Dimethylsulfonium 3-Carbomethoxyallylide. Preparation and Reaction with Electrophilic Olefins to Form Substituted Vinylcyclopropanes

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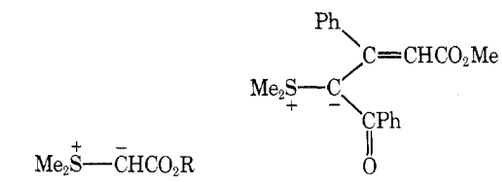
The title compound, **7**, from treatment of the corresponding sulfonium bromide, **6**, with sodium hydride and catalytic *tert*-butyl alcohol in tetrahydrofuran at 20°, has limited stability but has been treated with several Michael acceptors to produce novel vinylcyclopropanes in fair yields. One such product, **8**, has been thermally converted to a new disubstituted cyclopentene, **18**.

In recent years sulfur ylides have found a wide variety of applications in organic synthesis.[1,2] We wish to report the preparation of a new reagent in this category, dimethylsulfonium 3-carbomethoxyallylide[3a] (**7**), its reactions with electrophilic olefins to produce novel di- and trisubstituted vinylcyclopropanes, and the thermal rearrangement of one of these products to a representative new difunctional cyclopentene. Ylide **7** is a vinylog of the dimethylsulfonium carboalkoxymethylides (**1**).[4] Unsubstituted and alkyl- and aryl-substituted sulfonium allylides have also been previously investigated.[5] In addition, more highly stabilized derivatives of **7** have been reported, *e.g.*, **2**,[6] as well as oxosulfonium and aminooxosulfonium analogs, *e.g.*, **3**[2c,7] and **4**.[8]



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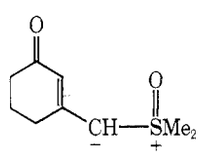

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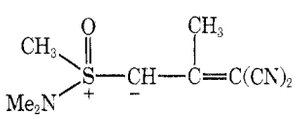

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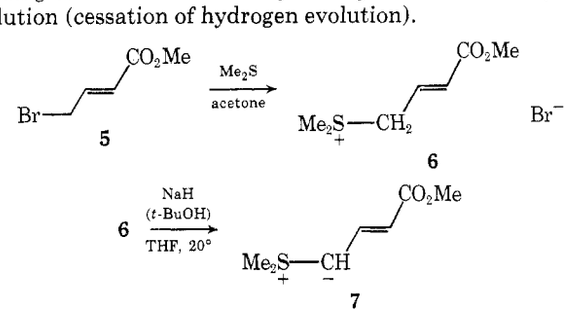
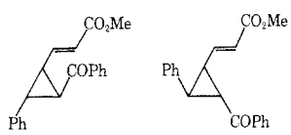
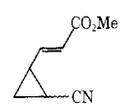
Results

3-Carbomethoxyallyldimethylsulfonium bromide (**6**) was prepared in 95% yield by treatment of methyl 4-bromocrotonate[9] (**5**) with excess dimethyl sulfide in acetone at room temperature. The nmr spectrum of **6** showed its configuration to be >95% trans. Conversion of the sulfonium salt to ylide **7** was achieved by reaction with sodium hydride in tetrahydrofuran (THF) in the presence of 0.05 equiv of *tert*-butyl alcohol under high-turbulence stirring at 20–22°. The ylide **7** has limited stability, decomposing to an intractable brown residue if allowed to stand at room temperature for 1 hr. It may be effectively utilized, however, by adding substrate immediately after generation of the ylide solution (cessation of hydrogen evolution).



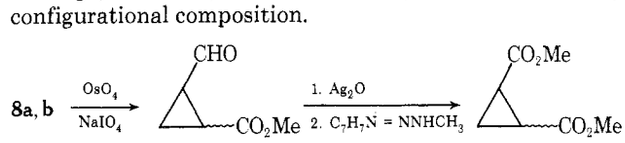
5 **6** **7**

Table I
Vinylcyclopropanes from Ylide 7

Substrate	Products	Yield, %
Methyl acrylate	**8a** (3%), **8b** (97%)	50
Dimethyl fumarate	**9**	57
Dimethyl maleate	**9**	60
Benzalacetophenone	 **10a** (45%) **10b** (55%)	50
Acrylonitrile	 **11**	20

Reaction of **7** with 1.0 equiv of several Michael acceptors produced the cyclopropane products presented in Table I. All are previously unreported compounds. The reactions were conducted at room temperature overnight, followed by conventional work-up.

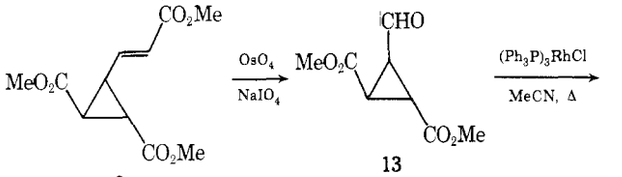
In this manner, methyl acrylate gave in 50% distilled yield a liquid product, bp 91–94° (2 mm), identified as 3% *cis*- and 97% *trans*-1-(*trans*-2-carbomethoxy)vinyl-2-carbomethoxycyclopropane, **8a** and **8b**, respectively. The constitution and double-bond configuration of **8** were determined by ir, nmr, and mass spectra and elemental analysis. Gas chromatography (gc) of the known degradation products dimethyl *cis*- and *trans*-1,2-cyclopropanedicarboxylate,[10] **12a** and **12b**, respectively, obtained by double-bond cleavage, oxidation, and esterification, established the ring-configurational composition.



