mediately rearrange to ocimene (VI).[7] Other possible reactions of the intermediate and the stereochemical properties of the intermediate were not considered.

Application of the same concept to the pyrolysis of β-pinene (II) leads to the biradical (VII) which unlike V is asymmetric. Models show that hydrogen atoms from the isopropyl residue (positions (9) and (10)) may be transferred either to positions (2) or (7). One would expect transfer to position (7) with the formation of an internal olefin (IX) to be favored over that to position (2) which leads to an exo-structure (VIII). Limonene (IX) so formed should be optically pure. Recombination of the biradical (VII) unlike that of V would regenerate an unracemized pinene. Bond fission between carbon atoms (3) and (4) would lead to myrcene (X).

Goldblatt and Palkin[8] report the vapor phase pyrolysis of β-pinene to lead to myrcene (X) and *l*-IX of "singularly high rotation." The rotation of the isolated limonene was about 10% under the maximum possible.[9] No VIII was reported. The small deficit in rotation of IX might originate from the presence of a little VIII.

Hunt and Hawkins[10] report that the isomerization of β-pinene proceeds as a first order reaction unaffected by small quantities of hydroquinone. Dilution with *dl*-IV does not affect the rate constants. The reported activation energy is about 48 kcal.

Data which critically test the prediction that recovered β-pinene would be unracemized have not been reported.

The proposed mechanism provides a stereochemical correlation between *l*-β-pinene and *l*-limonene.

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[7] The formation of ocimene was later reported, F. O. Rice, U. S. Patent 2,190,369, February 13, 1940. No other investigator has reported ocimene.

[8] L. A. Goldblatt and S. Palkin, THIS JOURNAL, **63**, 3517 (1941).

[9] Ref. 4, p. 152 gives 126.8°; ref. 8 reports 114.9°.

[10] H. G. Hunt and J. E. Hawkins, THIS JOURNAL, **72**, 5618 (1950).

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

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The Association of Tri-*p*-xenylmethyl

BY TING-LI CHU AND S. I. WEISSMAN

Recent measurements of the magnetic susceptibility of solutions in toluene of tri-*p*-xenylmethyl[1] show that over the temperature range 0 to 60° and the concentration range 0.018 to 0.032 mole per liter the molar susceptibility is constant. Use of the conventional correction for diamagnetism leads to a constant degree of association of 0.20.

In connection with other work we have investigated the absorption spectra of solutions of tri-*p*-xenylmethyl in toluene. We find that the Beer–Lambert law is obeyed over the concentration range 2×10^{-4} to 4.5×10^{-3} mole per liter, and that the molar extinction coefficient is independent of temperature over the range 10 to 40°. The shape of the absorption curves obtained by us is identical with those already given in the literature.[2,3] The molar extinction coefficient at the peak at 6150 Å. is 1525. These results indicate that tri-*p*-xenylmethyl is not associated in toluene solution.

Our solutions were prepared on the vacuum bench by the method already described by Lewis, Lipkin and Magel.[2] A solution of a weighed sample of pure tri-*p*-xenylcarbinol[4] in freshly distilled acetyl chloride was refluxed for 12 hours. The resulting solution was made up to a known volume and an aliquot pipetted into a Pyrex absorption cell. The cell was quickly attached to the vacuum line where all subsequent operations were carried out. The acetyl chloride was evaporated and the solid halide subjected to prolonged evacuation at about 80°. Any trace of acid remaining in the system was neutralized by introduction of triethylamine vapor. A measured volume of toluene and a trace of triethylamine (each dried over sodium–potassium alloy) were distilled into the cell containing the halide, and silver amalgam was then introduced by a vacuum dumper. The cell was sealed off under vacuum, and reduction effected by several minutes shaking of the solution with the amalgam. The free radical solutions prepared in this way remained unchanged during several days storage in the dark at room temperature.

