[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

2-Naphthyl-1-cyclopentanones and 1-Cyclohexanones[1,2]

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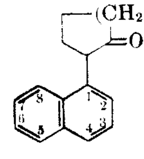
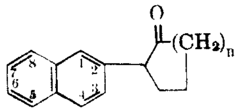
As possible intermediates for the preparation of disubstituted cycloalkenes bearing a naphthyl group[3] as one of the substituents we desired samples of the four possible 2-naphthyl-1-cyclopentanones and 1-cyclohexanones I–IV. II has been prepared previously in 2–15% yield by reaction of 1-naphthylmagnesium bromide on 2-chlorocyclohexanone.[4,5] Using the same general procedure as Orchin[4] we were able to secure similarly small yields of I (1.6%), III (4.4%), and IV (12%).



I: n = 1

II: n = 2



III: n = 1

IV: n = 2

Further investigation revealed a considerably improved alternate pathway to I and III based on (a) epoxidation *via* perbenzoic acid of the corresponding 1-(1- and 2-naphthyl)-1-cyclopentenes (derivable in turn from the same basic starting materials, *viz.* 1- and 2-bromonaphthalenes and cyclopentanone, as used in the Orchin procedure) followed by (b) molecular rearrangement of the crude oxirane[6] by heating with anhydrous zinc chloride (over-all yield *ca.* 45% for the two steps). The epoxide method applied to the production of IV, however, proved only slightly more suitable (18% conversion from the alkene) than the Orchin method, possibly due to the much greater facility for contraction of a six-membered ring over that of a five-membered ring during the rearrangement process.

Data relative to selected infrared absorption bands for I–IV are recorded in Table I, examination of which shows that I and III exhibit normal intense naphthyl bands between 700 and 900 cm.$^{-1}$ while II and IV exhibit abnormalities in the same region. The absence of a band at about 855 cm.$^{-1}$ in IV may possibly be ascribed to a steric hindrance by the cyclohexanone moiety to out-of-plane vibrations by the hydrogen in position 1,[cf. 7] while the band at 784-788 cm.$^{-1}$ in II may indicate a similar partial steric hindrance to hydrogen in position 2 and/or in position 8 [*cf.* spectra[8] of 1,2-dimethylnaphthalene (strongest band at 786 cm.$^{-1}$) and 1,8-dimethylnaphthalene (strong band at 773 cm.$^{-1}$ and medium band at 789 cm.$^{-1}$)]. The ultraviolet absorption spectra (see Table II) of I–IV show little variation from the corresponding 1- and 2-alkylnaphthalenes.[cf. 9]

EXPERIMENTAL[13]

2-(1-Naphthyl)-1-cyclopentanone (I). *Epoxide procedure.* A solution of 11 g. (0.057 mole) of purified 1-(1-naphthyl)-1-cyclopentene[14] in 200 ml. of 0.345 *M* perbenzoic acid[15] in chloroform was maintained at 0–5° for 24 hours. The mixture was treated with 50 ml. of 5% aqueous sodium hydroxide with occasional shaking at room temperature for 2–3 hours. The organic layer was washed with water and the solvent was removed under reduced pressure. Essentially according to the procedure of Winternitz and Mousseron[16] the residue was heated with 3 g. of fused zinc chloride at 105–115° for 30–40 minutes at 40 mm. pressure. The cooled mixture was extracted with benzene-ether. Combined organic extracts were washed once with 50 ml. of 1 *N* sulfuric acid and twice with water and then were distilled. The fraction boiling at 170–174° (0.8 mm.) crystallized from methanol; yield 5.5 g. (46%), m.p. 91–93°.

Chloro ketone procedure. The crude ketone obtained from interaction of the Grignard reagent from 81 g. (0.39 mole) of 1-bromonaphthalene, 6.2 g. (0.25 g.-atom) of magnesium, 200 ml. of anhydrous ether, and 100 ml. of anhydrous benzene with 44.5 g. (0.38 mole) of freshly prepared 2-chlorocyclopentanone[17] was purified essentially according to the procedure of Orchin for II[4] and crystallized from 30–60° petroleum ether, yield 0.85 g. (1.6%), m.p. 85–86°. Recrystallization of a sample from dilute methanol gave needles, m.p. 91–92°, undepressed on admixture with product from the epoxide procedure.