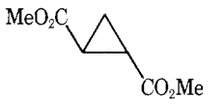
12a, cis, 3%
12b, trans, 97%

Reaction of **7** likewise with dimethyl fumarate generated a liquid product, bp 127–129° (0.12 mm), shown to be 1-(*trans*-2-carbomethoxy)vinyl-*trans*-2,3-dicarbomethoxycyclopropane (**9**). The assigned structure was supported by spectral data and elemental analysis, the nmr spectrum indicating only trans vicinal proton coupling across the double bond. The ring configuration in **9** was established by side-chain cleavage to produce a single aldehyde, **13**, whose nmr spectrum exhibited two methyl ester signals and which was decarbonylated[11] with tris(triphenylphosphine)chlororhodium to give only *trans*-1,2-dicarbomethoxycyclopropane, **12b**.

Similar reaction of ylide **7** with dimethyl maleate afforded in 60% yield after distillation the same product, **9**, as that from dimethyl fumarate, on the basis of ir and nmr spectra. Degradation of the product from maleic ester in the same fashion as that from fumarate, above, again yielded only *trans*-cyclopropane diester **12b**.

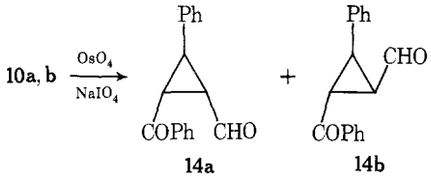


9 **13**

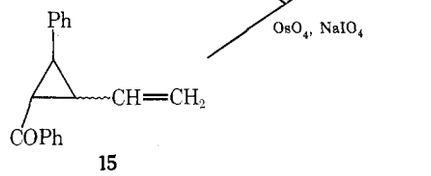


12b

Reaction between **7** and benzalacetophenone gave rise to a crude yellow oil which partially solidified on standing. Its monomeric content was indicated by degradation to be 45% methyl *trans*-3-(*cis*-2-benzoyl-*trans*-3-phenylcyclopropyl)-acrylate (**10a**) and 55% of the trans,trans,cis isomer, **10b**. Treatment of the crude product with osmium tetroxide–sodium metaperiodate produced a mixture of two aldehydes whose combined nmr spectrum was in accord with those of the separate isomeric aldehydes **14a** and **14b** obtained by Trost and coworkers[5e] from a similar degradation of isomeric 1-benzoyl-2-phenyl-3-vinylcyclopropanes (**15**). The **10a/10b** product ratio was taken to be that of the integrated aldehydic proton absorptions. A small amount (10% yield) of the major product, **10b**, was isolated as colorless needles, mp 109.0–110.0°, which had spectral properties and elemental analysis in agreement with the assigned structure. The yield of **10a,b** is estimated to be *ca.* 50%.



14a **14b**



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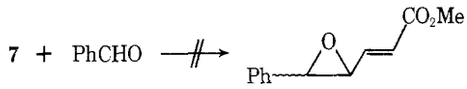
Less definitive results were obtained for reaction between **7** and acrylonitrile. Distillation of the product gave material of bp 109–116° (1.5 mm), in 32% yield for the anticipated vinylcyclopropanes. Isolation of the major gas-chromatographic fraction from a nonpolar column led to nmr evidence for 1-cyano-2-(*trans*-2-carbomethoxyvinyl)cyclopropane (**11**) (probably both isomers), as the principal product structure (*ca.* 20% yield). Addition of chemical shift reagent $Eu(fod)_3$[12] to the product mixture, however, allowed the resolution of six carbomethoxy proton signals. The minor products were not identified. It may be noted that anomalous results have been obtained in reactions of other sulfur ylides with α,β-unsaturated nitriles.[4d,13]

In view of the reactions of other sulfur ylides with carbonyl compounds to form epoxides,[1,2] reaction of **7** with benzaldehyde was undertaken. Nmr examination of the crude product, however, showed the presence of unreacted benzaldehyde and ylide decomposition products only; no evidence for the oxirane, **16**[2i], was found.



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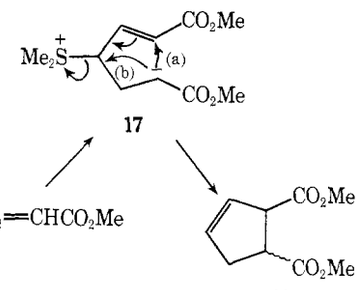
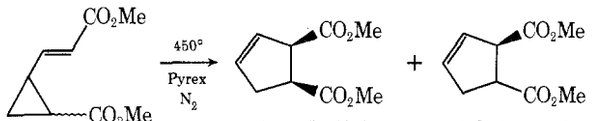
Our interest in ylide **7** was based on its potential for five-membered as well as three-membered carbocyclic ring synthesis with electrophilic olefins. Cyclopentene derivatives could be envisioned either from SN2′ ring closure subsequent to Michael addition, *e.g.*, **7** → **17** (path a) → **18**, or by the thermal rearrangement[14] of vinylcyclopropane products, *e.g.*, **8** → **18**.



