

EXPERIMENTAL

a) Reaction of 3-sulfolene with benzoyl peroxide and iodine. A three-necked flask fitted with a nitrogen inlet, a chemical stirrer, and reflux condenser connected with a gasometer was charged with 5.9 g (50 mM) of I, 18.37 g (75 mM) of benzoyl peroxide, and 12.7 g (50 mM) of iodine in 100 ml of carbon tetrachloride. The mixture was boiled for 48 hr. The gas collected was analyzed for its CO₂ content. The iodine that had not reacted was determined by titration with 0.1 N sodium thiosulfate solution, and the benzoyl peroxide iodometrically. The consumption of iodine was 12.5 mM (25%) and that of benzoyl peroxide 27.6 mM (36.8%), 3.0 mM of this (4%) having been consumed in the formation of CO₂. In order to eliminate the unchanged iodine and benzoyl peroxide, the reaction mixture was washed successively with aqueous solutions of Na₂SO₃ and NaHCO₃ and then with water. The wash waters were extracted with chloroform. The carbon tetrachloride and chloroform were eliminated in vacuum. Recrystallization of the residues from ether and carbon tetrachloride yielded 4.0 g (22%) of IV and 6.4 g (35%) of V. After three crystallizations, IV was obtained with mp 179–180° C (literature data [1] mp 179–180° C) and V with mp 122–124° C (literature data: 124.5–125° C).

b) The reaction of 3.3 g (25 mM) of II with 9.0 g (37.5 mM) of benzoyl peroxide and 6.3 g (25 mM) of iodine in 50 ml of carbon tetrachloride under similar conditions gave 2.0 mM (3%) of CO₂ and 5.0 g (53%) of VI. After two crystallizations, the product melted at 129–130° C (literature data: 130–131° C). The presence of traces of VII in the reaction products was detected by thin-layer chromatography.

c) The reaction of 3.3 g (20.1 mM) of III with 7.3 g (30.2 mM) of benzoyl peroxide and 5.1 g (20.1 mM) of iodine in 45 ml of carbon tetrachloride gave 3.0 mM (5%) of CO₂ and 0.9 g (11%) of VIII with mp 150–153° C (literature data: 156–157° C). The presence of traces of III in the reaction product with VIII was established by thin-layer chromatography.

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REACTION OF DIMEDONE WITH ALDEHYDES AND β-AMINOVINYL CARBONYL COMPOUNDS

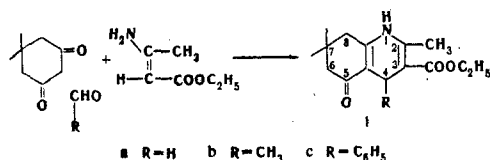
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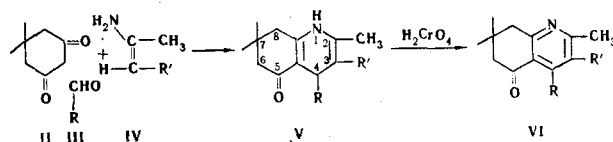
UDC 547.831.3:542.953:543.422.4.6

The unsymmetrical condensation of dimedone, an aldehyde, and various β-aminovinyl carbonyl compounds, and also bisacetonitrile, has given 3,4-disubstituted derivatives of 2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline (Va-f). Compounds Va, d, f have been oxidized with H₂CrO₄ to the corresponding 3,4-disubstituted 2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinolines (Via-c). The IR spectra of compounds Va-c, f and Via and the UV spectra of compounds Va, c, f, and Via, c have been recorded.

A preceding communication [1] described the unsymmetrical condensation of dimedone, an aromatic or aliphatic aldehyde, and an ester of β-aminocrotonic acid with the formation of a 4-substituted 3-ethoxy-carbonyl-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline (Ia-c).



Continuing our experiments, we tackled the problem of testing the possibility of a similar condensation with other β-aminovinyl carbonyl compounds. Condensation was carried out with acetylacetone imine, benzoylacetone imine, and bisacetonitrile, giving the corresponding 3,4-disubstituted derivatives of 2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline Va-f.



