

## ATTEMPTS TO SYNTHESIZE SOME ENONES

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**ABSTRACT:** In this report, we synthesised some model enones to reveal the true nature of their further transformation into dihydrofuran derivatives *via* [1,5]-ring closure reactions with carbenes.

**Key Words:**  $\alpha,\beta$ -unsaturated ketone, aldol condensation, benzylation

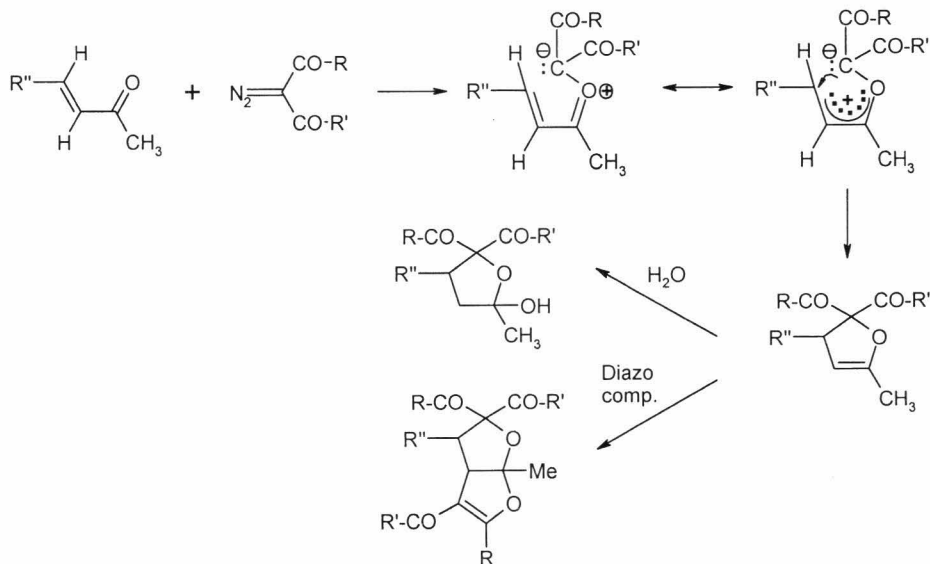
### BAZI ENONLARIN SENTEZİNE YÖNELİK ÇALIŞMALAR

**ÖZET :** Bu çalışmada karbenler ile [1,5]-halka kapanması reaksiyonu sonucu dihidrofuran türevlerinin oluşumunu yönlendirebileceği düşünülen enon bileşikleri sentezi üzerine çalışılmıştır.

**Anahtar Sözcükler:**  $\alpha,\beta$ -doymamış keton, aldol kondenzasyonu, benzoilasyon.

### INTRODUCTION

In recent years, we have been investigating the metal salt catalysed reactions of several  $\alpha$ -diazo- $\beta,\beta'$ -dicarbonyl compounds with  $\alpha,\beta$ -conjugated ketones and their derivatives [1,2]. As a result of these studies, we have published some results on the formation of dihydrofurans *via* 1,5-ring closure of the carbonyl ylid intermediates (Figure 1) [2].



**Figure 1.** Formation of dihydrofurans *via* 1,5-ring closure of the carbonyl ylids

There are also some recent reports [3-5] based on our studies [1,2].

The obtained dihydrofurans were observed to react further with a second molecule of the diazo compound, and/or with water.

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In order to reveal the true nature of the mechanisms of these reactions, the preparation of some model enone compounds, that would be suitable to force the reactions to follow desired paths, were needed. Through those attempts of synthesis we came across with both expected results, leading to known or new enones, and some unexpected products. It is authors' hope that the reporting these results in a separate paper might be useful for whom interested in synthesising enones.

