3(2H)Furanone Derivatives. Ring-Chain Tautomerism in the 1,3,4,6-Tetraketone Series (1)

M. Poje and K. Balenovic*

Department of Organic Chemistry, University of Zagreb, Strossmayerov trg 14, 41001
Zagreb, Croatia, Yugoslavia

Received August 23, 1978

Ring-chain tautomeric equilibria in the 1,3,4,6-tetraketone series 1 have been examined and the identification of the chain-form 2 and hydroxyfuranone 3 has been accomplished from [1]H-nmr spectra; the relative contribution of the two depends on the structure and also on the solvent. Conversions of 1 into 3(2H)furanones 4 and 5 involving the cyclic tautomer 3 are described.

The facility with which certain polycarbonyl compounds form cyclic tautomers is a phenomenon of considerable biological importance. The isolation of a number of hydroxylated 2-benzyl-2-hydroxy-3(2H)benzofuranones, cyclic tautomers of the open-chain α-diketones, together with dihydroflavonols of corresponding structures has thrown light on the biogenetical relations between chalcone, aurone, and flavonoid pigments in higher plants (2). Very little attention, however, has been paid to the potential role of such cyclic intermediates in accounting for the variety of different cyclization paths from the same polyketoacid stage in biogeneses of the polyketide type. Moreover, contrary to the well established ring-chain tautomerism in dicarbonyl compounds, only scattered reports on polycarbonyl systems have appeared in the literature (3-5).

On account of the close relationship between tautomerism and rearrangements, which are sometimes indistinguishable, certain characteristics of polycarbonyl model compounds 1 which combine the properties of α-, β-, γ-, and ε-diketones may be explained by ring-chain tautomeric equilibria. Instances of considerable interest are biogenetic type reactions (6) and oxidative rearrangements (1,7-9) of tetraketones 1, which are readily ac-

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cessible by Claisen condensation (9-11). Besides being an explanation for the unexpected reactivity, ring-chain tautomerism can also be a convenient rationalization for the spectral properties of 1,3,4,6-tetraketones 1.

Since spectroscopic measurements can be performed on relatively undisturbed molecules, they may become a valuable means of estimating the ring-chain tautomeric equilibria, particulary for those pairs which undergo rapid interconversions. This approach was successful in the study of 2,2,9,9-tetramethyldecane-3,5,6,8-tetrone (1a), where the [1]H-nmr spectrum at 35° in DMSO-d_6 showed an unsymmetrical pattern due to the superposition of the cyclic form 3a (85%) over the symmetrical pattern associated with the open-chain form 2a (15%). The tautomer 2a is characterized by a two-proton singlet at δ 6.69 as well as an eighteen-proton singlet at δ 1.20, and the tautomer 3a by a one-proton singlet at δ 5.47, an AB-quartet at δ 3.19 (J = 17.0, Δν = 28.8 cps) characteristic of diastereotopic methylene protons, and two nine-proton singlets at δ 1.16 and 1.06 corresponding to nonequivalent t-butyl groups. The intermolecular hydrogen exchange between 2a and 3a is fast on the nmr time scale and an averaged spectrum results, giving rise to a signal at δ 7.60 (OH). In deuteriochloroform, however, only the chain-form 2a can be detected, giving rise to three singlets at δ 15.50 (OH), δ 6.53 (=CH-), and δ 1.20 t-butyl).

The integration of the spectrum of an unsymmetrical tetraketone, 1-phenylheptane-1,3,4,6-tetrone (1e), indicated the presence of 84% of the two possible cyclic forms 3e/3f in a 6:1 ratio, and 16% of the chain-form 2e in DMSO-d_6. This was in good agreement with our proposal of the cyclic tautomers 3e,f being intermediates in the oxidation of 1e with lead tetra-acetate in acetic acid, which on rearrangement afforded two corresponding dehydroacetic acid analogues in a 3:1 ratio (1).

