Tetrahedron. Vol. 28, pp 1565 to 1573. Pergamon Press 1972. Printed in Great Britain

SYNTHESIS AND PROPERTIES OF *TRANS* 1-ARYL-2-BENZOYLCYCLOPROPANES AND THEIR VINYLOGES

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(*Received in the UK* 6 *September* 1971; *Accepted for publication* 14 *October* 1971)

Abstract – 1-Aryl-2-benzoylethylenes react with dimethyloxosulfonium methylide in dimethylformamide and form *trans* 1-aryl-2-benzoylcyclopropanes, the configuration of which was confirmed by double ^{13}C NMR spectroscopy. The reaction proceeds exclusively at the double bond adjacent to carbonyl group with 1-aryl-4-benzoylbuta-1,3-dienes and 1-aryl-6-benzoylhexa-1,3,5-trienes and leads to *trans* 1-(2′-(aryl)vinyl)-2-benzoylcyclopropanes and *trans* 1-(4′-arylbuta-1′,3′-dienyl)-2-benzoylcyclopropanes correspondingly. IR- and UV-spectroscopic evidence points to conjugation between the carbonyl group and the cyclopropane ring in all compounds. Mass-spectra of benzoylcyclopropanes are characterized by a common ion; the ratio of the intensity of this common ion to the intensities of the molecular ions for 1-aryl-2-benzoylcyclopropanes is correlated with the Hammett–Brown 6 constants. Polarographic behaviour of 1-aryl-2-benzoylcyclopropanes is also reported.

1-ARYL-2-BENZOYLCYCLOPROPANES (I) have been little studied. To date only I (R = H) has been described and recently some 1-aryl-2-benzoyl-3,3-dideuterocyclopropanes (aryl = Ph, *p*-tolyl, *p*-MeO-, *p*-fluoro-, *p*-chloro-, *m*- and *p*-bromophenyl) were synthesized.[1,2] Meanwhile compounds of type I may be of great interest for the investigation of some theoretical problems such as the transmission of substituent influence through cyclopropane rings.[2,4] We found[5] that for the evaluation of the transmission of electronic effects through a double bond and a conjugated double bond system in compounds of the type $PhCO(CH{=}CH)_nC_6H_4R$(II) mass spectrometry may be successfully used. The method is free from many shortcomings of other methods because mass spectrometric fragmentation reactions proceed in the gas phase at pressures which prevent molecular collisions and solvatation interactions between solvent and solute which takes place when measurements are taken in solution. Thus the mass spectrometic method allows more unambiguous results to be obtained. Compounds I and II are of the general type $PhCO{-}X{-}C_6H_4R$ and we hoped that the mass spectrometric method would give us a good correlation in the case of I. Therefore we decided to prepare I and the vinyloges 1-(2′-arylvinyl)-2-benzoylcyclopropanes(III) and 1-(4′-arylbuta-1′,3′-dienyl)-2-benzoylcyclopropanes (IV) (compounds of types III or IV were not described) and to evaluate the transmission capability of the cyclopropane bridge by the mass spectrometric method.

Among possible routes to I, III and IV the addition of the methylene group at the activated double bond by the action of dimethyloxosulfonium methylide (V) is doubtless the simplest and most accessible path. This method was proposed by

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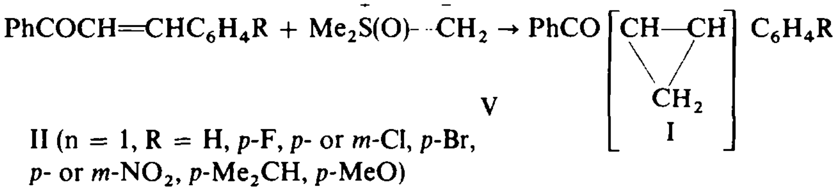
F. G. Corey and M. Chaykovsky,[6] who also used it for the synthesis of I (R = H). Corey did not establish the configuration of I (R = H) but considered it to be mixture of *cis* and *trans* isomers. Later C. Agami and J. Abouet[7] prepared I (R = H) by the same procedure and suggested that this compound has *trans* configuration on NMR spectral evidence. This suggestion was confirmed by D. H. Boykin *et al.*[1] who studied the NMR spectra of 1-phenyl-2-benzoyl-3,3-dideutero (and 3-mono-deutero)-cyclopropane prepared by the Corey method with dimethyloxosulfonium dideuteromethylide.

