water, acidification, and extraction (chloroform). Table I records the yields of β-keto sulfoxides (all crystalline solids) obtained with a variety of esters.[5,6]

TABLE I

CONVERSION OF ESTERS ($RCOOC_2H_5$) TO β-KETO SULFOXIDES ($RCOCH_2SOCH_3$) AND METHYL KETONES ($RCOCH_3$)

R	% yield of β-keto sulfoxide	% yield of methyl ketone
Phenyl	79	>98
Anisyl	>98	>98
α-Naphthyl	>98	89
α-Furyl	71	70
Cyclohexyl	98	98
n-Pentyl	70	>98
n-Heptadecyl	>98	>98

These keto sulfoxides react rapidly and cleanly with aluminum amalgam[7] in 90% tetrahydrofuran–10% water mixture to give ketones[8]

$$RCOCH_2SOCH_3 + Al\cdot Hg + H_2O \longrightarrow RCOCH_3$$
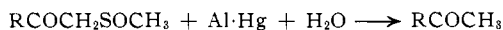
The yields given in Table I are indicative of the high efficiency of this reduction process. The reductive cleavage is not limited to the formation of methyl ketones, but seems to be characteristic of β-keto sulfoxides in general. Furthermore β-keto sulfones and β-keto sulfonamides also undergo the reaction as shown by eq. 2 and 3. β-Keto sulfonamides can be prepared from esters in high yield using the highly reactive di-

$$RCOCH_2SO_2CH_3 \xrightarrow{97\%} RCOCH_3 \xleftarrow{>98\%} RCOCH_2SO_2N(CH_3)_2 \quad (2)$$

R = cyclohexyl

(3)
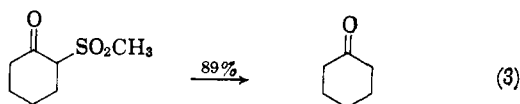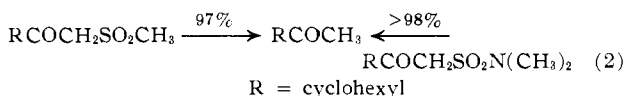
methylaminosulfonyl carbanion.[9]

This ketone synthesis is also applicable to certain polyfunctional esters. For example, dimethyl azelaate was converted via the β-keto sulfoxide route to undecan-2,10-dione in 82% yield.

The reductive fission of β-keto sulfoxides by aluminum amalgam permits a new and very flexible approach to the synthesis of five- and six-membered carbocycles, which should be especially useful for fused-ring systems. In general this approach consists of the following elements: (1) introduction of a one, two, or three carbon chain containing an attached sulfur substituent, for example at $C\alpha$ starting with a ketone; (2) introduction of other carbons and a functional group which can be converted to a carboxylic ester group, for example at

(5) The examples in which the yields of β-keto sulfoxides are below 90% are generally those cases in which the product was quite soluble in the aqueous phase and not completely recovered by simple extraction with chloroform.

(6) Satisfactory analytical data were obtained for the compounds described herein.

(7) Prepared by immersing aluminum foil in 2% aqueous mercuric chloride solution for 10–15 sec. and rinsing the amalgamated foil quickly with alcohol and ether, and used immediately for the reductions.

(8) In the case of conjugated aromatic keto sulfoxides the reaction was carried out for 10 min. at 0° with stirring using 10 g.-atoms of aluminum per mole of keto sulfoxide and ca. 60 ml. of 10% aqueous tetrahydrofuran per gram of keto sulfoxide (extended reaction times and higher temperature allow pinacol formation by further reduction). In the case of nonconjugated keto sulfoxides the reactants (same proportions) were heated at reflux temperature for 60–90 min. with stirring.

(9) This carbanion can be prepared in tetrahydrofuran solution as the lithium salt from N,N-dimethylmethanesulfonamide and n-butyllithium. It reacts with dimethyl sulfoxide to form the methylsulfinyl carbanion.

the carbonyl carbon of a ketone; (3) cyclization of a sulfone ester to an α-sulfonyl ketone; and (4) reductive removal of the α-sulfonyl grouping. Another application of the aluminum reduction to carbocycle synthesis is discussed in the following paper.[10]

(10) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., **86**, 1640 (1964).