17 **18**

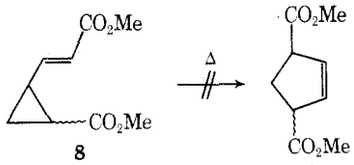
In fact, no cyclopentenoid products were detected from any of the reactions listed in Table I. Flow pyrolysis of product **8** over Pyrex beads at 450°, however, did provide a useful route to the cyclopentene system **18**. Distillation of



8a, cis, 3%
8b, trans, 97%

18a, cis, 49% **18b**, trans, 51%

the pyrolysate provided material of bp 101–105° (2 mm) shown to contain *cis*- and *trans*-3,4-dicarbomethoxycyclopentene, **18a** and **18b**, respectively, in a 49:51 ratio and 64% yield, plus 16% of unconverted **8**. Nmr integration showed the rearrangement product to possess two vinylic protons, ruling out double-bond position isomers of **18**. The constitution and configurational composition of **18** were established by hydrogenation to the corresponding *cis*- and *trans*-cyclopentane-1,2-dicarboxylic esters, whose gc retention times and spectra matched those of authentic samples. Alternative rearrangement **8** → **19** by cleavage of the bond between the side chain and methylene carbons was shown not to have occurred; *cis*- and *trans*-3,5-dicarbomethoxycyclopentenes **19** were prepared independently and shown by gc to be absent from the distilled pyrolysis product.

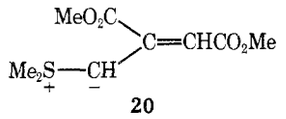


8 **19a**, cis
b, trans

Discussion

Carbomethoxyallylide **7** exhibits reactivity similar to that of the parent ester- and ketone-stabilized sulfonium ylides, $Me_2S^+C^-HCO_2R$, **1**, and $Me_2S^+C^-HCOPh$. Characteristically, these ylides add to electrophilic olefins to produce cyclopropanes[4c,d,h,6,15] but fail to generate oxiranes

from simple aldehydes and ketones.[4b,m,6,15-18] Oxosulfonium analog **3**, for comparison, is likewise useful for the formation of cyclopropanes from Michael acceptors,[2c] while the highly delocalized sulfonium ylide **2** is without apparent reagent properties.[6] An additional structural relative of **7**, dimethylsulfonium 2,3,-dicarbomethoxyallylide (**20**), is a



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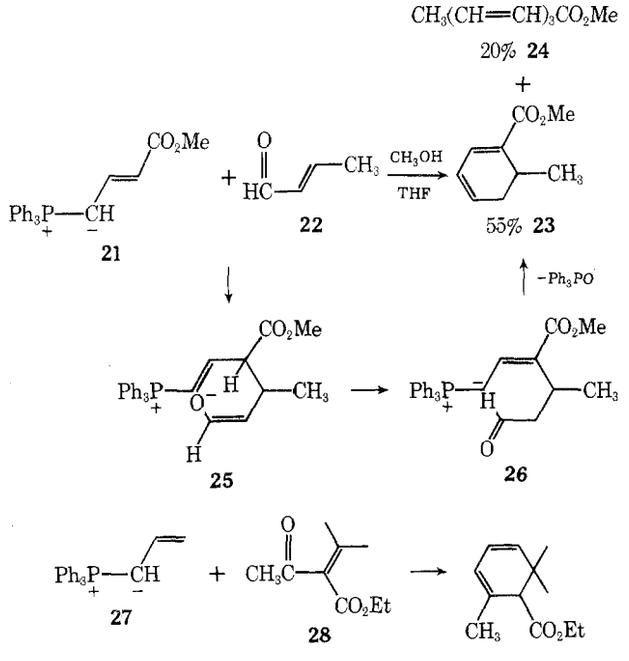
hypothetical intermediate in base-induced coupling of the corresponding sulfonium ion but has not been generated as an independent reagent.[3]

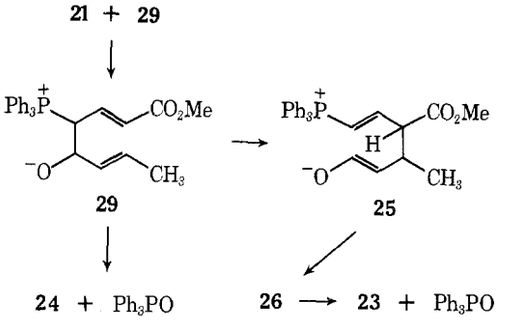
The reactions of **7** reported here are somewhat compromised by concurrent decomposition of the ylide. They are nevertheless of preparative importance, as the products are otherwise unknown polyfunctional compounds capable of diverse further transformations. It is likely that alternative base–solvent conditions can be found[1f,g,2a] to effect improved yields in reactions of **7**.

