CONDENSATION OF DIMEDONE N-METHYLIMINE WITH ISOPROPYLIDENE ARYLIDENEMALONATES

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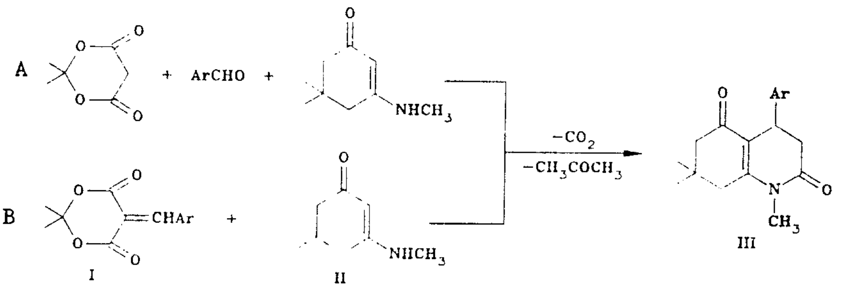
Condensation of dimedone N-methylimine with isopropylidene arylidenemalonates has given 4-aryl-1,7,7-trimethyloctahydroquinoline-2,5-diones, characterized by their IR, UV, and PMR spectra.

The use of isopropylidene arylidenemalonates (I) in the synthesis of heterocyclic compounds has received little attention, although it is certainly of interest in view of their accessibility and the mild conditions required for their reactions. Condensation of (I) with β-dicarbonyl compounds affords coumarins [1] and quinolines [2, 3]. In order to extend the synthetic possibilities of this reaction, and to examine the structures of the products, we have condensed dimedone N-methylimine (II) with some isopropylidene arylidenemalonates.



IIIa $Ar=C_6H_5$; b $Ar=p\text{-}O_2NC_6H_4$; c $Ar=m\text{-}O_2NC_6H_4$; d $Ar=o\text{-}O_2NC_6H_4$; e $Ar=p\text{-}ClC_6H_4$; f $Ar=p\text{-}CH_3OC_6H_4$; g $Ar=o\text{-}CH_3OC_6H_4$; h $Ar=2,4\text{-}(CH_3O)_2C_6H_3$; i $Ar=3,4\text{-}(CH_3O)_2C_6H_3$

The reaction proceeds satisfactorily in boiling alcohols with the elimination of acetone and loss of carbon dioxide. It has been shown that the condensation may be carried out either by generating (I) in the reaction mixture itself (from isopropylidene malonate and the aromatic aldehyde in the presence of piperidine as catalyst) (method A), or using previously isolated and purified (I) (method B). The condensation affords the 4-aryl-1,7,7-trimethyl-1,2,3,4,5,6,7,8-octahydroquinoline-2,5-diones (III).

The IR spectra of (III) show strong absorptoin at 1680-1720 cm^{-1} corresponding to stretching vibrations of the 5-carbonyl group, and at 1637-1657 cm^{-1}, which may be assigned to stretching vibrations of the 2-carbonyl group.

The UV spectra of (IIIa-i) show absorption with λ_{max} 293-305 nm, similar to that seen with dimedone N-methylimine (λ_{max} 290 nm), but of lower intensity (ε11,400-20,000 and ε 32,000, respectively). Local excitation of the phenyl chromophore (203-207 nm) is increased when a second methoxy-group is present in the aromatic ring [from ε 16,800 for (IIIf) to 25,400 for (IIIh) and ε 30,000 for (IIIi)].

In the PMR spectra of the quinolinediones (IIIa-i), the protons of the methyl groups in the 7-position of the octahydroquinolinedione, and those at nitrogen and in the methoxy-substituents, the 4-aryl substituent, and the proton in the 4-position are readily identifiable.

It is assumed that the signals for the methylene groups, seen at higher field (2.17-2.31 ppm, s), are attributable to the 6-CH$_2$ group, the multiplet splitting of the signal at 2.74-2.95 ppm to the protons in the 3-position, and the protons in the 8-position are magnetically nonequivalent (2.51-2.60 ppm, d, J = 8-12 Hz).

