In general, other conditions (24 hr, 25°) gave mixtures of the two ketones which could be separated by column chromatography or fractional crystallization, or more conveniently, directly hydrogenolyzed as described below.

Iodotricyclic ketone 11 (0.03 g) was stirred in 5 ml of ethanol with 2 drops of triethylamine and 10% palladium on carbon (0.03 g) at 25° in the presence of hydrogen (1 atm) for 15 hr. The mixture was filtered and the filtrate was concentrated to dryness. The residue was suspended in dilute sodium hydroxide and extracted with ether. Drying and concentration gave pure tricyclic ketone 2 (0.02 g, ~100%) which showed no trace of iodotricyclic ketone 11 by tlc.

5,5-Dimethyl-5,12b-*seco*-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizinium Iodide (12).—A solution of 0.2 g (0.827 mmole) of tricyclic amine 10 and 5 ml of methyl iodide in 20 ml of benzene was stirred at 0° for 1 hr then allowed to stand at 5–10° for 2.5 days. The precipitate was collected (~100%), washed well with benzene, and converted into the chloride form as described below. Iodide 12 had mp 154–157° after several crystallizations from methanol–ether (needles).

Tricyclic Ketone 2 from 5,5-Dimethyl-5,12b-*seco*-1,2,3,4,6,7,-12,12b-octahydroindolo[2,3-*a*]quinolizinium Iodide (12).—Tricyclic methiodide 12 (0.3 g, 0.8 mmole) was converted into the corresponding chloride by stirring it with 2 g of freshly prepared silver chloride in 60 ml of methanol for 25 hr at 25°. Filtration and concentration gave crude yellow oil (0.21 g) which was taken up in 5 ml of methanol and added dropwise to periodic acid (0.35 g, twofold excess) in 2 ml of 50% aqueous methanol. The mixture was stirred for 30 min at 25°. After the addition of aqueous thiosulfate, chloroform extraction gave a mixture of salts which were converted into the chloride form by ion exchange (Dowex 2-X4). The resulting residue was taken up in 25 ml of ethanol and stirred with 0.3 g of sodium thiophenoxide in 25 ml of ethanol for 30 min at 25°. The precipitate (sodium chloride) was removed and the filtrate was taken to dryness. The residue was refluxed for 40 hr under nitrogen with 110 ml of methyl ethyl ketone. Usual work-up (see earlier demethylation procedures) gave 0.17 g of dark amber residue. Chromatography on activity III basic alumina gave on benzene elution 0.04 g (20%) of recovered tricyclic amine 10. Further elution with benzene–chloroform (1:4) gave 0.075 g (30–40% based on unrecovered tricyclic amine 10) of a mixture of tricyclic ketone 2 and iodotricyclic ketone 11 (tlc).

Treatment of Tricyclic Ketone 2 with Diethyl Malonate Anion.—To 0.011 g (0.0005 g-atom) of sodium dissolved in 1 ml of dry ethanol was added 0.08 g (0.5 mmole) of diethyl malonate with stirring under nitrogen. After a few minutes 0.013 g (0.05 mmole) of tricyclic ketone 2 in 2 ml of ethanol was added. Examination of aliquots by ultraviolet spectroscopy over 8 hr showed only starting material. The mixture was treated with aqueous sodium hydroxide and extracted with chloroform. The chloroform layer was extracted with 10% hydrochloric acid which was then made basic with 10% sodium hydroxide and chloroform extracted. Drying and concentration of this chloroform extract gave 0.01 g (77%) of recovered tricyclic ketone 2 identified by spectral and tlc comparisons with starting material.

To 0.008 g (0.33 mmole) of sodium hydride in 1 ml of dry ethanol was added with stirring under nitrogen 0.10 g (0.62 mmole) of diethyl malonate. After a few minutes 0.079 g (0.31 mmole) of tricyclic ketone 2 was added. The mixture was stirred at 70–80° for 8 hr. Usual work-up gave 0.06 g (76%) of tricyclic ketone 2.

Treatment of Tricyclic Ketone 2 with Potassium Cyanide.—A solution of 0.023 g (0.09 mmole) of tricyclic ketone 2 and 0.006 g (0.9 mmole) of potassium cyanide in 15 ml of ethanol was stirred under nitrogen at 25° for 17 hr. Dilution of the reaction mixture with sodium hydroxide solution and ether extraction gave 0.023 g (100%) of tricyclic ketone 2 identified by spectral and tlc comparisons with authentic material. Refluxing this mixture in 2 ml of ethanol for 24 hr gave a 48% recovery of starting material. Reaction mixture aliquots were examined by ultraviolet and tlc but no reaction could be detected.

Registry No.—N-(Indole-3-acetyl)piperidine, 7774-14-3; **1**, 4802-79-3; **2**, 7774-20-1; *cis* **3**, 7774-16-5; *trans* **3**, 7774-17-6; **4a**, 7774-19-8; **4b**, 7774-18-7; **6a**, 7774-21-2; **6b**, 7774-22-3; **7a**, 7774-23-4; **7b**, 7784-64-7; **8**, 5912-12-9; **9**, 7774-24-5; **10**, 7262-67-1; **12**, 7774-27-8.