Betaines have been strongly implicated as intermediates in sulfur ylide reactions with electrophilic double bonds,[1,2f,4l,13] *e.g.*, **17** (path b) in the present instance. That both maleic and fumaric ester lead from ylide **7** to the same product, **9**, indicates that conformational equilibration in the corresponding intermediates is faster than ring closure, a situation reported for other reactions of stabilized ylides.[2g,4c,19,20] The system was not tested for maleate → fumarate conversion by reversible Michael addition.[2f,19]

A noteworthy contrast exists between the present reactions of sulfonium ylide **7** and those reported recently by Bohlmann and Zdero[21] for the triphenylphosphonium analog, **21**. With α,β-olefinic carbonyl compounds ylide **21** produces 1-carbomethoxy-1,3-cyclohexadienes as principal products, *e.g.*, **23**, along with minor amounts of normal Wittig products, *e.g.*, **24**. Büchi and Wüest[22] had earlier observed the abnormal reaction for the parent triphenylphosphonium allylide, **27**, and α-carbethoxyenone **28**. Both groups postulated the cyclization pathway to proceed by Michael addition on the part of the carbon γ to phosphorus, followed by activated hydrogen transfer to enolate oxygen and intramolecular Wittig reaction of the resultant aldehyde or ketone, as illustrated for **21**.



We would suggest an alternative mechanism, whereby both products emanate from initial carbonyl addition by the allylide α carbon. The first intermediate in this case, **29**, could partition itself between normal elimination of triphenylphosphine oxide, to produce **24**, and [3,3] sigmatropic rearrangement to **25**, which would lead to cyclized product **23** as previously proposed. This mechanism accords



with the characteristic 1,2 addition of representative Wittig reagents with conjugated enones and enals;[23] only in cases of pronounced steric hindrance around carbonyl is 1,4 addition observed.[23] Initial formation of **29**, moreover, would represent greater nucleophilicity of the phosphonium allylide at its α rather than γ carbon, a property established for sulfonium allylides here by product structures.[24] For rearrangement **29** → **25**, in competition with normal Wittig elimination, driving force would be provided by stabilization through conjugation of both the anionic and cationic[22,25] centers.[26-28]

The thermal rearrangement of vinylcyclopropane **8** to cyclopentene **18** proceeds, as generally observed, with cleavage of only the more substituted eligible ring bond[14g,l,n] and without the stereospecificity associated by orbital symmetry conservation[29] with a concerted sigmatropic reaction.[14d-f,i,j,n] For the symmetry-allowed pathway suprafacial with respect to the allyl moiety and with inversion of configuration at the migrating carbon, **8b** should produce wholly **18b**.[29] Doering and Sachdev have recently interpreted detailed related results in terms of a continuous diradical transition state.[14n]

Cyclopentene diester **18**, although produced nonstereospecifically, has a constitution suggestive of useful applications to prostaglandin synthesis.[30,31]

Experimental Section

General. Melting points (uncorrected) were obtained in capillary tubes with a Thomas-Hoover apparatus. Nuclear magnetic resonance (nmr) spectra were recorded on either a Varian A-60A or HA-100 spectrometer, using solutions in $CDCl_3$ or CCl_4 with internal tetramethylsilane. Infrared (ir) spectra were recorded on a Beckman IR-8 instrument either as thin films or as *ca.* 2% solutions in CCl_4. Mass spectra were obtained using a Varian M-66 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Analytical gas chromatography was performed with a Wilkens Aerograph Hy-Fi Model 600-C instrument with flame-ionization detector. The following columns were employed throughout most of this work, using nitrogen as the carrier gas at 20 psi: (A) 5-ft × ⅛-in. 10% butanediol adipate on 70–80 mesh Anakrom ABS (Analabs, Inc.); (B) 10-ft × ⅛-in. 10% butanediol adipate on 70–80 mesh Anakrom ABS; (C) 5-ft × ⅛-in. 2% SE-30 on 60–80 mesh Chromosorb G (acid washed, DMCS treated).

Methyl 4-bromocrotonate was prepared as described by Vogel[9] from methyl crotonate and *N*- bromosuccinimide.

3-Carbomethoxyallydimethylsulfonium Bromide (6). In a 250-ml round-bottomed flask was placed a mixture of 20.0 g (0.112 mol) of methyl 4-bromocrotonate, 14.0 g (0.224 mol) of dimethyl sulfide, and 50 ml of dry acetone. The flask was stoppered and magnetically stirred at room temperature for 48 hr. A quantitative yield of the white hygroscopic crystalline product was collected by vacuum filtration under nitrogen in a glove bag, mp 94.5–95.5°: ir

($CHCl_3$) 1741, 1661, 1251, 1041 cm^{-1}; nmr (60 MHz, $CDCl_3$) δ 6.68 (m, HC=CH), 5.01 (d, CH_2), 3.82 (s, CO_2CH_3), 3.40 (s, $S^+(CH_3)_2$). In $CDCl_3$ solution, the salt was observed by nmr to revert predominantly over several hours to methyl *trans*-4-bromocrotonate and dimethyl sulfide. Crystalline **6** was further found to decompose over several days under dry nitrogen to a white solid, not identified, insoluble in chloroform.