Anal. Calc'd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.74; H, 7.06.

The *2,4-dinitrophenylhydrazone*, prepared according to the directions of Shriner and Fuson,[18] crystallized from acetonitrile as orange needles, m.p. 212.5–213.5°.

Anal. Calc'd for $C_{21}H_{18}N_4O_4$: N, 14.35. Found: N, 14.63.

2-(2-Naphthyl)-1-cyclopentanone (III). *Epoxide procedure.* From 13 g. of purified 1-(2-naphthyl)-1-cyclopentene[14] was obtained 7.4 g. of ketone, b.p. 174–178° (1.5 mm.), or 6 g. (43%) after one crystallization from methanol, m.p. 80–83°, undepressed on admixture with product from the following procedure.

Chloro ketone procedure. From equimolar quantities (0.32 mole) of 2-bromonaphthalene, magnesium, and 2-chlorocyclopentanone was obtained 2.97 g. (4.4%) of ketone, m.p.

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[1] Abstracted in part from the Ph.D. thesis of Herman Ziffer, University of Oregon, June, 1955.

[2] Conducted under sponsorship of the Office of Ordnance Research, contract number DA-04-200-ORD-176.

[3] Klemm and Ziffer, *J. Org. Chem.*, **20**, 182 (1955).

[4] Orchin, *J. Am. Chem. Soc.*, **70**, 495 (1948).

[5] Orchin and Reggel, *J. Am. Chem. Soc.*, **73**, 2955 (1951); Huang, *J. Org. Chem.* **19**, 1363 (1954).

[6] Elderfield, *Heterocyclic Compounds*, John Wiley and Sons, Inc., New York, 1950, Vol. I, pp. 47–54; House, *J. Am. Chem. Soc.*, **77**, 3070 (1955).

[7] Colthup, *J. Optical Soc. Am.*, **40**, 397 (1950).

[8] American Petroleum Institute, Research Project 44, *Catalog of Infrared Spectral Data.*

[9] Friedel and Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, Inc., New York, 1951.

TABLE I

SOME CHARACTERISTIC INFRARED ABSORPTION MAXIMA FOR I–IV[a]

$\tilde{\nu}_{max.}$ in Cm.$^{-1}$ [b]					
I	II	III	IV	Probable Assignment	
		753^{VS}	753^{S}	2-Naphthyl[c]	out-of-plane hydrogen bending[d]
780^{VS}	$(774)^{S}$			1-Naphthyl[c]	
	$784–788^{VS}$				
797^{VS}	$(795)^{S}$			1-Naphthyl[c]	
		818^{VS}	815^{VS}	2-Naphthyl[c]	
		858^{S}	—[e]	2-Naphthyl[c]	
1125^{S}	1143^{S}	1141^{VS}	1120^{S}	Carbonyl[d]	
1515^{M}	1513^{W}	1506^{M}	1511^{W}	In-plane naphthalene skeletal vibrations[f]	
1602^{M}	1600^{M}	1607^{M}	1601^{WM}		
1700^{S}	1720^{VS}	1716^{VS}[g]	1700^{VS}	Carbonyl stretching[d,h]	
2875^{S}	2850^{M}	2865^{S}	2840^{M}	Methylene hydrogen stretching[i]	
2940^{VS}	2930^{SM}	2940^{S}	2925^{S}		
3070^{M}	3040^{M}	3040^{M}	3040^{M}	Aromatic hydrogen stretching[i]	

[a] Spectra were determined over the region 2–15μ (5000–667 cm.$^{-1}$) by Samuel P. Sadtler and Son, Inc., Philadelphia 2, Pennsylvania using potassium bromide pelletization. Complete curves are included in their Catalog of Spectra as numbers 7129–7132. [b] Numbers in parentheses represent shoulders, not true maxima. Intensity designations: VS (very strong), S (strong), SM (strong medium), M (medium), WM (weak medium), W (weak). [c] Usually 1-substituted naphthalenes show bands at 755–780 and 780–800 cm.$^{-1}$, while 2-substituted naphthalenes show bands at 720–760, 800–830, and 830–860 cm.$^{-1}$ [8,10] [Unpublished data from this laboratory]. [d] See ref. (7). [e] No *bona fide* third 2-naphthyl band is apparent in this spectrum. A weak band of inappropriate shape does occur at 864 cm.$^{-1}$ [f] See[11]. [g] Estimated from poorly traced peak. [h] It might be noted that no systematic differentiation between the cyclopentanone and cyclohexanone rings, as based on relative ring strains[10,12] is apparent here. [i] See [10].