Under most conditions, in polar protic solvents, the exchange rate between the two forms 2 and 3 is fast on the nmr time scale and an averaged spectrum results, which, because of its symmetrical appearance, tends to be
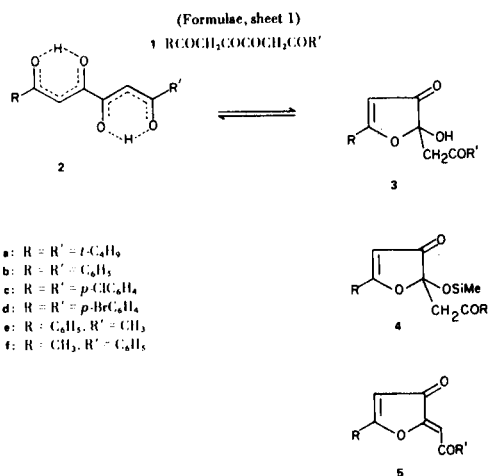
interpreted as evidence for the predominance of the chain tautomer. The ring-chain equilibria in protic solvents can be estimated from the ultraviolet spectra. The fact that tetraketone **1b** showed an intense absorption band at 370 nm in the dichloromethane, was taken as evidence that only the chelated dienol form **2b** exists in non-polar solvents. The same compound in methanol, however, showed three maxima at 364, 320 and 248 nm. It was concluded that the tetraketone **1b** contains appreciable amounts of the cyclic tautomer in protic solvents, because of appearance of two additional absorptions characteristic of less conjugated hydroxyfuranone form **3b** being in a mobile equilibrium with the open-chain form **2b**.

Careful choice of experimental conditions enabled the isolation and separation of both the yellow and of the highly unstable colourless form of 1,6-diphenylhexane-1,3,4,6-tetrone (**1b**) after neutralization of the aqueous solution of its disodium derivative. The infrared spectrum of the colourless crystals showed peaks at 1717 and 1688 cm^{-1} corresponding to the ring and aryl ketone, respectively. The ultraviolet spectrum in methanol showed maxima at 247 and 312 nm. The AB pattern in ^{1}H-nmr (DMSO-d_6)showed the presence of diastereotopic methylene protons, consistent with the structure of 2-hydroxy-2-phenacyl-5-phenyl-3(2H)furanone (**3b**). The infrared spectrum of the yellow crystals exhibited a broad band in the 1600-1490 cm^{-1} region, characteristic of conjugated chelates. The ^{1}H-nmr spectrum in deuterio-chloroform showed a symmetrical pattern in agreement with the structure **2b**. Mass spectra of **2b** and **3b** showed molecular ions at m/e 294, and an identical fragmentation pattern.

With the possibility in mind of tetraketone structures either of the open-chain **2** or the hydroxyfuranone **3** forms, we made the monotrimethylsilyl derivatives **4a-d** by reaction of tetraketones with trimethylsilyl chloride in dry pyridine. On treatment with diluted acids, trimethylsiloxyfuranones **4a-d** were quantitatively converted into parent tetraketones **1a-d**. The problem of structure determination was considerably simplified in dealing with derivatives which are not readily inter-convertible. Hence the structural assignment to the stable derivatives **4a-d** is more straightforward than to the parent hydroxyfuranones **3**. The compounds **4a-d** were characterized chemically and spectroscopically; all data were consistent with trimethylsiloxyfuranone structures **4**.

All attempts to convert tetraketones **1** into acylated derivatives of **2** or **3** failed. The reaction with acetic anhydride in pyridine proceeded with partial cleavage of tetraketones. Under same conditions, however, compounds **1c,d** underwent the cyclization into **5c,d** in high yields. The structures **5** were assigned on the basis

of its characteristic spectral properties, and (Z)-configurations of the exo-double bond from marked downfield shifts of hydrogens in cis-relation to ring carbonyl groups (**5c**, δ 6.97; **5d**, δ 6.96 in deuteriochloroform). It seems probable that the cyclization proceeds via intermediate 2-acetoxy-3(2H)furanone and subsequent base initiated β-elimination, where the p-halogens may be involved in the stabilization of the incipient double bond. The reverse ring-opening and conversion into parent tetraketones **1c,d** can be carried out by treatment of **5c,d** with 70% acetic acid in the presence of pyridine. Similarly, reactions of **5c,d** with o-phenylenediamine in benzene afforded quinoxaline derivatives of parent tetraketones **1c,d**.

The cleavage of the chain upon benzoylation of the disodium derivative of **1b** led to the formation of dibenzoylmethane (**6**) in a 25% yield. It seems likely that the cleavage is due to the hindrance to coplanarity and, consequently, to the destabilization of the form **2a** by electrophylic substitution on a polydentate system.

There is no reliable evidence for the existence of any keto-form among tetraketones **1**, presumably on account of steric hindrances. The dienol form **2**, or the cyclic tautomer **3** derived therefrom, appears to dominate in this class of compounds, in contrast to simple systems which are known to exist in keto-enol equilibria. The hindrances to coplanarity in the resonance-stabilized form **2a** by substitution, or a lower degree of enolization in polar solvents, appear to stabilize the cyclic form **3**.

