Preparation of an α-Unsubstituted 1-Indenone and Its Dimer[1]

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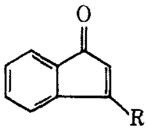
Attempts to prepare 1-indenones in which the C-2 is unsubstituted have been discouraging owing to the rapid polymerization of these compounds.[2] There are instances[3,4] when **1** (R = Ph) has been prepared in a transient state and isolated as a ketone derivative. Feeman and Amstutz report[5] the preparation of 6-chloro-3-(*p*-chlorophenyl)-1-indenone. In one case[6] the author claims to have obtained **1** (R = Ph) in the monomeric state, but without supporting data. On the other hand the preparation of 1-indenones where R = alkyl have been sketchily described,[7,8] with little convincing documentation. This Note describes the preparation of an alkylated analog of **1** where R = a tetramethylene bridge (**2**).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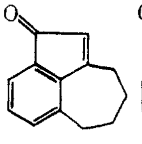
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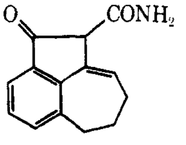
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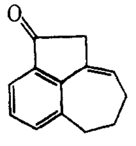
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Treatment of **3**[9] with refluxing hydrochloric acid yielded, along with the expected polymer, a low melting, light yellow product which lacked, as evidenced by infrared (ir) data, an amide or carboxylic acid group, and was a monomeric α,β-unsaturated ketone. The ultraviolet (uv) spectrum (see Table I) indicated that this substance possessed the indenone structure **2**.[10] Structure **2** was confirmed by the nuclear magnetic resonance (nmr) spectrum which indicated a vinylic proton, an allylic and benzylic multiplet, as well as methylene and aromatic absorption. Failure of **2** to polymerize readily, as expected, may be due to the large amount of steric crowding that would exist in placing these 5,6,7-fused-ring systems in a tight array.

TABLE I

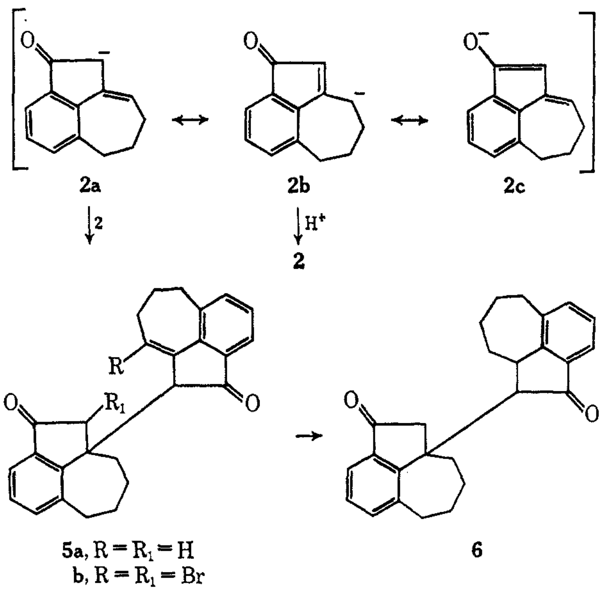
ULTRAVIOLET ABSORPTION DATA FOR **2**, **5a**, AND **5b**[a]

λ_{max}, mμ (log ϵ)		
2	5	5b
216 (4.18)	213 (4.34)	218 (4.29)
242 (4.49)	244 (4.38)	248 (4.03)
251 (4.34)		
266 (4.34)	268[b] (3.97)	
275[b] (4.20)	277[b] (3.91)	297 (3.30)
335 (3.60)	336 (3.25)	

[a] Spectra determined in 95% ethanol on a Bausch and Lomb Model 505 spectrophotometer. [b] Shoulder.

Hydrolysis of **3** in sodium hydroxide solution resulted in **2** and a second material, assigned structure **5a**. This compound was a high-melting white dimer of **2** possessing a nonconjugated ketone band and an uv spectrum characteristic of indanones[10] (see Table I). The nmr spectrum showed a methine singlet, a broad vinylic triplet, and aromatic and broad methylene multiplets in the ratio of 1:1:6:16. Even though a 1,2 cycloaddition dimer has been reported for 3-phenylindenone,[6] this possibility, along with a quasi Diels-Alder product was rejected, after considering the spectral data and chemical properties of **5a**. A Michael addition of anion **2a** to **2**, as illustrated in Scheme I, offers a reasonable explanation of formation of **5a** in alkaline solution.

SCHEME I



Compound **5a** absorbed 1 mol of hydrogen to produce **6**, but treatment with bromine produced a dibromide with evolution of hydrogen bromide. The brominated derivative retained its double bond but showed no vinylic hydrogens in its nmr spectrum. Addition of bromine to the double bond of **5a** followed by loss of hydrogen bromide would give the vinylic bromide, while substitution could produce the α-bromo ketone. Structure **5b** has been assigned on the basis of the two single protons characteristic of two different α hydrogens, one of which is similar to that of α-bromopropiophenone.[11]

Attempts to prepare 1 (R = CH_3, C_2H_5, i-C_3H_7) from the corresponding 2-carboxamide analog[10] under analogous conditions consistently led to yellow polymers while acid hydrolysis of 2-carboxamido-3-phenyl-1-indenone[10] produced a yellow dimer consistent in all aspects with that reported[6] for 3-phenylindenone (**1**, R = Ph).

