DECOMPOSITION OF DIAZOKETONES IN ORGANIC SULFIDES AND SULFOXIDES: CYCLOPROPANE FORMATION FROM DIAZOKETONES VIA SULFONIUM YLIDES^a

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Abstract—The catalytic decomposition of diazoketones in the presence of organic sulfides and sulfoxides, gives sulfonium and sulfoxonium ylides as the primary reaction products, the final products isolated depending upon the relative nucleophilicity of the sulfides compared to that of the corresponding ylides, and on the stability of the ylides. The mechanism, scope and limitations of a new method of cyclopropane formation from diazoketones are discussed. Some circumstantial evidence supporting a concerted process for Wolff rearrangement is presented.

INTRODUCTION

This paper reports the details on the decomposition of diazoketones in the presence of thioethers. Part of the results dealing with a new method of cyclopropane formation from diazoketones *via* sulfonium ylides have been reported.¹

At the time this work was undertaken only one paper dealing with the formation of sulfonium and sulfoxonium ylides by decomposition of diazocompounds in the presence of thioethers was known.² However, soon afterwards, Hochrainer refered to it³ as one of the potential methods for the preparation of sulfonium ylides, and more recently, the method has been applied to the preparation of carbonyl-stabilized sulfonium and sulfoxonium ylides.⁴

From our own work we have concluded that thioanisole is the most suitable thioether for the cyclopropane formation from diazoketones, since the more nucleophilic alkyl sulfides and sulfoxides lead to stable β -keto-sulfonium and sulfoxonium ylides rather than cyclopropanes.¹⁰

THERMAL AND CATALYTIC DECOMPOSITION OF DIAZOKETONES

According to some reviews,⁵ "purely thermal decomposition of diazoketones leads to cyclopropane derivatives; in the presence of copper compounds symmetrical diacylethylenes are formed". However, we could not find any experimental evi-

"Taken in part from doctoral theses of J. Quintana (1965-1968), and M. Torres, University of Barcelona, (1968-1970).

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dence supporting the cyclopropane formation in purely thermal decomposition of diazoketones. Actually, only a few references⁶ can be found reporting such a formal trimerization of "ketocarbenes", and the yields given are not greater than 1.4%. In fact, butenolides rather than cyclopropanes are the predominant products in such reactions.^{60, c}

In connection with a more ambitious project,⁷ we were interested in determining the optimal experimental conditions favoring cyclopropane formation rather than the normal dimerizations encountered in the decomposition of diazoketones.

Before examining the effect of thioethers in the catalytic decomposition of diazoketones, we examined the copper catalysed and the purely thermal decomposition of 1-diazo-3,3-dimethyl-2-butanone (diazomethyl-t-butylketone, Ia, $R=CMe_3$), the model we chose for our studies. The results are summarized in Chart I.

In agreement with previously reported results, 6a.8 we found that Cu-bronze induced decomposition of diazomethyl-t-butylketone in boiling benzene, gave trans-1,2-dipivaloylethylene (4, R=CMe₃) in 80% yield. In the presence of 2,3-dimethyl-2butene the catalytic decomposition leads to 1.1.2.2tetramethyl-3-pivaloylcyclopropane (7, R=CMe₃) in 43% yield, together with 57% yield of the diacylethylene 4.9 On the other hand, purely thermal decomposition in boiling xylene afforded 2,4-di-tbutyl-3-buten-4-olide (9, R=CMe_a) in 52% yield, identical to the product obtained from the photochemical decomposition.¹⁰ However, when diazomethyl-t-butylketone was decomposed, under atmosphere of nitrogen, with copper-bronze catalyst in thioanisole solution at 70°, trans-1,2,3-tripivaloylcyclopropane (6, R=CMe_a) was formed in high yield (80-90%).

These results demonstrated that the nature of the





products formed in the decomposition of diazoketones depends upon the relative nucleophilicity of the species present in the reaction mixture, as well as on the reaction conditions. In inert solvents, the catalytic decomposition of diazoketones gives a ketocarbene-copper complex 2 (or "deactivated" ketocarbene)* which is intercepted by the unreacted nucleophilic diazoketone to give an intermediate betaine 3a, nitrogen being then lost to yield trans-1,2-diacylethylene 4 (formally a "dimer"). In the presence of a nucleophilic olefin a competitive reaction takes place and a cyclopropylketone 7 is formed together with the dimer 4. In the photolytic and purely thermal decomposition, the free ketocarbene generated may undergo a Wolff rearrangement and the resulting electrophilic ketene (8) reacts with the unchanged diazoketone to give unsaturated lactones (butenolides 9).¹² However, some experiments reported later give circumstantial evidence that Wolff rearrangements, in the condensed phase, are probably concerted processes in which no ketocarbenes are involved. On the other hand, in the presence of a thioether and copper catalyst, the thioether is a nucleophile strong enough to compete effectively for the ketocarbene-copper complex, and a β -ketosulfonium ylide (1b) is formed in situ, the final products isolated depending upon the relative nucleophilicity of the thioether compared to that of the corresponding ylide, as well as on the stability of the ylides themselves. Whereas diazoketones in thioanisole solution give trans-1,2,3triacylcyclopropanes (6), the more nucleophilic alkyl sulfides and sulfoxides give the corresponding vlides (or their Hofmann degradation products in some instances).

CYCLOPROPANE FORMATION FROM DIAZOKETONES: SCOPE AND LIMITATIONS OF THE METHOD

The cyclopropane 1a formation from several diazoketones has been performed in solution of an inert solvent-usually benzene-, in the presence of 1.5-2.0 mol of thioanisole and a copper catalyst

^{*}The view that the transient intermediate in the copper catalyzed decomposition of diazoketones is some sort of a carbene-copper complex is supported by recent studies.¹¹

- usually anhydrous copper sulfate[†]. Table 1 gives the yields and the experimental conditions for a number of diazoketones.

The different diazoketones were chosen in order to evaluate the steric and electronic effects of the substituents on the yields of cyclopropanes. From Table 1 it must be concluded that in the series of aliphatic diazoketones the bulkier the substituent the better the yields. In the series of the aromatic diazoketones the yields are only moderate and the electronic character of the *para*-substituent does not effect them very much.

MECHANISMS OF CYCLOPROPANE FORMATION

Two alternative mechanisms can be visualized for the cyclopropane formation (Chart 1):

"Mechanism I", that proceeds through the dimer 4, and "Mechanism II" in which no dimer is involved and implies some stability for the intermediate betaine 3b.

In the preliminary communication^{1a} we favored "MechanismII" on the basis that if 1,2-diacylethylenes (dimer 4) were formed in the reaction, they should be the predominant products rather than the cyclopropanes; *i.e.*, since 1,2-diacylethylenes (4) are much less electrophilic than "ketocarbenes", they should accumulate in the reaction

$$la \longrightarrow 2 \xrightarrow{PhSMc} lb \xrightarrow{+2} 4 \xrightarrow{+1b} 5 \longrightarrow 6$$

However, the experimental results showed that cyclopropanes were almost the exclusive products, and no traces of dimers could be isolated. These results were consistent with "Mechanism II" which implies that the intermediate betaine 3b is stable and nucleophilic enough to capture a second "ketocarbene" giving the new betaine 5, which cyclizes to cyclopropane 6 by irreversible loss of thioanisole:

$$1a \longrightarrow 2 \xrightarrow[fast]{PhSMe} 1b \xrightarrow[fast]{+2} 3b \xrightarrow[fast]{+2} 5 \longrightarrow 6$$

Further experiments in solution of inert solvents (table 1), careful analyses by VPC, and application of spectroscopic techniques have given compelling evidence that "Mechanism I" is the predominant one. However, "Mechanism II" is also probably operating to some extent, and some circumstantial evidence will be given later.