We also chose the Corey method and tried the action of V on II (n = 1, 2, 3) in DMFA instead of DMSO originally used in the above syntheses of I (R = H) and the dideutero-derivatives. The exothermic reaction between unsubstituted II (n = 1) or III (n = 2) with electronegative substituents in the *meta* or *para* positions and V proceeded accordingly to the scheme:



II (n = 1, R = H, *p*-F, *p*- or *m*-Cl, *p*-Br, *p*- or *m*-NO_2, *p*-Me_2CH, *p*-MeO)

As a result I is formed in rather high yield. II (n = 1) with electronodonating substituents in the *para* position such as Me, oxy- and OMe groups reacts with V, but

TABLE 1. YIELDS AND CONSTANTS OF OBTAINED I

N	R	Yield %	M.p.	MW (found by mass spectrometry)
Ia	H	98	42–43·5	221
Ib	*p*-F	55	53-54	239
Ic	*p*-Cl	77	52-53	255
Id	*m*-Cl	50	40-41	255
Ie	*p*-Br	95	79–80·5	300
If	*p*-NO_2	83	105-107	266
Ig	*m*-NO_2	40	70-70·5	266
Ih	*p*-i-Pr	50	40–41	263
Ii	*p*-MeO	65	37-38	251

ANALYTICAL DATA

Compound	C%		H%		R%	
	Found	Calc.	Found	Calc.	Found	Calc.
Ib	79·40	79·90	5·39	5·41	–	–
Ic	74·85	75·20	5·10	5·11	13·99	13·85
Id	75·20	75·20	5·12	5·11	13·82	13·85
Ie	63·65	64·00	4·47	4·35	26·47	26·50
If	71·59	71·90	4·89	4·90	5·19	5·24
Ig	71·70	71·90	5·10	4·90	5·36	5·24
Ih	86·06	86·32	7·68	7·63	–	–
Ii	80·89	80·92	6·31	6·39	–	–

II (n = 1, R = p-Me_2N) is isolated unchanged from the reaction. It should be noted that we did not succeed in isolating I (R = p-OH) in pure form from the reaction mixture containing too much unreacted II (n = 1, R = p-OH). *Ortho* substituted II (n = 1) reacts with V results in a complex mixture of products from which we could not isolate in pure form *ortho* substituted I. Yields and some physical properties of I are given in Table 1.

The structure of I was confirmed by analytical data and IR- and UV-spectra (see below) and the purity checked by TLC.

TABLE 2. C^{13} CHEMICAL SHIFTS OF I
(in ppm, measured to low field from external TMS[a])

Compound	Ia[b]	Ib	Ic	Ie	If	Ii
Chemical shifts						
C_1, C_2	29·8–30·4	29·8	29·9–30·1	30·0	29·8–30·0	29·8–30·2
C_3	19·9	19·8	20·1	20·1	20·8	19·0
C_s^c	141·5	137·5	140·6	141·0	150·2	133·9
C_0^c	127·4	116·4	129·9	132·8	124·9	115·1
C_m^c	129·4	129·4	129·4	128·7	128·1	128·7
C_p^c	127·7	169·1	133·3	121·4	148·0	159·9
$C_{s'}^d$	138·8	138·9	139·0	138·8	138·7	139·7
$C_{o'}$, and $C_{m'}^d$	129·7-129·6	129·8–129·3	129·9–129·4	130·9–129·4	130·0–129·4	129·9 129·3
$C_{p'}^d$	133·6	134·1	134·2	134·2	134·5	134·2
C=O	196·8	198·1	197·8	197·5	197·3	198·3
C_x						55·4
Solvent	CCl_4	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
Conc. %	Sat.	60	70	60	80	60

[a] $\delta_{TMS} = 193·1 = \delta_{CS_2} = 129·0 - \delta_{C_6H_6} = 276 - \delta_{C_6H_{12}}$

[b] The assignment of carbons C_1, C_2, C_3, C_s, C_o, C_m and C_p in this compound was made in accordance with ref. 8

[c] The assignment of C_1, C_2 and C_3 carbons was made in accordance with ref. 8. The assignment of the Ph carbon signals in compound Ib, Ic, Ie, If and Ii was made in accordance with chemical shifts of monosubstituted benzene[9]

[d] The assignment of carbons $C_{s'}$: $C_{o'}$: $C_{m'}$ and C_p was made in accordance with chemical shifts of acetophenone[9]

The configuration was confirmed by double ^{13}C NMR spectroscopy, which may be successfully applied to determine the geometric configuration of cyclopropanes.[8] ^{13}C chemical shifts of some examples are given in Table 2.