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(1) Taken from the thesis of S. W. S., submitted to Indiana University in partial fulfillment of the requirements for the degree Doctor of Philosophy, June 1968.

(2) J. Deschamps, *C. R. Acad. Sci., Paris*, **246**, 3065 (1958).

(3) A. T. Blomquist and E. J. Mariconi, *J. Org. Chem.*, **26**, 3761 (1961).

(4) B. W. Rockett and C. R. Hauser, *ibid.*, **29**, 1394 (1964).

(5) J. F. Feeman and E. D. Amstutz, *J. Amer. Chem. Soc.*, **72**, 1522 (1950).

(6) R. de Fazi, *Gazz. Chim. Ital.*, **49**, 253 (1919).

(7) R. Stoermer and E. Laage, *Ber.*, **50**, 981 (1917).

(8) P. Besinet, R. Fraisse, R. Jacquier, and P. Viallefont, *Bull. Soc. Chim. Fr.*, 1377 (1960).

(9) E. Campaigne, R. Subramanya, and D. R. Maulding, *J. Org. Chem.*, **28**, 623 (1963).

(10) E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum, and D. R. Maulding, *ibid.*, **27**, 4428 (1962).

(11) The nmr spectrum of 2-bromopropiophenone (Sadtler No. 496) shows an α proton centered at δ 5.19 (CCl_4).

Experimental Section

All melting points, from a Mel-Temp capillary melting point apparatus, were corrected. Microanalyses were performed by Midwest Microlaboratories, Inc., Indianapolis, Ind. Infrared spectra were recorded with a Perkin-Elmer Model 137 Infracord. The nmr spectra were recorded on a Varian Model A-60 spectrometer, employing tetramethylsilane as an internal standard. Molecular weights were determined in chloroform on a Mechrolab vapor pressure osmometer, Model 301A.

Preparation of 6,7,8,9-Tetrahydro-2H-benz[*cd*]azulen-2-one (2).—A stirred, heterogeneous mixture of 22.7 g (0.1 mol) of **3**[9] and 150 ml of 15% hydrochloric acid solution was refluxed for 26 hr. After 4 hr a brown oil began to form on the acidic solution surface and, at the completion of the reflux period, this oil was separated and extracted with acetone. The orange insoluble material was filtered and recrystallized from dimethylformamide as dark yellow prisms (52%, based on weight recovery), mp >320°. This product was assumed to be a polymeric material of simplest empirical formula $C_{95}H_{80}N_5O_6$ (on basis of analysis).

Upon addition of water to the acetone extract, a second product was obtained which was filtered and recrystallized from benzene-hexane as light yellow plates. This material was identical with that substance which sublimed in the reflux condenser during the hydrolysis. Upon sublimation of this material *in vacuo* [82° (0.25 mm)], light yellow plates (20%, based on weight recovery), mp 88-90°, were obtained: λ_{max}^{KBr} 3.44 (CH), 5.92 (C=O), 6.28 μ (C=C); nmr ($CDCl_3$) δ 1.72–2.55 (4 H, m), 2.83–3.17 (4 H, m), 5.92 (1 H, s), 7.03–7.62 (3 H, m).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.78; H, 6.52; O, 8.88; mol wt, 184. Found: C, 84.61; H, 6.86; O, 8.84; mol wt, 186.

Compound **2** was also obtained by subjecting the initial brown oil to sublimation *in vacuo* at 82° (0.25 mm).

Preparation of Dimer 5a.—A yellow, homogeneous solution of 2.27 g (0.01 mol) of **3** in 50 ml of 15% sodium hydroxide solution was refluxed for 5 days with stirring (NH_3 evolution). After about 6 hr, a yellow material began to precipitate. At the conclusion of the reflux period the product was collected and recrystallized from ethyl acetate (42%), mp 252°, as white plates which could also be sublimed *in vacuo* [212° (0.3 mm)]: λ_{max}^{KBr} 3.41 (CH), 3.49 (CH), 5.82 (C=O), 6.19 μ (C=C); nmr ($CDCl_3$) δ 1.25–3.19 (16 H, m), 3.90 (1 H, s), 4.14 (1 H, t), 7.08–7.58 (6 H, m).

Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.78; H, 6.52; O, 8.88; mol wt, 368. Found: C, 85.05; H, 6.38; O, 8.71; mol wt, 358.

The reddish ethyl acetate mother liquor was evaporated and yielded a product which was sublimed *in vacuo* [82° (0.25 mm)], mp 88-90°, as light yellow needles (8%). This lower melting product was found to be identical with **2** by comparison with an authentic sample using thin layer chromatography employing ether-cyclohexane in a 1:1 ratio, and by comparison of ir spectra.