We may report, in addition, that α-naphthylphenyl-*p*-xenylmethyl also obeys Beer's law with a temperature-independent extinction coefficient. A mixture of this free radical with tri-*p*-xenylmethyl, however, does not obey Beer's law, nor is the absorption at fixed concentration independent of temperature. The two free radicals apparently associate in toluene solution.[5] According to our data ΔF^0 for the association is about -4 kcal. per mole at 25°, while ΔH is about -12 kcal. per mole.

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[1] P. W. Selwood and R. M. Dobres, THIS JOURNAL, **72**, 3860 (1950).

[2] G. N. Lewis, D. Lipkin and T. T. Magel, *ibid.*, **66**, 1579 (1944).

[3] It has been demonstrated (ref. 2) that unless extreme precautions are taken, tri-*p*-xenylmethyl is converted to another free radical of unknown constitution. The pure tri-*p*-xenylmethyl is blue-green, the other free radical red. In a recent paper Dobres and Selwood (THIS JOURNAL, **72**, 5731 (1950)) describe tri-*p*-xenylmethyl as "deep burgundy." Apparently our blue-green substance and the one studied by Dobres and Selwood are different.

[4] This material was generously supplied by Professor Lipkin. It is a portion of the preparation used in the work of Lewis, Lipkin and Magel.

[5] A result pointing in the same direction has been obtained by C. S. Marvel and Chester M. Himel, THIS JOURNAL, **64**, 2227 (1942).

DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY
SAINT LOUIS 5, MISSOURI

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Rate of Oximation and Extent of Enolization of Alkyl Aryl Ketones[1]

BY MARY J. CRAFT,[2] BILLY F. LANDRUM,[2] EDGAR C. SURATT[2] AND CHAS. T. LESTER[3]

We have previously reported the rate of oxime formation of four series of ketones.[4] We have ex-

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[1] This work was made possible through a contract with the Office of Naval Research.

[2] Taken from respective Ph.D. Dissertations, Emory University, 1950.

[3] Responsible co-author.

[4] (a) E. C. Suratt, J. R. Proffitt, Jr., and C. T. Lester, THIS JOURNAL, **72**, 1561 (1950); (b) M. J. Craft and C. T. Lester, *ibid.*, **73**, 1127 (1951).

tended this work to include some *p*-alkylphenyl alkyl ketones, phenyl isopropyl ketone and *p*-xylyl isopropyl ketone. These latter compounds and the former four series have also been treated with methylmagnesium bromide in an active hydrogen apparatus.[5] The new rate values are recorded in Table I; the active hydrogen determinations in Table II.

TABLE I

RATE OF OXIME FORMATION OF ARYL ALKYL KETONES AT 30°

Rate constant in liters/moles/sec. × 10^3

		Alkyl	
Aryl	Methyl	Ethyl	Isopropyl
Phenyl	24.6^a	14.5^a	2.22
p-Methylphenyl	16.2	9.90	1.79
p-Ethylphenyl	16.5	9.90	1.73
p-Isopropylphenyl	16.7	10.3	1.51
p-*t*-Butylphenyl	16.7	10.0	1.84
p-Xylyl	1.84^{4a}	0.863^{4a}	0.19

TABLE II

REACTION OF ARYL ALKYL KETONES WITH METHYLMAGNESIUM BROMIDE

E = % enolization; A = % addition

	Alkyl							
	Me		Et		*n*-Prop-*n*-Hept^a		Isoprop	
Aryl	E	A	E	A	E	A	E	A
Phenyl	9	88	4	96	3–4	92–99	2	100
p-Alkylphenyl^b	7–9	87–90	3–4	91–95	...	...	2–3	93–98
p-Xylyl	15	87	7	96	7–8	90–94	5	93
Carvacryl	18	80	8	88	8–9	81–87	...	....
Thymyl	25	71	21	75	19–21	70–81	...	....

[a] The range of values given embraces all the *n*-alkyl groups from propyl through heptyl. [b] The range of values embraces the compounds in which the *p*-alkyl groups were methyl, ethyl, isopropyl and *t*-butyl.