Table 1. Cyclopropanation of diazoketones R-CO-CHN₂

R	Solvent	Catalyst	Time (hr)	Temp (℃)	Yield (%)
Me ₁ C—	thioanisole	Cu	3	70	73.5a.b
Me ₁ C—	thioanisole/benzene	CuSO₄	2.5	60	84·2ª
Me CH-	thioanisole/OME	CuSO.	3	59	72·0°
Me—	thioanisole/benzene	CuSO.	4	0	10 ^{c. d}
Ph—	thioanisole	Cu	3	60	33.3ª
Ph—	thioanisole/hexane	Cu	3	60	38·7ª
p-MeOC ₆ H ₄ -	thioanisole/benzene	CuSO.	4.5	70	38-4ª
P-NO ₂ C ₆ H ₄ -	thioanisole/benzene	CuSO ₄	10	48	24·0ª

^aIsolated as pure, crystalline product; ^bYields as high as 97% have been obtained in some experiments; ^cProduct isolated by preparative v.p.c.; ^dDiazoacetone gives rather erratic results and the yield given has been determined by VPC and represents at least a minimum.

†Although it has been reported that di- μ -chlorodi- π allyldipalladium decomposes ethyl diazoacetate under very mild thermal conditions (0-10°),13 preliminary experiments have shown that the results are very complex with diazoketones either in solution of inert solvents or in the presence of nucleophilic olefins. On the other hand, cuprous acetylacetonate¹⁴ was a very effective catalyst for the dimerization of diazomethyl-t-butylketone: in benzene solution the reaction proceeds at room temperature to give 85% yield of a 3:1 mixture of trans- and cis-1,2-dipivaloylethylene (this isomer easily isomerizes, but it could be characterized by NMR spectroscopy since the olefinic protons appear at $\tau 3.3$, instead of 2.6 observed in the trans-isomer). Although the cyclopropanation proceeds also at room temperature the results were complex, the sulfonium ylide being the main product isolated (~ 41% yield), together with cyclopropane (7%) and dimer (12%).

Each of the individual steps proposed in Chart 1 has either adequate analogy in the literature or it has been demonstrated in this work.

The formation *in situ* of sulfonium ylides as intermediates is well substantiated because they can be isolated under certain experimental conditions (see below). On the other hand, it is well known that β -ketosulfonium ylides react with *trans*-1,2diacylethylenes¹⁵ to give 1,2,3-triacylcyclopropanes, the yields obtained depending upon the steric and electronic effects of the substituents (Table 2), and we have found that if diazoketones are decomposed under conditions for cyclopropane formations, *in the presence of a competitive dimer*, the sulfonium ylides formed *in situ* are intercepted to some extent by the dimer already present in the reaction mixture (Table 3).



Table 2. Reaction of β -ketosulfonium ylides with dimers in benzene solution

R	\mathbf{R}^{1}	R²	Yield %	cis- %	trans- %	Exp. conditions
Me	Ph	Ph	97.8		_	24 hr room temp
Me	CMe ₃	Ph	92.8	85.5	14.5	24 hr room temp
Me	Ph	CMe.	75.8	68.4	31.6	24 hr room temm
Me	CMe.	CMe.	0	_		24 hr room temp
Me	CMe.	CMe.	60.2	—		3 hr at 50°
Ph	CMe.	CMe.	22.2	_		48 hr room temm
Ph	CMe ₂	CMe.	38.5	_		96 hr room temp
Ph	CMe ₃	CMe ₃	27.3	_	-	3 hr at 70°

Table 3. Reaction of diazoketones with competitive dimers (Conditions for cyclopropane formation)

R ¹ —CO—CHN ₂ 1a	+	R [±] CH==CH 4	-COR ²
		C _eH_e/CuSO _e	RSMe
		R ² CO	COR ²

R	R	R²	1a : 4 (molar)	Yield %	Exp. conditions
Me	CMe ₃	CMe3	1:1	39 ·3	5 hr at 50°
Ph	CMe ₃	Ph	2:3	81ª	2 hr at 70°
Ph	Ph	CMe ₃	1:1	48 ∙4⁰	1 hr at 65°

^aA mixture of *cis*-1,2-dibenzoyl-*trans*-3-pivaloylcyclopropane (82%) and *trans*-1,2-dibenzoyl-3-pivaloylcyclopropane (18%). Excess of dimer recovered in 89%.

^bMixture of two isomers (ratio not determined); small amounts of *trans*-1,2,3-tribenzoycyclopropane (1.9%) and *trans*-1,2-dibenzoylethylene (12%), together with recovered *trans*-1,2-dipivaloylethylene (37.7%) were detected by VPC. Although different authors^{150,16} have reported that β -ketosulfonium ylides decompose under thermal and catalytic conditions to give *trans*-1,2,3triacylcyclopropanes (6), we have verified the stability of a number of them and found that, with the exception of methylphenylsulfonium phenacylide, they are too stable (Table 4) to account for the high yields usually obtained in the cyclopropane formation, mainly via the t-butyl derivative.

However, in agreement with the mechanisms proposed in Chart I, we have found that reaction of β -ketosulfonium ylides with diazoketones, in the presence of copper salts, also gives cyclopropanes.¹⁷ In fact, the reaction of a diazoketone with an ylide with different R-substituents should give different products depending upon the mechanism operating: "Mechanism I" should give a cyclopropane with two of the acyl groups coming from the ylide 1b, and "Mechanism II" a cyclopropane with two of the acyl groups from the diazoketone 1a (Chart II).

When such an experiment was performed by reacting two moles of diazomethyl-t-butylketone (1a, R=CMe₃) and one mole of methylphenyl-sulfonium phenacylide (1b', R=Ph), with anhydrous copper sulfate as the catalyst, the VPC analysis of the mixture showed not only the presence of both cyclopropanes, in 19.2 and 26.1% yield, respectively, but *trans*-1,2,3-tripivaloylcyclopro-





Table 4. Thermal and catalytic stability of β -ketosulfonium ylides



R	R'	Solvent	Catalyst	Temp (℃)	Time (hr)	Dec products
Me	Ph	THF	_	reflux	48	stable criss.c
Me	Ph	Benzene	CuSO₄	60	3	stable ^{cr15b}
Me	Ph	Cyclohexene	CuSO ₄	reflux	24	cyclopropan e (70%) +
						benzoyinorcarane ¹⁵⁰
Me	Ph	Thioanisole/benz.	CuSO₄	63	3	stable
Me	CMe ₃	THF	'	reflux	48	stable
Me	CMe ₃	Benzene	CuSO₄	40	4	stable
Me	CMe ₃	Cyclohexene	CuSO.	reflux	40	stable
Me	CMe ₃	Thioanisole/benz.	CuSO.	60	3	stabl e
Ph	Ph	Benzene	CuSO.	60	4	85-90% recovery ^{c/}
Ph	Ph	Thioanisole/benz.	CuSO₄	65	4.5	{100% decomposition 45% cyclopropane
Ph	CMe ₃	Benzene	CuSO.	68	3	stable
Ph	CMe ₃	Thioanisole/benz.	CuSO ₄	68	3	stable

pane in 27.7% yield,* together with small amounts (1.6 and 1.7%) of the two possible symmetrical dimers. No traces of the unsymmetrical dimer were detected. Although there is too much crossover to draw unequivocal conclusions, the results can be interpreted either in terms of both mechanisms operating competitively or taking into account only "Mechanism I", but not in terms of "Mechanism II" alone.

