lation, and in some cases before the second chromatography, each set of combined fractions was taken up in ether and extracted with 12% hydrochloric acid, thereby removing completely the substance which g.l.c. had shown to be present after but not before chromatography. One fraction of the initial chromatogram showed only the g.l.c. peak corresponding to this acid-soluble compound, and had $\lambda_{\max}^{\mathrm{CCl_4}}$ 2.95, 3.08, 5.90 (impurity?), 6.06 (all weak peaks); n.m.r. (CCl_4), 9.09 (s), 9.23 τ (s). This is thus tentatively characterized as 10-amino-1,1-dimethyl-*trans*-decalin, formed from the isocyanate during chromatography. The amine amounted to 0.24 g. (loss of weight on acid extraction), or the equivalent of an additional 19% of isocyanate III.

Isolation of the Amide IId.—The first amidic component to be eluted was isolated after two chromatograms as 0.047 g. (3.4% based on starting hydrazide IIc) of an oil which slowly crystallized. This was sublimed at *ca.* 60° (*ca.* 10^{-6} mm.) to afford the amide IId as white prisms, m.p. 75–77° (microscope hot stage); $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.1, 6.0, 6.2 μ (weak); n.m.r. (CCl_4), 9.16 (s), 9.20 τ (s). The infrared and n.m.r. spectra of this sample were identical with those of material prepared by ammonolysis of the acid chloride, and the melting point of a mixture was undepressed. Mixed fractions contained an additional 0.059 g. of IId (according to g.l.c.) bringing the total yield to 8%.

Isolation of the γ-Lactam.—The second amidic product to be eluted was obtained after acid washing and two chromatograms as 0.159 g. of an oil (11% based on starting hydrazide). Mixed fractions contained, according to g.l.c., an additional 0.038 g. (total yield 14%). The oily γ-lactam was distilled in a Hickman still at 0.05 mm. (bath 130–136°) to afford the analytical sample, $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.1, 5.9 μ; n.m.r. (CCl_4), 2.00 (s), 6.45 (s), 9.10 (s), 9.21 τ (s).

Anal. Calcd. for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76; mol. wt., 207. Found: C, 75.2; H, 10.0; N, 6.7; mol. wt., 207 (mass spectrum[13]),

Isolation of the δ-Lactam Ib.—The final amidic product after acid washing and two chromatograms amounted to 0.115 g. (8% based on starting hydrazide) of white plates, m.p. 134–139°; $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.12, 6.02 μ; n.m.r. (CCl_4), 1.65 (s), 170–205 c.p.s. (m), 9.72 τ (s). When the 160–220 c.p.s. region of the n.m.r. spectrum was scanned while a strong saturating rf field was applied 321 ± 10 c.p.s. to lower field from the 170–205-c.p.s. resonance, the 170–205-c.p.s. multiplet split to a symmetric AB quartet. Mixed fractions contained 0.013 g. bringing the total yield to 9%. After recrystallization from *n*-hexane the white prisms of δ-lactam Ib had m.p. 145.5–146.5°. The material sublimed readily at 100° (0.1 mm.) to afford the analytical sample, m.p. 145.5–146.5°.

Anal. Calcd. for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76; mol. wt., 207. Found: C, 75.6; H, 10.1; N, 7.0; mol. wt., 207 (mass spectrum[13]).

1,1-Dimethyl-*trans*-decalin-10-carboxamide (IId).—A 0.250-g. (0.0012 mole) sample of 1,1-dimethyl-*trans*-decalin-10-carboxylic acid (IIb), m.p. 90–95°, was converted to the acid chloride with 1 ml. of thionyl chloride and 2 drops of pyridine. The crude acid chloride in 25 ml. of benzene was added to a stirred mixture of 10 ml. of benzene[18] and *ca.* 40 ml. of anhydrous ammonia which was allowed to warm to room temperature overnight. The mixture was washed with water, dried over sodium sulfate, and concentrated *in vacuo* to 0.237 g. of tacky brown oil, which was chromatographed on 5 g. of Woelm neutral alumina (activity grade II) to afford 0.122 g. (48%) of oil which slowly crystallized. Sublimation at *ca.* 60° (*ca.* 10^{-6} mm.) afforded the amide IId as white prisms, m.p. 75–77° (microscope hot stage); $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.1, 6.0, 6.2 μ (weak); n.m.r. (CCl_4), 9.16 (s), 9.20 τ (s).

