mass spectrum M^+ *m/e* 178. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.90; H, 10.11. Found: C, 80.97; H, 9,95. Compound **10** was identical by ir, nmr, mass spectrum, glc retention time, and mixture melting point with an authentic sample prepared according to the procedure described by Krapcho and Lovey.[5]

General Procedure for the Decarbalkoxylation of β-Keto Esters 2–8. A mixture of 10 equiv of Dabco, 1 equiv of β-keto esters **2–8**, and 15 equiv of *o*-xylene was heated to reflux for 4 hr with constant stirring. The cooled prodct mixtures were analyzed by glc and mass spectral analysis. The corresponding ketones (**11–14**) were identical by comparison of mass spectra and glc retention time with those of authentic samples.[8]

Decarbomethoxylation of β-Keto Ester 9. A mixture of 1.158 g (3.0 mmol) of compound **9** and 3.371 g (30.1 mmol) of Dabco in 10.434 g (98.4 mmol) of *o*-xylene was heated at 85–92° for 1 hr with constant stirring. The chloroform extract of the acidified (0.6 *M* HCl) reaction mixture was washed with water, dried over anhydrous $MgSO_4$, and evaporated *in vacuo* to give 0.890 g of crude compound **15** in 72% yield by glc analysis. The crude product was purified through a column packed with silica gel and eluted with hexane–chloroform to give 0.541 g (67%) of crystalline compound **15**: mp 189–191°; λ_{max} (KBr) 2820, 1690, 1440, 1240, 1020 cm^{-1}; nmr ($CDCl_3$) δ 3.63 (6 H), 2.43 (10 H, multiplet); mass spectrum M^+ *m/e* 268. *Anal.* Calcd for $C_{13}H_{16}O_6$: C, 58.21; H, 5.97. Found: C, 58.06; H, 5.95.

Acknowledgments. We wish to thank the graduate school and the Biological and Physical Sciences Institute for partial financial support.

Registry No.—**1**, 19386-06-2; **2**, 40778-30-1; **3**, 94-02-0; **4**, 41302-34-5; **5**, 1655-07-8; **6**, 10472-24-9; **7**, 611-10-9; **8**, 6627-69-6; **9**, 6966-22-9; **10**, 1660-04-4; **15**, 51869-06-8; Dabco, 280-57-9.

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New Synthetic Reactions. A Convenient Approach to Methyl 3-Oxo-4-pentenoate

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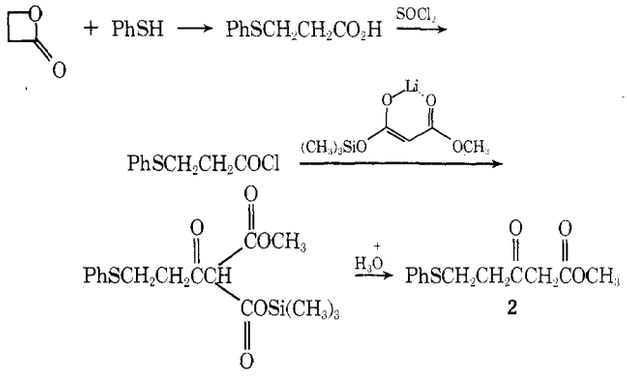
The utility of methyl 3-oxo-4-pentenoate (**1**) as an annelating agent in the synthesis of terpenes and alkaloids has been previously demonstrated.[1–4] Nevertheless, this reagent is not easily synthesized. The original method requires an acid-catalyzed elimination as the last step (eq 1) and proceeded in 7–12% overall yields from readily available starting materials. In our hands, this step never went

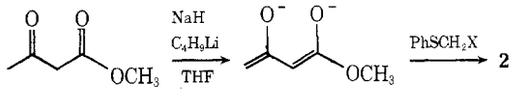
$$C_2H_5OCH_2CH_2COCH_2CO_2CH_3 \xrightarrow{TsOH} H_2C{=}CHCOCH_2CO_2CH_3 \quad (1)$$

to completion without substantial decomposition. An alternative approach based upon a retro Diels–Alder reaction to introduce the unsaturation proceeds in excellent yields (68% overall) but requires the availability of a special high-temperature pyrolysis apparatus.[5] The facility of dehydrosulfenylations as a method to introduce unsaturation conjugated to a carbonyl group suggested this reaction for the introduction of the double bond.[6] We wish to report utilization of this approach as a particularly convenient one for the preparatin of **1**. More generally, this methodology represents a novel approach to the introduction of a methylene group α to a carbonyl group.[7]