Comparison of the data with that of *the cis* and *trans* cyclopropanes[8] revealed that the C^{13} shifts of the C_1, C_2 and C_3 carbon atoms of the cyclopropane ring in I did not exceed those of *trans* cyclopropanes and that there were no signals in the region characteristic of *cis* cyclopropanes. In addition the substituents in the benzene ring of I have no influence on the ^{13}C chemical shifts of the carbon atoms in the cyclopropane ring and the ^{13}C chemical shifts of the carbon atoms in the Ph nucleus adjacent to C_1 in I (R = H) were close to those of *trans* phenylcyclopropane.[8] Thus we conclude that compound I possesses a *trans* configuration of the cyclopropane ring.

II (n = 2, 3, R = H, *p* = Br, *p*-MeO) reacts with V at the double bond adjacent to the carbonyl group and forms the unsaturated cyclopropane ketones III and IV in accordance with the scheme:

$$PhCO(CH{=}CH)_nC_6H_4R + V \rightarrow PhCO\left[\underset{CH_2}{CH{-}CH}\right](CH{=}CH)_{n-1}C_6H_4R$$

II (n = 2, 3, R = H, *p*-Br, *p*-MeO) III (n = 2), IV (n = 3)

Yields of III and IV were lower than those of I. When R = *p*-NO_2 only II (n = 2) reacted with V to give III (R = NO_2).

Yields and some properties of III and IV are given in Table 3.

TABLE 3. YIELDS AND CONSTANTS OF III AND IV

Compound	R	n	Yield	M.p.	MW (mass-spectrometry)
IIIa	H	1	65	83-85	247
IVa	H	2	55	98-100	271
IIIb	*p*-Br	1	90	92-93	326
IVb	*p*-Br	2	81	119-120	350
IIIc	*p*-NO_2	1	36	115-116	292
IIId	*p*-MeO	1	35	78-79	277
IVc	*p*-MeO	2	44	81-82	301

ANALYTICAL DATA

Compound	C%		H%		R%	
	Found	Calc.	Found	Calc.	Found	Calc.
IIIa	86·63	87·06	6·24	6·50		—
IVa	87·12	87·56	6·52	6·61	--	-
IIIb	66·02	66·20	4·88	4·63	24·52	24·49
IVb	68·13	68·51	5·00	4·86	22·55	22·30
IIIc	73·35	73·70	5·35	5·15	4·80	4·78
IIId	81·90	81·98	6·68	6·52	—	—
IVc	82·76	82·86	6·88	6·62	—	—

The structures of III and IV was confirmed from analytical data, IR and UV spectra and purity checked by TLC. In all solvent systems studied (C_6H_6–EtOAc or ether-n-hexane) III and IV gave one spot. All compounds (III and IV) revealed only one carbonyl group absorption in the IR characteristic of compounds of type I. The *trans* configuration of III and IV was accepted by analogy: introduction of additional double bonds in II would hardly change the reaction stereochemistry.

We have measured the IR spectra of I, III and IV. All compounds revealed in $CHCl_3$ bands at 1020–1050 cm^{-1} which in accordance with[10] can be accepted as characteristic of the cyclopropane ring. These compounds also have typical benzene ring absorption at 1590–1595 cm^{-1} and III and IV have additional absorption bands in the region 1600 cm^{-1} and 900–1000 cm^{-1} typical of double bonds and the C–H of *trans* double bonds. An intense absorption band of the carbonyl group at 1665–1670 cm^{-1} is present in IR spectra of all I, III and IV. It should be noted that the IR spectra of aroylcyclopropanes have not been extensively studied. Only in one work[2] was it mentioned that the carbonyl frequency of I (R = H, Ph) was lower than that of arylbenzoylethanes. Carbonyl frequencies of I compared to those of II and benzophenones or 1-aryl-2-benzoylethanes are given in Table 4.