EXPERIMENTAL

Ring-Chain Tautomeric Equilibrium of 2,2,9,9-Tetramethyldecane-3,5,6,8-tetrone (**1a**).

The open chain form **2a** (100%) had ^{1}H-nmr (deuteriochloroform): δ 15.50 (bs, 2H, OH), 6.53 (s, 2H, =CH-), 1.20 (s, 18H, CMe$_3$); ^{1}H-nmr (DMSO-d_6), open-chain form **2a** (15%): δ 7.60 (bs, 2H, OH), 6.59 (s, 2H, =CH-), 1.20 (s, 18H, CMe$_3$); and the cyclic form **3a** (85%): δ 7.60 (bs, 1H, OH), 5.47 (s, 1H, =CH-), 3.19 (d, d, 2H, CH$_2$, J = 17.0, $\Delta\nu$ = 28.8), 1.16 (s, 9H, COCMe$_3$), 1.06 (s, 9H, CMe$_3$).

Ring-Chain Tautomeric Equilibrium of 1-Phenylheptane-1,3,4,6-tetrone (**1e**).

The open-chain form **2a** (16%) had ^{1}H-nmr (DMSO-d_6): δ 8.00, 7.66 (umc, 5H, phenyl), 7.60 (bs, 2H, OH exchangeable with D$_2$O), 7.16 (s, 1H, =CH-), 6.57 (s, 1H, =CH-), 2.16 (s, 3H, CH$_3$); the cyclic form **3e** (72%): δ 8.00, 7.66 (umc, 5H, phenyl), 7.60 (bs, 1H, OH), 6.43 (s, 1H, =CH-), 3.11 (d, d, 2H, J = 15.6, Δν = 12.6), 2.23 (s, 3H, COCH$_3$), and the cyclic form **3f** (12%): δ 8.00, 7.66 (umc, 5H, phenyl), 7.60 (bs, 1H, OH), 5.56 (s, 1H, =CH-), 3.65 (d, d, 2H, CH$_2$, J = 15.5, Δν = 19.8), 2.12 (s, 3H, CH$_3$).

2-Hydroxy-2-phenacyl-5-phenyl-3(2H)furanone (**3b**).

To stirred 8% methanolic sodium hydroxyde (20 ml.), finely powdered **1b** (5.88 g., 0.02 mole) was gradually added. The precipitated disodium derivative of **1b** was collected, washed with methanol, and dried *in vacuo*. The yellow powder (6.1 g.) was resuspended in water, stirred at ice-bath temperature, and precooled 5% sulphuric acid added dropwise to pH 7. The crystalline precipitate was collected, washed with water, and dried *in vacuo* at -5°. Colourless crystals were separated mechanically and 0.15 g. (2.5%) of **3b**, m.p. 164-176°, was obtained. Attempts to purify this product by recrystallization failed; uv λ max (methanol): nm (log ε) 247 (4.05), 312 (4.01); the spectrum gradually changed to equilibrium showing maxima at 248 (4.00), 320 (4.00), and 364 (4.17), identical to those of the yellow form **2b** dissolved in methanol; ir (potassium bromide): ν max 1717, 1688, 1600, 1580, 1145, 845, 750, 690 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.06-7.24 (um, 11H, phenyl and OH exchangeable with deuterium oxide), 6.47 (s, 1H, =CH-), 3.72 (d, d, 2H, CH$_2$, J = 15.7, Δν = 20.3); ms: m/e (relative intensity) 294 (3.2, P), 238 (2.6), 190 (4.3), 189 (33.4), 148 (10.8), 147 (100.0), 120 (3.2), 105 (11.2), 103 (2.1), 102 (2.1), 91 (4.0), 79 (1.7), 78 (1.7), 77 (4.5), 70 (1.5), 69 (45.2), 44 (1.0), 43 (1.0). On standing the colourless form **3b** gradually changed to the yellow form **2b**, m.p. 178-9°.

The yellow form of 1,6-diphenylhexane-1,3,4,6-tetrone (**1b**) was recrystallized twice from chloroform and yielding 4.4 g. (74%) of **2b** as long yellow needles, m.p. 180° [lit. (10) m.p. 179-80°]; uv (dichloromethane): λ max nm (log ε) 370 (4.44); ir (potassium bromide): ν max 1600, 1580-1490, 1250, 767, 700 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 15.70 (bs, 2H, OH), 8.02-7.54 (um, 10H, phenyl), 7.13 (s, 2H, =CH-); mass spectra of **2b** and **3b** were identical.