Anal. Calcd. for $C_{13}H_{23}NO$: C, 74.59; H, 11.08; N, 6.69. Found: C, 75.0, 74.8; H, 10.9, 10.7; N, 6.75.

Acknowledgment.—We express thanks to the U. S. Public Health Service, National Institutes of Health, for a grant (A4215) in support of this work, and to Mr. A. O. Clouse for assistance with some of the n.m.r. determinations. The n.m.r. instruments were provided by grants from the U. S. Public Health Service and the National Science Foundation, to whom we are grateful.

(18) Mr. N. G. Schnautz in our laboratory has found that tetrahydrofuran is a superior solvent for this reaction.

4-*t*-Butyl-3-cyclohexenone and 4-*t*-Butyl-3-cyclohexenols

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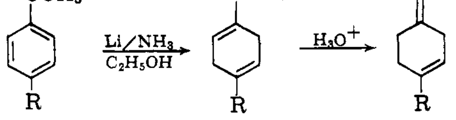
4-*t*-Butyl-3-cyclohexenone (I) was prepared from *p*-*t*-butylanisole. Reduction of I with lithium aluminum hydride gave 4-*t*-butyl-3-cyclohexenol (II). Addition of Grignard reagents to I gave 4-*t*-butyl-1-phenyl-3-cyclohexenol (III) and 4-*t*-butyl-1-methyl-3-cyclohexenol (IV). Nuclear magnetic resonance and infrared spectra of II–IV are discussed. The possibility of transannular intramolecular hydrogen bonding in II–IV and other 3-cyclohexenols is considered.

Preparations of 4-*t*-butyl-3-cyclohexenols were undertaken in order to permit study of transannular OH. . .π intramolecular hydrogen bonding in such compounds.[1] The key intermediate, 4-*t*-butyl-3-cyclohexenone (I), was prepared by a procedure analogous to that reported for synthesis of 4-isopropyl-3-cyclohexenone[2] and 4-methyl-3-cyclohexenone.[3]

Reduction of *p*-*t*-butylanisole with lithium in liquid ammonia plus ethanol presumably gave 4-*t*-butyl-2,5-dihydroanisole, which without isolation, was subjected to oxalic acid-catalyzed hydrolysis of the enol–ether function, to give 4-*t*-butyl-3-cyclohexenone (I), isolated by fractional distillation as a colorless liquid, b.p. 91° (8 mm.). Identification of I is based on ultraviolet spectra, infrared spectra, and gas chromatography, which when taken together, indicate a purity of 96 ± 2%, probable impurities being 4-*t*-butyl-2-cyclohexenone, *ca.* 3%; 4-*t*-butylcyclohexanone, up to 3%; and *p*-*t*-butylanisole, *ca.* 0.2%.



I

R = *t*-butyl

An earlier preliminary report of the preparation of I stated that "lithium metal in ethylenediamine has been used to reduce *t*-butylphenol in good yield to

(1) J. W. Larsen, B. S. thesis, Tufts University, 1962.

(2) N. A. Nelson and G. A. Mortimer, *J. Org. Chem.*, **22**, 1146 (1957), and references cited.

(3) E. A. Braude, and A. A. Webb, with (in part) M. U. S. Sultanbawa, *J. Chem. Soc.*, 3328 (1958).

4-*t*-butyl-3-cyclohexenone."[4] However, when we repeated the reaction under the conditions reported,[4,5] most of the *p*-*t*-butylphenol was recovered. A sixfold increase in the ratio of lithium to phenol gave a complex mixture including unconjugated ketones, but infrared spectra showed clearly that I was at best a minor product. Reggel, *et al.*,[5b] did not list 3-cyclohexenone among the products obtained by treatment of phenol with lithium in ethylenediamine. Furthermore, an attempt to prepare 4-methyl-3-cyclohexenone from *p*-cresol by this procedure[5] was unsuccessful; most of the *p*-cresol was recovered.[6] Therefore, this procedure[5] cannot be recommended for preparation of I, or other 3-cyclohexenones.[7]

Other conditions generally useful for direct reduction of phenols to 3-cyclohexenones have not come to our attention. Preparation of 6-methoxy-2-tetralone from 6-methoxy-2-naphthol in 64% yield by a modified Birch reduction affords an interesting special case.[8] Here, the β,γ-unsaturated bond is stabilized as part of a benzene ring. An alternative to the general method we used, analogous reduction of an N,N-dialkylaniline, has been investigated.[9]

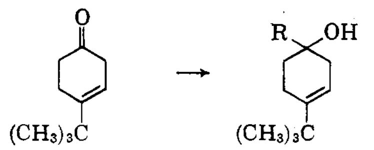
The 2,4-dinitrophenylhydrazone of I was compared to that of 4-*t*-butyl-2-cyclohexenone, prepared from I under conditions which allowed equilibration (Table I).