## EXPERIMENTAL

Melting points are uncorrected. IR: JASCO FT-IR 5300 apparatus, reported in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: in  $\text{CDCl}_3$ , 200 and 250 MHz Bruker apparatus, TMS as internal standard,  $\delta$  in ppm,  $J$  in Hz.  $^{13}\text{C}$  NMR at 50 and 63 Mhz. GC-MS: Hewlett-Packard instrument with HP-1 capillary column (24 m. long, packed with cross-linked phenylmethyl siloxane), EI-MS detector; column conditions:  $100^\circ\text{C}$  (5' isothermal), heat to  $280^\circ\text{C}$  with  $10^\circ\text{C}/\text{min}$ , 20' isothermal at  $280^\circ\text{C}$ ; He 0.54 bar.

*1-phenyl-2-methyl-1-pentene-3-one* (**1**) was prepared from the aldol condensation reaction between benzaldehyde and 3-pentanone with pyrrolidine as an amine catalyst [6]. The crude product was distilled (40 mm,  $163\text{-}165^\circ\text{C}$ ). Yield 65%. IR: 3071, 2946, 2893, 1697, 1446, 1214, 1036, 696. GC-MS (min): 10.94 (24%), 12.88 (76%). EI-MS ( $m/z$  %): *Z*-isomer: 174 (38) [ $\text{M}^+$ ], 145 (69), 117 (100), 115 (89), 91 (41), 77 (9), 65 (13), 63 (14), 51 (16), 39 (14). *E*-isomer: 174 (45) [ $\text{M}^+$ ], 145 (75), 117 (97), 115 (100), 91 (48), 77 (8), 65 (13), 63 (12), 51 (15), 39 (13).  $^1\text{H}$ -NMR: *E*-isomer (73.2%): 7.52 (vinyl), 7.40-7.14 (phenyl), 2.83 (q, 2H,  $J$ :7.2 Hz,  $-\text{CH}_2\text{CH}_3$ ), 2.06 (s, 3H,  $=\text{C}-\text{CH}_3$ ), 1.17 (t, 3H,  $J$ :7.2 Hz,  $-\text{CH}_2\text{CH}_3$ ). *Z*-isomer (23.1%): 7.52 (vinyl), 7.40-7.30 (phenyl), 2.79 (q, 2H,  $J$ :7.2 Hz,  $-\text{CH}_2\text{CH}_3$ ), 2.02 (s, 3H,  $=\text{C}-\text{CH}_3$ ), 1.12 (t, 3H,  $J$ :7.2 Hz,  $-\text{CH}_2\text{CH}_3$ ).