(11) National Institutes of Health Postdoctoral Fellow 1962–1964.

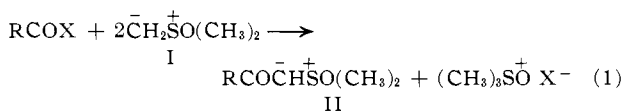DEPARTMENT OF CHEMISTRY   E. J. COREY
HARVARD UNIVERSITY   MICHAEL CHAYKOVSKY[11]
CABMRIDGE 38, MASSACHUSETTS

## Formation and Photochemical Rearrangement of β'-Ketosulfoxonium Ylides

Sir:

Dimethylsulfoxonium methylide (I)[1] can be acylated by treatment with reactive carboxylic acid derivatives such as acid chlorides and phenyl esters to give stable β-ketosulfoxonium ylides according to eq. 1. Thus, with benzoyl chloride and 2 equivalents of I in tetra-

$$RCOX + 2\bar{C}H_2\overset{+}{S}O(CH_3)_2 \longrightarrow$$

I

$$RCO\bar{C}H\overset{+}{S}O(CH_3)_2 + (CH_3)_3\overset{+}{S}O\ X^- \quad (1)$$

II

hydrofuran at 25° for 1 hr. the ylide II, R = C_6H_5, m.p. 119–120°, ultraviolet maxima 229, 283 mμ (ϵ 9500, 11,300) is formed in 92% yield.[2] Similarly, the ylide II, R = cyclo-C_6H_{11}, m.p. 198–199°, ultraviolet maximum 252 mμ (ϵ 13,600), is obtained in 87% yield. Reaction of the phenyl esters of Δ^1-cyclohexenyl carboxylic acid and Δ^1-cyclopentenyl carboxylic acid with I (1 equiv.) in tetrahydrofuran at reflux for 4 hr. also proceeds according to eq. 1 to give the respective products II, R = Δ^1-cyclohexenyl, m.p. 168.5–169.5°, ultraviolet maxima 228, 279 mμ (ϵ 11,400, 16,400) (92%), and II, R = Δ^1-cyclopentenyl, m.p. 145–146.5°, ultraviolet maxima 235, 284 mμ (ϵ 7500, 10,900) (85%).

Under the conditions used to effect reaction 1 with more reactive acid derivatives nonconjugated ethyl esters are unchanged. However, α,β-unsaturated ethyl esters undergo conjugate addition followed by cyclization as depicted in eq. 2 for ethyl Δ^1-cyclohexenyl carboxylate which is transformed into III, m.p. 205–


(2)

III
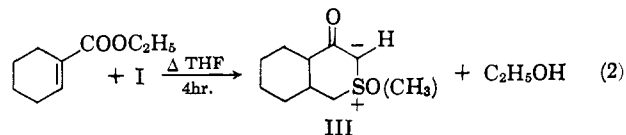
220° dec., ultraviolet maximum 245 mμ (ϵ 14,500). The structure III is assigned to this product on the basis of physical data and sequential conversion to IV, R = $SOCH_3$ (zinc–acetic acid, 0°), IV, R = SCH_3 (zinc–acetic acid, 110°), IV, R = $\overset{+}{S}(CH_3)_2$ (methyl iodide), and V (base). The last substance is identical with an authentic sample obtained from the methylene transfer reaction[1,3] of I with 1-acetylcyclohexene.

(1) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., **84**, 867 (1962).

(2) Satisfactory elemental analyses have been obtained for all new compounds reported herein. The β-ketosulfoxonium ylides studied all show carbonyl absorption in the infrared in the range 6.35–6.60 μ (chloroform solution); those derived from conjugated carbonyl systems, e.g., II, R = C_6H_5, absorb near the higher wave length. Ultraviolet data are for solutions in 95% ethanol.

(3) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., **84**, 3782 (1962).