TABLE 4. ν_{CO} OF p-RC_6H_4–X–COPh (IN $CHCl_3$, CM^{-1})

R X	H	i-Pr	OMe	F	Cl	Br	NO_2
CH—CH_2—CH	1666	1668	1667	1668	1670	1668	1670
CH=CH	1665	1663	1662	1667	1666	1667	1670
Without bridge[12]	1660	1658	—	—	1660	1661	—
CH_2CH_2	1685	—	1685	—	—	1687	—

As the data show, the substitution of –CH_2CH_2– in I for a double bond as well as by a cyclopropane ring leads to a considerably shift to lower frequencies of about 20 cm^{-1} and the ν_{CO} values of II (n = I) are only slightly lower than those of I. Thus the introduction of a cyclopropane ring influences the force constant of carbonyl group almost as much as a double bond. This confirms the capability of the cyclopropane ring to conjugate with the carbonyl group. It is of interest that the introduction of Ph in position 2 of PhCOCH=CH_2 (ν_{CO} 1677 cm^{-1} in CCl_4)[13] or benzoylcyclopropane (ν_{CO} 1677 cm^{-1} in CCl_4)[14] shifts ν_{CO} to lower frequencies by about 7 cm^{-1} (ν_{CO} or II (n = I, R = H) as well as I (R = H) is 1670 cm^{-1} [11, 15] This shows that the influence of the Ph group on the force constant of the C=O bond is transmitted through the double bond and the cyclopropane ring approximately to the same extent. It will be noted that I (R = H) and II (n = I, R = H) are characterized by higher ν_{CO} than benzophenone (ν_{CO} 5–6cm^{-1}).

It is known that *para* substituents with a positive inductive, mesomeric or hyperconjugative effect in a benzene ring decrease the double character of a carbonyl group and consequently its stretching frequency. On the other hand *para* substituents with a negative inductive or mesomeric effect cause the carbonyl frequency to increase. Among substituents obtained for I there are i-Pr (+T and hyperconjugative effects), MeO (+M and weak −I effects), halogen atoms (strong −I and weak +M effects) and NO_2 (strong −I and −M effects). But the ν_{CO} values of differently substituted I are very close to each other and substitution in the *para* position in all cases leads to the increase of ν_{CO} ($\Delta\nu_{CO}$ 1–4 cm^{-1}). Thus the nature of the substituent does not apprecialy influence the force constant of the C=O bond. The same weak action of the above substituents is observed also for substituted benzophenones and II (n = I). Due to small changes in the position of the carbonyl absorption it is impossible to evaluate precisely the transmission capability of the cyclopropane ring of I by IR spectroscopy.

The introduction of double bonds between a cyclopropane ring and a substituted phenyl ring does not cause any noticeable shifts of ν_{CO} (Table 5) as could be anticipated from the above results.

TABLE 5. ν_{CO} OF III AND IV (IN $CHCl_3$, CM^{-1})

Compound	ν_{CO}	Compound	ν_{CO}
IIIa	1668	IVa	1667
IIIb	1666	IVb	1668
IIIc	1668	IVc	1668
IIId	1669		

Electronic spectra of aroylcyclopropanes have also been little reported. UV spectra of benzoylcyclopropane and I (R = H) were measured and discussed by R. J. Mohrbacher and N. H. Cromwell[2] in comparison with those of 1-phenyl-2-benzoylethane. The authors found that the substitution of CH_2CH_2 for a cyclopropane ring caused a batochromic shift of about 10 nm and assigned this shift to conjugation between the benzoyl chromophore and the phenylcyclopropane ring. This batochromic shift is also observed when a phenyl group is introduced in the 2 position of 1-benzoylcyclopropane.

UV spectral data of I in comparison with those of some benzophenones are given in Table 6.

TABLE 6. ELECTRONIC SPECTRA OF SOME DERIVATIVES OF I AND BENZOPHENONES*

Compound	λ_{max} nm (ε 10^{-3})
Ia	244 (17·6): 273 (3·59): 279 (2·31)
Ib	243 (12·9): 275 (2·43): 281 (1·56)
Ic	248 (24): 226 (18·2): 238 (20·2): 287 (3·06): 304 (2·14): 313 (2·145)
Id	243 (18·3): 277 (2·16): 282 (1·9): 302 (1·4)
Ie	244 (22·4): 236 (20·1): 278 (4·88): 286 (3·82): 313 (3·33): 334 (1·87)
Ig	245 (35·7): 246 (19·5): 249 (33·4): 290 (3·6): 305 (2·62): 329 (2·4)
Ih	242 (17·8): 224 (14·1): 279 (4·12)
Ii	242 (16·8): 230 (18·3): 270 (8·5)
$PhCOC_6H_4R$-*p*	
R	
H	248 (20): 280 (2·85)
F	250 (19·5): 280 (1·75)
Br	253 (22): 259 (23·5)

