with the recorded melting point of 220° for 6-chloro-3(2H)-benzofuranone semicarbazone.[7]

Proof of Structure of IV by Conversion to 2-Chloro-4-methoxybenzoic Acid.—Two grams (0.01 mole) of IV was dissolved in 50 ml. of water containing 2 g. of NaOH and heated to the refluxing temperature. Methyl sulfate (2.5 g., 0.02 mole) was added slowly and the refluxing continued for 2 hours. At the end of this time, a solution of 8 g. of $KMnO_4$ in 100 ml. of water was added slowly and the refluxing continued for an additional hour. The manganese dioxide was then filtered off with suction, washed with water, and the combined filtrates made strongly acidic with concd. HCl. After cooling overnight in the refrigerator, the light yellow solid was filtered off with suction and recrystallized from dilute ethanol to yield 0.8 g. (42%) of short colorless needles, m.p. 204–205° with sublimation. The recorded melting point of 2-chloro-4-methoxybenzoic acid is 208° with sublimation.[8]

Anal. Calcd. for $C_8H_7O_3Cl$: C, 51.49; H, 3.78. Found: C, 51.61; H, 3.50.

2-Chloro-4-hydroxy-ω-(benzylmethylamino)-acetophenone Hydrochloride (V, R = CH_3).—2-Chloro-4-hydroxy-ω-chloroacetophenone (IV) (3.5 g., 0.017 mole) was added as a powder to 4.1 g. (0.034 mole) of N-benzylmethylamine[11] dissolved in an anhydrous mixture of 150 ml. of ether and 50 ml. of dioxane. The resulting red solution was shaken mechanically until crystals of N-benzylmethylamine hydrochloride were seen to form (about 5 hours) and then left to stand at room temperature for 3 days. The precipitated secondary amine hydrochloride was filtered off with suction and washed with a little dry ether. Absolute ethanol, saturated with dry HCl, was added dropwise to the combined filtrates until the yellow precipitate just began to redissolve. After the addition of 100 ml. of dry ether, the mixture was chilled in the refrigerator and the precipitate isolated by suction filtration. This substance was dissolved in a small quantity of absolute methanol, decolorized with Norit, and precipitated with dry ether to obtain 4.3 g. (78%) of colorless leaflets, m.p. 145–150° dec.

Anal. Calcd. for $C_{16}H_{17}Cl_2O_2N$: N, 4.29; ionic Cl, 19.87. Found: N, 4.18; ionic Cl, 10.73.

2-Chloro-4-hydroxy-ω-(benzylethylamino)-acetophenone Hydrochloride (V, R = C_2H_5).—This substance was prepared in a similar manner using 3.5 g. (0.017 mole) of IV and 4.6 g. (0.034 mole) of N-benzylethylamine.[11] The product was obtained as 3.0 g. (52%) of almost colorless leaflets, m.p. 177–180° dec.

Anal. Calcd. for $C_{17}H_{19}Cl_2O_2N$: N, 4.12; ionic Cl, 10.42. Found: N, 3.90; ionic Cl, 10.36.

2-Chloro-4-hydroxy-α-(methylaminomethyl)-benzyl Alcohol Hydrochloride (VI, R = CH_3).—Two grams (0.0061 mole) of V (R = CH_3) were placed in the hydrogenation flask with 40 ml. of absolute methanol and 0.1 g. of Adams catalyst and hydrogenated at a pressure of 47 lb./sq. in. at room temperature. At the completion of the reaction (about 5 hours), the catalyst was filtered off and the methanol removed *in vacuo*. The remaining oily solid was dissolved in a small quantity of hot acetone, separated from insoluble oils by decantation, and slowly cooled to 0°. The product was thus obtained as colorless prisms, m.p. 160–161°, with a yield of 1.0 g. (69%).

Anal. Calcd. for $C_9H_{13}Cl_2O_2N$: N, 5.88; ionic Cl, 14.89. Found: N, 5.69; ionic Cl, 14.91.

2-Chloro-4-hydroxy-α-(ethylaminomethyl)-benzyl Alcohol Hydrochloride (VI, R = C_2H_5).—This compound was prepared in the same manner from 2.0 g. (0.0059 mole) of V (R = C_2H_5), and was obtained as 0.98 g. (65%) of colorless prisms from absolute methanol-ether, decomposing at 160–170°.

