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TRISUBSTITUTED CYCLOPROPANES FROM THE REACTION OF STABLE SULPHONIUM YLIDES WITH α-HALOCARBONYL COMPOUNDS

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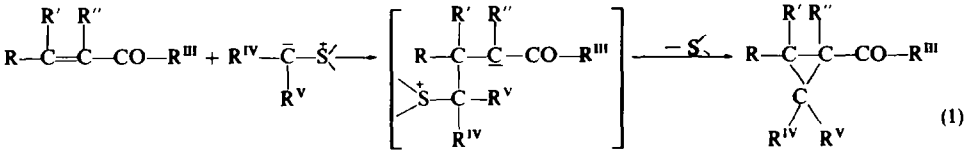
Abstract- The reaction between carbonyl-stabilized sulphonium ylides (II) and primary α-halocarbonyl compounds (I) affords cyclopropanes (III) arising from two ylidic units and one unit from the helo compound in good yields. Secondary halides also afford the expected cyclopropanes III. but considerable amounts of olefines (V) and symmetrically trisubstituted cyclopropanes (VII), derived from three ylidic units, are also obtained. Accurate NMR analyses permit the configuration of the cyclopropanes to be assigned.

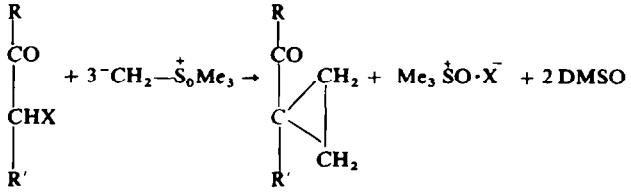
DURING the last decade sulphur ylides have been shown to be of great utility in the synthesis of cyclopropanes by various routes.[1-4] The most important method, which has been extensively investigated, and commented upon,[1] is that utilizing as starting material α,β-unsaturated carbonyl compounds with both stabilized sulphonium and unstabilized oxosulphonium ylides. The generally accepted pathway for this reaction is the following:



(1)

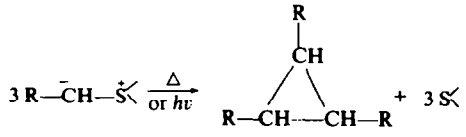
Eq 1 shows in this case that the cyclopropane ring arises from two olefinic carbons and the α-carbon of the ylide.

Two years ago we reported a different type of synthesis of cyclopropanes based on the reaction of dimethyloxosulphonium methylide with α-halo ketones and α-halo esters, whereby the cyclopropane ring arises from two ylidic carbon atoms and only one carbon from the substrate, the halo compound:[2c, 2e]



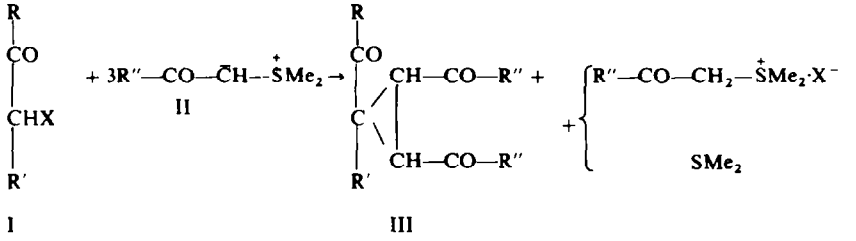
(2)

A third method of synthesis of cyclopropanes is based on a thermal or photochemical decomposition of ylides.[3] By this route symmetrically trisubstituted cyclopropanes are obtained where the cyclopropane ring is built up from the α-carbons of three moles of ylide:



(3)

With the aim of extending the synthetic utility of the reaction outlined in Eq 2, we reacted a number of differently substituted α-halo ketones and esters (I) with some stabilized sulphonium ylides (II), in order to obtain cyclopropanes of the general structure III:



(4)

I III

As far as we know only three examples of reactions between stabilized sulphonium ylides and α-halo carbonyl compounds yielding cyclopropanes are recorded. In two of these cases halo compounds were used structurally related to the ylide (R = R″ = OEt or Ph, R′ = H), so that the resulting cyclopropanes were symmetrically trisubstituted.[2a,b,d] In the third case (R = OEt, R′ = H, R″ = Ph) the cyclopropane was obtained in only 4% yield.[2a]

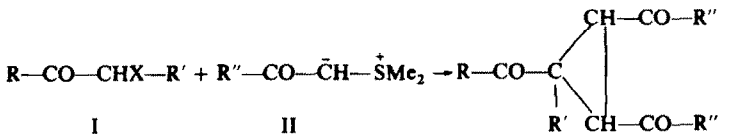
In our experiments the reactions, which were performed at room temperature in THF gave the expected cyclopropanes in most cases in quite satisfactory yields.

