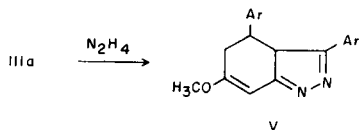


Table I
Physical and Analytical Data of Compounds III

Compound No.	Yield %	M.P. °C	Formula	Analysis Found %	
				C	H
a	42	141-142 Benzene	C ₂₀ H ₁₈ O ₃	78.43	5.88
				78.51	5.72
b	45	149-150 Ethanol	C ₂₀ H ₁₇ ClO ₃	70.58	5.00
				70.52	5.08
c	42	172-173 Ethanol	C ₂₀ H ₁₇ ClO ₃	70.58	5.00
				70.43	5.12
d	34	149-150 Ethylacetate	C ₂₀ H ₁₇ BrO ₃	62.17	4.61
				62.03	4.51
e	44	150-151 Ethanol	C ₂₁ H ₂₀ O ₄	75.00	5.95
				75.10	5.89
f	45	138-140 Ethanol	C ₂₁ H ₂₀ O ₄	75.00	5.95
				74.94	5.81
g	44	144-145 Ethanol	C ₂₁ H ₂₀ O ₃	78.75	6.25
				78.49	6.13



The ¹H nmr spectroscopic data for compounds IIIa-g in deuteriochloroform solution were carefully studied and are given in Table II. Our assignment of these structures is based upon the proton magnetic resonance studies of similar compounds [15]. These compounds show four important peaks at δ 5.32-5.46, 3.8-4.4, 4.48-4.94 and 2.64-2.92 with intensities corresponding to one hydrogen each except in some examples which correspond to two hydro-

gens. These peaks correspond to H-2, H-5, H-6 and H-4 respectively.

Since the carbon-13 spectra are more sensitive to changes in structures, an examination of the carbon-13 spectra of compounds IIIb and IIIg was undertaken. The results of this investigation are summarized in Table III.

The non-aromatic regions are characterized by the presence of eight signals. The shifts of the *O*- and *C*-methyl groups and the carbonyl function are derived from chemical shift theory [13]. The quaternary carbons C-1, C-3 and the Ar-C=O resonance at *ca.* 198, 177 and 195 ppm are distinguished from other signals by its multiplicity in the off-resonance experiments. In the case of the remaining carbons, C-2 resonates at 102.2, C-4, C-5, C-6 and CH₃O resonates at 35.8, 41.4, 56.0 and 59.2 ppm respectively for IIIb and resonates at 36.0, 41.7, 56.0 and 59.5 ppm respectively for compounds IIIg. The above assignments were made on the basis of model compounds [19] and single-frequency off-resonance decoupling.

EXPERIMENTAL

The ir spectra were obtained in Nujol mulls on a Beckman Acculab T-M spectrophotometer. The uv absorption spectra were recorded in methanol or chloroform on a Pye Unicam SP 8-200 spectrophotometer. The nmr spectra were taken on a Bruker WH 90 Ds spectrometer equipped with ASPECT 2000, 32 K Computer, operating at 22.63 MHz. Melting points are uncorrected. Elemental analysis were performed by Alfred Bernhardt Laboratories, Ruhr, Germany.

Preparation of Ethyl β-Methoxycrotonate II [20].

Ethyl acetoacetate (130 g) was mixed with redistilled trimethylorthoformate (106 g) and dry methanol (100 ml), and then concentrated hydro-

Table II
Spectral Data of Compounds III

Compound No.	Infrared (cm ⁻¹)	Bands (Nujol) [h] Assignments	Nuclear Magnetic Resonance Values [a] δ					
			H-2 [b]	H-4 [c]	H-5 [d]	H-6 [e]	OMe [f]	Ar-H [g]
a	1695	conjugated C=O	5.44	2.76	3.92	4.62	3.68	7.2-7.72
	1658	exocyclic C=O						
b	1687	conjugated C=O	5.44	2.72	3.9	4.6	3.7	7.1-7.76
	1665	exocyclic C=O						
c	1675	conjugated C=O	5.46	2.92	4.4	4.84	3.72	7.75-7.88
	1645	exocyclic C=O						
d	1685	conjugated C=O	5.4	2.7	3.88	4.56	3.68	6.86-7.77
	1650	exocyclic C=O						
e [i]	1675	conjugated C=O	5.32	2.64	3.8	4.48	3.6	6.52-7.66
	1645	exocyclic C=O						
f [j]	1685	conjugated C=O	5.4	2.86	4.08	4.96	3.68	6.56-7.8
	1655	exocyclic C=O						
g [k]	1690	conjugated C=O	5.44	2.75	3.9	4.9	3.7	6.82-7.8
	1660	exocyclic C=O						

[a] Deuteriochloroform was used as a solvent: [b] s, 1H. [c] s, 2H. [d] Sextet, 1H. [e] d, 1H, J_{5,6} = 11-13.5 Hz. [f] s, 3H. [g] m, 10H for compound a and 9H for compounds b-g. [h] Only absorption bands in the more significant range 1800-1500 cm⁻¹ were reported. [i] 3.56, s, 3H, OCH₃. [j] 3.7, s, 3H, OCH₃. [k] 2.2, s, 3H, CH₃.