Dimethylsulfonium 3-Carbomethoxyallylide (7). A 1000-ml three-necked creased (Morton) flask was equipped with a thermometer, a high-speed mechanical stirrer (G. K. Heller Co., Las Vegas, Nev., Model GT 21), and a gas-outlet tube leading to a tetrahydrofuran (THF) bubbler. In the flask was placed 350 ml of dry (4A molecular sieves) THF, 0.33 g (4.5 mmol) of *tert*-butyl alcohol, and 2.17 g (0.091 mol) of sodium hydride (3.56 g of a 61% mineral oil dispersion, washed twice with either anhydrous ether or hexane). 3-Carbomethoxyallyldimethylsulfonium bromide, **6**, (21.0 g, 0.087 mol), was weighed under nitrogen and transferred in one step to the stirred reaction mixture. The reaction temperature was maintained at 20–22° by means of a water bath, and the reaction mixture was stirred rapidly until hydrogen evolution had virtually ceased (*ca.* 2 hr). At this point the ylide solution was amber-yellow, but it turned brown if allowed to stand for 1 hr. Attempts to isolate the ylide by filtration of the solid and rotary evaporation of the solvents afforded only an undefinable brown residue.

Dimethyl *cis*- and *trans*-1,2-Cyclopropanedicarboxylate. The diesters were prepared by the method of McCoy.[10] They were readily separated as the corresponding diacids, the cis isomer being purified *via* the internal anhydride.

Dimethyl *cis*- and *trans*-1,2-Cyclopentanedicarboxylate. These diesters were prepared by the method of Latont and Bonnet[32] and separated in the same manner as the cyclopropane diesters.

Dimethyl *cis*- and *trans*-Δ^4-1,3-Cyclopentenedicarboxylate. The cis diester was obtained from the ozonolysis at −78° of norbornadiene followed by silver oxide oxidation and esterification, following the procedure of Grob and Pfaendler.[33] The trans diester was obtained in an equilibrium mixture with the cis by treatment of the latter with boiling methanolic sodium methoxide.

Reaction of Ylide 7 with Methyl Acrylate. Immediately after generation of the ylide solution (from 0.087 mol of sulfonium salt) using the technique described above, 7.49 g (0.087 mol) of methyl acrylate in 25 ml of THF was added in one portion. Moderate stirring was continued at room temperature for 16 hr. The reaction mixture was then poured into 1000 ml of water and transferred to a 3-l. separatory funnel. The aqueous layer was extracted with two 200-ml portions of ether, and the combined ether extract was washed once with 100 ml of water and then dried over anhydrous magnesium sulfate. Removal of the solvents on the rotary evaporator gave an amber liquid which after distillation through a heated 60-cm single-tantalum-helix column afforded 8.0 g (50%) of a clear colorless liquid, bp 91–94° (2 mm): ir (thin film) 3025, 2965, 1715, 1650, 1445, 1265, 1205, 1180, 1155 cm^{-1}; nmr (60 MHz, CCl_4) δ 6.42 (m, HC=CH), 5.85 (d, HC=CH, J = 15 Hz), 3.63 (s, CO_2CH_3), 2.47–0.93 (m, ring H); mass spectrum *m/e* 184 (molecular ion). *Anal.* Calcd for $C_9H_{12}O_4$: C, 58.70; H, 6.58. Found: C, 58.82; H, 6.64.

In a 100-ml round-bottomed flask was placed 1.0 g (5.44 mmol) of the product, **8**, and 24 ml of 3:1 dioxane–water. Approximately 20 mg of crystalline osmium tetroxide was added to this magnetically stirred solution,[34] and after several minutes the reaction mixture turned black. At this time 2.56 g (11.95 mmol) of sodium metaperiodate was added to the reaction mixture in small portions over 0.5 hr. After the addition the reaction was stirred at 25° for 3.5 hr and then suction filtered, and the salts were washed well with ether. The combined filtrate and washings were concentrated by rotary evaporation, and the residue was taken up in ether–water and transferred to a separatory funnel. The layers were separated and the aqueous phase was extracted with two additional 50-ml portions of ether. The combined ether extract was washed with 50 ml of brine, filtered through neutral alumina, and dried over anhydrous magnesium sulfate. Rotary evaporation of the solvent afforded 0.56 g of a residual crude yellow-brown oil, which had nmr properties (60 MHz, CCl_4) consistent with the expected aldehyde: δ 9.25 (d, J = 4 Hz, CHO), 3.65 (s, CO_2CH_3), 2.13 (m, ring H), 1.33 (m, ring H).

To a cold, magnetically stirred suspension of silver oxide (prepared by adding 1.06 g (6.26 mequiv) of silver nitrate to 0.25 g (6.26 mequiv) of sodium hydroxide in 20 ml of water) was added over a 5-min period the crude aldehyde (3.13 mmol, based on the assumption of 0.40 g of aldehyde). After stirring at 0° for 10 min, 0.63 *M* sodium hydroxide was slowly added until the solution was slightly alkaline (5.2 ml, 3.27 mequiv). The black silver metal was filtered (room pressure) and washed well with water. The resulting clear solution was then cooled and acidified to *ca.* pH 3 with 10% hydrochloric acid. The cloudy acidic layer was extracted with four 50-ml portions of ether, and the combined ether extract was washed once with water and dried over magnesium sulfate. Rotary evaporation of the ether gave 0.45 g of a yellow oil, which had nmr properties in accord with the expected acid (60 MHz, CCl_4): δ 9.01 (s, CO_2H), 6.36 (s, CO_2CH_3), 2.12 (m, ring H), 1.32 (m, ring H).