5-t-Butyl-2-pivaloylmethyl-2-trimethylsiloxy-3(2H)furanone (**4a**).

To a stirred solution of **1a** (5.08 g., 0.02 mole) in dry pyridine (15 ml.), trimethylsilyl chloride (3.26 g., 0.03 mole) was gradually added in the course of 30 minutes and then stirred for 12 hours at room temperature. The cold mixture (-10°) was diluted with water (30 ml.) and extracted with light petroleum (3 x 40 ml.). The extract was washed with cold water, dried, and the solvent removed *in vacuo*. A yellow oil remained (4.1 g.) which was treated with a little decolourizing charcoal in carbon tetrachloride. After removal of solvent repeated crystallization from light petroleum yielded 2.2 g. (34%) of **4a** as colourless prisms, m.p. 28-30°; uv (methanol): λ max nm (log ε) 266 (3.85); ir (neat): ν max 2970, 1723, 1717, 1593, 1253, 1174, 847 cm^{-1}. ^{1}H-nmr (carbon tetrachloride): δ 5.33 (s, 1H, =CH-), 3.02 (d, d, 2H, CH$_2$, J = 16.7, Δν = 12.7), 1.20 (s, 9H, COCMe$_3$), 1.08 (s, 9H, CMe$_3$), 0.16 (s, 9H, SiMe$_3$).

Anal. Calcd. for C$_{17}$H$_{30}$O$_4$Si: C, 62.53; H, 9.26. Found: C, 62.29; H, 9.53.

2-Phenacyl-5-phenyl-2-trimethylsiloxy-3(2H)furanone (**4b**).

To a well stirred suspension of finely powdered **1b** (8.82 g.,

0.03 mole) in dry pyridine (25 ml.), trimethylsilyl chloride (3.95 g., 0.036 mole) was added in the course of 30 minutes and then heated (60°) for further 6 hours. The resulting solution was cooled (-10°), diluted with water (25 ml.), and the olive-green crystals collected, washed with water, and dried. After treatment with a little decolourizing charcoal, two crystallizations from carbon tetrachloride gave 5.8 g. (53%) of **4b** as colourless plates, m.p. 126-8°. The analytical sample was obtained after two crystallizations from carbon tetrachloride, m.p. 130°; uv (methanol): λ max nm (log ε) 247 (4.04), 312 (4.00); ir (potassium bromide): ν max 1714, 1683, 1606, 1595, 1570, 1453, 1353, 1154, 1115, 898, 750, 690 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.69 (umc, 10H, phenyl), 6.15 (s, 1H, =CH-), 3.68 (d, d, 2H, CH$_2$, J = 15.5, Δν = 20.4), 0.17 (s, 9H, SiMe$_3$); ms: m/e (relative intensity) 367 (2.9, P + 1), 366 (8.7, P), 352 (1.1), 351 (7.5), 261 (1.0), 249 (1.0), 245 (1.2), 237 (4.7), 236 (1.6), 235 (9.4), 207 (3.6), 192 (3.1), 191 (3.1), 177 (5.7), 147 (3.6), 135 (2.8), 130 (3.5), 106 (4.7), 105 (55.3), 103 (15.7), 102 (100.0), 77 (15.1), 76 (3.4), 75 (13.4), 74 (2.9), 73 (27.5).

Anal. Calcd. for C$_{21}$H$_{22}$O$_4$Si: C, 68.82; H, 6.05. Found: C, 69.08; H, 6.09.

2-p-Chlorophenacyl-5-p-chlorophenyl-2-trimethylsiloxy-3(2H)furanone (**4c**).

To a suspension of **1c** (3.63 g., 0.01 mole) in pyridine (20 ml.), trimethylsilyl chloride (1.32 g., 0.012 mole) was added. After proceeding in the same manner as with **4b**, 2.1 g. (48%) of **4c** was obtained as colourless plates, m.p. 94-95° dec.; ir (potassium bromide): ν max 1717, 1684, 1609, 1594, 1489, 1412, 1407, 1365, 1257, 1184, 1176, 1122, 1092, 908, 845, 810 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.64, 7.54 (umc, 8H, C$_6$H$_4$), 6.15 (s, 1H, =CH-), 3.63 (d,d, 2H, CH$_2$, J = 15.5, Δν = 20.4), 0.17 (s, 9H, SiMe$_3$).

