

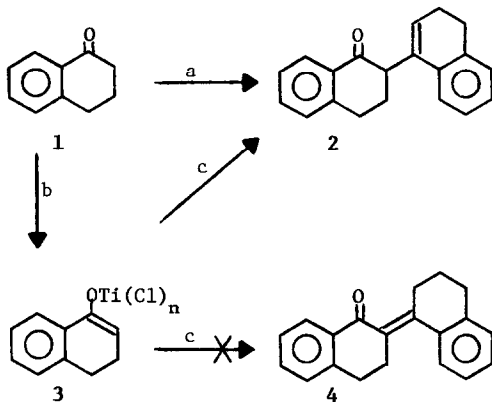
ALDOL DIMERIZATION OF 1-INDANONE AND 1-TETRALONES

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Abstract: The aldol dimerization of 1-indanone and 1-tetralones using titanium tetrachloride and triethylamine as condensing agents provides α,β - and β,γ -unsaturated ketones, respectively, in 53-58% yield.

Aldol dimerization of ketones has been extensively reviewed.² However, dimerization of 1-tetralones has not received wide attention despite the attractiveness of these products as precursors in the synthesis of α,β -linked polycyclic systems.³ For example, 1,2'-binaphthyl systems and hydrogenated derivatives free of the 1,1'- and 2,2'-isomers.³

The dimer product isolated from the acid-catalyzed, self-condensation of 1-tetralone (1) was previously reported to be the α,β -unsaturated ketone 4.^{3a} This structure has been corrected to that of the β,γ -unsaturated ketone 2.^{4a,4b} The yield of 2 in these earlier preparations^{4a,4b} was low but to date, it is the only pure compound reported from the reaction. We attempted improving the yield of 2 using acidic^{5a,b} and basic^{5c} reagents. Of these, Amberlyst-15^{5b} in refluxing xylene, was the most practical but the yield did not exceed 20%. Under comparable conditions, 6-methoxy-1-tetralone failed to react. We also tried using *p*-toluenesulfonic acid in ethylene glycol and toluene according to a patented procedure⁶ for dimerization of 6-methoxy-1-tetralone. The yield of dimer ketone was 12%.

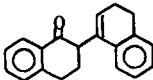
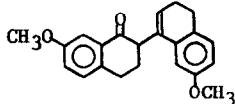
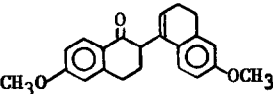
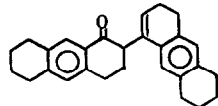
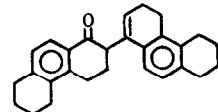
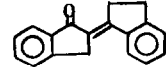


^a H^+ , $-\text{H}_2\text{O}$, Δ . ^b TiCl_4 , -10°C . ^c1-Tetralone, $(\text{CH}_3\text{CH}_2)_3\text{N}$.

Using equimolar quantities of 1 and the preformed enolate 3, in the presence of anhydrous triethylamine, gave 2 in 70% yield.⁶ We could not isolate or show that 4 is a product. This result prompted study of related ketones to gain information about the regioselectivity of formation of the compounds shown in Table I. Of these, 5, 7, and 8 are new.

Table I lists the dimer ketones prepared using preformed titanium enolates. In all cases involving self-condensation of 1-tetralones, the β,γ -unsaturated isomer was obtained as the isolated product. The α,β -unsaturated isomer is possibly present in the reaction mixture but we were unable to isolate or identify it. In comparison, applying this procedure to 1-indanone, we obtained the crystalline α,β -unsaturated ketone **9** free of the β,γ -isomer.

Table I. NMR and Yield Data for Dimer Ketones.

Dimer Ketone	% Yield	mp, °C	¹ H-NMR (δ from TMS)		¹³ C-NMR (ppm from TMS)	
			Vinyl ^a	Methine ^b	Carbonyl ^c	Methine ^d
2 	70	133-135 132-135 ^e	5.78	3.84	198.5 (197.4)	50.7
5 	70	123-127	5.77	f	198.5 (196.6)	50.4
6 	78	123-125 124-126 ^g	5.62	3.70	197.9 (197.8)	50.5
7 	74	160-163	5.68	3.84	198.3 (197.8)	50.1
8 	71	140-143	5.66	3.76	198.7 (197.5)	49.8
9^h 	53	142-143 ⁱ	j	j	194.6 (206.1)	j

^aVinyl triplet, J=4-5 Hz. ^bMethine triplet, J=6-7 Hz. ^cShift value of monomer ketone carbonyl is noted in parentheses. ^d α to C=O. ^eRef. 4b. ^fObscure. ^gRef. 4c. ^hStructure **9** is arbitrary. We have no evidence regarding its stereochemistry. ⁱ(Lit.⁷ 142-143 °C) Yellow crystals, failed to form oxime. ^jAbsent.

We attempted cross condensation of preformed enolate of 1-tetralone with 1-indanone as well as preformed enolate of 1-indanone and 1-tetralone. An intractable complex mixture re-

sulted in both cases. GC/MS studies showed these to be similar mixtures of C₁₈, C₁₉, and C₂₀ dimers.