In a 100-ml three-necked round-bottomed flask fitted with condenser, magnetic stirrer, and addition funnel was placed 0.45 g (3.12 mmol) of crude acid in 10 ml of anhydrous ether. To this stirred solution was added *via* the addition funnel 0.51 g (3.43 mmol) of 1-methyl-3-*p*-tolyltriazene (Willow Brook Laboratories, Inc., with accompanying data sheet) in 10 ml of ether. The reaction mixture was stirred at room temperature for 15 min and then boiled at reflux for 4 hr. After cooling to room temperature, the reaction mixture was transferred to a separatory funnel with the aid of additional ether and washed successively with two 25-ml portions of 10% hydrochloric acid, two 25-ml portions of 10% aqueous sodium bicarbonate, and once with 25 ml of water. After drying (magnesium sulfate), rotary evaporation gave 0.3 g of a slightly yellow liquid. Gas chromatography using column A at 150° revealed the presence of two components, identified as 97% *trans*- and 3% *cis*-dimethyl 1,2-cyclopropanedicarboxylate by comparison of retention times with those of the independently synthesized compounds (above). The nmr spectrum essentially matched that of the authentic trans diester (60 MHz, CCl_4): δ 3.65 (s, CO_2CH_3), 2.07 (m, ring H), 1.25 (m, ring H).

Reaction of Ylide 7 with Dimethyl Fumarate. To a freshly prepared ylide solution (from 0.087 mol of sulfonium salt, **6**) was added 12.6 g (0.087 mol) of dimethyl fumarate (Eastman) in 100 ml of THF, and the reaction was stirred at room temperature for 16 hr. After work-up (see above) there was obtained 19.2 g of brown viscous liquid. This material was distilled through a heated 60-cm single-tantalum-helix column to give 12.0 g (57%) of a very viscous, clear, colorless liquid (which turned cloudy upon standing), bp 127–129° (0.12 mm). Gas chromatography showed this material to be homogeneous: ir (thin film) 3080, 2970, 1720, 1655, 1445, 1330, 1260, 1180, 1140 cm^{-1}; nmr (60 MHz, $CDCl_3$) δ 6.92 (m, HC=CH), 6.10 (d, HC=CH, J = 16 Hz), 3.75 (s, CO_2CH_3), 2.57 (m, ring H); mass spectrum *m/e* 242 (molecular ion). *Anal.* Calcd for $C_{11}H_{14}O_6$: C, 54.50; H, 5.84. Found C, 54.73; H, 6.00.

Oxidation of 1.0 g (4.14 mmol) of the product (**9**) was conducted with catalytic osmium tetroxide and 1.95 g (9.1 mmol) of sodium metaperiodate, as described above, to yield after work-up 0.82 g of a yellow oil which had the nmr properties expected for aldehyde **13** (100 MHz, CCl_4): δ 9.28 (d, CHO, J = 5.5 Hz), 3.73 (s, CO_2CH_3), 3.72 (s, CO_2CH_3), 2.92 (t, ring H, J = 5.5 Hz), 2.50 (m, ring H). Only one aldehydic and two $-CO_2CH_3$ absorptions were observed in the nmr spectrum even with added Eu(fod)$_3$.[12] Gas chromatography showed only one component.

In a 25-ml round-bottomed flask with reflux condenser and magnetic stirrer was placed 50 mg (0.269 mmol) of the aldehyde, **13**, and 5 ml of acetonitrile.[11] This solution was then brought to a boil under reflux, and 0.25 g (0.269 mmol) of tris(triphenylphosphine)rhodium (I) chloride (Ventron) was added in small portions over a 1-day period. After boiling at reflux for 4 days, reaction was shown by gc to be complete. The acetonitrile was removed on the rotary evaporator and the residue taken up in EtOH and filtered. The filtrate was concentrated, taken up in ether, and filtered again. Concentration of the ethereal solution by rotary evaporation gave a yellow liquid. Gas chromatographic analysis of this liquid showed that the only product was dimethyl *trans*-1,2-cyclopropanedicarboxylate, **12b**, by comparison of retention time and nmr spectrum with those of authentic compound (see above).

Reaction of Ylide 7 with Dimethyl Maleate. This reaction was carried out as before using 10.0 g (0.0415 mol) of sulfonium salt **6** and 6.0 g (0.0415 mol) of dimethyl maleate in 30 ml of THF. After work-up 8.0 g of a yellow, viscous liquid was obtained. Short-path distillation afforded 6.0 g (60%) of a colorless, viscous liquid (which became slightly turbid upon standing), bp 140–145° (0.6 mm), homogeneous by gc. The ir and nmr spectra of this compound were identical with those of the product from the reaction with dimethyl fumarate.

Oxidative degradation and decarbonylation were carried out as with the fumarate-derived product, again producing aldehyde **13** and only the trans diester **12b**, by nmr and gc criteria.

Reaction of Ylide 7 with Benzalacetophenone (Chalcone).