Proton Spin Coupling in 1-Indanone[1]

ERNEST LUSTIG AND EDWARD P. RAGELIS

Division of Food Chemistry, Bureau of Science, Food and Drug Administration, Department of Health, Education, and Welfare, Washington, D. C. 20204

Received December 1, 1966

The alicyclic protons of 1-indanone represent an ideal system for the test of theory on magnitudes and signs of $^2J_{HH}$ and $^3J_{HH}$ values because the alicyclic ring is unstrained, unsubstituted, and rigid and the proton spectrum is well resolved. The corresponding A_2B_2 spectrum was completely analyzed. The two $^2J_{HH}$ values are of the same sign, and their sign is opposite that of the $^3J_{HH}$ values, in accordance with theory. Long-range coupling in 1-indanones is discussed, and the methods of preparing deuterated 1-indanones and their intermediates are described.

The determination of relative signs of proton–proton spin coupling constants has been of considerable interest during the last years.[2] It is generally accepted that in systems in which protons are bonded to ethane-like CC fragments, the coupling constants between vicinal protons ($^3J_{HH}$) have a sign opposite those between geminal protons ($^2J_{HH}$). The proofs of this were based either on the results of double-resonance experiments or on the analysis of spectra mostly of the ABC or ABX type. A_2B_2 spectra (from CH_2CH_2 groupings) have the advantage over ABX or ABC spectra (from CH_2CHR groupings) that effects of substituents on carbon atoms, which do affect both $^3J_{HH}$ and $^2J_{HH}$, are absent, and thus the conclusions regarding the relative signs are on a firmer basis. A further desirable requirement is that the CH_2CH_2 grouping be rigid,[3] so that uncertainties about the actual magnitude of $^3J_{HH}$ owing to motional averaging[4] do not arise.

Both of these requirements were met in the studies described in the first two reports on the subject in A_2B_2 systems: on metacyclophane[3] and on two 1,1,2,2-tetrasubstituted cyclobutanes.[5] Since in both cases the protons in the CH_2 group are nonequivalent, an ambiguity remains in the assignment of the J values

---

(1) Presented in part at the American Chemical Society Meeting in Miniature, May 7, 1965, University of Maryland, College Park, Md.

(2) For an introduction to the subject, *cf.* (a) A. A. Bothner-By in "Advances in Magnetic Resonance," J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965, p 195; (b) M. Barfield and D. M. Grant, ref 2a; (c) N. S. Bhacca and D. H. Williams, "Applications of N.M.R. Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 149; (d) R. C. Fahey, G. C. Graham, and R. L. Piccioni, *J. Am. Chem. Soc.*, **88**, 193 (1966).

(3) H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, **37**, 120 (1962).

(4) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1963).

(5) E. Lustig, *J. Chem. Phys.*, **37**, 2725 (1962).

to one $^2J_{HH}$ and three $^3J_{HH}$ values; such an ambiguity is inherent in the parameters extracted from A_2B_2 spectra.

However, in molecules in which the protons within a CH_2 group are equivalent, no such ambiguity arises, as then $^2J_{HH}$ and $^3J_{HH}$ are between equivalent and nonequivalent protons, respectively. A CH_2CH_2 system in which this is so, and which is rigid also, is that of the alicyclic protons of 1-indanone. An early analysis of its spectrum[6] yielded the parameters in Table I (column I) with good evidence that the signs of ^2J and$_{HH}$ $^3J_{HH}$ are opposite. Servis and Roberts later reached the same conclusion from the analysis of a similar A_2B_2 spectrum of 2,2-dibromocyclobutanone.[7] Although in the spectrum of this molecule only 2 × 7 distinct peaks are observed for 2 × 10 lines.[7b] the unperturbed high-field wing of the A_2B_2 portion of the 1-indanone spectrum (Figure 1) displays all 10 lines. This fact puts our conclusions on firm ground. Furthermore, as Servis and Roberts pointed out,[7] the results obtained from four-membered rings may not be generally applicable, because the bonding in such strained systems is not ethanelike, as required for predictions on $^3J_{HH}$ values based on Karplus' theoretical treatment.

Table I

Nmr Parameters (Hz) of the A_2B_2 System of the Alicyclic Protons of 1-Indanone (ω_0 = 60 MHz)

	I[a]	II[b]	III[c]	IV[d]
$(\omega_A - \omega_B)$	32.0(1.5)[e]	30.0	29.94(0.20)	31.0
J_A	±15.5(1.5)		±14.32(0.16)	1.9
J_B	±17.3(1.5)		±16.00(0.25)	3.8
$\lvert J_A - J_B \rvert$	1.8(0.3)	2.0	1.68	1.9
J'	±3.6(0.2)	3.7	±3.37(0.20)	3.5
J''	±9.2(0.2)	8.7	±8.45(0.18)	8.9

[a] Reference 6. [b] By direct analysis; *cf.* B. Dischler, *Z. Naturforsch*, **20a**, 888 (1965). [c] Refined by LAOCOON II: S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964); rms error = 0.075 Hz. [d] H. H. Hecht, *Theoret. Chem. Acta* (Berlin), **3**, 202 (1965). The spectrum reproduced there is less well resolved than ours (Figures 1, 2, and 4). [e] Values in parentheses denote probable errors.