In the meantime we found that when cyclopropanes are prepared in an inert co-solvent as described, and the mixture is cooled and the catalyst filtered off, the analysis shows that the yield of cyclopropane is *only* 30-35%, the main products being the dimer and the sulfonium ylide, present in almost equimolecular amounts, which then react very slowly to give more cyclopropane until only traces of them remain (Table 2).

Table 5 gives the results of three experiments run under identical conditions which were "frozen" after no more nitrogen was evolved, and then analysed (VPC) from time to time until constant values were observed. The ylide could be isolated by extracting the solution with water and then recovered from the aqueous solution by re-extraction with chloroform.

These results give compelling evidence that "Mechanism I" is actually operating, and all the

^{*}Probably arising from a competitive cyclopropanation of diazoketone induced by the thioanisole generated *in situ*.

observed facts are best interpreted if the generation of the ketocarbene-copper complex $(1a \rightarrow 2)$ is the rate limiting step.4c However, "Mechanism II" could also operate competitively to some extent since cyclopropane is already present in the "frozen" mixture, in spite of the slow reaction of the ylides with dimers, especially those having t-Bu groups, which in turn are those that give better vields of cyclopropane*. Some circumstantial and analogical evidence that this mechanism is probably operating is found in the fact that the much less nucleophilic B-ketosulfoxonium ylides, which are known not to react with dimers at all (Experimental), give about 8% yield of cyclopropane when reacted with diazoketones in the presence of copper catalyst.

 Table 5. "Frozen" mixtures from diazomethyl-tbutylketone (VPC analytical control)



% Yield of cyclopropane^a

l ime (days)	1st Operation	2nd Operation	3rd Operation	
0	_		32.0 ± 6.4	
1	48.0 ± 2.6	47.5 ± 2.8		
2	—	62.0 ± 1.8	56.5 ± 1.2	
3	$62 \cdot 0 \pm 2 \cdot 8$	64.3 ± 2.1	—	
5	67.0 ± 1.6	—	_	
6		_	65.5 ± 3.3	
7	69.0 ± 2.9	_	_	
9	_	68.0 ± 2.1	67.0 ± 1.5	
11	72.5 ± 1.2		_	
14	72.5 ± 1.4	_	_	
15		67.8 ± 3.6	79.5 ± 7.8	
17	_	78.0 ± 2.2	79.5 ± 1.6	
52	80.0 ± 1.4	81.0 ± 1.4	80.0 ± 1.5	

^aCorrected values (Experimental)

*The high yields of cyclopropane obtained when the mixture is not "frozen" is due to the increase of temp and polarity of the medium during the working-up process: benzene is eliminated under vacuum at $30-40^\circ$, but the remaining thioanisole solution is then evaporated to dryness at $70-80^\circ$.

The increase of cyclopropane initially present with increasing reaction temp is shown in the following table:

	React temp	React time	Initial vield	Final yield (30 days)
1.	52℃ ·	30 min	35.5%	$70.8 \pm 2.8\%$
2.	90°C	30 min	60.8%	$70{\cdot}5\pm3{\cdot}4\%$

FORMATION OF SULFONIUM AND SULFOXONIUM YLIDES IN THE REACTION OF DIAZOKETONES WITH SULFIDES AND SULFOXIDES: A NEW METHOD FOR CYCLOPROPANE FORMATION FROM DIAZOKETONES IN DIMETHYL SULFIDE

The results obtained in the catalytic decomposition of diazomethyl-t-butylketone (1a, $R=CMe_3$) in the presence of DMSO and thioethers other than thioanisole are summarized in Table 6.

Alkyl sulfides and sulfoxides are more nucleophilic species than thioanisole, and once the corresponding ylide is formed this is the final product (or its Hofmann degradation products in one case) because it cannot effectively compete with the sulfide for "ketocarbenes", and the reaction does not proceed further. On the other hand, the low nucleophilicity of diphenyl sulfide accounts for the low yield of cyclopropane.

Table	6.	Reactions	of	diazomethyl-t-butylketone	with
DM	SO	and thioeth	ers,	, in the presence of copper sa	ults

Thioether	Product	Yield (%)
Dimethyl sulfoxide (DMSO)	Ylide	44·0
Dimethyl sulfide	Ylide	47.7
Diethyl sulfide	Ylide	
	(and/	
	or decomposition	
	products from)	
Diphenyl sulfide	Cyclopropane	16-0
Thioanisole	Cyclopropane	80-1
Diphenyl sulfide Thioanisole	Cyclopropane Cyclopropane	16∙0 80∙1

Since the catalytic decomposition of diazoketones in inert solvents affords trans-1,2-diacylethylenes (dimer 4), and in the presence of dimethyl sulfide gives sulfonium ylides which, in turn, add to the former to yield cyclopropanes (Table 2), it is possible to induce cyclopropane formation in DMSO using threefold excess of the former. Thus, the catalytic decomposition of three moles of diazomethyl-t-butylketone in the presence of one mole of dimethyl sulfide and anhydrous copper sulfate as catalyst, in benzene solution, afforded trans-1,2,3tripivaloylcyclopropane in 40% yield. Although the yields are not as good as when cyclopropane formation is induced by thioanisole, the new method offers the advantage of using a lower boiling sulfide which can be easily eliminated at low temperature.

PURELY THERMAL DECOMPOSITION OF DIAZOKETONES IN THIOANISOLE: WOLFF REARRANGEMENT

Purely thermal decomposition of diazomethyl-tbutylketone (1a, R=CMe₃) in xylene solution, leads to a butenolide 9 (R=CMe₃) identical to that obtained in the photochemical decomposition.¹⁰ In order to explore whether Wolff rearrangement involves a free ketocarbene as intermediate, diazomethyl-t-butylketone has been decomposed in thioanisole solution at 135°, butenolide 9 being also formed as the sole product in this reaction (91% yield). Therefore, if the ketene 8 were formed from an intermediate ketocarbene, this should be intercepted—at least, partially—by the thioanisole to give the sulfonium ylide. However, the results show that the product from purely thermal decomposition is independent of the nature of the solvent,¹⁸ and most probably Wolff rearrangement is a concerted process* involving an oxirene 11 as intermediate:²⁰

columns being used (experimental conditions and retention time for significant compounds are also given):

Model F-21 (flame ionization detector):

(a) A $120 \text{ cm} \times \frac{1}{4}^n$ stainless steel column, filled with 5% NPGS on Chromosorb W. Retention times (Injector at 250° C; column at 150° ; flow of N₂ 30 ml/min):

trans-1,2-dipivaloylethylene -3.6 min; trans-1,2,3-triisobutyroylcyclopropane -8.8 min; trans-1,2,3-tripivaloylcyclopropane -12.4 min; trans-1,2,3-triacetylcyclopropane -16.0 min; trans-1-benzoyl-2-pivaloylethylene -20.8 min.