Anal. Calcd. for C$_{21}$H$_{20}$Cl$_2$O$_4$Si: C, 57.93; H, 4.63. Found: C, 58.20; H, 4.61.

2-p-Bromophenacyl-5-p-bromophenyl-2-trimethylsiloxy-3(2H)furanone (**4d**).

To a suspension of **1d** (4.52 g., 0.01 mole) in pyridine (20 ml.), trimethylsilyl chloride (1.32 g., 0.012 mole) was added. After proceeding in the same manner as with **4b**, the yield of **4d** was 2.3 g. (44%), m.p. 105° dec.; ir (potassium bromide): ν max 1717, 1690, 1608, 1591, 1485, 1408, 1368, 1257, 1130, 1071, 907, 840, 811 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.68, 7.63 (umc, 8H, C$_6$H$_4$), 6.15 (s, 1H, =CH-), 3.62 (d,d, 2H, CH$_2$, J = 15.5, Δν = 20.4), 0.17 (s, 9H, SiMe$_3$).

Anal. Calcd. for C$_{21}$H$_{20}$Br$_2$O$_4$Si: C, 48.81; H, 3.85. Found: C, 48.47; H, 3.97.

Hydrolysis of **4a-d**).

A solution of each **4a-c** (0.002 moles) in dioxane (10 ml.) was treated with 2% sulphuric or acetic acid (2 ml.). The reaction mixture was stirred for an hour at ambient temperature, and then diluted with water (20 ml.) to give parent tetraketones **1a-d** (9-11) in quantitative yields.

(Z)-2-p-Chlorophenacylidene-5-p-chlorophenyl-3(2H)furanone (**5c**).

To a suspension of finely powdered **1c** (3.63 g., 0.01 mole) in dry pyridine (10 ml.), acetic anhydride (10 ml.) was gradually added in the course of 30 minutes, and then heated (100°) for a further 30 minutes. In the course of the reaction the tetraketone dissolved, and a yellow precipitate occurred. The reaction mixture was cooled, and the product collected, washed with ether (3 x 2 ml.), and dried *in vacuo*. The crude product 3.2 g.,

was recrystallized from dichloromethane-light petroleum to give 3.07 g. (89%) of **5c** as yellow needles, m.p. 188° dec.; uv λ max (hexane): nm (log ϵ) 240 (4.33), 316 (4.55), 364 (4.05); ir (potassium bromide): ν max 1704, 1674, 1640, 1600, 1409, 1300, 1280, 1250, 1091, 1015, 997, 863, 811 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.73 (umc, 8H, C_6H_4), 6.97 (s, 1H, =CH-), 6.31 (s, 1H, =CH-); ms: m/e (relative intensity) 348 (12.1, P + 4), 346 (63.1, P + 2), 344 (95.0, P), 319 (10.6), 317 (61.0), 315 (12.2), 283 (11.3), 281 (34.0), 235 (5.5), 233 (14.0), 207 (25.5), 205 (10.7), 154 (14.2), 152 (42.6), 141 (38.3), 139 (100.0), 138 (29.8), 136 (88.0), 113 (25.6), 111 (73.1), 101 (25.0), 75 (22.7), 69 (92.2).

Anal. Calcd. for $C_{18}H_{10}Cl_2O_3$: C, 62.63; H, 2.91. Found: C, 62.73; H, 2.81.

(Z)-2-p-Bromophenacylidene-5-p-bromophenyl-3(2H)furanone (**5d**).

After proceeding in the same manner as with **5c**, tetraketone **1d** (4.52 g., 0.01 mole) gave 3.9 g. (91%) of **5d** as yellow needles, m.p. 194-195° dec.; uv λ max (hexane): nm (log ϵ) 243 (4.43), 318 (4.65), 366 (4.15); ir (potassium bromide): ν max 1704, 1674, 1643, 1600, 1406, 1299, 1250, 1070, 1012, 997, 867, 810 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.79 (umc, 8H, C_6H_4), 6.96 (s, 1H, =CH-), 6.31 (s, 1H, =CH-); ms: m/e (relative intensity) 436 (54.0, P + 4), 434 (100.0, P + 2), 432 (53.6, P), 407 (31.0), 405 (60.0), 403 (31.7), 355 (31.5), 327 (26.5), 325 (28.9), 281 (28.8), 267 (26.5), 253 (32.9), 251 (44.2), 198 (24.2), 196 (21.3), 185 (68.0), 183 (71.3), 182 (44.3), 180 (44.8), 157 (34.2), 155 (36.1), 135 (39.5), 119 (37.1), 101 (47.4), 91 (27.1), 73 (76.3), 69 (84.2).