In 1-indanone the CC bond angles of the CH_2CH_2 grouping can reasonably be expected to be *ca.* 109°. Thus 1-indanone exhibits ideal conditions for comparing experimental results with theory: no substituents on H-bearing C atoms, rigidity of the CC skeleton, no ambiguities in the assignment of ^3J *vs.*$_{HH}$ $^2J_{HH}$, and a completely resolved spectrum.

However, the analysis of the A_2B_2 portion of the 1-indanone spectrum presents a problem inasmuch as the origin of this band, and thus the line positions as measured from the origin, are ill-defined; because of long-range coupling with protons of the aromatic ring, the fine structure in the low-field wing of the A_2B_2 part is perturbed (Figures 1 and 2) and the origin of the otherwise symmetrical A_2B_2 pattern cannot be accurately located. Of the various attempts to circumvent this difficulty (see Results and Discussion, part B3) only the substitution of all aromatic protons by deuterons finally led to a satisfactory solution (Figure 3). Now, the low-field portion of the band for the alicyclic protons exhibits almost all the fine structure of the high-field portion (Figure 4), even though some line broadening of the low-field lines owing to HD coupling is still observed. On this basis the line positions relative to the center of the A_2B_2 band could be located accurately for the determination of reliable nmr parameters (Table I).

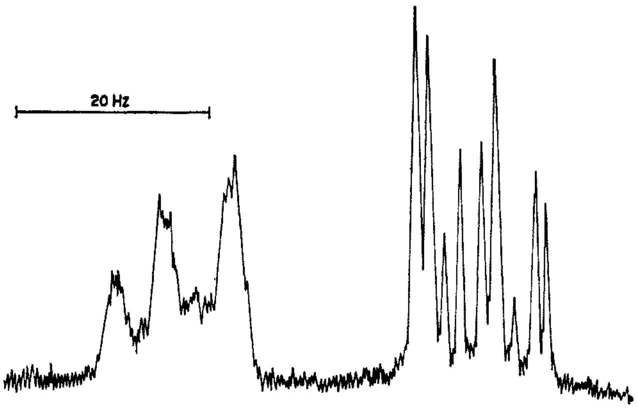

Figure 1.—Nmr spectrum of alicyclic protons in 1-indanone.

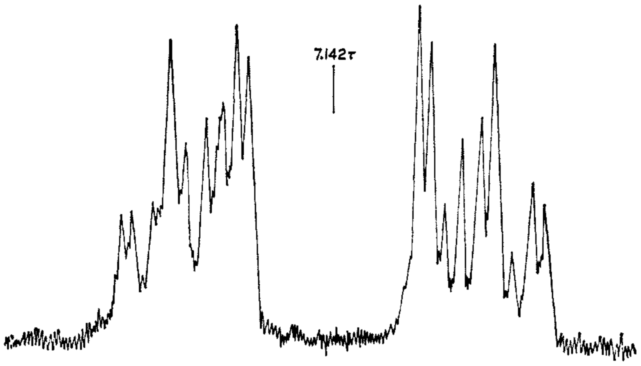

Figure 2.—Nmr spectrum of low-field portion of alicyclic protons of 1-indanone.

Analysis of the A_2B_2 Band of the 1-Indanone Spectrum.—An approximate value for $|\omega_A - \omega_B| \equiv \delta$ was found from the second moment of the spectrum, and this made it possible to identify the *ab* subpattern of the 𝒜 type (peaks 2 and 10), which is a function of δ and $|J' + J''|$. Then, with the aid of known relations,[8] the 2 × 4 ℬ-type lines were tentatively assigned to peaks, 3, 4, 6 or 7, and 8; they are functions of δ as well as of $|J' - J''|$ and $|J_A - J_B|$. The values for the parameters that can be obtained in this way agree quite well (Table I, column II) with those reported by Hecht[9] (*cf.* Table I, column IV).

However, disagreement appears when the entire spectrum, which includes also the other nonanalytical lines of the 𝒜 type, is fitted to obtain the remaining parameter $|J_A + J_B|$. The only practical method of doing this proved to be the computation of spectra with δ, J', J'', and $J_A - J_B$ fixed and $J_A + J_B$ varying at discrete intervals between −40 and +30 Hz. In this way the whole gamut of reasonable values for J_A and J_B, with like and unlike signs, and with signs equal to and opposite those of J' and J'', was covered.

Absence of serious discrepancies with experiment was noted only in spectra computed with values of J_A and J_B close to the final ones (Table I, column III). For a

---

(6) E. Lustig, quoted in ref 1a, p 213.