TABLE I

COMPARISON OF 2,4-DINITROPHENYLHYDRAZONES OF 2-CYCLOHEXENONES AND 3-CYCLOHEXENONES

4-Substituent	Ref.	Solvent	Δ^2 λ_{max} mμ	Δ^2 ε	Δ^3 λ_{max} mμ	Δ^3 ε
H	*a*	A[b]	378	27,400	362	22,650
Me	*c*	B[d]	375	28,000	360	22,400
	e	B	. . .	. . .	365	22,600
i-Pr	*a*	A	379	27,300	364	23,150
	f	B	376	28,100	363	22,400
	g	B	376	29,300	. . .	. . .
C_6H_{11}	*h*	A	382	28,100	364	23,700
t-Bu		B	375	29,200	362	23,900

[a] See ref. 2. [b] Chloroform. [c] See ref. 9. [d] Ethanol. [e] See ref. 3. [f] M. D. Soffer and M. A. Jevnik, *J. Am. Chem. Soc.*, **77,** 1003 (1955). [g] K. G. Lewis, *J. Chem. Soc.*, 2765 (1951). [h] A. L. Wilds and N. A. Nelson, *J. Am. Chem. Soc.*, **75,** 5360 (1953).



I

II, R=H
III, R=phenyl
IV, R=methyl

4-*t*-Butyl-3-cyclohexenol (II) was prepared by reduction of 4-*t*-butyl-3-cyclohexenone (I) with lithium aluminum hydride in ether solution, by analogy with preparation of 4-methyl-3-cyclohexenol.[3] The presence and position of the double bond in the alcohol II was confirmed by absorption in the infrared spectrum at 3050 cm.$^{-1}$ (vinyl C—H str.) and 1645 cm.$^{-1}$ (probably C=C str.), and by absorption in the n.m.r. spectrum centered at 4.65 τ (integrated intensity, 0.8 proton). A broad band centered at 6.1 τ (0.8 proton) may be attributed to the C-1 tertiary hydrogen. Other assignments are 8.47, hydroxyl hydrogen; 7.5–8.5, ring methylenes (7.0 protons, including the OH); and 8.96 τ, the *t*-butyl group (9.0 protons).

4-*t*-Butyl-1-phenyl-3-cyclohexenol (III) was prepared by addition of phenyl Grignard reagent to I in ether solution. The infrared spectrum of III was consistent with presence of a hydroxyl group, a phenyl group, a *t*-butyl group, and absence of a carbonyl group. The n.m.r. spectrum confirmed the position of the double bond. Absorption centered at 4.5 τ (integrated intensity, 1.0 proton) may be attributed to the single vinyl hydrogen. Other assignments are 2.4–2.8, phenyl; 7.4–8.4, ring methylenes; 8.04, hydroxyl hydrogen; and 8.92 τ, the *t*-butyl group.

4-*t*-Butyl-1-methyl-3-cyclohexenol (IV) was prepared by addition of methyl Grignard reagent to I in ether solution. The presence and position of the double bond in IV was confirmed by infrared absorption at 3052 cm.$^{-1}$ and n.m.r. absorption centered at 4.63 τ (integrated intensity, 0.9 proton). Other assignments are 8.40, hydroxyl hydrogen (confirmed by addition of deuterium oxide, which by converting OH to OD, caused this band to disappear); 7.6–8.1, allylic ring methylenes; 8.1–8.6, nonallylic ring methylene; 8.76, methyl; and 8.94 τ, the *t*-butyl group. The analogous preparation of 4-isopropyl-1-methyl-3-cyclohexenol was reported by Wallach and Heyer, who based their assignment of position of the double bond upon chemical methods.[10]

Several attempts to prepare 1,4-di-*t*-butyl-3-cyclohexenol by addition of *t*-butyllithium or *t*-butyl Grignard reagent to I were unsuccessful.[1] Infrared spectra of the product mixtures differed little from that of I. The very small quantities of hydroxyl-containing product obtained showed both hydroxyl and carbonyl absorption. Rather than addition to the carbonyl group, the strongly basic reagents apparently abstracted a proton from C-2 of I to give its enolate anion, a small fraction of which then added to a second molecule of I to give very small amounts of condensation products.