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA FOR I–IV

I[a]		II[b]		III[a]		IV[a]	
$\lambda_{max.}$ mμ	log ε	$\lambda_{max.}$[c] mμ	log ε	$\lambda_{max.}$[c] mμ	log ε	$\lambda_{max.}$[c] mμ	log ε
225	4.92	222–225	4.88	227	4.86	226	5.04
		(262)	3.57	268	3.67	268	3.67
274	3.85	272	3.79	276	3.70	276	3.69
283	3.92	282	3.84			(286)	3.49
293	3.77	292	3.80				
				304	2.70	(302)	2.58
314	2.80	313	2.62	(313)	2.48		

[a] Spectra were determined by means of a Beckman model DU spectrophotometer using cyclohexane as solvent. [b] Using 95% ethanol as solvent.[9] [c] Values in parentheses represent shoulders, not true maxima.

78–82°. Recrystallization of a sample from methanol produced platelets, m.p. 84.5–85°.

Anal. Calc'd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.34; H, 6.76.

The *2,4-dinitrophenylhydrazone*[18] crystallized from ethyl acetate as orange needles, m.p. 162–163°.

Anal. Calc'd for $C_{21}H_{18}N_4O_4$: N, 14.35. Found: N, 14.35.

2-(2-Naphthyl)-1-cyclohexanone (IV). *Chloro ketone procedure.* From equimolar quantities (0.38 mole) of 2-bromonaphthalene, magnesium, and 2-chlorocyclohexanone[19] there resulted 32 g. of crude naphthyl ketone, b.p. 110–235° (2.5 mm.), purified *via* the *semicarbazone* (washed with water, crystallized from dioxane, m.p. 168–170°) to give 6.7 g. (12%) of once-crystallized IV (from methanol), m.p. 78–82°. Recrystallizations of a sample from the same solvent yielded cream-white needles, m.p. 83.5–84.5°.

Anal. Calc'd for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.62; H, 7.23.

The *2,4-dinitrophenylhydrazone*[18] crystallized from ethyl acetate as light orange needles, m.p. 194–194.5°.

Anal. Calc'd for $C_{22}H_{20}N_4O_4$: N, 13.85. Found: N, 13.80.

Epoxide procedure. From 5 g. of purified 1-(2-naphthyl)-1-cyclopentene[14] was obtained 1.7 g. of ketone, b.p. 172–175° (1.1 mm.), or 0.95 g. (18%) after one crystallization of the distillate from methanol, m.p. 83.5–84.5°, undepressed on admixture with product from the chloro ketone procedure.

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(10) Gilman, *Organic Chemistry*, John Wiley and Sons, Inc., New York, 1953, Vol. III, Chap. 2.

(11) Vago, Tanner, and Bryant, *J. Inst. Petroleum*, **35**, 293 (1949); Broomfield, *J. Inst. Petroleum*, **38**, 424 (1952); McClellan and Pimentel, *J. Chem. Phys.*, **23**, 245 (1955).

(12) Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen and Co., Ltd., London, 1954, pp. 127–128.

(13) Melting points are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

(14) Klemm and Hodes, *J. Am. Chem. Soc.*, **73**, 5181 (1951).

(15) Gilman and Blatt, *Org. Syntheses*, Coll. Vol. I, 2nd ed., 431–434 (1941).

(16) Winternitz and Mousseron, *Bull. soc. chim. France*, [5], **16**, 713 (1949).

(17) Godchot and Taboury, *Compt. rend.*, **156**, 332 (1913).

(18) Shriner and Fuson, *The Systematic Identification of Organic Compounds*, 3rd ed., John Wiley and Sons, Inc., New York, 1948, p. 171.

(19) Newman, Farbman, and Hipsher, *Org. Syntheses*, **25**, 22 (1945).