(7) (a) K. L. Servis and J. D. Roberts, *J. Phys. Chem.*, **67**, 2885 (1963). (b) Technical Report 25, under Office of Naval Research Contract Nonr 220 (26), Task No. NR 055-388, Aug 1963.

(8) See Table I, footnote *b*.

(9) See Table I, footnote *d*.

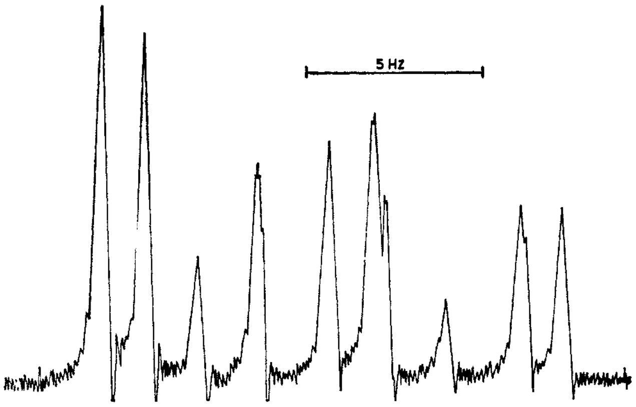

Figure 3.—Nmr spectrum of alicyclic protons in 4,5,6,7-d_4-1-indanone.

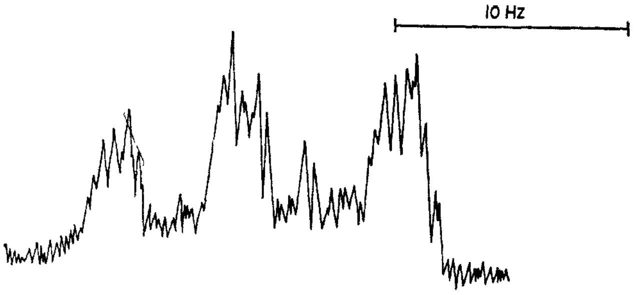

Figure 4.—Nmr spectrum of high-field portion of alicyclic protons of 1-indanone.

fair comparison of Hecht's and our values, the (computed) spectrum based on the former had to be moved 0.8 Hz downfield, so that the rms deviation for these spectra was minimized. Apart from the rather high deviation of 0.4 Hz and three lines differing from our observed lines by more than 0.4 Hz, two lines appearing in the spectrum computed with Hecht's values were not observed in our spectrum at all: one upfield by 0.2 Hz from peak 1, and another one upfield by 0.5 Hz from peak 10, both about $^1/_8$ as intense as their low-field neighbors. Resolution and signal-to-noise ratio in our experiments were sufficient to detect these lines if present. Further confidence in the correctness of our parameters is justified by the small rms error in fitting of 0.075 Hz, after ten iterations.[10]

Results and Discussion

A priori distinction between ω_A and ω_B, J_A and J_B, and J' and J'' is not possible in A_2B_2 spectra, and these parameters must be assigned on the basis of analogies with related molecules or the study of deuterated compounds.

A. Chemical Shifts.—The fairly obvious assumption that the low-field band broadened by long-range coupling belonged to the 3 protons was confirmed experimentally by substituting deuterons for the 2 protons (**5**): the well-resolved, high-field band disappeared, while the low-field triplet-like band collapsed into a single peak 2 Hz broad at τ 6.90. Furthermore, since the spectrum could be analyzed very accurately as an A_2B_2 system, *i.e.*, with the only two chemical shifts, only two types of protons exist in this system and hence the cyclopentenone portion of the molecule seems to be planar on the nmr time scale.

B. Spin Coupling between Protons. 1. Geminal.—Also, in the saturated part of a five-membered rigid ring system which can be considered as representative of most unstrained molecules, we have now unambiguously proved the signs of $^2J_{HH}$ and $^3J_{HH}$ to be opposite. Both $^2J_{HH}$ values are lower than -12.4 Hz, the value observed for CH_4. This finding is in qualitative agreement with substantiated predictions made by Barfield and Grant,[11] and with further considerations by Pople and Bothner-By,[12] that π bonds adjacent to geminal protons should make a negative contribution to $^2J_{HH}$. In 1-indanone this contribution would be expected to be equal, if the dihedral angles between π bonds (from the benzene ring and the carbonyl group) and the HCH planes were equal. That the two $^2J_{HH}$ values here differ by about 1.7 Hz is not necessarily significant in this connection. At any rate, it must be remembered that in ring compounds "the quantitative relationships (for dihedral angles; *cf.* above) are not as clear as those for freely rotating compds." [11]

Whereas the values of 3.9 and 1.8 Hz reported elsewhere[9] for the two $^2J_{HH}$ values in 1-indanone are incorrect, as shown by our analysis, and out of line with $^2J_{HH}$ values in similar bonding situations,[13] our values of about -14.3 and -16.0 Hz are in accord with such $^2J_{HH}$ values. No decision can be made as to the assignment of these two values to J_{22} and J_{33}, because in molecules closely related to 1-indanone these J values do not show any obvious relation to the 2 or 3 position. For example, in cyclopentenones[14,15] J_{22} values range from 11 to 18 Hz and in substituted 1-indanones[16] J_{33} values range from 14 to 18 Hz; 18 Hz was reported for J_{22} in a 3,3-disubstituted 1-indanone.[17] Stereospecifically deuterated 1-indanones may eventually make it possible to assign J_A and J_B to J_{22} and J_{33}.