Intramolecular hydrogen bonding between the hydrogen of a hydroxyl group and the π-electrons of a carbon–carbon double bond has been reported for *endo*-bicyclo[2.2.1]hept-2-en-5-ol (V).[11] The infrared spectrum of V shows absorption bands at 3622 and 3592 cm.$^{-1}$ ($\Delta\nu$, 30 cm.$^{-1}$).[11] The 3592-cm.$^{-1}$ band has been attributed to an intramolecular OH. . . .π hydrogen bond.[11] Since V may be thought of as a 3-cyclohexenol locked in a boat conformation by the

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[4] L. S. Smith, E. D. Woolfolk, and W. McLemore, "5th Report on Research under Sponsorship of the Petroleum Research Fund," *Am. Chem. Soc.*, 50 (1961).

[5] (a) L. S. Smith, private communication; (b) L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22,** 891 (1957).

[6] W. A. Pearson, Ph.D. thesis, University of Minnesota, 1958, pp. 89–90.

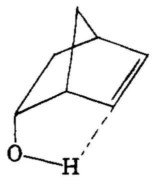
[7] The apparent discrepancy between ref. 4 and work reported herein has been resolved. Prof. L. S. Smith kindly furnished a sample labeled "4-*tert*-butyl-3-cyclohexenone, m.p. 99.0–99.5°," isolated after treatment of *p*-*t*-butylphenol with lithium in ethylenediamine. This sample supported the result reported herein for run 1, (84% recovery of *p*-*t*-butylphenol). We found that Prof. Smith's sample of "4-*tert*-butyl-3-cyclohexenone" gave the same melting point and infrared spectrum as *p*-*t*-butylphenol.

[8] N. A. Nelson, R. S. P. Hsi, J. M. Schuck, and L. D. Kahn, *J. Am. Chem. Soc.*, **82,** 2573 (1960).

[9] B. B. Millward, *J. Chem. Soc.*, 26 (1960), and references cited.

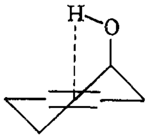
[10] O. Wallach and R. Heyer, *Ann.*, **362,** 280 (1908).

[11] P. von R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80,** 6691 (1958).

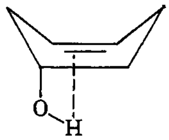


V

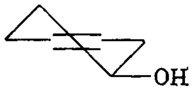
bridging methylene group, the corresponding conformation of a flexible 3-cyclohexenol also might be expected to exhibit similar intramolecular hydrogen bonding. Examination of models of 3-cyclohexenol suggested the existence of conformations in which intramolecular hydrogen bonding appeared to be possible, such as VIa and VIb, as well as conformations in which intramolecular hydrogen bonding is not possible, such as VIc and VId.



VIa



VIb



VIc

VId

Infrared spectra of alcohols II, III, and IV were compared with those of *p*-menth-1-en-4-ol and 1,2,3,4-tetrahydro-2-naphthol. None of these five alcohols exhibited a clearly resolved doublet near 3600 cm.$^{-1}$; no evidence for strong transannular intramolecular hydrogen bonding was observed. Evidence for weak transannular intramolecular hydrogen bonding in such compounds might be obtained by infrared spectroscopy by analysis of the hydroxyl stretching vibration absorption band shape under high resolution as a function of temperature in direct comparison with compounds such as V.

Experimental[12]

***p*-*t*-Butylanisole.**—*p*-*t*-Butylphenol, m.p. 98–99° (from benzene), 750 g. (5.00 moles) was converted to its methyl ether as reported.[13] Distillation of the product through a 100-cm. vacuum-jacketed column packed with $^1/_8$-in. i.d. glass helices yielded a center fraction of 450 g. (50%), b.p. 98–99° (11 mm.); $\lambda_{\max}$ 223 mμ (ε 10,200).