IV   V
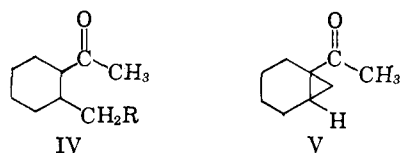
One of the most interesting properties of β-ketosulfoxonium ylides is their susceptibility to photochemical fission of the dipolar S–C bond by ultraviolet irradiation. The ylides II, R = C_6H_5 or cyclo-C_6H_{11}, upon excitation with 253 mμ radiation (low-pressure mercury arc) are transformed smoothly according to eq. 3, presumably via keto carbene and ketene intermediates. The combination of (1) and (3) is a process of chain extension

$$\overset{-}{RCOCHSO(CH_3)_2} \xrightarrow[R'OH]{h\nu} RCH_2COOR' + (CH_3)_2SO \quad (3)$$

II

R' = H, CH_3
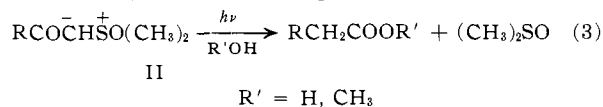
which is analogous to the Arndt–Eistert sequence.

Cyclic β-ketosulfoxonium ylides decompose by a pathway which parallels (3). Irradiation of the cyclic ylide III in methanol at 253 mμ produces the sulfoxide ester VI, infrared maximum 5.74, 9.5 μ, in 80% yield; in water the corresponding carboxylic acid is formed. This reaction opens a new route to carbocycles: oxidation of VI with peracetic acid affords the corresponding sulfone which undergoes cyclization with potassium t-butoxide to give the keto sulfone VII, R = SO_2CH_3, and this in turn is converted by treatment with aluminum amalgam[4] to $trans$-hydrindan-2-one (VII, R = H, 60% over-all yield from III), shown to be the pure

III   VI   VII
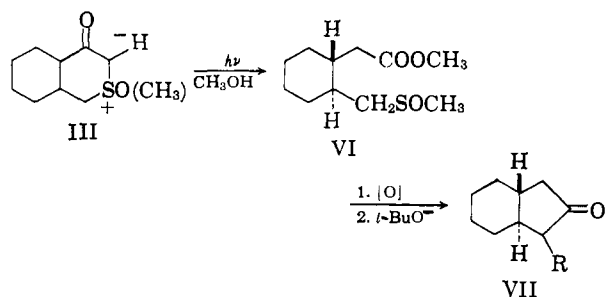
$trans$ isomer by vapor phase chromatography and conversion to known solid derivatives.[5] The stereospecific formation of $trans$-hydrindan-2-one is of special interest. Preliminary studies indicate that the reaction of I with ethyl esters of Δ^1-cycloalkenyl carboxylic acids produces $trans$-fused cyclic ylides in preference to the cis isomers.

Starting from ethyl cinnamate and I, 3-phenylcyclopentanone[6] was synthesized via the cyclic β-ketosulfoxonium ylide[7] by a sequence corresponding to III → VII in 30% over-all yield.

This new carbocycle synthesis can in some cases be modified to permit the synthesis of cis-fused ring systems. For example, the ylide II, R = Δ^1-cyclopentyl, undergoes cyclization upon heating in methanol at reflux (15 hr.) to give a cyclic product (55%) analogous to III but largely cis-fused since it is converted to cis-pentalan-2-one by a sequence of the type III → VII.

The parent member of the new class of cyclic β-ketosulfoxonium ylides VIII has also been prepared

(4) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 86, 1639 (1964).
(5) W. Hückel and H. Friedrich, Ann., 451, 132 (1926).
(6) W. Borsche and W. Menz, Chem. Ber., 41, 190 (1908).
(7) E. J. Corey and M. Chaykovsky, Tetrahedron Letters, No. 4, 169 (1963).

from I and ethyl acrylate; m.p. 181–185° dec., ultraviolet maximum 241 mμ (ϵ 15,800).

