, m.p. 149–150°, 3,5-dinitrobenzoate, m.p. 123°.

(9) H. Schmidt, *Ber.*, **77**, 544 (1944).

(10) H. C. Brown and P. A. Tierney, THIS JOURNAL, **80**, 1552 (1958).

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RECEIVED DECEMBER 4, 1958

THE SYNTHESIS OF DIPHENYLCYCLOPROPENONE

Sir:

To date no stable compound is known containing a carbonyl group in a three-membered ring. For this reason cyclopropenones are of special interest, for although the greater expected strain in the unsaturated cyclic ketones would seem likely to make them even less stable than the saturated compounds, cyclopropenones should be aromatic (being the analogs in the two-π-electron system of tropone in the six).[1] So, the preparation of a cyclo-

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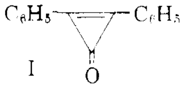
(1) Our calculations, using the L.C.A.O. method with all the usual approximations, except that α_0 is taken as $\alpha_C + \beta$, show that cyclopropenone should have a vertical resonance energy of 1.4β, and that this value is essentially the same for diphenylcyclopropenone if one corrects for the stilbene system. It is thus possible that our observed stability will also be found for the simpler cyclopropenone.

propenone seemed attractive as additional demonstration of the validity of such analogies.[2]

We considered that the interesting reaction between a carbene and a ketene acetal to furnish a cyclopropanone ketal, which has been described by McElvain,[3] could be adapted to this purpose. Since diphenylcyclopropenes are formed readily by base-catalyzed eliminations from appropriately substituted cyclopropanes,[4] we selected the reaction of phenyl ketene dimethyl acetal[5] with benzal chloride and potassium *t*-butoxide. The expected product was the dimethyl ketal of diphenylcyclopropenone (I), but we find that with neutral aqueous processing, this hydrolyzes,[6] the only crystalline product isolated being (I) itself, m.p. 121–121.5° from cyclohexane–benzene. Calcd. for $C_{15}H_{10}O$: C, 87.35; H, 4.89; mol. wt., 206. Found: C, 87.71, 87.52; H, 4.87, 4.93; mol. wt. (cryoscopic, CBr_4), 198. In the ultraviolet the compound shows maxima (CH_3CN) at 297 (4.3), 282 (4.25), 226 (4.13), and 220 (4.16) mμ, with a shoulder at 310 mμ (4.04). Its infrared spectrum (in CCl_4) is in striking agreement with the proposed structure, with weak absorption at 3.4 μ (aromatic C–H), a strong band at 5.40 μ (C=O stretching), and rather strong bands at 6.1 (conjugated C=C), 6.7 and 6.9 (benzene ring) and 7.45 μ (C=O bending). The only other major absorptions are two bands (in CS_2) at 13.0 and 14.5 μ (monosubstituted benzene).

As further evidence, we have studied thermal decomposition. While the melting at 121° is reversible, heating to 130–140° causes evolution of a gas which we have identified as carbon monoxide.[7] From the residue one can isolate, in 20% yield, diphenylacetylene identical with authentic material. This mode of decomposition is not surprising for (I), but the relatively high temperature at which it occurs, and the fact that (I) can be isolated from hydroxylic medium, show that the cyclopropenone system must have strong resonance stabilization indeed to compensate for its high angle strain.


I

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[2] The stable *s*-triphenylcyclopropenyl cation, reported by R. Breslow and Chin Yuan, THIS JOURNAL, in press, furnishes a similar analogy to tropylium ion.

[3] S. M. McElvain and P. L. Weyna, Amer. Chem. Soc. Meeting Abstracts, Chicago, Sept., 1958, p. 1-P.

[4] S. F. Darling and E. W. Spanagel, THIS JOURNAL, **53**, 1117 (1931).

[5] S. M. McElvain and J. T. Venerable, *ibid.*, **72**, 1661 (1950).

[6] The ready hydrolysis must occur because the intermediate in the reaction is a derivative of a cyclopropenyl cation.

[7] E. G. Voiret and A. L. Bonaimé, *Ann. chim. anal.*, **26**, 11 (1944).