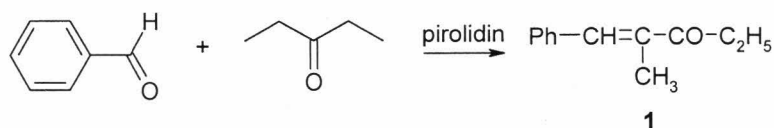
*2,5-dimethyl-3,4-diphenyl,4-hydroxycyclo-2-pentenone* (**2**) was prepared from the aldol condensation reaction between benzil and 3-pentanone [7]. Recrystallisation from ether gave light yellow crystals. Yield 73%. Mp:  $146\text{-}148^\circ\text{C}$ . IR: 3435, 3024, 2982, 2930, 1697, 1614, 1446, 1373, 1334, 1234, 1062, 991, 931. GC-MS (min): 20.56 (93%), 20.64 (7%). EI-MS ( $m/z$  %): *Z*-isomer (93%): 278 (61) [ $\text{M}^+$ ], 263 (100), 235 (28), 205 (19), 201 (10), 145 (10), 115 (60), 91 (22), 77 (53), 51 (18). *E*-isomer (7%): 278 (59) [ $\text{M}^+$ ], 263 (100), 235 (30), 205 (18), 201 (8), 145 (6), 115 (55), 105 (54), 91 (18), 77 (51), 51 (15).  $^1\text{H}$ -NMR: *Z*-isomer (93%): 7.29-7.11 (phenyl), 2.73 (q, 1H,  $J$ : 7.32 Hz,  $\text{CH}-\text{CH}_3$ ), 2.30 (br.s, 1H, OH, disappears on addition of  $\text{D}_2\text{O}$ ), 1.97 (s, 3H,  $=\text{C}-\text{CH}_3$ ), 1.21 (d, 3H,  $J$ :7.39 Hz,  $=\text{C}-\text{CH}_3$ ). *E*-isomer (7%): 7.99-7.63 (phenyl), 2.91 (q, 1H,  $J$ :7.2 Hz,  $\text{CH}-\text{CH}_3$ ), 2.30 (br.s, 1H, OH, disappears on addition of  $\text{D}_2\text{O}$ ), 2.02 (s, 3H,  $=\text{C}-\text{CH}_3$ ), 0.73 (d, 3H,  $J$ :7.2 Hz,  $=\text{C}-\text{CH}_3$ ).  $^{13}\text{C}$ -NMR: *Z*-isomer (93%): 209.0 (CO), 167.6 (Ph-C=C), 145.5 (Ph-C), 137.6 (PhC-C=), 133.5 (PhC=C), 130.2-124.3 (phenyl), 84.9 (C-OH), 56.0 (CH-CH<sub>3</sub>), 10.0 (C=C-CH<sub>3</sub>). *E*-isomer (7%): 206.0 (CO), 166.3 (Ph-C=C), 141.5 (PhC-C(OH)), 137.4 (PhC-C=), 132.9 (Ph-C=C), 130.2-124.3 (phenyl), 82.5 (C-OH), 55.7 (CH-CH<sub>3</sub>), 9.9 (=C-CH<sub>3</sub>).

*Tetrahydrobenzophenone* **8** was prepared from benzoyl chloride and cyclohexene by means of the Friedel-Crafts method [8]. The crude product was distilled (40 mm,  $200\text{-}205^\circ\text{C}$ ). Yield ca. 15%. GC-MS (min): 14.30 (24.3%), 14.47 (4.9%), 15.13 (44.2%), 15.88 (8.1%), 16.91 (11.4%), 17.06 (5.9%), 19.44 (1.2%). EI-MS ( $m/z$  %): (**8-10**)  $t_{\text{R}}$ : 14.30 (24.3%) 186 (24) [ $\text{M}^+$ ], 157 (10), 129 (6), 115 (5), 105 (100), 91 (3), 77 (75), 53 (9), 51 (27);  $t_{\text{R}}$ : 14.47 (4.9%) 186 (3) [ $\text{M}^+$ ], 157 (2), 128 (1), 115 (2), 105 (100), 91 (2), 77 (45), 53 (5), 51 (15);  $t_{\text{R}}$ : 15.13 (44.2%) 186 (67) [ $\text{M}^+$ ], 157 (25), 129 (11), 115 (9), 105 (83), 91 (5), 77 (100), 53 (16), 51 (42); (**5-7**)  $t_{\text{R}}$ : 15.89 (8.1%) 204 (6) [ $\text{M}^+$ ], 186 (17), 157 (7), 120 (13), 105 (100), 91 (4), 77 (47), 51 (11);  $t_{\text{R}}$ : 16.91 (11.4%) 204 (1) [ $\text{M}^+$ ], 187 (12), 146 (12), 133 (4), 105 (100), 91 (1), 77 (48), 51 (15);  $t_{\text{R}}$ : 17.06 (5.9%) 204 (1) [ $\text{M}^+$ ], 186 (3), 145 (11), 133 (4), 105 (100), 91 (1), 77 (47), 51 (14), 41 (7); (**11**)  $t_{\text{R}}$ : 19.44 (1.2%) 268 (40) [ $\text{M}^+$ ], 225 (5), 207 (7), 163 (89), 133 (7), 121 (11), 105 (100), 95 (36), 81 (46), 77 (87), 67 (35), 51 (17), 41 (23).

