from hexane to yield 29.9 grams (65%) of *N*-dodecyl-1-hydroxy-2-naphthamide, mp 66–7° C.

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Received for review July 16, 1970. Accepted April 29, 1971. This work was supported by the Air Force Avionics Laboratory, ASD, Wright-Patterson Air Force Base, under Contract No. F-33615-67-C-1801.

Synthesis of Adamantyl Alkyl Ketones

YOSHIAKI INAMOTO[1] and HIROKAZU NAKAYAMA
Industrial Research Laboratory, Kao Soap Co., Ltd., 1334 Minatoyakushubata, Wakayama 640-91, Japan

A series of adamantyl-1 alkyl ketones was prepared by alkylation of ethyl adamantyl-1-carbonylacetate followed by hydrolysis and decarboxylation. Infrared, nuclear magnetic resonance, and mass spectra were measured, which revealed that the influence of the adamantyl group on ir and nmr spectral properties of the rest of the molecule is just the same as that of *t*-butyl group.

A series of adamantyl alkyl ketones reported here was synthesized as intermediates in the preparation of surface active agents for the purpose of studying the surface activity of the adamantyl group. In a homologous series of adamantyl-1 alkyl ketones, only the first two members are known: adamantyl methyl ketone, prepared by Stetter and Rauscher (*9*) by decarboxylation of adamantyl-1-carbonylacetic acid, as well as by Hala and Landa (*3*) by reaction of adamantanecarboxylic acid with acetic acid over thorium oxide catalyst at elevated temperature; and adamantyl-1 ethyl ketone, synthesized by Lauria et al. (*5*) by the reaction of adamantylcarbonyl chloride with diethylcadmium. However, neither of the last two methods seems satisfactory for the preparation of higher homologs of the series. In fact, we observed that the reaction of di-*n*-decylcadmium with adamantylcarbonyl chloride by the method of Lauria et al. (*5*) gave *n*-eicosane as a major product (21% yield), only a 2.6% yield of adamantyl-1 *n*-decyl ketone (isolated as 2,4-dinitrophenylhydrazone) having been obtained.

Our method of preparation consists in alkylation of ethyl adamantyl-1-carbonylacetate with an appropriate alkyl halide, followed by hydrolysis and decarboxylation. Ethyl adamantyl-1-carbonylacetate can be alkylated in the usual manner with an alkyl halide in the presence of sodium ethoxide, while hydrolysis of the resultant β-ketoesters is best effected by alkaline, rather than acid, hydrolysis by use of potassium hydroxide in 95% ethanol at room temperature. Use of boiling diluted sulfuric acid, even in the presence of some acetic acid, resulted in an incomplete hydrolysis, probably owing to small solubility of the β-ketoesters, and this is especially so for ones with higher alkyl group. Potassium salts of alkylated β-ketoacids thus obtained are easily decarboxylated on acidification with heating to give the desired adamantyl-1 alkyl ketones, which are listed, together with 2,4-dinitrophenylhydrazone, in Table I.

The first two members of the series [mp's: Me, 53–54°C (*9*), 54°C (*3*); Et, 30–32°C] and those with an alkyl group of the carbon number greater than 11 are solid, while those with *n*-propyl through *n*-nonyl are liquid at room temperature.

Some characteristic features are found in the ir, nmr, and mass spectra of these ketones. In the infrared spectra, the carbonyl stretching frequency has a constant value of 1700 cm^{-1}, and three absorption bands around 1100 cm^{-1} (absorptions due to skeletal vibration of C—CO—C) assume the values 1070–1080 cm^{-1}, 1045–1055 cm^{-1}, and 1020–1030 cm^{-1}, irrespective of the size and structure of the alkyl groups.