* I was measured in n-hexane (our data): benzophenone was measured in cyclohexane[13]

From data I is characterized by an intense maximum of the benzoyl chromophore shifted by about 4–10 nm in comparison with that of 1-phenyl-2-benzoylethane (λ_{max} (n-heptane) 238 nm (ε 12,400) (II)). Thus the benzoyl chromophore interacts with the cyclopropane ring in all the investigated ketones and the conjugation between the carbonyl group, the cyclopropane ring and the substituted phenyl group in I is close to that between the benzoyl group and phenyl nucleus in benzophenone. The nature of substituents in the benzene ring influences the position of the benzoyl chromophore maximum: therefore electronic spectral data cannot be used for an accurate evaluation of the transmission of substituent influence through cyclopropane rings. It is of interest that in chalcone II (R = H) the benzoyl chromophore is characterized by λ_{max} (n-hexane) 226 (ε 10,000).[16]

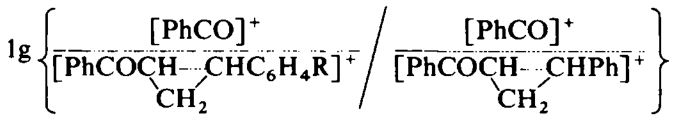
The benzoyl chromophore is also revealed in the electronic spectra of III and IV (Table 7).

TABLE 7. ELECTRONIC SPECTRA OF III AND IV (EtOH)

Compound	λ_{max} nm (ε 10^{-3})
IIIa	248 (22·7): 282 (13·7): 304 (6·15): 430 (6·2)
IIIb	255 (21·7): 226 (11·9): 274 (22·6): 355 (3·88)
IIIc	244 (20·2): 333 (19·5)
IIId	252 (23·7): 277 (20·9): 385 (1·67)
IVa	240 (14·3): 225 (11·5): 234 (12·1): 250 (8·1): 298 (20·2)
IVb	241 (20·1): 226 (16): 234 (18·3): 251 (16·6): 304 (37): 313 (36): 385 (3·58)

The UV spectra of III and IV also contain intense maxima due to conjugation of C_6H_4R with the double bonds.

After a preliminary investigation we found that I, III and IV have besides molecular ions a general ion $PhCO^+$. This enabled us in accordance with previous work[5] to determine more exact quantitative characteristics of the transmission properties of cyclopropane rings in the above compounds. A detailed study revealed that in the case of I the magnitudes



$$\lg\left\{\frac{[PhCO]^+}{[PhCO\underset{\diagdown CH_2 \diagup}{CH - CH}C_6H_4R]^+}\Bigg/\frac{[PhCO]^+}{[PhCO\underset{\diagdown CH_2 \diagup}{CH - CH}Ph]^+}\right\}$$

were linearly related to the σ-constants of Hammett.

The final graph is shown in Fig. 1.

The ratio of intensity of the ion $[PhCO]^+$ (*m/e* 105) to the intensity of the molecular ion gives $\rho = 0{\cdot}354$ ($r = 0{\cdot}98$). As I is an analogue of benzophenone for which M. M. Bursey and F. W. McLafferty[17] found $\rho = 1{\cdot}01$, the transmission coefficient for the cyclopropane ring $\pi' = 0{\cdot}35$. Thus the cyclopropane ring is situated by its capability to transmit the influence of the substituent between the double bond in II (n = 1) ($\pi' = 0{\cdot}72$) and two double bonds in II (n = 2) ($\pi' = 0{\cdot}25$).[5] The magnitude of π' for the cyclopropane ring is close to a reported value.[18]

Finally we investigated the polarographical behaviour of I because polarography is a convenient method for the evaluation of the reactivity of polarographicly active