Anal. Calcd. for $C_{18}H_{10}Br_2O_3$: C, 49.80; H, 2.32. Found: C, 49.99; H, 2.36.

Ring-Opening of **5c,d**.

A suspension of each **5c,d** (0.002 mole) in 70% acetic acid (10 ml.) and pyridine (1 ml.) was refluxed for two hours. The reaction mixture was diluted with water and the resulting solid collected, and crystallized from glacial acetic acid.

Compound **1c** was obtained as pale yellow leaflets, yield 80%, m.p. 229° [lit. (11) m.p. 229°]. Compound **1d** was obtained as pale yellow prisms, yield 82%, m.p. 217-218° [lit. (11) m.p. 217°].

Quinoxaline Derivatives of **1c** and **1d**.

A solution of each **5c,d** (0.001 mole) in benzene (10 ml.) was refluxed with an equimolar amount of o-phenylenediamine. The quinoxaline derivative of **1c**, m.p. 225° [lit. (11) m.p. 225°], and the quinoxaline derivative of **1d**, m.p. 244° [lit. (11) m.p. 244°], were obtained in quantitative yields.

Benzoylation of **1b**. 1,3-Diphenylpropane-1,3-dione (**6**).

To a suspension of finely powdered disodium derivative of **1b** (3.1 g., 0.009 mole) in anhydrous benzene (30 ml.), benzoyl chloride (5.0 g., 0.036 mole) was added, and the reaction mixture refluxed for an hour. The residue was covered with ethanol (15 ml.) and 1.0 g. (38%) of **1b** separated as yellow needles, m.p. 179°. The mother liquor was evaporated to dryness and the dark red oily residue heated in ligroin (40 ml.) under stirring for an hour. The orange-yellow solution was filtered, and the crude product purified by chromatography on silica gel (20 g., 70-230 mesh ASTM, Merck) with ligroin. After removal of the solvent the colourless needles were recrystallized from light petroleum to give 0.5 g. (25%) of **6** as colourless needles, m.p. 78° [lit. (12) m.p. 78°]; ir (potassium bromide): ν max 1600, 1580-1500 cm^{-1}. ^{1}H-nmr (deuteriochloroform): δ 16.80 (bs, 1H, OH), 7.95, 7.50 (umc, 10H, phenyl), 6.77 (s, 1H, =CH-).

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.04; H, 5.37.

REFERENCES AND NOTES

(1) Part XIX. Part XVIII: M. Poje, B. Gašpert and K. Balenović, *Rec. Trav. Chim. Pays-Bas*, in press.

(2) A. Mustafa, "The Chemistry of Heterocyclic Compounds", Vol. 29, Wiley-Interscience, New York, N. Y., 1974, Chapter 5.

(3) P. R. Jones, *Chem. Rev.*, **63**, 461 (1963).

(4) P. E. Walter, *Russ. Chem. Rev.*, **42**, 464 (1973); *ibid.*, **43**, 665 (1974).

(5) R. Escale and J. Verducci, *Bull. Soc. Chim. France*, 1203 (1974).

(6) K. Balenović and M. Poje, *Tetrahedron Letters*, 3427 (1975).

(7) K. Balenović, *Experientia*, **2**, 1 (1946); *Rec. Trav. Chim. Pays-Bas*, **67**, 282 (1948).

(8) K. Balenović, Dj. Cerar and L. Filipović, *J. Org. Chem.*, **10**, 1556 (1956).

(9) K. Balenović, A. Deljac, B. Gašpert and Ž. Štefanac, *Monatsh. Chem.*, **98**, 1344 (1967).

(10) E. Bröme and L. Claisen, *Ber.*, **21**, 1134 (1888); P. F. Schmidt, *Ber.*, **28**, 1206 (1895).

(11) D. Keglević, M. Malnar and T. Tomljenović, *Ark. Kemi*, **26**, 67 (1954).

(12) C. F. H. Allen, R. D. Abell and J. B. Normington, *Org. Synth.*, Coll. Vol. 1, 205 (1941).