The nmr spectrum of every ketone, with the exception of those for the methyl and the ethyl ketones, consists of five signals: the signal due to the protons of the alkyl methylene group adjacent to the carbonyl group (7.58 τ, triplet, $J = 7$ Hz), that due to the terminal methyl protons (9.11 τ), that due to the protons on the rest of the alkyl carbon atom(s) (8.4–8.9 τ), that due to $H\gamma$'s (*2*) (protons on the tertiary carbon atoms of the adamantane ring, 7.99 τ, broad singlet), and that due to $H\beta$'s and $H\delta$'s (*2*) (protons on the secondary carbon atoms of the adamantane ring, 8.22 τ, doublet, $J = 2$ Hz). Here again, these chemical shifts values are all the same throughout the series, irrespective of the size and shape of the alkyl groups. In addition to this, these spectral characteristics of the alkylcarbonyl moiety of the ketone molecule are not altered very much by changing the adamantane ring into a tertiary alkyl group. For example, *n*-butyl *t*-butyl ketone (*1, 12*) is found to have a similar ir carbonyl stretching frequency (1710 cm^{-1}) and nmr signals ($—COCH_2—$: 7.58 τ, *t*, $J = 7$ Hz; $—COCH_2CH_2CH_2—$: 8.4–8.9 τ, complex m; $—CH_3$: 9.12 τ, *t*, $J = 7$ Hz). Thus it is clear that the spectral properties of these adamantyl alkyl ketones are just as expected, and the adamantyl group does not exert any unusual influence on the spectral properties of the rest of the molecule.

In the mass spectra of the series of the ketones, the adamantyl cation (Ad^+, m/e 135) appears always as the base peak (relative intensity, 100). The parent peaks appear in relatively low intensities (0.2–8.2), and other important peaks appearing commonly throughout the series are those of adamantylcarbonyl

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[1] To whom correspondence should be addressed.

Table I. Adamantyl-1 Alkyl Ketones

Alkyl	Ketone Bp [°C (mm)]	Ketone n_D (Temp., °C) [mp, °C]^a	2,4-Dinitrophenylhydrazone, mp, °C^a
C_2H_5	71 (0.2)^b	[30–32]^c	168–169^d
$CH_3(CH_2)_2$	68–72(0.1)	1.4967(25)	157–158
$CH_3(CH_2)_3$	98–103(0.1)	1.4936(24)	175–177
$CH_3(CH_2)_4$	112–114(0.3)	1.4925(24)	174–176.5
$(CH_3)_2CH(CH_2)_2$	108–118(0.3)	1.4948(24)	165–168
$CH_3(CH_2)_5$	126–128(0.4)	1.4916(24)	126–128
$(CH_3)_2CH(CH_2)_3$	130–133(0.4)	1.4916(23)	142–143.5
$CH_3(CH_2)_6$	132–133(0.3)	1.4903(23)	122.5–125.5
$CH_3(CH_2)_8$	162–163(0.3)	1.4890(23)	106–108
$CH_3(CH_2)_{10}$	192–194(0.25)	[27]	93–94
$CH_3(CH_2)_{12}$	197–203(0.4)	[35.5–37]	88–89.5
$CH_3(CH_2)_{14}$	215–220(0.25)	[45.5–46.5]	84–86
$CH_3(CH_2)_{16}$	228–233(0.6)	[48–51]	82–84
$CH_3(CH_2)_{18}$	235–239(0.35)	[55.5–57.5]	85–86

[a] Melting points are uncorrected. [b] Lit. (*5*), bp 81–82°C/0.5 mm. [c] Lauria et al. (*5*) do not give the melting point. [d] Lit. (*5*), mp 160°C.

(AdCO$^+$, m/e 163), alkylcarbonyl with the same alkyl group as in the original ketone (RCO$^+$), 2-alkylketene with the alkyl group one carbon less than that in the original ($R'{-}CH{=}C{=}O^+$), and adamantyl methyl ketone ($AdCOCH_3^+$, m/e 178). The relative intensities of these peaks never exceed 10, thus the characteristic feature of the mass spectra of adamantane derivatives is manifesting itself also in these spectra.