As expected, the titanium enolate method is sensitive to steric effects. Dimerization of 3,5,8-trimethyl-1-tetralone, as a trial case, gave no more than a trace of dimer with starting material recovered.

To verify the structure assignments suggested for **2**, **5**, **6**, **7**, **8**, and **9** ¹H- and ¹³C-NMR spectra were obtained. Comparison of carbonyl resonances in the ¹³C-NMR spectra of **2**, **5**, **6**, **7**, and **8** with those of the respective monomer ketone shows little change in chemical shift from TMS, whereas the spectrum of **9** shows a 12 ppm carbonyl upfield shift from that of 1-indanone.

Ketones **2**, **5**, **7**, and **8** show a carbonyl deshielding of 1 to 2 ppm with respect to their corresponding monomer ketone. This is due to substitution α to the carbonyl in the dimer ketones. Compound **9** shows a ¹³C shielding effect on the carbonyl group due to contribution from neighboring carbon-carbon double bond. This is due to increased electron density at the carbonyl carbon from the conjugated π system. Thus, ¹³C-NMR clearly shows absence of conjugation in ketones **2**, **5**, **7**, and **8** as was observed for **9**. There is a consistent shift of the vinyl proton resonance and also that of the methine proton α to the carbonyl group in the β,γ-unsaturated ketones **2**, **5**, **6**, **7**, and **8** as given in Table I. These high absorptions are absent in the spectrum of **9**.

High resolution mass spectral data for the compounds in Table I verified the empirical formulae. The elemental analyses in Table II also confirmed the empirical formulae of **5**, **7**, and **8**.

Table II. High Resolution Mass Spectral and Elemental Analyses Data.

Compound	Formula	Calculated Mass	Observed Mass	Calculated (Found) %	
				C	H
2	C ₂₀ H ₁₈ O	274.2357	274.2340		
5	C ₂₂ H ₂₂ O ₃	334.1569	334.1560	79.00 (79.09)	6.64 (6.81)
6	C ₂₂ H ₂₂ O ₃	334.1569	334.1554		
7	C ₂₈ H ₃₀ O	382.2297	382.2285	87.91 (88.10)	7.91 (7.87)
8	C ₂₈ H ₃₀ O	382.2297	382.3210	87.91 (87.94)	7.91 (8.00)
9	C ₁₈ H ₁₄ O	246.1044	246.1073		

General Procedure for the Preparation of β,γ-Unsaturated Ketones.⁶ **3,3',4,4'-Tetrahydro-1',2'-binaphthalen-1(2H)-one.** To 200 mL of olefin-free *n*-hexane was added 69.9 g (56.0 mL, 0.51 mol) TiCl₄ in an N₂ atmosphere. The mixture was cooled by an

ice-salt water bath to $-10\text{ }^{\circ}\text{C}$ and a solution of 66 mL (72.5 g, 0.5 mol) of 1-tetralone (1) in 850 mL CH_2Cl_2 was added rapidly, with vigorous stirring, to give a fluffy, yellow precipitate. Subsequently, a solution of 66 mL (72.5 g, 0.5 mol) of 1 and 148 mL ($1^{\wedge}7.5$ g, 1.1 mol) of triethylamine diluted to 850 mL with CH_2Cl_2 was added. The ensuing red-black solution was stirred at $-10\text{ }^{\circ}\text{C}$ for 40 min and then allowed to warm to room temperature. After 16 h, the black product was treated with 1.6 L H_2O (3x), dried (MgSO_4), and concentrated. The product was washed with 200 mL of 2-propanol and the wash was filtered to give a combined yield of 96 g (70%) of 2. Recrystallization from 1 L of 2-propanol gave 70 g of white crystals: mp $130\text{--}133\text{ }^{\circ}\text{C}$ [lit.^{4b} $133\text{--}135\text{ }^{\circ}\text{C}$]; $^1\text{H-NMR}$ (CDCl_3) δ 8.1 (m, 1, ArH peri to carbonyl), 7.00–7.55 (m, 7, ArH), 5.77 (m, 1, C-2' vinyl H), 3.83 (t, 1, C-2 methine H), 3.00 (m, 2, C-4' H), 2.64–2.85 (m, 2, C-4), 2.1–2.45 (m, 4, C-3, C'H); mass spectrum m/z (M^+ , 100).

Preparation of 5,6,7, 8 and 9. Application of the above procedure to the appropriate monomer ketone gave the following colorless dimeric ketones. The yields and other data are found in Tables I and II.

- 7,7'-Dimethoxy-3,3',4,4'-tetrahydro-1',2-binaphthalen-1(2H)-one (5).
 6,6'-Dimethoxy-3,3',4,4'-tetrahydro-1',2-binaphthalen-1(2H)-one (6).
 3,3',4,4',5,5',6,6',7,7',8,8'-Dodecahydro-1',2-bianthracen-1(2H)-one (7).
 3,3',4,4',5,5',6,6',7,7',8,8'-Dodecahydro-1',2-biphenanthrene-1(2H)-one (8).
 2-[2',3'-Dihydro-1'H-inden'1'-ylidene]-2,3-dihydro-1H-inden-1-one (9).

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References and Footnotes

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