4-*t*-Butyl-3-cyclohexenone (I).—A procedure reported for preparation of 4-methyl-3-cyclohexenone was employed.[3] To a stirred mixture of anhydrous ether (530 ml.) and liquid ammonia (1400 ml.) in a three-necked flask fitted with a mechanical stirrer, Dry Ice-filled dewar condenser, and addition funnel, was added 145 g. (0.884 mole) of *p*-*t*-butylanisole. After 15 min., lithium, 24.6 g. (3.5 g.-atoms), in the form of 2-cm. pieces of $^1/_8$-in. wire, was added during 30 min. Then absolute ethanol, 215 ml. (3.66 moles), was added dropwise during 30 min. Stirring was continued until the blue color was discharged and most of the ammonia had evaporated. Then 660 g. of crushed ice was added. The mixture was extracted with ether and the ether extracts were washed with water. The combined ether extracts were concentrated to 440 ml. Then 440 ml. of saturated aqueous oxalic acid solution was added to the ether solution and stirred for 12 hr. The ether layer was separated, combined with ether extracts of the aqueous layer, washed with 6% aqueous sodium bicarbonate, washed with water, dried over anhydrous sodium sulfate, and the ether removed (20 mm.) to yield 140 g. of yellowish oil.

The combined product from three runs was distilled through the 100-cm. column. The center fraction, 156 g. (35%), b.p. 91°-(8.0 mm.)–92°(8.6 mm.), was used below. The infrared spectrum showed a strong sharp band at *ca.* 1720 cm.$^{-1}$, attributable to an unconjugated carbonyl group. Direct comparison of infrared spectra indicated that no more than a few per cent of *p*-*t*-butylanisole or 4-*t*-butylcyclohexanone could be present. No absorption attributable to a hydroxyl group was observed. A characteristic weak band at *ca.* 1340 cm.$^{-1}$ was noted. Gas chromatography on a 3.0-m. 9% 1,2,3-tris(2-cyanoethoxy)propane on 60–80-mesh Chromosorb W column at 100°, showed the presence of only 0.2 ± 0.1% *p*-*t*-butylanisole (retention time 3.1 min.) in the sample of 4-*t*-butyl-3-cyclohexenone (retention time 4.6 min.). No other peaks and no shoulders were observed. No more than a few per cent of 4-*t*-butylcyclohexanone (retention time 5.3 min.) could have escaped detection. The ultraviolet spectrum indicated that the sample contained less than 3% 4-*t*-butyl-2-cyclohexenone, assuming for the latter, at 225 mμ, an ε of 12,000, and assuming an ε of zero for all other components (except *p*-*t*-butylanisole).[14]

4-*t*-Butyl-3-cyclohexenone 2,4-Dinitrophenylhydrazone.—To 1.0 g. (6 mmoles) of 4-*t*-butyl-3-cyclohexenone in 240 ml. of ethanol (95%) was added 24 ml. (6 mmoles) of 2,4-dinitrophenylhydrazine in ethanol–phosphoric acid solution.[15] Recrystallization of the product from ethanol gave orange, needle-like crystals, m.p. 172.5–175°; $\lambda_{\max}$ 362 (23,900), 229 mμ (ε 17,000).

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 58.03; H, 6.11; N, 16.86.

4-*t*-Butylcyclohexanone 2,4-dinitrophenylhydrazone was prepared for comparison from 4-*t*-butylcyclohexanone by the preceding procedure. The orange crystals gave m.p. 152–155°; lit.[16] m.p. 151.5–152.5°.

4-*t*-Butyl-2-cyclohexenone 2,4-dinitrophenylhydrazone.—To a hot solution of 0.54 g. (2.7 mmoles) of 2,4-dinitrophenylhydrazine in 20 ml. of absolute ethanol and 2.5 ml. of concentrated hydrochloric acid was added 0.41 g. (2.7 mmoles) of 4-*t*-butyl-3-cyclohexenone in 5 ml. absolute ethanol. The solution was heated for 5 min. under reflux. The cooled solution yielded bright red crystals, which, after recrystallization from ethanol, gave m.p. 167.5–169.5°; $\lambda_{\max}$ 375 (29,200), 251 mμ (ε 17,000).

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.92; H, 6.08; N, 16.87.