The results, summarized in Table 1, show that the reaction is of wide applicability. The ready availability of starting materials, good yields, smooth reaction conditions and the easy isolation of the cyclopropanes from the reaction mixture make this method a useful and versatile tool for the synthesis of cyclopropyl carbonyl compounds, even though several other methods have been already described for the synthesis of these compounds.[5*]

It can be seen from Table 1 that yields are good either with keto- or ester-stabilized ylides. As far as the halo carbonyl compound is concerned, it should be noted that bromo compounds seem to be more convenient than the corresponding chloro

* According to the literature [1b; H. J. Bestmann, K. Rostock and H. Dornauer, *Angew. Chem.* **78**, 335 (1966); H. J. Bestmann, K. Rostock and H. Dornauer, *Chem. Ber.* **103**, 685 (1970)] phosphonium ylides usually react with α-halo carbonyl compounds in a different way. Triphenylarsonium phenacylide has been recently reported to give tribenzoylcyclopropane upon reaction with phenacyl bromide in moderate yields [A. W. Johnson and H. Schubert, *J. Org. Chem.* **35**, 2678 (1970)].

TABLE 1. CYCLOPROPANES FROM α-HALO CARBONYL COMPOUNDS AND SULPHONIUM YLIDES



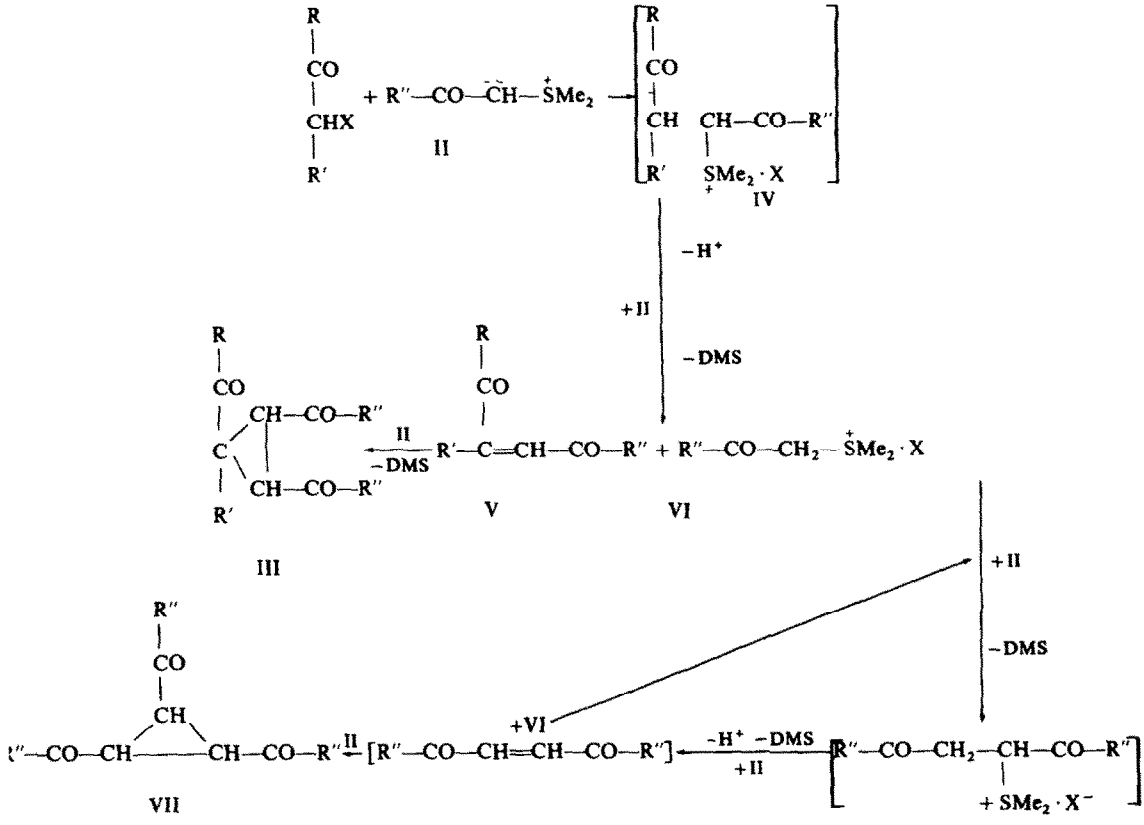
	R	R	X	R″	Yield %	Mp, °C[a]	Crystallized from	Formula	Required % C	Required % H	Found % C	Found % H
a[b]	p-$CH_3C_6H_4$	H	Br	Ph	70	~122	benzene–hexane	$C_{25}H_{20}O_3$	81·5	5·5	80·8	5·6
b[b]	p-$CH_3OC_6H_4$	H	Br	Ph	81	~129	benzene–hexane	$C_{25}H_{20}O_4$	78·1	5·2	78·2	5·5
c	p-$NO_2C_6H_4$	H	Br	Ph	85	155	chlorof.–hexane	$C_{24}H_{17}NO_5$	72·2	4·3	72·7	4·1
d[b]	p-BrC_6H_4	H	Br	Ph	68	~153	benzene–hexane	$C_{24}H_{17}BrO_3$	66·5	4·0	66·5	3·7
e[b]	β-$C_{10}H_7$	H	Br	Ph	84	~149	chlorof–hexane	$C_{28}H_{20}O_3$	83·1	5·0	82·7	5·0
f[+,c]	Me_3C	H	Br	Ph	87	162	benzene–hexane	$C_{22}H_{22}O_3$	79·0	6·6	79·4	6·6
f[+,+,c]	Me_3C	H	Br	Ph		153	benzene–hexane	$C_{22}H_{22}O_3$	79·0	6·6	79·1	6·6
g	Me	H	Br	Ph	65	95	hexane	$C_{19}H_{16}O_3$	78·1	5·5	78·5	5·4
h	Me	H	Cl	Ph	22	95	hexane					
i	Ph	H	Br	OMe	50	~59	[d]	$C_{14}H_{14}O_5$	64·1	5·4	64·0	5·2
j[e]	Ph	H	Br	OEt	90	63	ether–hexane	$C_{16}H_{18}O_5$	66·2	6·2	65·7	6·2
k	Me	H	Br	Ph	89	81	ether–hexane	$C_{19}H_{16}O_4$	74·0	5·2	74·5	5·1
l	Me	H	Br	p-$CH_3C_6H_4$	56	105	ether–hexane	$C_{21}H_{20}O_4$	75·0	6·0	74·8	5·9
m	Me	H	Br	p-$CH_3OC_6H_4$	48	85	ether–hexane	$C_{21}H_{20}O_6$	68·5	5·5	69·0	5·4
n	Ph	Ph	Br	Ph	15[f]	172	[d]	$C_{30}H_{22}O_3$	83·7	5·1	84·1	5·0
o	Ph	Ph	Br	p-$CH_3C_6H_4$	15[g]	151	[d]	$C_{32}H_{26}O_3$	83·8	5·7	83·5	5·9