EXPERIMENTAL

All the reactions have been performed in atmosphere of purified N_2 , and extensive precautions were taken to preclude the presence of even traces of moisture, mainly in the reactions involving ylides. MPs are uncorrected, and have been determined on a Kofler microscope.

UV. IR, and NMR spectra were recorded on Perkin Elmer Spectrometers, Model 157-UV, 457 and R-10, respectively. All the compounds prepared throughout the work showed correct spectra, even if they are not explicitly mentioned in the text. The following general remarks on NMR spectra are pertinent:

Sulfonium ylides. As observed,²¹ when the NMR spectra of the ylides were recorded under strictly anhydrous conditions the methine proton appeared as a sharp singlet, and addition of a trace of water produced a dramatic line broadening.

The diethyl sulfonium ylides, as well as other diethyl sulfur derivative,²² exhibit NMR spectra typical of systems possessing a methylene group with two non-equivalent (diastereotopic) protons²³ (two double quartets).

1,2,3-*Triacylcyclopropanes*. The NMR spectra of 1,2,3triacylcyclopropanes with three identical acyl groups show always a typical pattern of an AB₂ system ($J/\Delta \nu =$ 0.15), with $J_{AB} \sim 6$ Hz, indicating the *trans*- is the only isomer present.

When one of the three acyl groups is different, as in the case of 1,2/3-dibenzoyl-pivaloylcyclopropane and 1,2/3benzoyl-dipivaloylcyclopropane, then two isomers are possible (apart from the *all-cis*) which show typical patterns of AB₂ and ABC systems in the NMR.^{150,24} very useful indeed for quantitative analysis of the mixtures. The ABC systems show a quartet centered at τ 5.84 and a double quartet at 6.44, with coupling constants of the order of $J_{AB} = 9.8$, $J_{BC} = 6.1$ and $J_{AC} = 5.1$ Hz.

VPC were performed with Perkin Elmer Gas Chromatographs, Model F-21 and 990, the following types of (b) A 25 cm $\times \frac{1}{4}$ " stainless steel column, filled with 5% NPGS on Chromosorb W. Retention time (Injector at 250°; column at 210°; flow of N₂ 30 ml/min):

trans-1,2-dibenzoylethylene - 5.0 min

Retention times (Injector at 250°; column at 220°; flow of N_2 30 ml/min):

1.2/3-benzoyl-dipivaloylcyclopropane (two isomers)-1.7 min; 1.2/3-dibenzoyl-pivaloylcyclopropane (two isomers) -12.6 min.

Model 990 (flame ionization detector)

A 150 cm \times 1/8" stainless steel column, filled with 2.5% NPGS on Chromosorb G. Retention time (Injector at 200°; column at 150°; flow of N₂ 30 ml/min):

trans-1,2-dipivaloylethylene – 1.6 min; *trans*-1,2,3-tripivaloylcyclopropane – 12.0 min.

The areas of the peaks were corrected according to a calibration chart previously plotted with standard mixtures, and all the experimental data obtained in VPC analyses were statistically processed as described by J. D. Hinchen,²⁵ using an Olivetti Programma 101.

Diazoketones. Aliphatic diazoketones were prepared according to Arndt-Eistert²⁶ and aromatic diazoketones, as described by Newman and Beal.²⁷

The yields and physical constants are given in Refs 10, 26c, 27-29.

Sulfonium salts

(A) The dialkylsulfonium salts were prepared by reaction of the dialkylsulfdes and the α -halocarbonyl compound in MeOH soln. The procedure is illustrated by dimethyl(α -pivaloylmethyl)sulfonium chloride:

A mixture of 8.6 g (64 mmol) α -chloropinacolone and 29 ml dimethyl sulfide, in 43 ml anhydr MeOH, was refluxed for 72 hr. The mixture was evaporated under vacuum, the crystalline residue filtered off, and washed with ether. Recrystallization from MeOH-ether afforded 6.0 g (47.5% yield) dimethyl(α -pivaloylmethyl)sulfonium chloride, m.p. 156–157° (Found: C, 48.69; H, 8.79; Cl, 17.80; S, 16.12. C₈H₁₇ClOS requires: C, 48.88; H, 8.72; Cl, 18.04; S, 16.30.

The dimethylphenacylsulfonium bromide, which has already been described,³⁰ was prepared in 93% yield, m.p. 143-143.5° (Found: C, 45.82; H, 4.93; Br, 30.61; S, 11.90.

^{*}Similarly, Curtius rearrangement also seems to take place through a concerted mechanism because no nitrene products have yet been found from thermolyses of acyl azides.¹⁹

C1:0H1:2BrOS requires: C, 45:98; H, 5:02; Br, 30:60; S, 12:28.)

(B) The methylphenylsulfonium salts were prepared by methylation of the corresponding sulfides with dimethyl sulfate **and** further treatment with KBr as described.^{16a, 31} In the case of the methylphenyl(α -pivaloylmethyl)sulfonium salt the product was prepared *in situ* as described in the following section.

Sulfonium and sulfoxonium ylides

The sulfonium and sulfoxonium ylides prepared throughout this work are listed in Table 7. The procedures used are illustrated with the following examples:

(A) Sodium hydroxide method.³² A stirred mixture of 3.2g (15.4 mmol) phenyl(α -pivaloylmethyl) sulfide (prepared from sodium phenolate and α -bromopinacolone in 76.3% yield, cf31 as a low m.p. crystalline solid, m.p. 26.5-27°. (Found: C, 69·44; H, 7·55. C12H16OS requires: C, 69.19; H, 7.74) and 2.3 ml (23 mmol) dimethyl sulfate was heated at 100° for 1½ hr. After cooling, the sulfonium sulfate separated as a gel. To the stirred, ice-cooled, mixture NaOHaq (7.6 g in 90 ml water) was added and cooled down to $0-5^\circ$. After stirring for $1\frac{1}{2}$ hr, the soln was extracted several times with chloroform. The extract was dried and evaporated to give the methylphenylsulfonium α pivaloylmethylide (2.1 g, 62.6% yield) which, after recrystallization from petrol ether and drying over P₂O₅, showed m.p. 83·84°; IR (KBr) 1540 cm⁻¹; NMR, τ (in DCCl₃) 2.1-2.6 (m)(5H), 5.95 (s)(1H), 6.9 (s)(3H) and 8.8 (s)(9H). (Found: C, 69.69; H, 8.15; S, 14.57, C₁₃H₁₈OS requires: C, 70.24; H, 8.16; S, 14.39.)

(B) Sodium hydride method.³² 2·2g (43·7 mmol) NaH (50% dispersion in mineral oil) were added to a stirred

suspension of 6.7g (34.4 mmol) dimethyl(α -pivaloylmethyl)sulfonium chloride in 170 ml dry THF. The system was then connected to a gas meter and stirred for 3 hr until the evolution of H₂ stopped (800 ml, 100%). The mixture was filtered and the soln evaporated *in vacuo* under rigorous anhydrous conditions to give dimethylsulfonium α pivaloylmethylide (3.9g, 71.6% yield) which, after recrystallization from benzene-petrol ether, gave m.p. 115.5– 116° (polymorphic change at 72–73°); IR (KBr) 1530 cm⁻¹; NMR, τ (DCCl₃) 6.2 (broad)(1H), 7.1 (s)(6H), 8.9 (s)(9H)(Found: C, 59.58; H, 10.35; S, 19.80. C₈H₁₆OS requires: C, 59.95; H, 10.06; S, 20.00.)