2. Vicinal.—If the five-membered ring (*cf.* above) has a planar configuration, the dihedral angles are approximately 0 for the 2 and 3 protons that are *cis* with respect to each other, and are *ca.* 120° for the *trans* pair. Thus even a qualitative application of the Karplus relation leaves little doubt that $J' = 8.45$ and $J'' = 3.37$ Hz are $^3J_{cis}$ and $^3J_{trans}$, respectively.

3. Longe-Range (Interannular).—In the related molecule indene, the aromatic ring proton next to the CH_2 group proved to be responsible for the major part of the broadening of the CH_2 doublet, as shown by the effect of substituting methyl groups for aromatic protons (one at a time) on the line width of the CH_2 doublet components.[18] However, in monomethyl-1-indanones with methyl groups in the 4, 5, and 7 positions,[19] the low-field portion of the A_2B_2 band remained blurred. Since it was not clear whether the protons on the aromatic ring or on the methyl groups

---

[10] The best fit was obtained by assigning peak 7 to the $\mathcal{B}$ group. Lines can be assigned unambiguously to $\mathcal{A}$ and $\mathcal{B}$ groups in A_2B_2 systems by using double resonance and multiple quantum transitions: E. Lustig, E. P. Ragelis, N. Duy, and J. A. Ferretti, submitted for publication.

[11] M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

[12] J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

[13] See Table I, footnote *c*.

[14] J. D. Edwards, Jr., and N. Ichikawa, *J. Org. Chem.*, **29**, 503 (1964).

[15] P. J. Kropp, *J. Am. Chem. Soc.*, **85**, 3779 (1963).

[16] D. N. Kevill, G. A. Coppens, M. Coppens, and N. H. Cromwell, *J. Org. Chem.*, **29**, 382 (1964).

[17] B. W. Rockett and C. P. Hauser, *ibid.*, **29**, 1394 (1964).

[18] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 592 (1963).

[19] H. O. House and G. H. Rasmussen, *J. Org. Chem.*, **28**, 31 (1963). We are greatly indebted to Professor House for copies of monomethyl-1-indanone spectra.

are long range coupled to the 3 protons, 4,5,6,7-tetramethyl-1-indanone (**4**) was synthesized. Even in the spectrum of this compound the 3-proton band showed the same complex splitting pattern as in the other 1-indanones mentioned; it is therefore concluded that some unspecified $CH_3 \cdots CH_2$ coupling exists and that methyl substitution cannot be applied in all cases to pinpoint coupling between protons bonded on fused aromatic and alicyclic rings.

That aromatic as well as methyl protons can be involved in such long-range coupling was demonstrated by a double-resonance experiment:[20] when a second radio-frequency field was applied at the frequency of the only aromatic (5) proton in 7-hydroxy-4,6-dimethyl-1-indanone,[21] a sharpening of some of the peaks in the 3-proton band was noted, but it still did not yield the desired mirror image of the 2-proton band. 1-Indanones with "nmr-inactive" substituents are thus needed to establish which aromatic protons are coupled with the 3 protons.

Experimental Section

Preparations.—Friedel–Crafts acylation of 1,2,3,4-tetramethylbenzene (prehnitene) with 3-chloropropionyl chloride yielded 54% of 3-chloropropio-2,3,4,5-tetramethylphenone (**1**) and 10% of 2,3,4,5-tetramethylphenyl vinyl ketone (**2**) which readily resinified on standing (**3**). Cyclization of the 3-chloropropio-2,3,4,5-tetramethylphenone in concentrated sulfuric acid gave 4,5,6,7-tetramethyl-1-indanone (**4**) in 38% yield, together with 14% of 3-chloropropionic acid occurring from keto cleavage. 1-Indanone was converted to 2,2-d_2-1-indanone (**5**) in 85% yield by the base-catalyzed exchange of the protons in the 2 position with heavy water. Isotopically pure 3-chloropropiophenone-d_5 (**6**) was synthesized in 68% yield by the action of 3-chloropropionyl chloride on benzene-d_6 and was cyclized, in sulfuric acid-d_2, to 2,2,4,5,6,7-d_6-1-indanone (**7**) in 35% yield at 100° for 2.5 hr, or to 4,5,6,7-d_4-1-indanone (**8**) in 21% yield at 85° for 1 hr. 2,2,4,5,6,7-d_6-1-Indanone (**7**) was converted to 4,5,6,7-d_4-1-indanone (**8**) in 74% yield *via* the base-catalyzed exchange of the deuterons in the 2 position with light water.