The synthesis of the requisite phenylthio derivative **2** initially paralleled a modified route for the formation of the ethoxy precursor.[8] While three steps are required, **2**

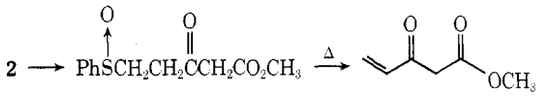


was prepared in 62–76% overall yield. A more convenient one-step synthesis of **2** involved the alkylation of the dianion of methyl acetoacetate[9] with halomethyl phenyl sulfide. Alkylation proceeds in about 40% yield with chloro-



methyl phenyl sulfide, but in 63–80% yield with iodomethyl phenyl sulfide. Equally important to the increased yield with the latter reagent was the formation of fewer side products.

Oxidation to the sulfoxide proceeds nearly quantitatively with sodium metaperiodate at room temperature. Heating the sulfoxide in refluxing chloroform for 12 hr followed by evaporation of the solvent and distillation *in vacuo* produced methyl 3-oxo-4-pentenoate in 97% yield. This three-step synthesis produces methyl acryloylacetate in an overall yield of 60–76% from readily available materials. The alternative five-step route proceeded in an overall yield of 60–72%.



Experimental Section

Infrared spectra were determined on a Beckman IR-8 spectrophotometer. Nmr spectra were determined on a Varian Associates Model A-60A spectrometer. Chemical shifts are given in δ units, parts per million relative to TMS as an internal standard. Mass spectra were taken on a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 eV.

All reactions were carried out under nitrogen. Thick layer chromatography was performed in 1.5-mm layers of silica gel PF-254 (E. Merck AG, Darmstadt). Removal of solvents from products normally involved rotary evaporation at water aspirator pressure followed by evacuation of the flask to approximately 1 mm to remove the last traces of the solvent.

3-Phenylthiopropionic Acid. A neat mexture of 19.41 g (269

mmol) of β-propiolactone and 28.5 g (259 mmol) of phenyl mercaptan was stirred at 80° for 24 hr. The flask was then fitted with a distillation column and heated to 60° (4 mm) for 1 hr to remove unreacted starting materials. The remaining 41.8 g (89% yield) of yellow oil was essentially pure (>95%) 3-phenylpropionic acid: ir (CCl_4) 3125–2940 (acid OH), 1712 (acid C=O), 687 cm^{-1} (Ph); nmr (CCl_4) δ 11.45 (s, 1 H, $-CO_2H$), 7.3 (M, 5 H, (Ph), 3.2 (AA', 2 H, $-SCH_2-$), 2.6 (BB', 2 H, $-CH_2CO_2-$); mass spectrum *m/e* (rel intensity) 182 (59), 123 (47), 111 (10), 110 (100), 109 (50), 77 (16).

Anal. Calcd for $C_9H_{10}O_2S$: mol wt, 182.040. Found: mol wt, 182.040.

3-Phenylthiopropionyl Chloride. To 119 g (71.8 ml, 1.0 mol) of thionyl chloride was added 122.1 g (0.67 mol) of 3-phenylthiopropionic acid in 1–2-g portions over a 15-min period. The reaction mixture was stirred at 40° for 4 hr. Excess thionyl chloride as removed by vacuum distillation (40–60°, 4 mm). The remaining brown liquid (121.5 g, 90% yield) was essentially pure (>95%) acid chloride which was utilized directly in the next step. The material could be further purified by vacuum distillation to give a yellow oil: bp 120–127° (0.5 mm); ir (CCl_4) 1795 (acid chloride C=O), 690 cm^{-1} (Ph); nmr (CCl_4) δ 7.25 (m, 5 H, Ph), 3.05 (s, 4 H, $-SCH_2CH_2COCl$ coincidental chemical shifts).