To a freshly prepared ylide solution (from 0.087 mol of sulfonium salt **6**) was added 18.1 g (0.087 mol) of chalcone (Aldrich) in 25 ml of THF, and the reaction mixture was stirred for 16 hr. After work-up, 25 g of a viscous yellow oil was obtained which partially solidified upon standing. Collection and recrystallization of the solid material from ether–pentane yielded 2.5 g (8.7 mmol, 10%) of white solid, mp 109–110°: ir (CCl_4) 3090, 3060, 2970, 1730, 1680, 1655, 1260, 1150, 1035, 705 cm^{-1}; nmr (60 MHz, CCl_4) δ 7.97 (m, aromatic H), 7.43 (m, aromatic H), 7.20 (broad s, aromatic H), 6.35 (m, HC=CH), 5.88 (d, HC=CH, J = 15 Hz), 3.57 (s, CO_2CH_3), 3.25 (m, ring H), 2.68 (m, ring H). *Anal.* Calcd for $C_{20}H_{18}O_3$: C, 78.40; H, 5.93. Found C, 78.06; H, 5.94.

Attempted refinement of the remaining oily product by crystallization and by chromatography was unsuccessful (evidently the consequence of closely similar amounts of isomers **10a** and **10b**).

Identification of the pure crystalline product as **10b** was carried out by oxidative degradation with osmium tetroxide and sodium periodate, as described above, to produce aldehyde **14b**, whose nmr spectral properties were fully in accord with those listed for this compound by Trost, *et al.*[5e]

The composition of the original oily product mixture (before separation of the crystalline component) was determined by side-chain cleavage of 1.34 g of this material in the same manner to yield after work-up 0.47 g of brown oil, whose nmr spectrum was a composite of those reported[5e] for **14a** and **14b**. The vinylcyclopropane product ratio was taken to be that of the derived aldehydes by nmr integration in the –CHO region, 45% **14a** (δ(CHO) 9.57, J = 6.0 Hz) and 55% **14b** (δ(CHO) 9.15, J = 5.0 Hz).

Reaction of Ylide 7 with Acrylonitrile. To a freshly prepared ylide solution (from 0.087 mol of sulfonium salt) was added 4.87 g (0.087 mol) of acrylonitrile in 25 ml of THF, and the reaction was stirred for 16 hr. After work-up there remained 10.3 g of a viscous amber liquid, which upon distillation through a 60-cm single-tantalum-helix column afforded 4.15 g (32%) of a clear colorless liquid, which turned cloudy upon standing, bp 109–116° (1.5 mm). The product was purified by slow filtration through coarse-grade filter paper to remove a small amount of another liquid phase. The major component of this product was obtained enriched but not pure by preparative gas chromatography (5-ft × ⅜-in. SE-30 on Chromosorb W): ir (thin film) 3043, 2975, 2873, 2253, 1717, 1658, 1445, 1272, 1214, 1159 cm^{-1}; nmr (60 MHz, $CDCl_3$) δ 6.22 (m, HC=CH), 3.70 (broad s, CO_2CH_3), 2.20 (m, ring H), 1.37 (m, ring H). The impure nature of the product precluded elemental analysis.

Reaction of Ylide 7 with Benzaldehyde. To a freshly prepared solution of ylide (from 0.087 mol of sulfonium salt) was added 9.22 g (0.087 mol) of benzaldehyde in 20 ml of THF, and the reaction mixture was stirred for 16 hr. After work-up there was obtained a yellow liquid, indicated by nmr to contain essentially only unreacted benzaldehyde and ylide decomposition products.

Pyrolysis of 1-(*trans*-2-Carbomethoxy)vinyl-2-carbomethoxycyclopropane (8a,b). Vinylcyclopropane **8** (4.0 g, 0.017 mol) was added dropwise from an addition funnel onto a 35-cm Pyrex-bead-packed column maintained at 450° and under a slow stream of nitrogen. The product was collected in a 100-ml three-necked flask fitted with a Dry Ice condenser and containing 25 ml of ether cooled to −78°. After the pyrolysis, the ether was evaporated, and the crude residue was distilled through a short-path column, yielding 3.2 g (80%) of a clear colorless liquid, bp 101–105° (2 mm). Gc of the reaction mixture using column C at 120° showed one major peak (relative area 80) and two overlapping minor peaks (combined area 20). The principal minor constituent had the same retention time as that of the starting material, **8b**. On column B at 175° the major product was resolved into two peaks, shown to be cyclopentenes **18a,b**, as follows.

The predominant signals in the integrated nmr spectrum (60 MHz, CCl_4) of the distilled product were appropriate to a dicarbomethoxycyclopentene with two vinylic protons: δ 5.65 (m, HC=CH), 3.65 (s, CO_2CH_3), 3.57 (m, ring H), 3.25 (m, ring H), 2.63 (m, ring H). Hydrogenation of 0.6 g of product, at 60 psi over 5% palladium-on-charcoal in ether, produced a liquid whose two major components had gc retention times identical with those of *cis*- and *trans*-1,2-dicarbomethoxycyclopentane (see above) in the ratio of 49:51, respectively. The assignments were reinforced by essentially matching nmr spectra of the hydrogenation product (taking account of impurities) and a 1:1 mixture of the authentic epimeric cyclopentane diesters.

The absence (<0.5%) of the constitutionally isomeric diesters **19a,b** was established cleanly by gc comparison with the authentic compounds (see above) using column B at 175°.