V: a R = C₆H₅; R' = COCH₃; d R = CH₃; R' = CN VI: a R = C₆H₅; R' = COCH₃
 b R = H; R' = COCH₃; e R = H; R' = CN b R = CH₃; R' = CN
 c R = C₆H₅; R' = CN f R = C₆H₅; R' = COC₆H₅; c R = C₆H₅; R' = COC₆H₅

The synthesis was carried out in ethanol with para-formaldehyde, acetaldehyde, and benzaldehyde. The synthesis with benzaldehyde gave good results. The

Table 1
Products of the Reaction of Dimedone with β -Aminovinyl
Carbonyl Compounds

Com- pound	Solvent* for crys- tallization	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
				C	H	N	C	H	N	
Va	1	198—200	C ₂₀ H ₂₃ NO ₂	77.45	7.62	4.62	77.62	7.49	4.53	41.0
VIa	2	107—108	C ₂₀ H ₂₁ NO ₂	77.93	7.00	4.05	78.14	6.89	4.56	51.0
Vb	3	209—211	C ₁₄ H ₁₉ NO ₂	72.48	8.25	6.11	72.07	8.21	6.00	20.0
Vc	4	230—232	C ₁₉ H ₂₀ N ₂ O	78.27	6.32	10.2	78.11	6.87	9.55	68.0
Vd	4	198—200	C ₁₄ H ₁₈ N ₂ O	72.54	7.77	12.13	73.01	7.88	12.16	68.0
VIb	4	84	C ₁₄ H ₁₆ N ₂ O	73.22	7.03	12.65	73.64	7.06	12.27	54.0
Ve**	4	234—236	C ₁₃ H ₁₆ N ₂ O	72.04	7.44	12.55	72.16	7.46	12.95	37.5
Vf	4,5	208—209	C ₂₅ H ₂₅ NO ₂	80.31	6.66	3.71	80.81	6.78	3.77	35.6
VIc	1	157—158	C ₂₅ H ₂₃ NO ₂	8.21	6.36	3.51	81.27	6.27	3.79	76.0

* (1) 40% ethanol; (2) ethanol + H₂O; (3) 30% ethanol; (4) 95% ethanol; (5) dimethylformamide.

** In the same way as for Va, to separate the desired product from the bisdimedonylmethane formed as an impurity, the reaction mixture was treated with a saturated solution of NaHCO₃.

Table 2
Spectroscopic Characteristics of the Compounds Synthesized

Com- pound	Bands of maximum absorption*		
	Medi- um**	IR spectra, cm ⁻¹	UV spectra, nm (in ethanol)
Va	PO	1663 (m), 1601 (m)	252 (10700)
	HB	3289 (m), 3220 (m)	401 (5240)
VIa	PO	1686 (m), 1660 (m), 1627 (sh), 1548 (m)	280 (11680)
Vb	PO	1696 (sh), 1679 (s), 1654 (sh), 1594 (s), 3288 (m)	
	DE	1694 (s), 1616 (m), 1592 (s), 3408 (sh), 3360 (w)	
Vc	PO	1657 (m), 1608 (s), 2212 (s)	230 (20000)
	HB	3243 (m), 3186 (s)	361 (11700)
Vf	PO	1654 (m), 1601 (s)	266 (17600)
	HB	3256 (m), 3188 (sh)	384 (4900)
VIc	—	—	241 (21300)

* m—medium; s—strong; w—weak; sh—shoulder.

** PO—paraffin oil; HB—hexachlorobutadiene; DE—dichloroethane.

reaction took place less satisfactorily with acetaldehyde and paraformaldehyde. It was impossible to obtain products of the condensation of acetaldehyde with dimedone and benzoylacetone imine or acetylacetone imine. When paraformaldehyde was used, a large amount of bisdimedonylmethane was obtained as a by-product, this being isolated and identified by means of its melting point, behavior in paper chromatography, and UV spectra. To separate them from the bisdimedonylmethane, the condensation products **Vb** and **e** were treated with a saturated solution of NaHCO_3 . Compounds **Va**, **d**, **f** were oxidized with chromic acid to the corresponding 3,4-disubstituted 2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinolines (**VIa-c**). Attempts to oxidize compound **Vf** with H_2O_2 and chloranil were unsuccessful. After **Vf** had been boiled with chloranil in xylene for 15 hr, the starting material was recovered. Thus, the best oxidizing agent available to us was chromic acid. We have studied the IR spectra of compounds **Va**, **b**, **c**, **f** and **VIa**. The IR spectra were taken in paraffin oil and hexachlorobutadiene and, in the case of compound **Vb**, also in dichloroethane solution. The IR spectra of similar compounds have been considered previously [2, 3]. In the $6\text{-}\mu$ region, compounds **Va-f** absorb in a similar manner to the 4-substituted derivatives of 3-ethoxycarbonyl-2-7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinolines that we have described previously. In the $3\text{-}\mu$ region ν_{NH} appears. The UV absorption spectra of compounds **Va**, **c**, **f**, and **VIa**, **c** are similar to those of the compounds described previously [1].