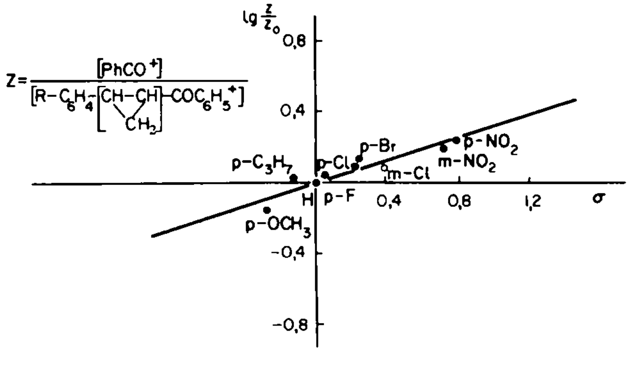


FIG 1. The correlation graph

groups. Polarography of cyclopropane ketones of type I has not been studied before. I is reduced at a dropping mercury electrode in 50% DMFA at pH 2·5 (HCl–KCl buffer) and forms one (Ia, Ic, Id, Ie), two (Ib, Ih) or three (Ii) waves (Table 8).

TABLE 8. HALF WAVE POTENTIALS AND DIFFUSION CURRENTS OF SOME I AND II [depolarisator concentration 0·1 mM, 50% DMFA, pH 2·5 (0·05 M HCl–KCl)]*

Compounds I	$E_{\frac{1}{2}}$ mV	i_d μA	Compounds II (n = 1), R	$E_{\frac{1}{2}}$ mV	i_d μA
Ia	1000	0·25	H	640	0·13
Ib	930	0·12	*p*-F	640	0·14
	1070	0·09			
Ic	916	0·27	*p*-Cl	610	0·12
Ie	912	0·29	*p*-Br	605	0·14
Ih	875	0·17	*p*-i-Pr	640	0·11
	1000	0·15			
Ii	870	0·10	*p*-MeO	670	0·12
	992	0·03			
	1127	0·07			
Id	910	0·28			

* In this conditions $PhCOCH_2CH_2Ph$ has $E_{\frac{1}{2}}$ 1164 mV

The waves of I are of diffusion character (the wave heights are linearly connected with $\sqrt{H}$). The summed height of two waves of Ib or Ih or three waves of Ii is roughly equal to that of the single wave of Ia and the height. of the latter is twice as much as that of II (n = 1). The wave of II is a single electronic type.[19] As I and II (n = 1) are close to each other the reduction of I is most likely to be a two electron process. I is reduced at less negative potentials than 1-benzoyl-2-phenylethane but at more negative potentials than II (n = 1). This also points out the conjugation between the cyclopropane ring and the carbonyl groups which enhances the reactivity of the carbonyl group towards polarographic reduction.

EXPERIMENTAL

UV spectra were measured with SP-700 spectrometer. IR spectra were recorded on a UR-10 spectrometer. ^{13}C NMR spectra were measured with NM-4H-100 spectrometer (JEOL) with NSS-system for observation of resonance signals of heavy nuclei. Mass spectra were measured with MX-1303 mass spectrometer with direct sample introduction. The ionization voltage was 50 eV, emission current 1 mA and the temperature of the ionization chamber 130°. The reproducibility of the mass spectra (over some months) was about 6% (relative).

Polarogrammes were registered by a pen-recording polarograph PE-315. The electrolytic cell was thermostated at 23 ± 0·1°. A capillary with beak was used, m = 0·46 mg/sec, t = 1·4 sec. Ionic strength of solution was constant and equal to 0·05 m. $E_{\frac{1}{2}}$ and was measured towards the outer saturated calomel electrode pH of solutions was measured by a pH meter LPM-60M with a glass electrode. Stock solutions of 1 were prepared in dry DMFA. The investigated solutions were deoxygenated with bubbling pure argon for 20 min. TLC was made on 13 × 18 cm plates with an unfixed thin layer (1 mm) of Al_2O_3 (II grade activity) detection was by iodine vapours.

Synthesis of I. 5·52 g (0·026 M) of crystalline trimethyloxosulfonium iodide were added all at once to a suspension of 0·6 g (0·025 M) NaH in 50 ml of dry DMFA. After hydrogen evolution ceased a solution of 0·025 M of II (n = 1, 2 or 3) in 20 ml DMFA were added in one portion to the mixture. After the exothermic reaction had ceased the mixture was stirred for 1 hr at room temp and poured into 60 ml 3% HCl and ice. The mixture was extracted with ether (3 × 50 ml), dried ($MgSO_4$) and evaporated. I, III and IV were crystallized from hexane. The analytical data and properties of obtained compounds are given in Tables 1 and 2.

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