(C) Basic alumina method.³³ A soln of 1.0g (3 mmol) dimethylphenacylsulfonium bromide in MeOH was adsorbed on a chromatographic column filled with 30 g basic alumina,³⁴ and then eluted with chloroform. The chloroform solution was evaporated, and the residue dried over P₂O₃, to give dimethylsulfonium phenacylide (0.499 g, 72:3% yield), m.p. 78-79° after recrystallization from CHCl₃-CCl₄:^{130, 18c, 32} IR (CH₂Cl₂) 1520 cm⁻¹; NMR τ (DCCl₃) 1.7-2.5 (m)(5H), 5.45 (broad)(1H), 6.98 (s)(6H).

(D) "Ketocarbene" Method.¹⁰ See under "Catalytic decomposition of diazoketones in the presence of organic sulfides and sulfoxides".

(E) Dimethylsulfoxonium methylide method.³⁵ The sulfoxonium ylides have been prepared according to the method developed by Corey and Chaykovsky. The procedure is illustrated with dimethylsulfoxonium α -pivaloyl-methylide.

A solution of 6.0g (50 mmol) pivaloyl chloride in 50 ml THF recently distilled over CaH₂, was added dropwise to a stirred 0.5N soln of dimethylsulfoxonium methylide³⁵⁰ in THF (200 ml, 0.1 mol), and the mixture stirred 1 hr at

Ylide	Method	Yield (%)	М.р. (°С)	Ref.
Me, Ś—ĈH—COPh	Α	69.6	78–79°	15b, 16c, 32
-	В	80.0	78-79°	32
	С	72·3	78-79°	
EtzŠ—ĒH—COPh Me	Α	81·2	_*	
Ś−ĒH−COPh	В	77-6	111-113	15 <i>a</i>
Ph Me ₂ Š—ČH—COPh	Ε	92·1	117-118	35
Me.Š—ČH—COCMe	А	88-8	115-116	
	В	71-6	115-116	
	D	47.7	115-116	
ELS-CH-COCMe	Α	65-9	_•	
	D	?	*	
Ме				
ŚĈHCOCMe₃	Α	62-6	83-84	
Ph				
Me ₂ S – CH – COCMe ₃	D	49-5	170-171	
U O	Е	93·4	170-171	

Table 7. Sulfonium and sulfoxonium ylides

*Highly unstable and hygroscopic compound, characterized by I.R. and N.M.R. spectroscopy (Obtained from sulfonium salt prepared in situ) room temp. The mixture was filtered to remove the trimethylsulfoxonium chloride and the crystals thoroughly washed with ether. The soln was evaporated to dryness to give dimethylsulfoxonium α -pivaloylmethylide as white crystals, m.p. 170–171° after recrystallization from CHCl₃-CCl₄ (8.0g, 93.4% yield); IR (KBr) 1560 cm⁻¹; NMR, τ (DCCl₃) 5.4 (s)(1H), 6.52 (s)(6H), 8.86 (s)(9H)(Found: C, 54.47; H, 9.04; S, 17.96. C₈H₁₆O₂S requires: C, 54.53; H, 9.15; S, 18.16.)

Dimethylsulfoxonium phenacylide^{35a} was prepared in 92% as a crystalline solid, m.p. 117-118°; IR (KBr) 1525 cm⁻¹; NMR, τ (DCCl₃) 1·9-2·6 (m)(5H), 4·8 (s)(1H), 6·4 (s)(6H)(Found: C, 60·92; H, 6·34; S, 16·42. C₁₀H₁₂O₂S requires: C, 61·22; H, 6·16; S, 16·51).

Stability of sulfonium ylides. The thermal and the catalytic stability has been tested under different conditions. The results are listed in Table 4. The procedure is illustrated with the following example:

A soln of methylphenylsulfonium α -pivaloylmethylide (53 mg) in dry benzene (2 ml), containing anhyd CuSO₄ (20 mg) was heated at 68° for 2 hr under N₂. The mixture was cooled, the catalyst filtered off and the soln evaporated under vacuum; the residue was analysed by spectroscopic (IR and NMR) and chromatographic (TLC and VPC) techniques, the ylide being recovered almost quantitatively (> 90%).

Catalytic decomposition of diazoketones

(A) In inert solvents. trans-1,2-dipivaloylethylene. To a soln of 5 g (39 mmol) diazomethyl-t-butylketone in 25 ml anhyd benzene 0.5 g copper-bronze (precipitated from CuSO₄ soln by 80% aqueous hydrazine), was added and the mixture refluxed for 24 hr. The benzene soln was columned through silica-gel to remove the colloidal Cu, the solvent evaporated under vacuum and the remaining pale yellow crystalline solid recrystallized from benzene to give 3.1 g (80% yield) trans-1,2-dipivaloylethylene, m.p. 110–111°C; λ_{max} (EtOH) 235 nm ($\epsilon = 9.800$); IR (C₂Cl₄) 1680–1690 cm⁻¹; NMR, τ (CCl₄) 2-6 (s)(2H), 8-8 (s)(18H)(Found: C, 73.44; H, 10.33; M.W., 198. C₁₂H₂₀O₂ requires: C, 73.43; H, 10.27; M.W., 196).

(B) In 2,3-dimethyl-2-butene: 1,1,2,2-tetramethyl-3pivaloylcyclopropane. A soln of 6.0g (47 mmol) diazomethyl-t-butylketone in 22 ml 2,3-dimethyl-2-butene was added dropwise to a suspension of 200 mg copper-bronze in 50 ml of the same olefin heated at 110-120°, and the mixture was refluxed for 3 hr. The catalyst was removed by columnation through silica-gel and elution with benzene, the soln concentrated under vacuum, and the remaining soln kept in the refrigerator: the trans-1,2 dipivaloylethylene (2.65 g, 57% yield) was filtered, and the residue evaporatively distilled at 0.5 torr to give 3.73g (43% yield) impure 1,1,2,2-tetramethyl-3-pivaloylcyclopropane. An analytic sample was prepared by VPC (Found: C, 79.12; H, 12.05. $C_{12}H_{22}O$ requires: C, 79.06; H, 12.16).

The VPC analysis of another operation gave 60% yield of the dimer and 37% of cyclopropylketone.

Catalytic decomposition of diazoketones in thioanisole: Cyclopropane formation from diazoketones via sulfonium ylides

(A) Synthesis of 1,2,3-triacylcyclopropanes. The results are summarized in Table 1, and the general procedure is illustrated with the cyclopropane from diazomethyl-tbutylketone: 3.72g (30 mmol) thioanisole and 0.4ganhyd CuSO, were added to a soln of 2.52g (20 mmol) diazomethyl-t-butylketone, and the mixture heated to the decomposition temp (~ 60°) until no more evolution of N₂ was observed (2½ hr). The mixture was cooled, the catalyst filtered off and the solvent evaporated under vacuum. The thioanisole was eliminated at 70-80°/0·1 torr, and the solid residue recrystallized from petrol ether to give 1.6g (84.2% yield) *trans*-1,2,3-tripivaloylcyclopropane, m.p. 161-162° (mixed m.p. with an authentic sample prepared according to the method of Charpentier-Morize and Collard,³⁸ 160-161°).