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RECEIVED NOVEMBER 29, 1958

RESOLUTION OF A NON-HETEROCYCLIC QUATERNARY PHOSPHONIUM IODIDE

Sir:

We wish to report the first completely successful resolution of a quaternary phosphonium salt in which the phosphorus atom is not a member of a heterocyclic ring. Both enantiomorphs of methylethylphenylbenzylphosphonium iodide have been obtained by way of the *d*(−)-dibenzoylhydrogentartrate and *l*(+)-dibenzoylhydrogentartrate salts. The iodides were found to be optically stable even in solution, and this fact disposes of the suggestion that the numerous previous failures[1] to resolve asymmetric phosphonium salts of the type $RR_1R_2R_3P^+,X^-$ were attributable to their rapid racemization in solution by a dissociation-equilibrium mechanism[2]

$$RR_1R_2R_3P^+,X^- \rightleftarrows RR_1R_2P + R_3X$$

The only previous successful resolutions of phosphonium salts have been with compounds in which the phosphorus atom was a member of a heterocyclic ring. Holliman and Mann,[3] proceeding through the *d*-camphorsulfonate, were on one occasion able to isolate pure crystalline dextrorotatory 2-phenyl-2-*p*-hydroxyphenyl-1,2,3,4-tetrahydroisophosphinolinium bromide, but later they were unable to repeat their initial success. Recently, Hart and Mann[4] accomplished the resolution of P-spiro-bis-1,2,3,4-tetrahydrophosphinolinium iodide into its dextro and levo isomers *via* the *d,l*-phosphonium *l*-menthoxyacetate.

Racemic methylethylphenylbenzylphosphonium iodide, m.p. 166–167°, was prepared by the method of Meisenheimer, *et al.*[1f,5] Treatment with silver *d*(−)-dibenzoylhydrogentartrate,[6] in methanol gave the phosphonium *d*(−)-dibenzoylhydrogentartrate, which was crystallized several times from *n*-propyl alcohol. There was obtained a diastereoisomer of m.p. 142–143°, $[\alpha]^{25}D$ − 54.0° (*c* 1.281 in methanol).

Anal. Calcd. for $C_{34}H_{33}O_8P$: C, 68.00; H, 5.67; P, 5.17. Found: C, 68.21; H, 5.73; P, 5.48.

By treatment of the dibenzoylhydrogentartrate with ammonium iodide in absolute methanol there was obtained dextrorotatory methylethylphenylbenzylphosphonium iodide, m.p. 159–160°, $[\alpha]^{25}D$ +24.0° (*c* 0.824 in methanol).

Anal. Calcd. for $C_{16}H_{20}PI$: C, 51.90; H, 5.39; P, 8.38; I, 34.35. Found: C, 51.67; H, 5.65; P, 8.44; I, 34.38.

By the action of silver *L*(+)-dibenzoylhydrogentartrate on racemic methylethylphenylbenzylphosphonium iodide the dextrorotatory dibenzoylhydrogen tartrate, m.p. 142–143°, $[\alpha]^{25}D$ +54.0° (*c* 1.100

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[1] (a) A. Michaelis, *Ann.*, **315**, 19 (1901); (b) A. Michaelis, *ibid.*, **315**, 43 (1901); (c) E. Wedekind, *Ber.*, **45**, 2933 (1912); (d) W. J. Pope and C. S. Gibson, *J. Chem. Soc.*, **101**, 735 (1912); (e) L. G. Radcliffe and W. H. Brindley, *Chemistry and Industry*, **42**, 64 (1923); (f) J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt and W. Samuel, *Ann.*, **449**, 213 (1926); (g) G. Kamai, *J. Gen. Chem.* (*U.S.S.R.*), **2**, 524 (1932); (h) G. Kamai and L. A. Khismatullina, *Doklady Akad. Nauk. S.S.S.R.*, **92**, 69 (1953); (i) G. Kamai and L. A. Khismatullina, *J. Gen. Chem.* (*U.S.S.R.*) (in English Translation), **26**, 3815 (1956). It should be pointed out that Kamai and Khismatullina[1h] reported that they had achieved some concentration of the diastereoisomers of allylbutylphenylbenzylphosphonium *d*-bromocamphorsulfonate, but attempts to prepare the enantiomorphic optically active bromides by metathesis with potassium bromide failed.

[2] F. G. Mann, *J. Chem. Soc.*, 65 (1945).

[3] F. G. Holliman and F. G. Mann, *ibid.*, 1634 (1947).

[4] F. A. Hart and F. G. Mann, *ibid.*, 4107 (1955).

[5] These authors were unable to resolve the cation *via* the *d*-bromocamphorsulfonate.

[6] D. M. Coyne, W. E. McEwen and C. A. VanderWerf, THIS JOURNAL, **78**, 3061 (1956).