[a] Uncorrected. [b] Values are reported corresponding to the mixture of two geometric isomers of structures III[+,+] and III[+,+,+] (see page 3565). Relative amounts are reported under Table 2. [c] Two geometric isomers IIIf[+,+] and IIIf[+,+,+] (see page 3572). [d] Crude, from chromatography. [e] For III j see Ref 1p. [f] Vn (24%) and VIIn (18%) were also obtained. [g] Vo (30%) and VIIo (33%) were also obtained.

compounds (cf IIIg *vs* IIIh), though a deeper investigation in this respect should be made. It is also observed that both ketones and esters, either aliphatic or aromatic, can be used for this synthesis quite satisfactorily.

When secondary halides were used (In, o) the cyclopropanes III were obtained in lower yields and olefines of structure V were isolated along with a certain amount of the symmetrically trisubstituted cyclopropanes VII arising from the ylide reacting with its own conjugate acid (VI).†

In consideration of these results and on the basis of the previous reports on the synthesis of cyclopropanes by sulphur ylides,[1–4] a reasonable pathway for these reactions can be outlined as follows:

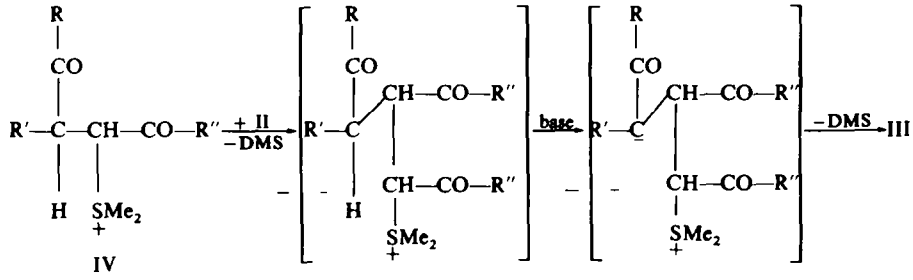


The high yields in III obtained when R′ = H show that in these cases, after the first step of the sequence, the reaction of II with V to afford the cyclopropane III is much faster than the competing reaction of II with its own conjugate acid (VI) which would afford the symmetrically trisubstituted cyclopropane VII. On the contrary, with secondary halides (In, o) the lower yields in III, the moderate yields in olefin V and the obtainment of substantial amounts of VII, would indicate that the step V → III and also the formation of V occur at slower rate, comparable with that of the forma-

† The formation of symmetrically substituted cyclopropanes from sulphonium ylides through the corresponding sulphonium salts has already been observed.[2a,b,4]

tion of VII,† presumably for steric reasons. According to the proposed mechanism, the olefine Vn, when treated with IIa, in the usual conditions employed in the synthesis of III from I (THF, 12 hr, room temp), gave the expected cyclopropane IIIn.