Other 1,2,3-triacylcyclopropanes prepared from diazoketones are listed:

trans-1,2,3-triacetylcyclopropane, m.p. 75-76° (10% yield, as determined by VPC)(characterized by IR and NMR spectroscopy).

trans-1,2,3-triisobutyroylcyclopropane, m.p. $66-67^{\circ}$ (72% yield) (Found: C, 71·10; H, 9·73. C₁₅H₂₄O₃ requires: C, 71·39; H, 9·59).

trans-1,2,3-tribenzoylcyclopropane, m.p. $217 \cdot 5 - 218^{\circ}$ (38.7% yield)⁶ (Found: C, 81.05; H, 5.11. C₂₄H₁₈O₃ requires: C, 81.32; H, 5.13).

Trans-1,2,3-tri(4-methoxybenzoyl)cyclopropane, m.p. $151-153^{\circ}$ (38·4% yield)(Found: C, 73·17; H, 5·45. C₂₇H₂₄O₆ requires: 72·96; H, 5·44).

trans-1,2,3-tri(4-nitrobenzoyl)cyclopropane, m.p. 248° dec (24% yield)(Ratts and Yao,¹⁸⁰ give m.p. 265-266°) (Found: C, 58.96; H, 3.30; N, 8.87. $C_{24}H_{15}N_2O_9$ requires: C, 58.90; H, 3.09; N, 8.59).

(B) "Freezing" of the cyclopropane reaction: Characterization and analysis of the intermediates. Three different experiments were run simultaneously under identical conditions in order to test the repeatability²⁵ of the method.

A soln of 504 mg (2 mmol) diazomethyl-t-butylketone and 744 mg (3 mmol) thioanisole, in 2 ml dry benzene containing 80 mg anhyd CuSO₄, was heated at 60° until no more evolution of N₂ was observed (2 hr). The mixture was cooled, the catalyst filtered off and thoroughly washed with benzene. The benzene soln was analysed by VPC The results of three experiments are given in Table 5. Since sulfonium ylides are not suitable for VPC analysis, aliquot parts of the benzene solns were eventually extracted from time to time with water, and the aqueous solns re-extracted with chloroform, dried and evaporated to dryness, and the ylide weighed and characterized by IR and NMR spectroscopy. The results were always in agreement with those from VPC analysis.

Reaction of sulfonium ylides with dimers

The results are summarized in Table 2, and the general procedure is illustrated by the following examples:

(A) A solution of 256 mg (1.4 mmol) dimethylsulfonium α -pivaloylmethylide and 335 mg (1.4 mmol) trans-1,2dibenzoylethylene in 15 ml dry benzene was stirred at room temp for 22 hr. The mixture was evaporated under vacuum, the residue columned on silica-gel, eluted with benzene, and the resulting product recrystallized from benzene-petrol ether to give 440 mg (92.8% yield) of an isomeric mixture of 1,2/3-dibenzoyl-pivaloylcyclopropane, m.p. 164-165° (Found: C, 79.07; H, 6.77. C₂₂H₂₂O₃ requires: C, 79.02; H, 6.63.) From the NMR spectrum it was calculated that 85.5% was the isomer cis-1,2-dibenzoyl-trans-3-pivaloylcyclopropane (AB₂ system), and 14.5% trans-1,2-dibenzoyl-3-pivaloylcyclopropane (ABC system).¹³⁰

(B) The reaction of dimethylsulfonium phenacylide with *trans*-1,2-dipivaloylethylene at room temp for 24 hr afforded 75.8% yield of a mixture of 1,2/3-benzoyldipivaloylcyclopropanes (68.4% cis- and 31.6% trans-), m.p. 161-162° (polymorphic change at 149-150°)(Found: C, 76.50; H, 8.39. C₂₀H₂₈O₃ requires: C, 76.40; H, 8.33.)

(C) The reaction of either dimethyl- or methylphenylsulfonium α -pivaloylmethylide with *trans*-1,2-dipivaloylethylene was always very slow, even at higher temp, as shown in Table 2.

Attempted reaction of sulfoxonium ylides with dimers

A soln of 95 mg (0.53 mmol) dimethylsulfoxonium α pivaloylmethylide and 106 mg (0.53 mmol) *trans*-1,2dipivaloylethylene in 5 ml anhydrous benzene was refluxed for 24 hr. Evaporation of benzene under vacuum gave 201 mg crystalline material which NMR spectrum showed to be the mixture of unreacted starting products.

Similarly, no reaction took place when the more reactive *trans*-1,2-dibenzoylethylene was substituted for *trans*-1,2-dipivaloylethylene.

Reaction of diazoketones with dimers

The results are summarized in Table 3. The procedure is illustrated with the following example: 2 ml thioanisole and 50 mg anhydrous CuSO₄ were added to a soln of 252 mg (2 mmol) diazomethyl-t-butylketone and 748 mg (3 mmol) trans-1,2-dibenzoylethylene in 3 ml dry benzene, and the mixture heated at 70° for 2 hr, until no more evolution of N₂. The mixture was cooled, the catalyst filtered off and the solvent evaporated under vacuum. Fractional crystallization of the remaining semicrystalline residue from benzene afforded 542 mg (81% yield) of an isomeric mixture of 1,2/3-dibenzoyl-pivaloylcyclopropanes (82% of cis-dibenzoyl and 18% of trans-dibenzoyl), identical with the product from the reaction of the corresponding ylide with the same dimer (see above), together with 325 mg of recovered trans-1,2-dibenzoylethylene.

Reaction of diazoketones with ylides

The general procedure is illustrated with the following examples:

(A) Reaction of diazomethyl-t-butylketone with methylphenylsulfonium α -pivaloylmethylide. (a) To a soln of 0.396 g (3.1 mmol) diazomethyl-t-butylketone and 1.40 g (6.3 mmol) methylphenylsulfonium α -pivaloylmethylide in 7 ml dry benzene, were added 0.10 g anhyd CuSO₄, and the mixture heated to the decomposition temp (52°), until no more evolution of N₂ (1 hr). The mixture was cooled, the catalyst filtered off and the soln washed with water to remove excess of ylide. From the aqueous soln, by extraction with chloroform, were recovered 0.6 g ylide (42.8%). VPC analysis of the benzene soln showed the presence trans-1,2,3-tripivaloylcyclopropane (66.9%) and trans-1,2-dipivaloylethylene (33% yield).

(b) A similar reaction using two mol of diazoketone *per* mol of ylide gave much more dimer than cyclopropane-(1:0-4), no ylide being recovered.