Anal. Calcd. for $C_{10}H_{15}Cl_2O_2N$: N, 5.55; ionic Cl, 14.06. Found: N, 5.46; ionic Cl, 13.89.

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[11] The N-alkylbenzylamines were prepared from the corresponding N-benzylidenealkylamines by catalytic reduction using a palladium-on-charcoal catalyst.

COMMUNICATIONS TO THE EDITOR

DEUTERIUM ISOTOPE EFFECTS ON THE AIR OXIDATION OF CUMENE

Sir:

In spite of the large body of data on the air oxidation of hydrocarbons,[1] no direct evidence has been presented that would indicate the nature of the termination reaction. The reaction $2RO_2\cdot \rightarrow ROOR + O_2$ is the most common proposal. The kinetically important propagation reaction of air oxidations is much better understood and is accepted as involving the formation of alkyl radicals by reaction of alkyl peroxy radicals with hydrocarbons. The stabilization of free radicals by resonance[2] is well established, but evidence for hyperconjugative resonance stabilization rests mostly on addition reactions to C=C bonds.[2] The relative reactivities of toluene and cumene toward various free radicals[3] indicate that adjacent methyl groups can affect the rate by as much as a factor of 18.9, but this is complicated by polar effects. In the oxidation of ring substituted cumenes, polar substituents have a small effect with a ρ value of -0.4.[4]

In order to learn more about the stabilization of free radicals and the nature of the chain terminating step, the rates of oxidation of cumene and β-deutero cumenes were determined. To the extent that hyperconjugative stabilization is important the rates should be slower for the deuterated compound.[5] On the other hand, if the chain terminating step involved breaking a C–H bond this step should be greatly inhibited and the net result would be an increase in the rate of oxidation.

The deuterocumene was prepared from deutero-acetone and phenylmagnesium bromide. The resulting carbinol was dehydrated with iodine catalyst and the olefin hydrogenated to cumene using Adams catalyst with methanol as the solvent. The cumene was washed with concentrated sulfuric acid and distilled before use in the oxidation experiments. Two different samples of deutero-cumene were prepared and analyzed by optical density measurements in the 3.4 μ region on a

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[1] L. Bateman, *Quarterly Reviews*, **8**, 147 (1954).

[2] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1955, pp. 381–476.

[3] G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4578 (1955).

[4] G. A. Russell, Abstracts of Papers, 128th Meeting Am. Chem. Soc., Minneapolis, Minn., **128**, 18-O (1955).

[5] E. S. Lewis and C. E. Boozer, THIS JOURNAL, **76**, 791 (1954).

Beckman IR-2 spectrophotometer. The analysis revealed only about 1.4 and 3.0 atoms of deuterium per mole for samples A and B, respectively. The oxidations were carried out at 65° using azodiisobutyronitrile as the catalyst and chlorobenzene as the solvent. A sensitive constant pressure apparatus was used to measure the volumes of oxygen consumed. The results are summarized in Table I.

TABLE I

THE RELATIVE RATE OF OXIDATION OF CUMENE AND DEUTEROCUMENE

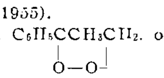
Compound	Added inhibitor	k_H/k_D
Deuterocumene A	None	0.91
Deuterocumene B	None	0.85
Deuterocumene A	*p*-Nitrophenol	1.05
Deuterocumene B	*p*-Nitrophenol	1.07
Deuterocumene A	2,4-Dichlorophenol	1.19
Deuterocumene B	2,4-Dichlorophenol	1.27

From the data in Table I it can readily be seen that both of the effects discussed above are in operation. The two effects were separated by the addition of an inhibitor to replace the usual termination step.[6] The ratio of the inhibited rates represent the secondary isotope effect and indicate that hyperconjugation is important in stabilizing free radicals. The effect on the chain terminating step is much larger since it completely overshadows the secondary effect, even though the over-all rate of oxidation is proportional to the inverse square root of the termination rate constant. Such an effect probably means that the chain terminating step involves scission of a β-carbon-hydrogen bond and could be written thusly[7]

$$2C_6H_5C(CH_3)_2OO \longrightarrow C_6H_5\text{–}C(CH_3)_2OOH + C_6H_5C(CH_3)=CH_2 + O_2$$

Acknowledgment.—The authors are indebted to the Research Corporation for a Frederick Gardner Cottrell grant which made this work possible.