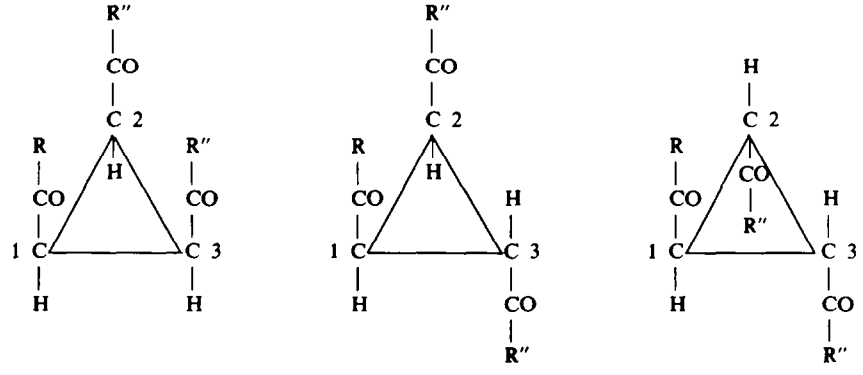
Another possible path to the cyclopropanes III, which also would be conceivable,[2a] would involve a direct displacement of dimethylsulphide from IV by the ylide, followed by cyclization to III:



At present no data are available to distinguish between these two possibilities. However, even if this alternative seems acceptable when using nonstabilized ylides,[2e] in this case it seems to be less likely, for the formation from IV of an intermediate olefin V, stabilized by two carbonyl groups, by a β-elimination, should be preferred to the direct displacement of DMS.

Structures

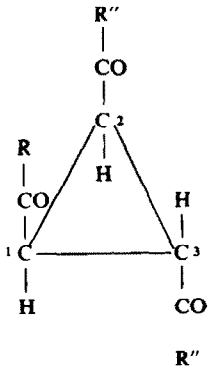
Cyclopropanes of general structure III (R′ = H) may exist in three different configurations, III^{+} (1r, 2c, 3c),* III^{++} (1r, 2c, 3t) and III^{+++} (1r, 2t, 3t), the first of these with all the three substituents in a *cis* relationship. the other two with only two substituents in a *cis* arrangement.



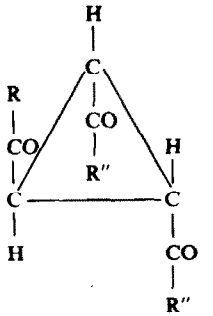
* It should be observed in this respect that even a minimum amount of VI would suffice for the complete conversion of the ylide II into the symmetric cyclopropane VII in a chain reaction process.

† *Rules for IUPAC Notation for Organic Compounds* p. 75. Longmans, London (1961).

TABLE 2. CHEMICAL SHIFTS (δ, PPM) AND COUPLING CONSTANTS (C/S) OF CYCLOPROPANES



III'



III+++

Compound	R	R''	H^1	H^2	H^3	J_{12}	J_{13}	J_{23}	CH_3	solvent
IIIa++ a,b	p-$CH_3C_6H_4$	Ph	3·73	3·73	4·22 or 4·20		5·6	5·6	2·32[c]	$CDCl_3$
			3·55	3·55	4·31		5·5	5·5	1·95[c]	C_6D_6[3]
IIIa+++ b	p-$CH_3C_6H_4$	Ph	4·20 or 4·22	3·73	3·73	5·6	5·6		2·39[c]	$CDCl_3$
			4·31	3·55	3·55	5·5	5·5		2·02[c]	C_6D_6
IIIb++ b,d	p-$CH_3OC_6H_4$	Ph	[e]	[e]	4·23				3·80[c]	$CDCl_3$
					4·34		5·6	5·6	3·18[c]	C_6D_6[3]