## RESULTS

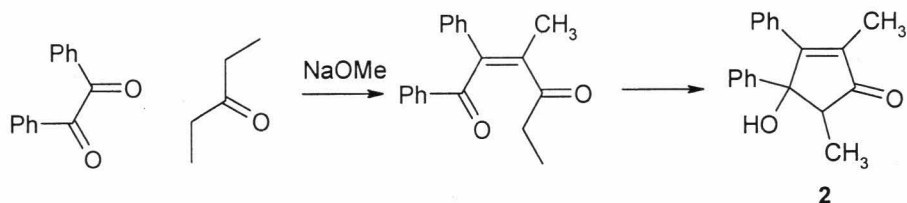
Aldol condensation reaction and Friedel-Crafts type olefin acylation reaction were used for the syntheses of appropriate enones.

Reaction of benzaldehyde and diethyl ketone in basic medium [6] afforded the expected enone **1** as a mixture of geometric isomers (76% *E*, 24% *Z*) in 65% yield (Figure 2).



**Figure 2.** Reaction of benzaldehyde and diethyl ketone

Reaction of benzil with diethyl ketone in basic medium [7] resulted with formation of 2,5-dimethyl-3,4-diphenyl-4-hydroxycyclopent-2-ene-1-one **2** as a mixture of geometric isomers (93% *E*, 7% *Z*) in 73% yield (Figure 3).



**Figure 3.** Reaction of benzil with diethyl ketone

Friedel-Crafts type benzylation of cyclohexene by the procedure of Christ and Fuson [8, see also 9] gave results rather different from those reported by the cited authors. The product distribution was attributed to the suggested mechanism of the reaction as shown in Figure 4.