Table III

Carbon-13 Chemical Shifts (δ) for Compounds III

	IIIb	IIIg [b]
C-1	198.155	198.480
C-2	102.229	102.229
C-3	177.098	177.488
C-4	35.875	36.070
C-5	41.464	41.724
C-6	56.086	56.021
Ar-C=O	195.100	195.555
CH ₃ O	59.271	59.596
Aromatic Carbons	139.859, 137.974	138.364, 136.804
	133.165, 129.785	132.905, 129.466
	128.680, 127.511	128.680, 127.966, 127.121

[a] Deuteriochloroform was used as a solvent. [b] 20.992, CH₃.

chloric acid (0.5 ml) was added. The mixture was distilled immediately to give ethyl β -methoxycrotonate (144 g, 100 %), bp 188-194°.

6-Aroyl-5-aryl-3-methoxy-2-cyclohexenones III. General Procedure.

A mixture of 1,3-diaryl-2-propen-1-ones I (0.05 mole), 75 ml of dry THF and ethyl β -methoxycrotonate (II) (0.05 mole) was added to a suspension of sodium hydride (0.05 mole) in 75 ml of dry THF at 0°. The mixture was stirred for 10 hours at 0°, quenched with water (15 ml) and acidified with dilute hydrochloric acid to pH 7. The water layer is extracted with ethyl acetate (3 \times 100 ml). The combined ethyl acetate solutions were dried with magnesium sulfate. After evaporation of the solvent under vacuum, crystallisation of the residue from the appropriate solvent, the corresponding products were obtained (Table I).

REFERENCES AND NOTES

- [1] R. Hansel, J. Schulz, A. Pelter and M. T. Ayoub, *Z. Naturforsch.*, **33b**, 1020 (1978).
- [2] R. Hansel, M. T. Ayoub and A. Pelter, *Z. Naturforsch.*, **34b**, 1576 (1979).
- [3] A. Pelter, M. T. Ayoub, J. Schulz, R. Hansel and D. Reinhardt, *Tetrahedron Letters*, 1627 (1979).
- [4] M. T. Ayoub, M. Y. Shandala, A. Pelter and G. M. Gussab Bashi, *J. Chem. Soc., Perkin Trans. I*, 697 (1981).
- [5] M. Y. Shandala and N. H. Al-Jobour, *J. Chem. and Eng. Data*, **21**, 118 (1976); *ibid.*, 120 (1976).
- [6] M. Y. Shandala, H. N. Al-Jallo, N. H. Al-Jobour and F. Al-Hajjar, *ibid.*, **21**, 115 (1976).
- [7] M. Y. Shandala and N. W. Al-Jobour, *Aust. J. Chem.*, **29**, 1583 (1976).
- [8] M. Y. Shandala, A. Al-Khashab, N. H. Al-Jobour and M. Al-Arab, *J. Prakt. Chem.*, **6**, 321 (1979).
- [9] N. Al-Jobour and M. Y. Shandala, *J. Heterocyclic Chem.*, **17**, 941 (1980).
- [10] M. Y. Shandala, A. Y. Al-Khashab, M. Afzal and S. S. Ahmad, *J. Heterocyclic Chem.*, **17**, 1605 (1980).
- [11] E. Smismann and A. Voldeng, *J. Org. Chem.*, **29**, 3161 (1964).
- [12] Y. Anghelova and C. Ivanov, *Chem. Ber.*, **106**, 2643 (1973).
- [13] Y. Anghelova, *Synthesis*, 343 (1974).
- [14] J. Martelli, D. Danion and R. Carrie, *Tetrahedron*, **30**, 3063 (1974).
- [15] C. Ivanov and T. Tcholakova, *Synthesis*, 392 (1981).
- [16-18] M. Y. Shandala and M. T. Ayoub (under publication).
- [19] J. B. Sothers, "Carbon-13 NMR spectroscopy", Academic Press New York, 1972.
- [20] H. Brinkhoff, British Patent 1,137,466 (1967); *Chem. Abstr.*, **70**, 77348x (1969).