IIIb^{+++} [b]	p-$CH_2OC_6H_4$	Ph	4·18	3·72	3·72	5·7	5·7		3·86 [c]	$CDCl_3$
			4·30	3·53	3·53	5·6	5·6		3·26 [c]	C_6D_6
IIIc^{++} [f]	p-$NO_2C_6H_4$	Ph	3·869	3·643	4·191	9·22	5·60	5·72		$CDCl_3$
IIId^{++} [f,g]	p-BrC_6H_4	Ph	3·661	3·772	4·219	9·53	5·67	5·71		$CDCl_3$
IIIe^{++} [b,h]	β-$C_{10}H_7$	Ph	3·90	3·82	4·30	9·7	5·73	5·72		$CDCl_3$
IIIe^{+++} [b]	β-$C_{10}H_7$	Ph	4·41	3·81	3·81	5·7	5·7			$CDCl_3$
IIIf^{++} [f]	t-C_4H_9	Ph	3·362	3·511	4·023	9·7	5·4	5·8	1·14	$CDCl_3$
IIIf^{+++} [f]	t-C_4H_9	Ph	3·723	3·498	3·498	5·67	5·67		1·27	$CDCl_3$
IIIg^{++} [f]	Me	Ph	3·130	3·563	4·050	9·58	5·47	5·78	2·23	$CDCl_3$
IIIi^{+++}	Ph	COOMe	3·78	2·73	2·73	5·6	5·6		3·76	$CDCl_3$
			3·82	2·65	2·65	5·6	5·6		3·35	C_6D_6
IIIj^{+++}	Ph	COOEt	3·76	2·70	2·70	5·6	5·6		1·27	$CDCl_3$
IIIk^{++} [f]	COOMe	Ph	2·928	3·397	3·944	9·66	5·42	5·69	3·56	$CDCl_3$
IIIl^{++} [f]	COOMe	p-$CH_3C_6H_4$	2·935	3·404	3·954	9·60	5·26	5·76	2·38 [i]	$CDCl_3$
									3·59	
IIIm^{++} [f]	COOMe	p-$CH_3OC_6H_4$	2·905	3·374	3·909	9·78	5·44	5·68	3·61	$CDCl_3$
									3·84	
									3·86	

[a] IIIa^{++}/IIIa^{+++} = 1·0 after one crystallization. [b] III^{++} and III^{+++} analyzed in mixture. [c] The assignment of the ν_{CH3} signals has been made on the assumption that methyls laying *cis* to a phenyl group are slightly shielded, as shown in the case of the couple IIIf^{++}–IIIf^{+++} and in the spectrum of the *trans* tri-*p*-tolylcyclopropane (VII, R″ = p-$CH_3C_6H_4$) which shows one CH_3 signal at 2·42 and a $2CH_3$ signal at 2·37 ppm. [d] IIIb^{++}/IIIb^{+++} = 0·6 after one crystallization. [e] Signals partially overlapped with those of IIIb^{+++}. [f] Spectrum calculated. [g] After one crystallization IIId^{++} was contaminated with 20% of IIId^{+++}, whose spectrum could not be completely analyzed because of substantial overlapping of the signals. The part A of its AX_2 spectrum appears at 4·17 ppm. [h] IIIe^{++}/IIIe^{+++} = 1 after one crystallization. [i] Two overlapped CH_3 signals.

On the basis of the mechanism proposed for their synthesis, one should "a priori" expect any of the three possible isomers. presumably the less hindered or a mixture. also in consideration of the fact that the synthesis of cyclopropanes from olefines (Eq 1), which repeats the last step (V → III) of this synthesis, has been proved to be only partially stereospecific.[1f,g,m,6] Moreover, since the cyclopropanes are obtained in a basic medium where equilibration could take place in any of the intermediates one would expect a mixture of geometric isomers.*

Actually in no case could the less stable "all *cis*" cyclopropane (III^+) be isolated. Instead, in some cases (IIIc, g, k, l, m) only the isomer III^{++} was isolated, in two cases (IIIi, j) the only isolated isomer was III^{+++} and finally in five cases (IIIa, b, d, e, f) a mixture of the less hindered isomers III^{++} and III^{+++} was obtained. Their relative amounts (after one crystallization) are reported in Table 2.

The structures of the cyclopropanes were assigned mainly on the basis of spectroscopic measurements.

NMR spectra

The NMR parameters for the cyclopropanes III are reported in Table 2. It is noteworthy that the values of coupling constants fall in a very narrow range, that is between 9·2 and 9·8 c/s and between 5·2 and 5·8 c/s. These values are perfectly in line with the predicted values for J_{cis} and respectively J_{trans} in cyclopropanes.[7]

We can exclude the "all *cis*" configuration III^+ for all the cyclopropanes since one coupling constant of 5·5–5·8 c/s is always present, and this value is too low to be attributed to a vicinal *cis* interaction.[7] Consequently the only two possible configurations are III^{++} and III^{+++}, the latter leading to a symmetrical three spin spectrum (AX_2 or AB_2), the former to a non symmetrical one (ABC or ABX).

TABLE 3. METHYLENE PMR CHEMICAL SHIFT (δ, C/S) OF BROMOMETHYL CARBONYL COMPOUNDS

R	Chemical shift (ppm)[a]
β-$C_{10}H_7$	4·55
p-$NO_2C_6H_4$	4·46
C_6H_5	4·43
p-$CH_3C_6H_4$	4·42
p-BrC_6H_4	4·39
p-$CH_3OC_6H_4$	4·38
CH_3	3·88
CH_3O	3·84

[a] In $CDCl_3$ (c = 0·2 molar).