(B) Reaction of diazomethyl-t-butylketone with methylphenylsulfonium phenacylide ("Crossed Experiments"). A soln of 1.10g (8 mmol) diazomethyl-t-butylketone and 1.0g (4 mmol) methylphenylsulfonium phenacylide in 7 ml dry benzene, containing 0.10g anhyd CuSO₄, was slowly heated up to 54°, at which temp a smooth evolution of N₂ began. The mixture was kept under these conditions for 4 hr, and finally heated at 70° for 30 min to ensure the complete decomposition. The catalyst was filtered off, the solvent removed and the thioanisole evaporated at high vacuum. The residue was dissolved in benzene and analyzed by VPC to give: *trans*-1,2-dipival-oylethylene – 1.7%; *trans*-1,2-dibenzoylethylene – 1.6%; *trans*-1.2-pivaloylethylene* – 0%; *trans*-1,2,3-tripivaloylcyclopropane (two isomers) – 26·1%; 1,2/3-dibenzoyl-pivaloylcyclopropane (two isomers) – 19·2%; *trans*-1,2,3-tribenzoylcyclopropane – 0%; Unidentified products – 23·6%.

(C) Reaction of diazomethyl-t-butylketone with sulfoxonium ylides. Circumstantial and analogical evidence favoring "Mechanism II". (a) To a soln of 369 mg (2·9 mmol) diazomethyl-t-butylketone and 258 mg (1·5 mmol) dimethylsulfoxonium α -pivaloylmethylide in 7 ml dry benzene, were added 70 mg anhyd CuSO₄ and the mixture slowly heated up to 70°C, at which temp, a smooth evolution of N₂ started. The mixture was heated until no more N₂ was evolved (~ 3 hr), and then cooled at room temp. The catalyst was filtered off, and the soln washed with water to remove all traces of ylide and DMSO, dried with NaSO₄ and the solvent eliminated under vacuum. VPC analysis of the soln showed the formation of *trans*-1,2.dipivaloylethylene in 83-5% yield, and *trans*-1,2.3-tripivaloylcyclopropane in 7·2% yield.

(b) A similar reaction at 80–85° for 5 hr of diazomethylt-butylketone (1.3 mmol) with dimethylsulfoxonium phenacylide (0.7 mmol), in benzene solon (3 ml) containing anhyd CuSO₄ (50 mg), gave a mixture of *trans*-1,2-dipivaloylethylene (as the major component), *trans*-1-benzoyl-2-pivaloylethylene and 1,2/3-benzoyl-dipivaloylcyclopropane, though no reliable figures can be given.

Catalytic decomposition of diazoketones in the presence of organic sulfides and sulfoxides

The results are summarized in Table 6, and the general procedure is illustrated by the following examples:

(A) Reaction of diazomethyl-t-butylketone with dimethyl sulfide. 1·1g (0·18 mol) dimethyl sulfide and 0·25 g anhyd CuSO₄ were added to a soln of 1·5 g (12 mmol) diazomethyl-t-butylketone in 7 ml dry benzene, and the mixture slowly heated up to 40° until no more evolution of N₂ (1½ hr). The catalyst was filtered off, and the solvent removed under vacuum to give a crystalline residue which, after washing with ether and recrystallization from benzene-petrol ether (0·91g, 47·7% yield), was identified as dimethylsulfonium α -pivaloylmethylide, m.p. 115-116°, identical in all respects with an authentic sample prepared from the sulfonium salt as described above.

(B) Reaction of diazomethyl-t-butylketone with diethyl sulfide. 1.3 g (13 mmol) diethyl sulfide and 0.20 g anhyd CuSO, were added to a soln of 1.1 g (9 mmol) diazomethyl-t-butylketone in 7 ml dry benzene, and the mixture left at room temp until no more evolution of N_2 (~ 3 hr). The catalyst was filtered off, and the solvent removed under vacuum at low temp: the residue was a highly unstable syrup which was characterized by IR spectroscopy (strong band at 1530 cm⁻¹) as the diethyl-sulfonium α -pivaloylmethylide.

When copper-bronze was substituted for anhyd CuSO, the reaction proceeded at higher temp, the products isolated being that of a Hofmann degradation identified by NMR spectroscopy as the ethyl(α -pivaloylmethyl)

^{*}A sample of *trans*-1-benzoyl-2-pivaloylethylene for direct comparison, was prepared by catalytic decomposition of an equimolecular mixture of diazomethyl-t-butyl-ketone and diazoacetophenone.

sulfide (b.p. $80-82^{\circ}/15$ torr): τ (CCl₄) 6.7 (s)(2H), 7.2-7.6 (g)(2H), 8.7 (t)(3H) and 8.8 (s)(9H), and 2,2,7,7-tetramethyl-4,5-diethylthioocta-3,6-dione, m.p. 128-129°

$$Et-S-CH-COCMe_3$$

 \downarrow
 $Et-S-CH-COCMe_3$

5.7 (s)(2H), $7 \cdot 2 - 7 \cdot 7$ (double quartet)(4H), $8 \cdot 6 - 8 \cdot 9$ (m)(24H)(Found: M.W. 312 \cdot 3. $C_{16}H_{30}O_2S_2$ requires 318 \cdot 54).

(C) Reaction of diazomethyl-t-butylketone with dimethyl sulfoxide. A soln of 1.3 g (10 mmol) diazomethylt-butylketone and 1.6g (20 mmol) DMSO in 7 ml dry benzene, containing 0.20g anhyd CuSO4, was heated at 40° until no more evolution of N₂ ($\sim 2 \text{ hr}$). The mixture was cooled to room temp, enough chloroform was added to re-dissolve the ppt, the catalyst filtered off, and the solvent partially evaporated under vacuum: the crystalline product (fraction A) was filtered, washed with petrol ether, and dried. The mother liquors were extracted with water, and the aqueous soln re-extracted with chloroform. The chloroform extract was dried with NaSO4 and evaporated to dryness (fraction B). Recrystallization of fraction A and B from CHCl₃-CCl₄ afforded 0.9 g (49.5% yield) of pure dimethylsulfoxonium α -pivaloylmethylide, m.p. 170-171°, identical in all respects to the product prepared according to the method of Corey and Chaykovsky³⁵ (see above).

Cyclopropane formation from diazomethyl-1-butylketone in dimethyl sulfide.

To a soln of 1.26 g (10 mmol) diazomethyl-t-butylketone and 0.206 g (3.3 mmol) dimethyl sulfide in 7 ml dry benzene, were added 0.20 g anhyd CuSO₄ and the mixture slowly heated up to 40° until no more evolution of N₂. The catalyst was filtered off, the solvent removed under vacuum, and the residue columned on silica-gel. Eluation with cyclohexane-benzene (95:5) gave 0.39 g (40% yield) *trans*-1,2,3-tripivaloylcyclopropane, m.p. 159–160°, identical with an authentic sample.

Purely thermal decomposition of diazomethyl-t-butylketone

A soln of 2.0g (15.8 mmol) diazomethyl-t-butylketone in 12 ml thioanisole was heated up to 130–135° for 15 hr, until the evolution of N₂ ceased. The thioanisole was evaporatively distilled at 0.6 torr, and the residue (1.4 g, 91% yield) was characterized as 2,4-di-t-butyl-3-buten-4-olide¹⁰ by UV, IR and NMR spectroscopy. A pure sample, m.p. 42-42.5° was prepared by VPC; λ_{max} 219 nm ($\epsilon = 1094$) (EtOH); IR (KBr) 1810 cm⁻¹ (VS); NMR, r(CCl₄) 4.94-4.97 (d, J = 3.4 Hz)(1H), 7.15-7.18 (d, J = 3.4 Hz) (1H), 8.82 (s)(9H) and 8.98 (s)(9H).