Physicochemical Determinations.—Melting points are corrected. Unless stated otherwise, the infrared spectra were determined with a Beckman IR-5 spectrometer. Molecular weights were determined on a Model 301 Mechrolab vapor pressure osometer. For nmr spectroscopy a Varian A-60 spectrometer with carefully calibrated sweep and suitably modified sweep circuitry was used with a sweep rate of 0.05 Hz/sec and a chart scale of 0.5 Hz/cm (Figure 1). Samples of 1-indanone and 4,5,6,7-d_4-1-indanone were vacuum degassed 15% solutions in CS_2 ($\sim$2 *M*); samples of other compounds were either neat liquids or undegassed CS_2, $CDCl_3$, or CCl_4 solutions of solids. For the final iterative analysis by computer with the aid of the program LAOCOON II,[7] the average of eight out of twelve traces was used; four traces were rejected because one or more lines deviated from the mean by more than 0.15 Hz.

Preparation of 3-Chloropropio-2,3,4,5-tetramethylphenone (1).—In a 100-ml, three-necked Morton flask equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser fitted with a drying tube, were placed 40 ml of dry carbon disulfide and 18.7 g (0.140 mole) of anhydrous aluminum chloride. To this stirred mixture was added a solution consisting of 13.4 g (0.0999 mole) of 1,2,3,4-tetramethylbenzene, 15.0 g (0.188 mole) of 3-chloropropionyl chloride, and 5 ml of dry carbon disulfide over a 90-min period.

After the reaction mixture was stirred for an additional 3 hr at room temperature, the carbon disulfide was removed under reduced pressure. The dark, viscous residue which remained was added to 300 g of cracked ice containing 25 ml of concentrated hydrochloric acid. The crude solid which separated was collected, washed with four 200-ml portions of cold water, dried, and recrystallized from 150 ml of methanol containing 2 g of decolorizing charcoal.

The yield of impure 3-chloropropio-2,3,4,5-tetramethylphenone (**1**) was 12.1 g (54%), mp 53–57°.

The above phenone (**1**), which was contaminated with hydrogen chloride, was purified by dissolving it in 75 ml of ether, washing the ether solution with two 25-ml portions of cold saturated sodium bicarbonate solution and three 25-ml portions of cold water, and drying the ether solution over sodium sulfate. The ether was removed under reduced pressure and the residue (10.5 g) was recrystallized from 130 ml of hot *n*-heptane to yield 8.0 g (36%) of 3-chloro-2,3,4,5-tetramethylphenone (**1**), mp 56.6-57.5°.

Anal. Calcd for $C_{13}H_{17}ClO$: C, 69.48; H, 7.63; Cl, 15.77. Found: C, 70.06; H, 7.63; Cl, 15.35.

The above methanolic mother liquor was diluted with 50 ml of water and extracted with three 50-ml portions of ether. The total ether extract was washed with two 25-ml portions of saturated sodium bicarbonate solution and two 25-ml portions of water, and then was dried over Na_2SO_4. The ether was removed under reduced pressure and the residual orange oil was vacuum distilled through a Kontes short-path distillation apparatus to yield 2.0 g of a product: bp 94–95° (0.45 mm), $n^{28}\text{D}$ -1.5508. This product, which readily polymerized upon standing, was identified by its nmr and infrared spectra as 2,3,4,5-tetramethylphenyl vinyl ketone (**2**). The nmr spectrum consisted of 15 lines. Two lines at τ 7.83 and 7.90 were assigned to the methyl protons, twelve lines between τ 3.13 and 4.32 were assigned to the vinyl protons, consistent with an ABC spectrum; and one line at τ 3.07 was assigned to the lone proton of the aromatic ring. The spectrum and line intensities were consistent with the structure of 2,3,4,5-tetramethylphenyl vinyl ketone. The infrared spectrum (KBr disk) showed absorption bands at 6.01 (vs, C=O), 3.43 (s, CH_3, asymmetrical), 3.15 (sh, CH_3, symmetrical, 6.25 (m, C=C), 6.42 (w, C=C), 10.12 (m, CH=C), 10.66 (m, $C{=}CH_2$), and 11.48 (m, CH) μ.

One gram of the polymerized 2,3,4,5-tetramethylphenyl vinyl ketone (**2**) was purified by dissolving it in 10 ml of CCl_4 and reprecipitating it by adding the solution to 550 ml of methanol. The poly(2,3,4,5-tetramethyl vinyl ketone) (**3**) had a polymer melt temperature of 200° and a number average molecular weight of 9700. The infrared spectrum (KBr disk) showed absorption bands at 5.98 (S, C=O), 3.44 (M, CH_3, asymmetrical), 3.51 (Sh, CH_3, symmetrical), 12.72 (S), and 13.14 (S, CH_2CH_2) μ.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.33; H, 8.93.