The spectra of all compounds except IIIa, b, e, i, j, have been completely analyzed. Compounds IIIa, b, e, i, j^{+++} show an AX_2 and compound $IIIf^{+++}$ an AB_2 pattern. With regard to the unsymmetrical cyclopropanes showing ABX (IIIe. f. d^{++}) or ABC (IIc. g. k. l. m^{++}) spectra. the assignment of the signals has been made on the assumption that since carbonyl groups exert a deshielding effect on the *cis* hydrogens in cyclopropanes,[7] the signal at the lowest field must arise from the hydrogen laying

* An attempt of equilibration of $IIIf^{++}$ in the presence of IIa for 12 hr at room temperature in THF failed, $IIIf^{++}$ being recovered unchanged. On the contrary the equilibration took place quickly in the presence of NaOMe (see after).

TABLE 4. IR SPECTRA OF CYCLOPROPANES III (IN NUJOL)[a]

Compound	1799–1700	1699–1600	1599–1500	1499–1300	1299–1200	1199–1100	1099–1000	999–800	799–600
					cm^{-1}				
IIIa[b]		1670, 1605		1325, 1300	1220	1180	1015	827	732, 709
IIIb[b]		1670, 1600	1510	1370, 1320	1220	1170	1020		712
IIIc^{++}		1690, 1670, 1600	1525	1345	1220		1020	858	758, 718, 707
IIId[b]		1670	1590	1320	1220	1175	1070, 1010	825	728, 705
IIIe[b]		1670	1595	1460, 1320	1220	1180	1015	825	755, 715
IIIf^{++}		1695, 1670	1595	1330	1220		1020		700
IIIf^{+++}		1690, 1670	1595	1320	1215		1080, 1010		782, 732, 710, 692
IIIg^{++}	1720	1670		1330, 1300	1220	1180	1020		708
IIIi^{+++}	1760, 1730	1670	1595	1330, 1300	1215	1155	1060, 1020	970, 897	716, 685
IIIj^{+++}	1740	1670		1330, 1305	1205	1180	1090, 1010	898, 870	710
IIIk^{+++}	1730	1670	1595	1330, 1310	1220, 1205		1040, 1020	918	755, 710
IIIl^{++}	1730	1680, 1670, 1605		1320, 1300	1205	1180	1020		742
IIIm^{++}	1730	1665, 1600	1505	1330	1260, 1220	1165	1020	850, 810	762
IIIn		1680, 1670, 1605	1580	1335	1260, 1215	1175	1015		752, 728, 718, 705
IIIo		1670, 1610		1350	1270, 1230, 1205	1180	1030, 1015	840	768, 760, 728, 700

[a] Only prominents peaks are reported. [b] Mixture of two isomers III^{++} and III^{+++}. Relative amounts are reported under Table 2.

cis to two carbonyls. while the signals at higher field must arise from the two hydrogens laying *cis* to only one carbonyl. We have indeed observed such a deshielding effect in the symmetrical compounds III^{+++}, where there are no structural ambiguities. The two hydrogens at higher field in III^{++} compounds have been assigned on the basis of the substituent's nature. In Table 3 we have reported for comparison the chemical shifts of the methylene protons of some bromomethyl carbonyl compounds with the same substituents as in the cyclopropanes. However the extrapolation from the data of Table 3 should be taken with great caution especially in the case of IIIc, d, e, where a rather large degree of ambiguity still remains.

With regard to the cyclopropanes IIIa, b, d, e, f, which have been obtained as a mixture of two isomers of structures III^{++} and III^{+++}, one of these (IIIf) has been resolved by chromatography and the spectra taken separately. Apparently the most abundant* (63% of the whole mixture) was the less stable isomer $IIIf^{+++}$. The equilibration between the two forms is very rapid in $CDCl_3$ in the presence of CD_3ONa (III^{++}/III^{+++} ratio = 1·6 after a few min at room temperature). A similar equilibration (III^{++}/III^{+++} ratio = 1·5) has been observed for a 2:3 mixture of $IIIb^{++}$ and $IIIb^{+++}$.

IIIa, b, d, e were recorded and analyzed without previous separation of the two forms III^{++} and III^{+++}. It should be observed that, as far as the cyclopropanes protons are concerned, both $IIIa^{++}$ and $IIIa^{+++}$ give the same spectrum in C_6D_6, deceptively showing the same pattern typical of an AX_2 system, while only very tiny differences are observed in $CDCl_3$ solution.