Catalytic Reduction of 5a.—A solution of 1.0 g (3.0 mmol) of **5a** in 100 ml of absolute ethanol was shaken with 0.8 g of platinum oxide in an atmosphere of hydrogen for 4 hr, after which the catalyst was removed and washed with warm ethanol. The ethanol mother liquors were combined and evaporated under a stream of air, leaving a white crystalline residue of **6** recrystallized from methanol as cream prisms (70%): mp 187-189°; λ_{max}^{KBr} 3.40 (CH), 3.49 (CH), 5.87 μ (C=O). Quantitative hydrogenation indicated an uptake of 1 mol of hydrogen.

Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.32; H, 7.03; O, 8.64; mol wt, 370. Found: C, 84.22; H, 7.05; O, 8.92; mol wt, 367.

Bromination of 5a.—A solution of 1.84 g (5.0 mmol) of **5a** in 320 ml of glacial acetic acid was stirred briefly at 0° before the dropwise addition of 1.60 g (0.01 mol) of Br_2 in 10 ml of glacial acetic acid. The addition to the stirred, cold acetic acid solution required 15 min. After stirring at room temperature for 1 hr, the red solution was poured over ice and the resulting aqueous solution was allowed to stand overnight, yielding a yellow product (67%). The product was collected by filtration, washed with water, and recrystallized from tetrahydrofuran-water as white needles: mp 182-182.5°; λ_{max}^{KBr} 3.41 (CH), 3.51 (CH), 5.87 (C=O), 6.22 μ (C=C); nmr (CF_3COOH) δ 1.70–2.38 (14 H, m), 4.00 (1 H, s), 5.15 (1 H, s),[11] 7.12–7.78 (6 H, m).

Anal. Calcd for $C_{26}H_{22}O_2Br_2$: C, 59.32; H, 4.18; Br, 30.39; mol wt, 526. Found: C, 59.33; H, 4.50; Br, 29.89; mol wt, 522.

Extraction of the aqueous mother liquor with three 50-ml portions of chloroform followed by drying of the extracts with anhydrous calcium chloride, filtration, and evaporation yielded no additional products.

Registry No.—2, 17791-29-6; 5a, 17791-30-9; 5b, 17791-31-0; 6, 17818-08-5.

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An Unusual Coupling of Cyclohexenone Cyclic Ketals

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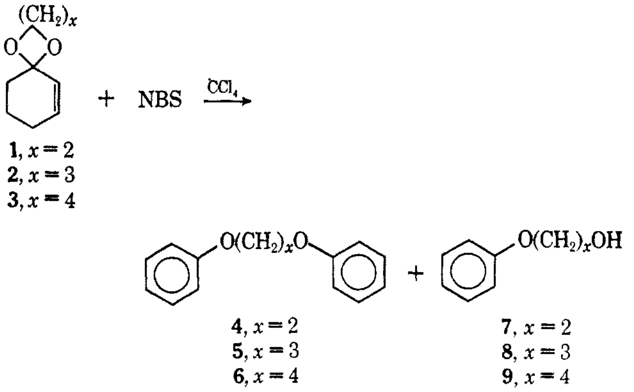
In a recent Note,[1] the preparation of 4-bromo-2-cyclohexenone ethylene ketal was reported as arising from the reaction of 2-cyclohexenone ethylene ketal and N-bromosuccinimide (NBS), using azobisisobutyronitrile and ultraviolet (uv) light as catalysts. When the reaction between 2-cyclohexenone ethylene ketal and NBS which had been recrystallized from water was carried out, a dramatically different result was obtained.



1, $x = 2$
2, $x = 3$
3, $x = 4$

4, $x = 2$
5, $x = 3$
6, $x = 4$

7, $x = 2$
8, $x = 3$
9, $x = 4$

When cyclic ketal **1** was treated with 1 equiv of NBS in refluxing carbon tetrachloride, a vigorous exothermic reaction occurred after only several minutes. Removal of the succinimide and evaporation of the solvent left a material whose ir spectrum showed strong absorption at 8.05, 13.36 and 14.45 μ. Elution chromatography of the crude reaction mixture yielded a white,[2] crystalline compound (**4**) and a much smaller amount of a colorless oil (**7**), bp 68–70° (3 mm). Compound **4** displayed the following: a mass spectrum with the parent peak at *m/e* 214 and intense fragments at *m/e* 121 and 107; uv absorption maximum at 220 mμ with weak absorption at 270 and 277 mμ; and pertinent ir bands at 6.26, 6.71, 8.05, 11.31, 12.54, 13.36 and 14.45 μ. The nmr spectrum of **4** displayed signals at δ 4.25 (2 H, s), 6.84 (3 H, m), and 7.25 (2 H, m). The melting

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[1] M. Graff and W. H. Gilligan, *J. Org. Chem.*, **32**, 3203 (1967).

[2] This material darkened slowly upon standing, probably indicating the presence of a small quantity of a presently unidentified bromine-containing material.