Preparation of 4,5,6,7-Tetramethyl-1-indanone (4).—In a 35-ml, round-bottom flask provided with a magnetic stirrer and with a reflux condenser fitted with a drying tube were placed 3.0 g (0.013 mole) of 3-chloropropio-2,3,4,5-tetramethylphenone (**1**) and 25 ml of concentrated sulfuric acid (sp gr 1.84). The mixture was stirred for 80 min over the range 30–50°,[22] cooled to room temperature, and added to 200 g of cracked ice. The crude 4,5,6,7-tetramethyl-1-indanone (**4**) which precipitated was collected, washed with 100 ml of water, and dried. Three recrystallizations from methanol with cooling acetone in solid carbon dioxide mixture and one final recrystallization from *n*-hexane gave 0.90 g (38%) of 4,5,6,7-tetramethyl-1-indanone (**4**): mp 151–153°, oxime mp 215–216° (lit.[23] mp 152–153°, oxime mp 214–215°). The infrared spectrum (KBr disk) of 4,5,6,7-tetramethyl-1-indanone (**4**) showed absorption bands at 3.36 (sh, CH_3, asymmetrical), 3.45 (m, CH_3, symmetrical), 5.92 (vs, C=O), and 6.33 (m, C=C) μ. Ether extraction of the above aqueous phase yielded 0.2 g (14%) of 3-chloropropionic acid, easily identified by its nmr and infrared spectra.

Preparation of 2,2-d_2-1-Indanone (5).—In a 25-ml, round-bottom flask equipped with a Dean–Stark trap and a magnetic stirrer were placed 2.0 g (0.015 mole) of 1-indanone, 11.0 g (0.544 mole) of deuterium oxide (99.7% isotopic purity), 0.10 g (0.00072 mole) of anhydrous potassium carbonate, and 8.0 ml of dry dioxane.[24] The stirred, yellow-orange solution was brought to reflux and 4 ml of the distillate was collected, causing the reaction mixture to become turbid. At this point, the heat was removed; the reaction mixture was cooled to room temperature with stirring and extracted with two 20-ml portions of ether.

---

(20) We are grateful to Mr. Ross Pitcher (Varian Associates) for carrying out the double-irradiation experiment.

(21) We are grateful to Dr. C. K. Cain (McNeill Laboratories) for a sample of this compound.

(22) The yield drops to 17% if one uses a temperature of 100° for 2 hr.

(23) G. Baddeley, G. Holt, and S. M. Makar, *J. Chem. Soc.*, 3289 (1952).

(24) The dioxane was dried over Molecular Sieves 4A.

The ether extracts were combined, washed with two 20-ml portions of cold water, and dried over magnesium sulfate. After the ether was removed under reduced pressure, the residue was recrystallized from 25 ml of petroleum ether (30–60°) to yield 1.7 g (84%) of 2,2-d_2-1-indanone (5), mp 39–40°. The nmr spectrum in the alicyclic region showed only one absorption peak at τ 6.90 corresponding to the protons in the 3 position of 1-indanone.

Preparation of 3-Chloropropiophenone-d_5 (6).—This compound was prepared in the same manner reported[25–27] for 3-chloropropiophenone. A solution of 26.6 g (0.21 mole) of 3-chloropropionyl chloride in 40 ml of benzene-d_6 was treated with 32 g (0.24 mole) of anhydrous aluminum chloride in 60 ml of dry carbon disulfide[27] and stirred for 75 min. The carbon disulfide was removed under reduced pressure and the dark residue was added to 500 g of cracked ice containing 50 ml of concentrated hydrochloric acid. The solid which separated was collected, dried, and recrystallized twice from a solution of 80% *n*-pentane and 20% *n*-heptane to yield 24.8 g (68%) of 3-chloropropiophenone-d_5 (6), mp 47.5–48.5° (lit[26,27] for 3-chloropropiophenone, mp 47–48°). The nmr spectrum showed no hydrogen absorption in the aromatic region. The ethylene region exhibited a typical A_2B_2 pattern.

Preparation of 2,2,4,5,6,7-d_6-1-Indanone (7).—3-Chloropropiophenone-d_5 (6) was cyclized in the manner reported[27] for the cyclization of 3-chloropropiophenone. A mixture of 1.7 g (0.0098 mole) of 3-chloropropiophenone-d_5 (6) and 20 g of sulfuric acid-d_2[28] was heated at 100° for 2.5 hr in a flask equipped with a magnetic stirrer and a reflux condenser fitted with a drying tube. The dark mixture was then cooled to room temperature and added to 150 g of cracked ice. The small amount of yellow solid that precipitated (0.1 g) was collected and washed with five 50-ml portions of cold water. The aqueous phase was extracted with four 50-ml portions of ether, and the combined ether extracts were washed with four 50-ml portions of water and dried over potassium carbonate. Removal of the ether left a yellow solid (0.6 g) which, when combined with the original solid and recrystallized from *n*-hexane containing a small amount of decolorizing charcoal, gave 0.45 g (35%) of 2,2,4,5,6,7-d_6-1-indanone (7),[29,30] mp 41–42° (lit.[27] for 1-indanone, mp 40–41°). The nmr spectrum showed only one absorption peak at τ 6.90 for the methylene hydrogens in the 3 position of 2,2,4,5,6,7-d_6-1-indanone (7). The 2,2,4,5,6,7-d_6-1-indanone (7) was converted to 4,5,6,7-d_4-1-indanone (8), mp 37–38°, in the manner previously described for the conversion of 1-indanone to 2,2-d_2-1-indanone (5), except that light water was used.