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Registry No.—**6**, 52919-94-5; **7**, 52919-95-6; **8a**, 52919-96-7; **8b**, 52949-89-0; **9**, 52919-97-8; **10a**, 52919-98-9; **10b**, 52949-90-3; *cis*-**11**, 52919-99-0; *trans*-**11**, 52949-91-4; **12a**, 826-34-6; **12b**, 826-35-7; **13**, 52920-00-0; **14a**, 27557-63-7; **14b**, 27557-62-6; **18a**, 52949-92-5; **18b**, 52949-93-6; methyl acrylate, 96-33-3; dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6; chalcone, 94-41-7; acrylonitrile, 107-13-1; methyl *trans*-4-bromocrotonate, 6000-00-6; dimethyl sulfide, 75-18-3; *cis*-1-carbomethoxy-2-formylcyclopropane, 52920-01-1; *trans*-1-carbomethoxy-2-formylcyclopropane, 35501-84-9; *cis*-1,2-cyclopropanedicarboxylic acid monomethyl ester, 31420-47-0; *trans*-1,2-cyclopropanedicarboxylic acid monomethyl ester, 52920-02-2; benzaldehyde, 100-52-7.

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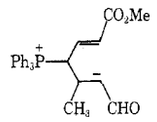

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from **21** + **27**, because of its inferior leaving group,[1a] resulting in reversion to reactants and slower but productive formation of **25**. We would favor the alternative mechanism proposed in the text on the basis of the typical preference of Wittig reagents for 1,2 addition to enones and enals.
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Synthesis and Reactions of 5-Cyclononynone

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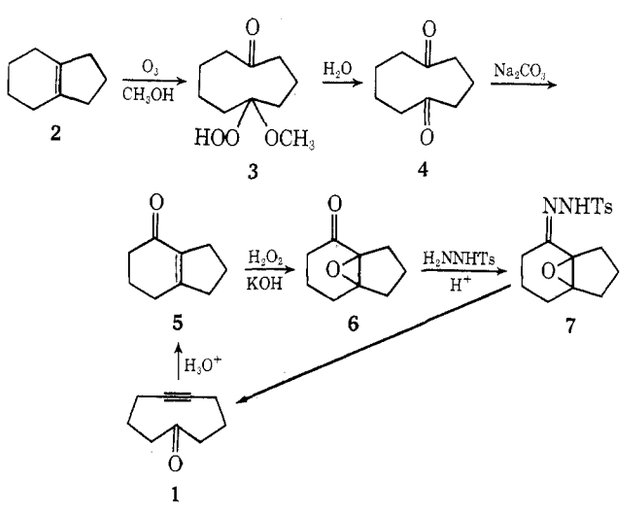
The previously unknown 5-cyclononynone (1) has been synthesized in an overall yield of 20% from 4,5,6,7-tetrahydroindan (2). As part of the synthesis, a very effective method of preparing bicyclo[4.3.0]-1(6)-nonen-2-one (5) has been developed. Fragmentation of the tosylhydrazone of the α,β-epoxy ketone 6 gave directly the strained cycloalkynone 1. A number of reactions of 1 have been investigated, including partial hydrogenation to yield *cis*-5-cyclononenone (10), which in turn could be converted by photoisomerization to *trans*-5-cyclononenone (11). A Diels–Alder reaction of 1 with 2,5-dimethyl-3,4-diphenylcyclopentadienone (12) resulted in the formation of the novel adduct 13. Acid-catalyzed transannular cyclization of 1 gave the bicyclic ketone 5 as the only product. All attempts to show that the optically active *l*-menthydrazone of 1 was a mixture of two diastereomers, because of the restricted rotation in the nine-membered ring, were unsuccessful.

A recent review[1] on the synthesis of cycloalkynes of medium sized rings indicated that no cyclononynone had yet been reported although 5-cyclodecynone had been prepared[2] and a Diels–Alder adduct of the very reactive 2-cyclooctynone had been isolated.[3] This report outlines the synthesis of the strained 5-cyclononynone (1) and describes a number of its reactions.

Synthesis of 5-Cyclononynone (1). The synthetic approach employed the well-known fragmentation reaction of the tosylhydrazone of an α,β-epoxy ketone.[2] The required ketone (6) was prepared from 4,5,6,7-tetrahydroindan (2) as outlined in Scheme I. Ozonolysis of 2 in methanol would be expected to yield hydroperoxide 3 which upon treatment with water would hydrolyze to 4, analogous to the ozonolysis of 9,10-octalin in methanol as reported by Criegee.[5-7] After this ozonolysis procedure no attempt was made to purify diketone 4 as previous reports[8] indicated it very readily underwent intramolecular aldol condensation. Thus, treatment of our hydrolyzed ozonolysis product with aqueous sodium carbonate solution gave the unsaturated ketone 5 in 50% yield from 2. This preparation of 5 is superior both in availability of starting material and overall percentage yield to those procedures previously reported.[9]

Epoxy ketone 6 was readily prepared from 5 by treatment with alkaline hydrogen peroxide.[10] Reaction of 6 with

Scheme I



2 3 4 5 6 7 1

tosylhydrazine in acetic acid–methylene chloride at −20° followed by warming to room temperature gave 5-cyclononynone (1) in 56% yield. All the spectral properties are consistent with this structure (see Experimental Section). In the infrared spectrum of 1 no absorption for –C≡C–