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3-Acetyl-2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline (Va). A mixture of 2 g (~ 0.015 mole) of dimedone, 1.42 g (~ 0.015 mole) of acetylacetone imine, and 1.52 g (~ 0.015 mole) of benzaldehyde was boiled in 30 ml of ethanol for 1 hr, assuming a dark yellow color. After the solvent had been distilled off, dilution with half a volume of water and storage at $0\text{-}4^\circ\text{C}$ for 2 days gave a yellow crystalline precipitate. Yield 1.8 g (41%), mp $198\text{-}200^\circ\text{C}$ (after three crystallizations from 40% ethanol). The substance dissolves

in methanol, benzene, dioxane, and acetic acid. In a solution of sodium methoxide it gives a dark yellow coloration. Found, %: C 77.45; H 7.62; N 4.62. Calculated for $\text{C}_{20}\text{H}_{23}\text{NO}_2$, %: C 77.62; H 7.49; N 4.53.

3-Acetyl-2,7,7-trimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydroquinoline (VIa). An aqueous solution of 1 g of chromic anhydride was added in small portions to a solution of 2 g (~ 6.5 mM) of **Va** in 50 ml of acetic acid heated to $70\text{-}80^\circ\text{C}$ until the color changed to dark green. After the mixture had been evaporated to half volume and had been diluted with water, a yellow crystalline substance deposited. Yield 1.01 g (51%), mp $107\text{-}108^\circ\text{C}$ (from ethanol + water). Found, %: C 77.93; H 7.00; N 4.05. Calculated for $\text{C}_{20}\text{H}_{21}\text{NO}_2$, %: C 78.14; H 6.89; N 4.56.

3-Acetyl-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline (Vb). This was obtained in a similar manner to **Va** from 2 g (~ 0.015 mole) of dimedone, 1.4 g (~ 0.015 mole) of acetylacetone imine and 0.45 g (~ 0.015 mole) of paraformaldehyde, boiled for 3 hr in 40 ml of ethanol. After the solvent had been distilled off, to separate the desired product from the bisdimedonylmethane formed as an impurity the dry residue was treated with a saturated solution of NaHCO_3 and the mixture was filtered. Yellow crystalline substance, yield 0.6 g (20%), mp $209\text{-}211^\circ\text{C}$ (after three crystallizations from 30% ethanol). In a solution of sodium methoxide it gave a dark yellow coloration. Found, %: C 72.48; H 8.25; N 6.11. Calculated for $\text{C}_{14}\text{H}_{19}\text{NO}_2$, %: C 72.07; H 8.21; N 6.0. The bisdimedonylmethane was identified by its mp of $139\text{-}190^\circ\text{C}$ (literature $191\text{-}191.5^\circ\text{C}$), paper chromatography in the butyl acetate-methanol-0.25% ammonia solution (95:5:25) system, R_f 0.94, and its UV spectrum in ethanol (263-264nm).

The constants, yields, and spectroscopic characteristics of the substances synthesized are given in Tables 1 and 2.

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N-SUBSTITUTED 1,3-DIMETHYL-2-IMINOBENZIMIDAZOLINE

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The N-alkylation, N-arylation, and N-acylation of 1,3-dimethyl-2-iminobenzimidazoline are reported.

N-Substitution in the 2-iminobenzimidazoline series has not previously been studied. Our experiments have

shown that the action of alkylating agents on 1,3-dimethyl-2-iminobenzimidazoline (I) [1] leads to the formation of benzimidazolium salts (II) which, on treatment with alkali, are converted into 2-alkylimino-1,3-dimethylbenzimidazolines (III). Similarly, 1,2-dibromoethane reacts with I to form IV and V.