Preparation of 4,5,6,7-d_4-1-Indanone (8).—A mixture of 5.00 g (0.0287 mole) of 3-chloropropiophenone-d_5 (6) and 100 g of sulfuric acid-d_2 was stirred under a nitrogen atmosphere at 85° for 1 hr. The reaction mixture was cooled, added to cracked ice, and extracted with three 150-ml portions of ether. The combined ether extracts were washed with 50 ml of ice–water and dried over potassium carbonate. The ether solution was concentrated to 5 ml and chromatographed on 42–60 mesh alumina (Alcoa, Type F-1). Elution with 150 ml of petroleum ether (30–60°) gave 0.90 g (21%) of 4,5,6,7-d_4-1-indanone (8), mp 37–38°.

Registry No.—1-Indanone, 83-33-0; **1**, 716-28-9; **2**, 10036-00-7; **4**, 711-43-3; **5**, 10036-02-9; **6**, 10036-03-0; **7**, 10036-04-1; **8**, 10036-05-2.

Acknowledgment.—We thank Dr. Jo-Yun T. Chen of this division for the infrared measurements and interpretations and Mr. N. Duy for able assistance with nmr spectroscopy.

---

[25] W. J. Hale and E. C. Britton, *J. Am. Chem. Soc.*, **41**, 845 (1919).

[26] J. B. Conant and W. R. Kirner, *ibid.*, **46**, 240 (1924).

[27] A. Rahman and A. E. Gastaminza, *Rec. Trav. Chim.*, **81**, 645 (1962).

[28] The carbon disulfide was dried over Molecular Sieves 4A.

[29] 98% D_2SO_4 of a minimum isotopic impurity of 99% deuterium.

[30] 2,2,4,5,6,7-d_6-1-Indanone (7) was also obtained in 53% yield by heating the reaction mixture for 1 hr at 100°.

The Alkaline Hydrogen Peroxide Oxidation of Phenyl-2-propanones[1a]

DREXEL D. JONES AND DONALD C. JOHNSON[1b]

The Institute of Paper Chemistry, Appleton, Wisconsin

Received August 17, 1966

The alkaline hydrogen peroxide oxidations of phenyl-2-propanones have been found to proceed by two competitive mechanisms. Product analyses and kinetic studies revealed the primary reaction to involve cleavage to a benzaldehyde and acetic acid. A slow competitive cleavage also occurs to produce the benzyl alcohol and acetic acid. A slow competitive cleavage also occurs to produce the benzyl alcohol and acetic acid which apparently result from the intermediate ester formed in a Baeyer–Villiger oxidation. The primary oxidation was found to be first order with respect to both oxidant and substrate. Hydroperoxide anion was shown to be the reactive peroxide species from studies of the effects of sodium hydroxide concentration and peroxide species concentration on reactivity. Evidence was found suggesting that the enol tautomer is the reactive substrate. The mechanism proposed involves attack of the hydroperoxide anion on the enol as the rate-determining step. Cleavage then is thought to occur by a concerted process with attack on the original carbonyl carbon atom by a second hydroperoxide anion.

The aromatic products obtained from the alkaline hydrogen peroxide oxidation of various lignin-related model compounds were recently investigated.[2] Ketones having a carbonyl group β to the ring, phenyl-2-propanones, reacted when either a hydroxyl or methoxyl substituent was present at the *para* position of the ring. When the carbonyl group was α to the ring, only the ketone having the hydroxyl substituent was reactive. From the unique reactivity of the phenyl-2-propanones and product analysis, Reeves suggested that oxidation of these ketones involved the ring-conjugated enol tautomer. Such a postulation is feasible since the enol content of pure phenyl-2-propanone is nearly 3%, 2×10^4 times as high as that for acetone.[3] The purpose of the present investigation was to determine the mechanism of the alkaline peroxide oxidation of the phenyl-2-propanones.

Experimental Section

All melting points were determined with N.B.S. calibrated total immersion thermometers. The melting points of the ketones and their semicarbazones all showed satisfactory agreement with literature values. Three ketones, deoxybenzoin (Matheson Coleman and Bell), 4-phenyl-2-butanone (K & K), and phenyl-2-propanone (K & K), were commercially available.

Phenyl-2-propanones.—Several of the phenyl-2-propanones were prepared by condensing the appropriate substituted benzaldehyde with nitroethane. The resulting nitropropene was

---

[1] (a) A portion of a thesis submitted by D. D. Jones in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence University, Appleton, Wis., June 1966. (b) To whom inquiries should be addressed.

[2] R. H. Reeves and I. A. Pearl, *Tappi*, **48**, 121 (1965).

[3] A. Gero, *J. Org. Chem.*, **19**, 1960 (1954).