4-*t*-Butyl-3-cyclohexenol (II).—To a stirred solution of lithium aluminum hydride, 0.71 g. (0.019 mole), in 13 ml. of anhydrous ether heated under reflux, was added dropwise a solution of 5.0 g. (0.033 mole) of 4-*t*-butyl-3-cyclohexenone in 13 ml. of anhydrous ether during 1.5 hr. After an additional 2.5 hr. of continued heating, an excess of 10% hydrochloric acid (22 ml.) was added to the cooled mixture. The ether layer plus ether washings of the aqueous layer were combined, washed with water, dried over anhydrous sodium sulfate, and concentrated. The residue, 4.3 g., solidified at room temperature. Recrystallization from pentane gave white crystals, m.p. 86–86.5°.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.53; H, 11.79.

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(12) Spectral data were recorded by use of Perkin-Elmer Model 21 and 421 DG, and Beckman DK-2 spectrophotometers. Ultraviolet spectra were recorded in 95% ethanol solutions; infrared spectra in dried "Spectranalyzed" carbon tetrachloride solutions. We are indebted to Dr. D. P. Hollis for the n.m.r. spectra, recorded with a Varian A-60 spectrometer, chloroform-*d* solutions, and internal tetramethylsilane reference at the Spectroscopy Applications Laboratories, Varian Associates, Palo Alto, Calif. Microanalyses were determined by Dr. S. M. Nagy. Boiling points and melting points are uncorrected.

(13) W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, Jr., and L. C. Gibbons, *J. Am. Chem. Soc.*, **69**, 2451 (1947).

(14) M. D. Soffer and A. C. Williston, *J. Org. Chem.*, **22**, 1254 (1957), reported values for the analogous compounds: 4-isopropyl-2-cyclohexenone, λmax 227 mμ (ε 12,370); 4-isopropyl-3-cyclohexenone, no max. 210–360 mμ (ethanol).

(15) G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

(16) E. L. Eliel and M. N. Rerick, *ibid.*, **82**, 1367 (1960).

The infrared spectrum of a 0.06 M solution in carbon tetrachloride showed absorption bands at 3616 (strong, sharp), 3050 (weak, sharp), and 1645 cm.$^{-1}$ (very weak).

4-*t*-Butyl-1-phenyl-3-cyclohexenol (III).—To 1.20 g. (0.0494 g.-atom) of magnesium turnings in 40 ml. of dry ether was added dropwise with stirring a solution of 13.2 g. (0.0840 mole) of bromobenzene in 30 ml. of dry ether. The mixture was stirred for 1 hr. A solution of 5.00 g. (0.0329 mole) of 4-*t*-butyl-3-cyclohexenone in 25 ml. of dry ether was added dropwise with stirring during 45 min. at 0°. After 1 hr. of continued stirring at 0°, the reaction mixture was poured into ice–water, saturated ammonium chloride solution was added, and the layers were separated. The water layer was extracted with ether. The combined ether layers were washed until neutral with water, dried over anhydrous sodium sulfate, and the ether was removed under reduced pressure. Volatile components of the resulting oil were removed at 25° (0.03 mm.), leaving a solid residue. Two crystallizations from nitromethane gave 0.64 g. (8%) of white crystals, m.p. 74–74.5°. Further recrystallizations from nitromethane yielded a sample for analysis, m.p. 77.5–78.5°.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.42; H, 9.63. Found: C, 83.17; H, 9.69.

The infrared spectrum of a 0.005 M solution[12] showed absorption bands at 3604, 3090, 3062, and 3030 cm.$^{-1}$.

4-*t*-Butyl-1-methyl-3-cyclohexenol (IV).—A solution of 5.00 g. (0.0329 mole) of 4-*t*-butyl-3-cyclohexenone in 25 ml. of anhydrous ether was added to the Grignard reagent prepared from 1.20 g. (0.0494 g.-atom) of magnesium turnings and 11.8 g. (0.0833 mole) of iodomethane in 50 ml. of anhydrous ether. The reaction was carried out as previously described.

The final dried ether solution was concentrated under reduced pressure. The solid residue, m.p. 65°, readily sublimed at 20 mm. Four resublimations yielded white needle-like crystals, 1.0 g. (18%), m.p. 75–75.5°, which showed infrared absorption peaks at 3607 and 3052 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.15; H, 11.90.

Reaction of *p*-*t*-Butylphenol with Lithium in Ethylenediamine. Run 1.—The reported procedure was followed.[4,5] To 7.76 g. (0.0517 mole) of *p*-*t*-butylphenol in 200 ml. of ethylenediamine, was added 2.80 g. (0.40 g.-atom) of lithium metal wire during 2 hr. at 90–100° (nitrogen atmosphere). The mixture was heated at reflux 2 hr. longer. Ultraviolet analysis of the product isolated by ether extraction was consistent with presence of 84% *p*-*t*-butylphenol.