EXPERIMENTAL

Reagent. Methyl iodide, ethyl iodide, *n*-propyl iodide, *n*-butyl bromide, *i*-butyl bromide, *n*-amyl bromide, *i*-amyl bromide, and *n*-hexyl bromide were used after one distillation of commercially available reagents through a 1-ft Vigreux column. *n*-Octyl bromide, bp 61–63°C/2 mm, n_D^{23} 1.4510 [lit. (*6*), bp 106°C/39 mm, n_D^{20} 1.4527], *n*-decyl bromide, bp 82–83°C/2 mm, n_D^{23} 1.4543 [lit. (*10*), bp 124°C/20 mm, n_D^{20} 1.4558], lauryl bromide, bp 119–122°C/2 mm, n_D^{23} 1.4570 [lit. (*7*), bp 122°C/4 mm, n_D^{20} 1.4586], myristyl bromide, bp 145–147°C/5 mm, n_D^{24} 1.4584 [lit. (*6*), bp 145.7–147.0°C/5 mm, n_D^{20} 1.4608, n_D^{30} 1.4564], cetyl bromide, bp 173–175°C/2 mm, n_D^{24} 1.4600 [lit. (*13*), bp 178°C/9 mm, n_D^{20} 1.4520], and stearyl bromide, bp 176–179°C/2 mm, mp 26–27°C [lit. (*13*), bp 175°C/2 mm, mp 27.4–27.6°C] were synthesized by the method of Kamm and Marvel (*4*). Ethyl adamantyl-1-carbonylacetate, bp 135°C/0.5 mm [lit. (*9*), bp 108–110°C/0.06 mm], n_D^{20} 1.5060, was prepared by the reaction of adamantylcarbonyl chloride with ethyl ethoxymagnesiomalonate according to the method of Stetter and Rauscher (*9*). Adamantyl methyl ketone was synthesized by hydrolysis and decarboxylation of ethyl adamantyl-1-carbonylacetate (*9*). *t*-Butyl *n*-butyl ketone was prepared according to the method of Foley et al. (*1*): bp 165–166°C [lit. (*1*), bp 167.0–169.0°C], n_D^{26} 1.4144 [lit. (*1*), n_D^{20} 1.4149]; oxime, mp 59–59.5°C [lit. (*12*), mp 59.5–60.6°C]; 2,4-dinitrophenylhydrazone, mp 122–122.5°C.

General Procedure for Preparing Adamantyl-1 Alkyl Ketones. To a solution prepared from 30 ml of absolute ethanol and 1.15 grams (0.05 mole) of sodium is added 12.5 grams (0.05 mole) of ethyl adamantyl-1-carbonylacetate, and the solution is stirred for 15 min at room temperature. Appropriate alkyl halide (0.06 mole) is then added to the above solution. The reaction is stirred at room temperature for 12 hr and then refluxed for 2 hr when methyl iodide, ethyl iodide, or *n*-propyl iodide is used as the alkylation reagent. When butyl or higher bromide is used, the reaction is heated under reflux immediately after the addition of the halide, heating having been continued for 6 hr. The ethanol is removed from the reaction mixture on a steam bath, and the residue is poured onto 50 ml of cold water. The organic layer is taken up in ether, the ether extract being washed first with 1% sulfuric acid until the washings become distinctly acidic and then successively with saturated sodium bicarbonate solution and water until neutral. The ether solution is dried over anhydrous sodium sulfate, and distilled, finally under reduced pressure, until the boiling point of the distillate reaches 135°C/0.5 mm to remove the solvent as well as excess and any unreacted starting materials.

The distillation residue is dissolved in a solution of 2.80 grams of potassium hydroxide in 60 ml of 95% ethanol, the mixture being stirred at room temperature overnight. The ethanol is evaporated to dryness under reduced pressure in a bath below 50°C. Sixty ml of 5% sulfuric acid is added to the residue, and the mixture is carefully heated to reflux, heating being continued for another 2 hr. The cooled-down reaction mixture is extracted with ether and the ethereal extract, after being washed successively with saturated sodium bicarbonate solution and water, is dried over anhydrous sodium sulfate and fractionally distilled under reduced pressure to give the products listed in Table I. Yields vary from one ketone to another, but average about 80%. 2,4-Dinitrophenylhydrazones are prepared in the usual manner (*8*).

Measurements of Spectra. In ir spectroscopy, Shimadzu IR 27-C spectrophotometer with a sodium chloride prism was used, the samples being applied as liquid or solid films on a sodium chloride plate. Nmr spectra were taken on Japan Electron Optics Laboratory JNM-3H-60 at 60 MHz, at room temperature, in carbon tetrachloride solvent with TMS as internal standard. Mass spectroscopy was made on Hitachi RMU-6D, operated at the ionization voltage and temperature of 80 eV and 250°C, respectively.

Elemental analyses (C, H, N) of the new compounds in agreement with theoretical values were obtained and submitted for review.

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RECEIVED for review October 8, 1970. Accepted May 3, 1971.