The transformations described above are easily carried out and are of practical value in synthesis. The photochemical reactions are especially interesting, and these are being studied further.

(8) National Institutes of Health Postdoctoral Fellow 1962–1964.

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HARVARD UNIVERSITY   MICHAEL CHAYKOVSKY[8]
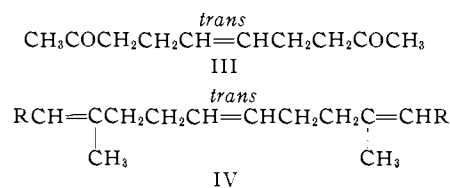CAMBRIDGE 38, MASSACHUSETTS

A New Synthetic Approach to Medium-Size Carbocyclic Systems

Sir:

In the first stage of an investigation directed at the total synthesis of the naturally occurring substance humulene (I), a study has been made of the reaction of a doubly allylic α,ω-dihalide with nickel carbonyl as a model cyclization process. This communication describes the results of these experiments[1] and the successful synthesis of 1,6-dimethylcyclododeca-1,5,9-triene (II); the new knowledge which has been obtained suggests simple synthetic routes to humulene and related structures and thus provides a key to these hitherto unsolved problems.

I   II
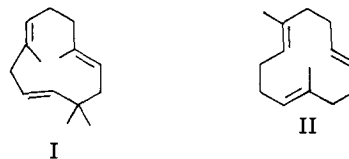
Dec-5-ene-2,9-dione (III)[2] was synthesized by alkylation of ethyl β-dimethylaminocrotonate with $trans$-

$$trans$$
$$CH_3COCH_2CH_2CH{=}CHCH_2CH_2COCH_3$$

III

$$trans$$
$$RCH{=}\overset{|}{C}CH_2CH_2CH{=}CHCH_2CH_2\overset{|}{C}{=}CHR$$
$$\overset{|}{C}H_3 \qquad\qquad\qquad \overset{|}{C}H_3$$

IV

1,4-dibromo-2-butene[8] followed by hydrolysis and decarboxylation; m.p. 41–42°, infrared maximum 5.81 μ, n.m.r. peaks at 5.20 δ (2 olefinic H) and 1.98 δ (2 CH_3CO).[4] The diketone III was converted to diethyl 3,10-dimethyldodeca-2,6,10-triene-1,12-dioate (IV, R = $COOC_2H_5$) by the procedure of Wadsworth and Emmons,[5] and this was reduced by lithium aluminum hydride to 1,12-dihydroxy-3,10-dimethyldodeca-2,6,10-triene (IV, R = CH_2OH). The n.m.r. spectrum of the diol IV, R = CH_2OH, so obtained indicated it to be a mixture of 80% all-$trans$ isomer and 20% cis, $trans$, $trans$ isomer[6]; as expected the Wittig process leading to

(1) This approach to cyclization seemed worthy of study because of the known coupling of simple allylic halides by nickel carbonyl to give 1,5-dienes [I. D. Webb and G. T. Borcherdt, J. Am. Chem. Soc., 73, 2654 (1951)] and the catalytic action of low-valent nickel compounds in the trimerization of 1,3-butadiene to 1,5,9-cyclododecatrienes [G. Wilke, Angew. Chem., 75, 10 (1963)]. More recently the coupling of allylic acetates has been reported [N. L. Bauld, Tetrahedron Letters, No. 19, 859 (1962)].
(2) Satisfactory analytical and spectroscopic data were obtained for all new compounds reported.
(3) See (a) S. A. Glickman and A. C. Cope, J. Am. Chem. Soc., 67, 1017 (1945); (b) G. Eglinton and M. C. Whiting, J. Chem. Soc., 3052 (1953).
(4) N.m.r. chemical shifts expressed as p.p.m. downfield displacement from tetramethylsilane as internal standard and measured at 60 Mc.
(5) W. S. Wadsworth and W. D. Emmons, J. Am. Chem. Soc., 83, 1733 (1961).
(6) See R. B. Bates and D. M. Gale, ibid., 82, 5749 (1960), for the n.m.r. methodology.