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TABLE 1. 4-Aryl-1,7,7-trimethyloctahydroquinoline-2,5-diones

Compound	Empirical formula	mp, °C	IR spectrum, cm^{-1}		UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	PMR spectrum, δ, ppm (J, Hz)								Yield, %	
			5-CO	2-CO		$C(CH_3)_2$, (s 6H)	$6\text{-}CH_2$ (s 2H)	$8\text{-}CH_2$ (d, 2H)	$3\text{-}CH_2$ (m, 2H)	$N\text{-}CH_3$ (s 3H)	$O\text{-}CH_3$ (s)	4-CH (t 1H)	4-Ar	A	B
IIIa	$C_{18}H_{21}NO_2$	152...154	1697	1645	204 (11,2), 227 pl (3,8), 303 (11,4)	1,12	2,29	2,51 ($J=9$)	2,80...2,88	3,19		4,34	7,11...7,18 (m, 5H)	42	39
IIIb	$C_{18}H_{20}N_2O_4$	192...194	1695	1643	203 (20,0), 215 pl (12,0), 293 (20,0)	1,12 (d $J=1$)	2,31	2,55 ($J=8$)	2,83...2,93	3,22		4,46	7,24...8,11 (q, 4H)	70	82
IIIc	$C_{18}H_{20}N_2O_4$	124...126	1693	1640	206 (18,0), 217 pl (13,0), 300 (15,8)	1,13	2,32	2,60 ($J=10$)	2,86...2,93	3,22		4,44	7,38...7,98 (q, 4H)	46	44
IIId	$C_{18}H_{20}N_2O_4$	172...174	1680	1647	204 (20,4), 219 pl (13,0), 301 (16,0)	1,10	2,17	2,57 ($J=8$)	2,88...2,95	3,22		4,79	6,86...7,99 (m 4H)	65	65
IIIe	$C_{18}H_{20}ClNO_2$	181...183	1693	1653	204 (16,0), 219 pl (14,0), 302 (13,8)	1,10	2,29	2,51 ($J=8$)	2,75...2,87	3,18		4,31	6,90...7,32 (q, 4H)	57	61
IIIf	$C_{19}H_{23}NO_3$	124...126	1697	1641	203 (16,8), 226 (14,0), 286pl (12,0), 302 (15,6)	1,11	2,28	2,52 ($J=8$)	2,74...2,86	3,18	3,72 (3H)	4,28	6,68...7,07 (m, 4H)	39	35
IIIg	$C_{19}H_{23}NO_3$	159...161	1687	1657	204 (17,6), 220 (11,8), 302 (15,8)	1,16 (d $J=4$)	2,27	2,58 ($J=12$)	2,73...2,84	3,20	3,80 (3H)	4,58	6,69...7,24 (m, 4H)	58	73
IIIh	$C_{20}H_{25}NO_4$	178...180	1720, 1702	1655	206 (25,4), 222 pl (10,8), 288 pl (9,2), 305 (11,8)	1,16	2,29	2,57 ($J=11$)	2,71...2,78	3,20	3,78 (6H)	4,52	6,21...6,71 (m, 3H)	49	34
IIIi	$C_{20}H_{25}NO_4$	152...154	1700	1637	207 (30,0), 228 pl (13,2), 287 pl (14,0), 302 (15,4)	1,12	2,30	2,51 ($J=8$)	2,78...2,88	3,19	3,80 (6H)	4,30	6,62...6,74 (m, 3H)	39	43

EXPERIMENTAL

IR spectra were obtained on a Specord IR-75, UV spectra on a Specord UV-VIS spectrophotometer in ethanol, and PMR spectra on a Tesla BS 487-C (80 MHz) in $CDCl_3$, internal standard TMS.

The elemental analyses for (III) were in agreement with the calculated values.

Dimedone N-methylimine was obtained as described in [5], and the isopropylidene arylidenemalonates as described in [6].

4-Aryl-1,7,7-trimethyl-1,2,3,4,5,6,7,8-octahydroquinoline-2,5-diones (IIIa-i). A. To a solution of 1.44 g (10 mmoles) of isopropylidene malonate in 10 ml of ethanol was added 1-2 drops of piperidine and 10 mmoles of the aromatic aldehyde, the mixture heated on the water bath for a few minutes, and 1.53 g (10 mmoles) of dimedone N-methylimine added. After heating on the water bath for 0.5-1 h, the solution was evaporated and placed in the refrigerator. The solid which separated was filtered off and recrystallized from ethanol.

B. A mixture of 10 mmoles of the malonate (I) and 1.53 g (10 mmoles) of (II) in 10 ml of ethanol was boiled on the water bath until all the (I) had dissolved, and no more gas was evolved. The products were isolated and purified as in method A.

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