[6] G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, THIS JOURNAL, **77**, 3238 (1955).

[7] A referee suggested  $C_6H_5\underset{\lfloor O-O \rfloor}{CCH_3CH_2}$. or $C_6H_5COCH_3 + CH_2O$ as other possible products.

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C. E. WIGHTMAN III

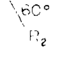
RECEIVED FEBRUARY 27, 1956

INFRARED ANALYSIS OF α-HALOCYCLOPENTANONES

Sir:

The well known *differences*[1] between substituted cyclopentane and cyclohexane rings stand in marked contrast to *similarities* recently found[2] when planar four center reactions were studied. These similarities, which might have arisen from common stereochemistry, led us to consider that when a carbon atom in the cyclopentane ring is puckered out of the plane about 0.7 Å.,[3] two adjacent *trans* groups will be coplanar much like two adjacent diaxial substituents on the chair form of the cyclohexane ring.

This communication which presents spectral evidence that α-halocyclopentanones are not planar lends support to these views. We have employed the method of R. N. Jones[4] and E. J. Corey[5] which distinguishes between axial and equatorial halogen atoms α- to a carbonyl group, to establish the hitherto unknown carbonyl frequency shifts due to the intermediate position of a halogen atom in a planar α-halocyclopentanone (I, R_1 = Br, Cl, R_2 = H).



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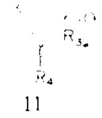

II

By measuring the α-halocamphors[6] where the rigid $R-\overset{|}{C}-\overset{|}{C}=O$ geometry, in projection, is virtually the same as in a planar cyclopentanone,[7] we have obtained for α-bromine a shift of 14 cm.$^{-1}$ and α-chlorine a shift of 18–19 cm.$^{-1}$. These are intermediate[4,5c] or borderline values[5a,b] between those reported for axial and equatorial halogens in six membered rings.

The good agreement (Table I) between the shifts for α-chlorocamphor (II, R_3 = H, R_1 = Cl) and α′-chlorocamphor (II, R_3 = Cl, R_4 = H) and the further shift for dichlorocamphor are in keeping with their assigned geometry.

TABLE I[a]

Ketone	ν_{max} C=O, cm.$^{-1}$	Δν, cm.$^{-1}$
Camphor	1744	. .
α-Bromo-	1758	14
α,α′-Dibromo-	1766	22
α-Chloro-	1763	19
α′-Chloro-	1762	18
α,α^1-Dichloro-	1774	30
2-Indanone[b]	1753	. .
1-Bromo-	1766	13
1-Chloro-[c]	1772	19
Cyclopentanone	1742	. .
1-Bromo-	1750	8
1-Chloro-	1755[5c]	13

[a] Measured in carbon tetrachloride solution on a Perkin–Elmer Model 21 Double Beam Infrared Spectrophotometer. [b] Kindly prepared by Mr. Elmer Maurer, Eastern Regional Research Laboratories, Phila. 18, Pa. [c] Prepared as in reference 8, m.p. 70.0–70.5°. *Anal.* Calcd. for C_9H_7OCl: Cl, 21.28. Found: Cl, 21.33, 21.39.

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[1] H. C. Brown, J. H. Brewster and H. Schechter, THIS JOURNAL, **76**, 467 (1954).

[2] F. V. Brutcher, Jr., and T. Roberts, Abstracts of Papers, 127th Meeting, American Chemical Society, Cincinnati, Ohio, April, 1955, p. 39N.

[3] Derived from the bicyclo[2.2.1]heptane ring system which has a puckered five membered ring with this geometry. It is considerably larger than the 0.2Å. puckering reported by Kilpatrick, Pitzer and Spitzer, THIS JOURNAL, **69**, 2483 (1947), for cyclopentane itself.

[4] R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2828 (1952).

[5] (a) E. J. Corey and H. J. Burke, *ibid.*, **77**, 5418 (1955); (b) E. J. Corey, T. H. Topie and W. A. Wozniak, *ibid.*, **77**, 5415 (1955); (c) E. J. Corey, *ibid.*, **75**, 2301, 3297 (1953).

[6] J. Simonsen and L. N. Owen, "The Terpenes," Vol. II, Cambridge University Press, Cambridge, England, 1949, Chap. 5.

[7] R. C. Cookson, *J. Chem. Soc.*, 282 (1954).