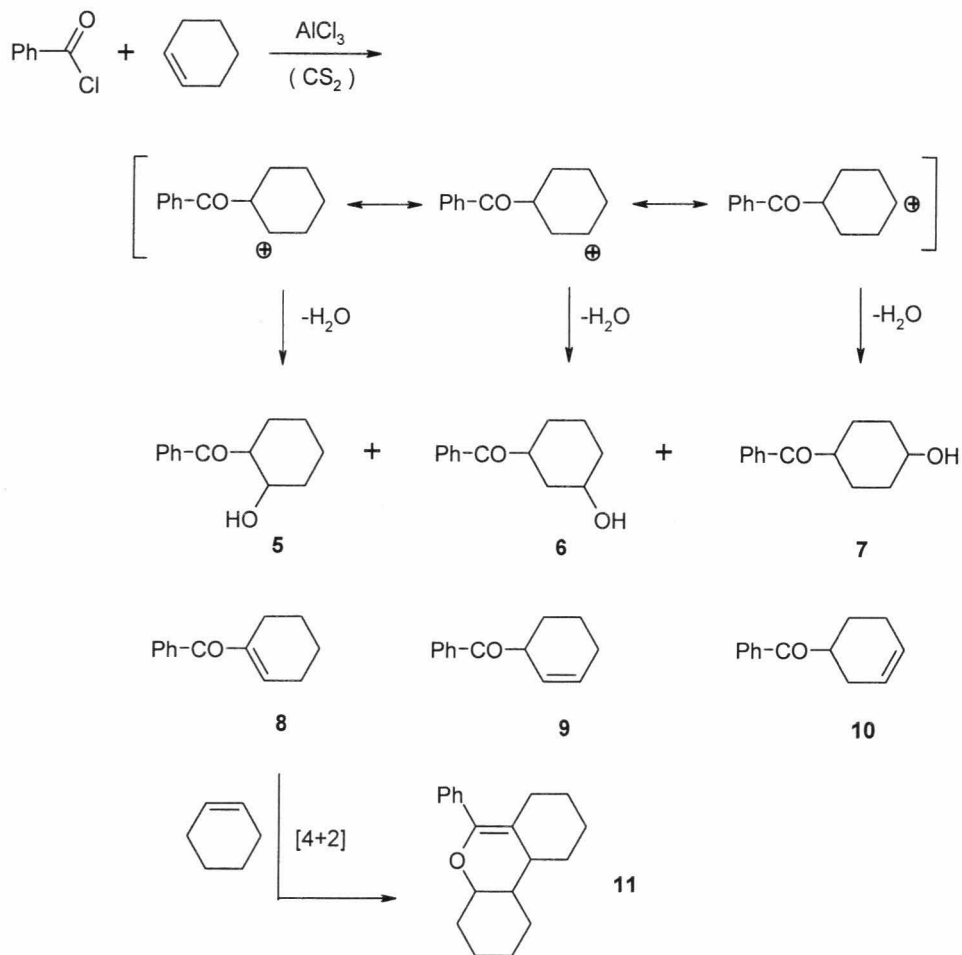


Figure 4. Products from benzoylation of cyclohexene

## DISCUSSION

Under the conditions of this work, benzylidene diethyl ketone **1**, was obtained expectedly as a mixture of geometric isomers of *E* and *Z* with a yields of 76% and 24% respectively by a smooth reaction. The same product was obtained by different methods as reported in the literature [10, 11]. Koester and Pourzal [10] used  $\text{R}^2\text{BOCOR}^1$  as catalyst. On the other hand, Gaudemar has obtained compound **1** as a minor product only in his experiments [11].

The initial condensation product from the reaction of benzil and diethyl ketone smoothly ring closed by aldolisation and afforded product **2**. The same enone was reported to be obtained by different methods in comparable yields earlier [12-14]. This reaction might be useful for further syntheses of cyclopentadienones.

Benzoylation of cyclohexene gave three isomeric hydroxy compounds **5-7** (25.4% total), three isomeric unsaturated ketones **8-10** (73.4% total) and a Diels-Alder adduct (**11**, 1.2%). On the other hand, Christ and Fuson [8] reported the formation of only two products, one of them being **8** with 40% yield while leaving the second product unidentified.

Reactions of these enones with carbenes are currently under study.

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## REFERENCES

- [1] Sezer Ö., Daut A., Anaç O., *Helv. Chim. Acta*, 78, 2036-2041 (1995).
- [2] Anaç O., Daut A., *Liebigs Ann./Recueil*, 1249-1254 (1997).
- [3] Maas G., Muller A., *J.F.Praktische Chemie, ChemikerZeitung*, 340 (4), 315- 322 (1998).
- [4] Hamaguchi M, Matsubara H, Nagai T., *J Org.Chem.*, 66 (16), 5395-5404 (2001).
- [5] Ferreira VF, Pereira LOR, de Souza MCBV et al., *Quim Nova*, 24 (4), 540-553 (2001).
- [6] Locksley H.D., Rainey D.K., *J. Chem. Soc. Perkin Trans. 1*, 23, 3001-3006 (1972).
- [7] Allen C.F.H., Rosener H.B., *J. Am. Chem. Soc.*, 49, 2110-2113 (1927).
- [8] Christ R.E., Fuson R.C., *J. Am. Chem. Soc.*, 893-897 (1937).
- [9] Wallach, *Liebigs Ann. Chem*, 305, 274 (1899).
- [10] Koester R., Pourzal A., *Ger. Offen.* 2, 417, 357 (1975) (*Chem. Abstr.* 84, 16961j (1976)).
- [11] Gaudemar F.B., *Ann. Chim.*, 3, 52-107 (1958).
- [12] Kraiman E.A., *Macromol. Syn.*, 2, 110-113 (1966).
- [13] Yates P., Yoda N., Brown W., Mann B., *J. Am. Chem. Soc.*, 80, 202-205 ., (1958).
- [14] Baranyovits F.L.C., Downes J.E., *Brit. Pat.* 1,052,951 (1966) (*Chem. Abstr.* 66, 94727e (1967))