IR and mass spectra

The IR spectra of the cyclopropanes, whose prominent peaks are reported in Table 4, all show an intense band in the 1020 cm^{-1} region, typical of the cyclopropane ring.[8] On the contrary, the band in the 860 cm^{-1} region, which has been observed in several cyclopropanes, seems not to be reliable for correlation.[8,9] A consistent band near 1220 cm^{-1} could be due to the aromatic ketone.[10] A remarkable consistency of a band in the 1330 cm^{-1} region is also observable. A peculiarity is shown by IIIi, whose spectrum in the carbonyl region shows a very strong band at 1760 cm^{-1} along with the normal ester band, of lower intensity, at 1730 cm^{-1}. This unusually high frequency band might be interpreted in terms of field effect due to the proximity of the two ester groups.[9] However conformational effects and other special effects might also come into play.[8,9]

The mass spectra of the cyclopropanes IIIa–m, all showing the molecular ion, are in accord with the given structures. In most cases, when a benzoyl group is present, the 105 *m/e* signal is the base peak. Other characteristic peaks correspond to M^+–RCO (except IIIj) and M^+–R″CO (except IIId). The RCO and R″CO peaks are always present, with the exception of IIIf, m for the former and IIIj for the latter.

EXPERIMENTAL

IR spectra were determined in nujol with a Perkin–Elmer Mod. 137 Infracord spectrometer. NMR spectra were recorded on a Varian A-60 or Varian HA-100 instrument; chemical shifts (δ, ppm) were measured from TMS as internal standard; the second order spectra were calculated with the aid of

* After one crystallization of the crude mixture from benzene–hexane.

LAOCOON III iterative procedure, RMS 0·02–0·1.[11] Mass spectra were measured on a Hitachi–Perkin–Elmer RMU6D spectrometer at 70 eV. Column chromatographies were performed on silica gel 0·05–0·20 mm (Merck–Darmstadt) using hexane–ether as eluent.

General procedure for the synthesis of cyclopropanes IIIa–m

0·03 moles of ylide II were prepared from the corresponding sulphonium salts by treatment with NaH in THF (100 ml) for 14 hr at room temp under stirring.[12] After filtration through celite a soln of the α-halo compound (0·01 moles in 30 ml of THF) was added dropwise while stirring under N_2. After 6–12 hr the soln was filtered, extended with Et_2O or $CHCl_3$, washed with 2N HCl, H_2O and dried over Na_2SO_4. After evaporation of solvent the crude cyclopropane, dissolved in $CHCl_3$, was percolated through silica gel and crystallized. (Table 1).

Special procedures. The mixture of IIIf^{++} and IIIf^{+++} obtained from If and IIf was resolved by preparative tlc (silica gel) using a 7:3 mixture of hexane–Et_2O. The major Rf isomer was IIIf^{++}. The cyclopropane IIIg was contaminated by a small amount (<5%) of *trans*-tribenzoylcyclopropane (VII, R″ = C_6H_5), separated by chromatography (hexane–ether 9:1) and identified (IR spectrum) with an authentical sample. Before crystallization IIIk was chromatographed using a 97:3 hexane–Et_2O mixture.

Reaction of dimethylsulphonium phenacylide with desyl bromide. The reaction was run on 0·03 moles of ylide (general procedure) during 24 hr. The ethereal extracts were concentrated and a ppt of *trans*-tribenzoylcyclopropane (VII, R″ = Ph) was obtained and filtered. The compound was identified by comparison (IR spectrum) with an authentical sample. The filtered solution was chromatographed; Vn, m.p. 120° (lit.[13] 129°) was eluted first with hexane–Et_2O 98:2; IR: 1670, 1660, 1600, 1265, 1230, 1180, 1020, 870, 800, 768, 738, 728, 700; NMR ($CDCl_3$): 6·92 (1H, s, =CH—CO); Mass: 312 *m/e* (M^+). IIIn was then eluted with hexane–Et_2O 95:5; further purification was needed by prep. tlc (silica gel) C_6H_6 as eluent; NMR ($CDCl_3$): 4·50 (1H, d, J = 6 c/s), 4·96 (1H, d, J = 6 c/s).