There is qualitative agreement between rate of oximation and extent of enolization. For any given series of ketones containing the same acyl group the following approximation exists, oximation rate: phenyl = *p*-alkylphenyl > *p*-xylyl = carvacryl > thymyl. Enolization: phenyl = *p*-alkylphenyl < *p*-xylyl = carvacryl < thymyl.

The *p*-xylyl, carvacryl and thymyl methyl ketones give enolization values in close agreement with those reported by Kadesch[6] for the appropriate 4,7-dialkyl-α-indanones. These latter compounds have been termed "partially hindered ketones."[7]

Experimental

Ketones.—The *n*-alkyl ketones derived from benzene, *p*-xylene, 2-*p*-cymene and 3-*p*-cymene have been described.[4] The other ketones were all prepared by a suitable Friedel-Crafts reaction.[8] The *p*-alkylphenyl alkyl and phenyl isopropyl ketones will be described later. The *p*-xylyl isopropyl ketone had the following properties: b.p. 115° at 5 mm.; d_{30} 0.9747; n^{30}D 1.5134; *Anal.* Calcd. for $C_{10}H_{16}O$: C, 81.8; H, 9.09. Found: C, 81.7; H, 9.17.

Rates of Oximation.—The medium and method were the same as that previously described.[4] The methyl and ethyl ketones were run in solution 0.05 *M* with respect to ketone and hydroxylamine hydrochloride. The isopropyl *p*-xylyl ketone was run, using 0.2 *M* solution of ketone and 0.1 *M* solution of amine. The other isopropyl ketones were run using 0.1 *M* each of ketone and hydroxylamine. The *k* values reported are averages of duplicate runs that agreed within 5%.

Active Hydrogen Determinations.—The measurements were made in duplicate, adding excess methylmagnesium bromide in dibutyl ether to 0.002 *M* amounts of each ketone. In an effort to obtain maximum reaction, the mixture was heated at 50° for 5 min. The values for enolization were reproducible to ±1%; those for addition to ±3%.

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DEPARTMENT OF CHEMISTRY
EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA

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[5] C. T. Lester and J. R. Proffitt, Jr., THIS JOURNAL, **71**, 1877 (1949).

[6] R. G. Kadesch, *ibid.*, **66**, 1207 (1944).

[7] A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 821.

[8] C. T. Lester and E. C. Suratt, THIS JOURNAL, **71**, 2262 (1949).

The Reduction of Cholestenone Enol Acetate by Sodium Borohydride[1]

BY WILLIAM G. DAUBEN AND JEROME F. EASTHAM

In a continuation of the study of the conversion of cholestenone to cholesterol[2] it has been found that the enol acetate of cholestenone is reduced by sodium borohydride to yield approximately 75% cholesterol. Previously this reduction had been carried out with lithium aluminum hydride and cholesterol obtained in only 35% yield.[2] Use of the borohydride greatly simplifies the experimental technique required for the reduction. Whereas with the aluminum hydride anhydrous ether is employed as a solvent and the reaction is carried out in an atmosphere of nitrogen, the reduction can now be conducted in methanolic solution with no special precautions for anhydrous conditions. The work-up and isolation of products is essentially that previously described.[2]

In contrast to the results with lithium aluminum hydride, no cholestenone is obtained from the reaction when excess sodium borohydride is employed if the reaction is allowed to continue for a sufficient length of time. Similar to the earlier results, however, is the evidence that the four isomeric stenols, cholesterol, epicholesterol, and the two Δ^4-stenols (Δ^4-cholesten-3α-ol and Δ^4-cholesten-3β-ol), are formed in the reduction, with the cholesterol preponderating. A limited study of the effect of conditions for the reaction has been made. Low temperature and addition of hydride to ester ("inverse mixing") seem to favor the proportion of cholesterol. Thus, under otherwise similar conditions,

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[1] This work was supported by a grant from the University of California Cancer Fund.

[2] W. G. Dauben and J. F. Eastham, THIS JOURNAL, **73**, 3260 (1951).