Run 2.—The reaction as in run 1 was repeated with 3.88 g. (0.0259 mole) of *p*-*t*-butylphenol in 200 ml. of ethylenediamine and 8.4 g. (1.20 g.-atom) of lithium. The product contained some *p*-*t*-butylphenol (16% by ultraviolet analysis) and about 20% unconjugated ketones (infrared analysis at 1720 cm.$^{-1}$). The infrared spectrum did not show a detectable absorption band at *ca.* 1340 cm.$^{-1}$.

Acknowledgment.—We wish to thank the National Science Foundation for support of this work.

Aza-Aromatic Substitution. III. Spectral Studies on the Nature of Bromine Complexes with the Quinoline System[1a,b]

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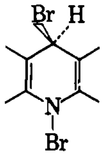
Spectral studies of bromine complexes of quinoline derivatives, both as solid complexes and as solution species, were undertaken. By consideration of the infrared spectrum, ultraviolet spectrum, and solution combining ratios and stability constants it is concluded that the principal species present is a 1:1 quinoline–bromine molecular complex of the *n*-donor type IV. Re-evaluation of previous reports on purported quinoline–bromine complexes reveals that such isolated compounds were undoubtedly quinolinium perbromides. The relevance of complexes, such as IV, as catalysts in aromatic and aza-aromatic bromination is suggested.

The recently observed facility with which quinoline undergoes selective bromination in the pyridinoid ring[1b] contravenes previous views concerning the reactivity of aza-aromatic heterocycles.[3] The interaction of quinoline and bromine in carbon tetrachloride led to the formation of an intermediate complex I which underwent smooth decomposition at 80° to yield 3-bromoquinoline. Isolation of the novel orange adduct I and iodometric analysis showed it to be an equimolar quinoline–bromine complex.[1b] Although similar halogen addition compounds of aza-aromatic heterocycles and their hydrogen halide salts have been known for some time,[4] the possible role of such adducts in electrophilic aromatic and aza-aromatic substitution makes further information concerning their structure and electronic character most desirable. Thus, the catalytic role of pyridine in aromatic bromination has been ascribed to the intermediate N-bromopyridinium bromide serving as a source of bromine cations.[5] Similar considerations tend to implicate quinoline–bromine adducts in the bromination of quinoline itself.[1]



II

However, the structure of such 1:1 adducts, especially with polynuclear nitrogen heterocycles, has been the subject of some disagreement. The older view of such adducts as being 1,2- or 1,4- addition products of the aza-aromatic heterocycle II[6] has little physical evidence to recommend it as such,[5] although similar structures are often postulated in rationalizing certain aspects of pyridine chemistry.[7] A second structural possibility for such complexes is dicoordinate complexation of the type $(R_3N)_2Br^+Br_3^-$ (III). That perchlorates of

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[1] Previous papers in this series: (a) J. J. Eisch, *J. Org. Chem.*, **27**, 4682 (1962); (b) **27**, 1318 (1962). (c) To whom inquires should be addressed at the Department of Chemistry, Catholic University of America, Washington 17, D.C.

[2] *Cf.* H. S. Mosher in "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 402.

[3] G. M. Badger, "Chemistry of Heterocyclic Compounds," Academic Press, New York, N. Y., 1961, p. 311.

[4] *Cf.* (a) H. Maier-Bode and J. Altpeter, "Das Pyridin und seine Derivate," W. Knapp, Halle, Germany, 1934, pp. 78–79; (b) A. B. Prescott and P. F. Trowbridge, *J. Am. Chem. Soc.*, **17**, 859 (1895); (c) P. F. Trowbridge, *ibid.*, **21**, 66 (1899); (d) D. M. Williams, *J. Chem. Soc.*, 2783 (1931); (e) A. I. Popov, *et al.*, *J. Am. Chem. Soc.*, **79**, 570, 4622 (1957).

[5] R. M. Acheson, T. G. Hoult, and K. A. Barnard, *J. Chem. Soc.*, 4142 (1954).

[6] A. Senier and P. C. Austin, *ibid.*, 1196 (1904).

[7] *Cf.* E. E. Garcia, C. V. Greco, and I. M. Hunsberger, *J. Am. Chem. Soc.*, **82**, 4430 (1960).