Reaction of dimethylsulphonium p-*methylphenacylide* (IIo) *with desyl bromide.* The reaction was run on 0·03 moles of IIo as above. The crude reaction mixture was resolved by chromatography; Vo, [m.p. 158° after sublimation (lit.[13] 158°)] was eluted first, with hexane–Et_2O 98:2; Mass: 326 *m/e* (M^+), 249 (M^+-C_6H_5), 221 (M^+-C_6H_5CO), 119 ($CH_3C_6H_4CO$, 105 base peak (C_6H_5CO). IIIo was then eluted with hexane–Et_2O 97:3: NMR ($CDCl_3$): 2·42 (6H, s), 4·46 (1H, d, J = 6 c/s), 4·92 (1H, d, J = 6 c/s). Finally *trans*-tri-*p*-toluyloyclopropane (VII, R″ = *p*-$CH_2C_6H_4$) was eluted with hexane–Et_2O 90:10; m.p. 148° from $CHCl_3$–hexane; IR: 1680, 1670, 1615, 1410, 1320, 1230, 1210, 1180, 1045, 1030, 1020, 898, 832, 817, 746; NMR ($CDCl_3$): 2·37 (6H, s, $2CH_3$), 2·42 (3H, s, CH_3), 3·70 (2H, d, J = 5·3 c/s), 4·19 (1H, m), 7·05–7·45 (6H, m, aromatics), 7·80–8·25 (6H, m, aromatics); Mass: 396 (M^+), 277 (M^+-$CH_3C_6H_4CO$), 119 *m/e* ($CH_3C_6H_4CO$). (Found: C, 82·0; H, 6·3; $C_{27}H_{24}O_3$ requires: C, 81·8; H, 6·1%).

Reaction between Vn *and dimethylsulphonium phenacylide.* 0·002 moles of Vn in THF (10 ml) were reacted with the ylide (0·006 moles) in THF (20 ml). After 20 hr at room temp the obtained cyclopropane was purified by prep. tlc (silica gel, C_6H_6) and identified by IR.

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REFERENCES

[1] Several reviews have appeared in which this subject has been treated. See for instance,
[a] J. Bloch, *Ann. Chim.* **60**, 419 (1965);
[b] A. W. Johnson, *Ylid Chemistry* p. 304. Academic Press, New York (1966);
[c] A. Hochreiner, *Österr. Chem. Zeitg.* **67**, 297 (1966);
[d] H. König, *Fortsch. Chem. Forsch.* **9**, 487 (1968);
[e] T. Durst, *Advances in Organic Chemistry* (Edited by E. C. Taylor and H. Wynberg), Vol. **6**, p. 285, Interscience. New York (1969)
[f] C. Agami, *Bull. Soc. Chim. Fr.* 1391 (1967);
[g] C. Agami and C. Prevost, *Ibid.* 2299 (1967);
[h] S. R. Laudor and N. Punja, *J. Chem. Soc.* (C) 2495 (1967);
[i] D. E. Evans, G. S. Lewis, P. J. Palmer and D. J. Weyell, *Ibid.* 1197 (1968);
[l] G. A. Caplin, W. D. Ollis and I. O. Sutherland, *Ibid.* 2302 (1968);

[m] G. B. Payne, *J. Org. Chem.* **32**, 3351 (1967);
[n] J. Casanova and D. A. Rutolo, *Chem. Comm.* 1224 (1967);
[o] H. Nozaki, D. Tunemoto, S. Matubara and K. Kondo, *Tetrahedron* **23**, 545 (1967);
[p] G. B. Payne, U.S.P. 3,397,223 *Chem. Abstr.* **69**, 105998 (1968)
2 [a] H. Nozaki, M. Takaku and K. Kondô, *Tetrahedron* **22**, 2145 (1966);
[b] A. W. Johnson and R. T. Amel, *Tetrahedron Letters* 819 (1966);
[c] P. Bravo, G. Gaudiano, C. Ticozzi and A. U. Ronchi, *Ibid.* 4481 (1968);
[d] A. W. Johnson and R. T. Amel, *J. Org. Chem.* **34**, 1240 (1969);
[e] P. Bravo, G. Gaudiano, C. Ticozzi and A. U. Ronchi, *Gazz. Chim. Ital.* **100**, 566 (1970)
3 [a] F. Krollpfeiffer and H. Hartmann, *Chem. Ber.* **83**, 90 (1950);
[b] K. W. Ratts and A. N. Yao, *J. Org. Chem.* **31**, 1689 (1966)
4 B. M. Trost, *J. Am. Chem. Soc.* **89**, 138 (1967)
5 J. M. Conia, *Angew. Chemie* Intern. Edn., **7**, 570 (1968)
6 E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.* **87**, 1353 (1965)
7 H. Booth, *Progress in Nuclear Magnetic Resonance Spectroscopy* (Edited by J. W. Emsley, J. Feeney and L. H. Sutcliffe) Vol. **5**, p. 167. Pergamon Press, Oxford (1969)
8 C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York (1963)
9 L. J. Bellamy, *Advances in Infrared Group Frequencies.* Methuen, London (1968)
10 L. J. Bellamy, *The Infrared Spectra of Complex Molecules* pp. 131, 148. Methuen, London (1958)
11 S. Castellano and A. A. Bothner-By, *J. Chem. Phys.* **41**, 3863 (1964)
12 A. J. Speziale, C. C. Tung, R. W. Ratts and A. Yao, *J. Am. Chem. Soc.* **87**, 3460 (1965)
13 C. F. H. Allen and H. B. Rosener, *Ibid.* **49**, 2110 (1927)