In xylene solon, at 135-140° for 22 hr, the yield of butenolide was 52.3%, estimated by NMR spectroscopy using benzoic acid as internal standard.

REFERENCES

- ¹⁶F. Serratosa and J. Quintana, *Tetrahedron Letters* 2245 (1967); ⁶J. Quintana, F. Serratosa and M. Torres, International Symposium on Synthetic Methods and *Rearrangements in Alicyclic Chemistry*. Oxford, 21-24 July (1969); The Chemical Society. Abstracts, p. 26
- ²J. Diekmaan, J. Org. Chem. **30**, 2272 (1965).
- ³A. Hochrainer, Angew. Chem. Internat. Edn. 6, 962 (1967)

- ⁴⁰W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Letters* 1979 (1969); W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Am. Chem. Soc.* 91, 2786 (1969); W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *Ibid.*, 91, 5164 (1969); W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.* 37, 1721 (1972); W. Ando, S. Kondo, K. Nakayma, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaido, and T.
- Migita, J. Am. Chem. Soc. 94, 3870 (1972);
- ^bF. Dost and J. Gosselck, *Tetrahedron Letters* 5091 (1970);
- ^cH. House, W. F. Fischer, Jr., M. Gall, T. E. McLaughlin, and N. P. Peet, J. Org. Chem. **36**, 3429 (1971)
- ⁵B. Eistert Newer Methods of Preparative Organic Chemistry, Vol. I, p. 531. Interscience, New York (1948); F. Weygand and H. J. Bestmann, Neuere Methoden der Präparativen Organischen Chemie, Band III, p. 280. Verlag Chemie, Weinheim/Bergstr. (1961)
- 6aCh. Grundmann, Liebig's Ann. 536, 29 (1938);
- ^bP. Yates and T. J. Clark, *Tetrahedron Letters* 435 (1961);
- ^cSee also, H. Strzelecka and M. Simalty-Siemiatycki, C. R. Acad. Sc., Paris 252, 3821 (1961)
- ⁷For a preliminary account see, J. Font, F. López, and F. Serratosa, *Tetrahedron Letters* 2589 (1972)
- ⁶P. Yates, J. Am. Chem. Soc. 74, 5376 (1952)
- ⁹J. Novák, J. Ratusky, V. Sneberg, and F. Sorm, Chem. Listy 51, 479 (1957); Chem. Abstr., 51, 10508e (1957)
- ¹⁰K. B. Wiberg and Th. W. Hutton, J. Am. Chem. Soc. 76, 5367 (1954)
- 11aW. R. Moser, Ibid. 91, 1135 and 1141 (1969)
- ^bG. W. Cowell and A. Ledwith, *Quart. Rev.* 24, 119 (1970)
- ¹²See, for example, W. Kirmse Carbene Chemistry p. 118, Academic Press, New York-London (1964) and refces therein
- ¹³R. K. Armstrong, J. Org. Chem. 31, 618 (1966)
- ¹⁴J. E. McMurry and T. E. Glass, *Tetrahedron Letters* 2575 (1971)
- ^{15a}H. Nozaki, M. Takaku, and K. Kondo, *Ibid.* 251 (1965); *Tetrahedron* 22, 2145 (1966);
- ^bB. M. Trost, J. Am. Chem. Soc. 88, 1587 (1966); Ibid. 89, 138 (1967)
- ^cJ. Casanova, Jr., and D. A. Rutolo, Jr., J.C.S. Chem. Comm. 1224 (1967)
- ^dH. Nozaki, D. Tunemoto, S. Matubara, and K. Kondo, *Tetrahedron* 23, 545 (1967)
- ^{16a}F. Krollpfeiffer and H. Hartmann, Chem. Ber. 83, 90 (1950);
- ^bK. W. Ratts and A. N. Yao, J. Org. Chem. 31, 1689 (1966);
- ^cA. W. Johnson and R. T. Amel, *Tetrahedron Letters* 819 (1966); J. Org. Chem. 34, 1240 (1969).
- ¹⁷cf. T. Sato and J. Higuchi, *Tetrahedron Letters* 407 (1972)
- ^{18a}J. Sauer and K. K. Mayer, *Ibid.*, 319 (1968);
- ^bcf. W. Lwowski, Angew Chem. Internat. Edn. 6, 897 (1967)
- ¹⁹Cited by T. L. Gilchrist and C. N. Rees, Carbenes, Nitrenes and Arynes p. 31. Nelson, London (1969)
- 200 I. G. Csizmadia, J. Font, and O. P. Strausz, J. Am. Chem. Soc. 90, 7360 (1968); D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *Ibid.* 92, 1768 (1970); MOSAN 44 (1970); C. Strausz, *Ibid.* 92, 1768 (1970); C. Strausz, *Ibid.*
 - ⁶S. A. Matlin and P. G. Sammes, *J.C.S. Chem. Comm.* 11 (1972);
- See, however, Z. Majerski and C. S. Redvanly, *Ibid.* 694 (1972)

- ²¹S. H. Smallcombe, R. J. Holland, R. H. Fish, and M. C. Caserio, *Tetrahedron Letters* 5987 (1968)
- 22K. W. Ratts, Ibid., 4707 (1966)
- ²³K. Mislow and M. Raban, Topics in Stereochemistry, Vol. 1, p. 1, Interscience, New York (1967)
- ²⁴J. V. Emsley, J. Feeney, and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. 1, pp. 320 and 372. Pergamon Press, London (1965)
- ²⁵J. D. Hinchen, J. Gas Chromatography 5, 641 (1965), and refces therein
- ²⁸⁰F. Arndt, B. Eistert, and W. Parlade, *Angew. Chem.* 40, 1099 (1927);
- ^bBer. Dtsch. Chem. Ges. 60, 1364 (1927);
- "F. Arndt and J. Amende, Ibid. 61, 1122 (1928);
- ^dF. Arndt and B. Eistert, *Ibid.* 68, 200 (1935)
- ²⁷M. S. Newman and P. Beal, J. Am. Chem. Soc. 71, 1506 (1949)
- ²⁸R. H. Eastman, Ibid. 79, 5503 (1957)
- ²⁹P. Karrer and J. Schkri, Helv. Chim. Acta 28, 820 (1945)

^{30a}H. Bohme and W. Krause, Chem. Ber. 82, 46 (1949);

^bA. J. Speziale, C. C. Tung, K. W. Ratts, and A. N. Yao, J. Am. Chem. Soc. 87, 3460 (1965)

- ³¹F. Krollpfeiffer, H. Hartmann, and F. Schmidt, *Liebigs* Ann. 563, 15 (1949)
- ³²K. W. Ratts and A. N. Yao, J. Org. Chem. 31, 1185 (1966)
- ³³F. Serratosa, J. Chem. Ed. 41, 564 (1964); 46, 302 (1969)
- ³⁴J. Castells and G. A. Fletcher, J. Chem. Soc. 3245 (1956)
- ³⁵⁹E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc. 86, 1640 (1964); 87, 1357 (1965);
- ^bR. Kuhn and H. Trischmann, *Liebigs Ann.* 611, 117 (1958); E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc. 84, 867 (1962)
- ³⁶M. Charpentier-Morize and P. Collard, Bull. Chim. Soc. Fra, 1982 (1962)