Iodomethyl Phenyl Sulfide. A solution of 83.9 g (80.0 ml, 0.675 mol) of thioanisole in 500 ml of methylene chloride was heated to reflux. A solution of 90.0 g (54 ml, 0.667 mol) of sulfuryl chloride (technical grade) in 150 ml of methylene chloride was added dropwise over a 1.25-hr period. Reflux was continued for 2 hr, and then the reaction was allowed to cool to room temperature. The contents of the flask were then transferred to a 2-l. round-bottomed flask and the solvent was removed by rotary evaporation *in vacuo* to give 104 g (98.6% yield) of chloromethyl phenyl sulfide as a yellow liquid. The product was sufficiently pure to be used in the next reaction, but could be further purified by distillation: bp 66° (0.2 mm) [lit.[10] bp 103–104° (12 mm)]; ir (CCl_4) 720, 690 (Ph), 653 cm^{-1} (CCl); nmr (CCl_4) δ 7.3 (m, 5 H, Ph), 4.82 (s, 2 H, $-CH_2Cl$).

A solution of 16.0 g (0.107 mol) of sodium iodide in 85 ml of acetone (reagent grade) was added to 15.88 g (0.100 mol) of chloromethyl phenyl sulfide and the reaction mixture was stirred at room temperature for 11 hr. The reaction mixture was then diluted with 100 ml of water and extracted with 2 × 100 ml of ether. The combined ether layers were washed with 25 ml of 5% aqueous sodium thiosulfate solution and 3 × 50 ml of saturated aqueous sodium chloride solution and dried over magnesium sulfate. The solvent was removed by rotary evaporation *in vacuo* to give 22.8 g (91% yield) of nearly pure (>95%) iodide as a yellow oil which was utilized directly in the next step: ir (CCl_4) 690 cm^{-1} (Ph); nmr (CCl_4) δ 7.3 (br s, 5 H, Ph), 4.48 (s, 2 H, $-CH_2I$). (Note: This material darkens rapidly on standing and should be used immediately after preparation.)

Methyl 3-Oxo-5-phenylthiopentanoate (2). Method A (From 3-Phenylthiopropionyl Chloride). A stirred solution of 19.0 g (100 mmol) of trimethylsilyl 2-methoxycarbonylacetate[8] in 100 ml of anhydrous ether (Mallinckrodt) was cooled to −78° and 69 ml (100 mmol) of *n*-butyllithium (1.45 *M* in hexane) was injected dropwise through a septum. The reaction mixture was stirred at −78° for 20 min, and then 10.0 g (50 mmol) of 3-phenylthiopropionyl chloride in 80 ml of dimethoxyethane (distilled from sodium benzophenone ketyl immediately before use) was added dropwise over a 1-hr period. A white precipitate formed over the course of the addition. Upon completion of the addition the reaction mixture was allowed to warm to room temperature over a 2-hr period and then stirred at room temperature for 12 hr. At the end of this period the reaction mixture was a clear, colorless solution with a thick, white gum on the walls of the flask. The reaction mixture was quenched with 50 ml of water and about 100 ml of solvent was removed by rotary evaporation *in vacuo*. The white suspension was poured into 200 ml of water and extracted with 300 ml of ether. The ether layer was washed with 100 ml of 1 *N* hydrochloric acid and 3 × 100 ml of saturated aqueous sodium chloride solution. The ether layer was dried over magnesium sulfate and solvent was removed by rotary evaporation *in vacuo* to give 11.2 g (93% yield) of sufficiently pure (>85%) sulfide **2** to be utilized directly in the oxidation step. Preparative tlc of a 0.519-g portion of this sample with chloroform (R_f 0.28) gave 0.422 g of methyl 3-oxo-5-phenylthiopentanoate (**2**) (77%, based on 3-phenylthiopropionyl chloride): ir (CCl_4) 1744 (ester C=O), 1724 (ketone C=O), 1235 (CO), 690 cm^{-1} (Ph); nmr (CCl_4) δ 7.1 (m, 5 H, Ph), 3.55 (s, 3 H, $-CO_2CH_3$), 3.32 (s, 2 H, $-COCH_2CO_2-$), 2.9 (m, 4 H, $-SCH_2CH_2CO-$); mass spectrum *m/e* (rel intensity) 238 (12), 225 (20), 218 (33), 196 (16), 185 (14), 164 (29), 159 (44), 144 (35), 143 (75), 136 (55), 127 (13), 123 (22), 110 (40), 109 (46), 108 (24), 101 (28), 69 (85), 65 (20), 58 (32), 57 (30), 55 (100).

Anal. Calcd for $C_{12}H_{14}O_3S$: mol wt, 238.006. Found: mol wt, 238.006.

Method B (From Methyl Acetoacetate). A 57% dispersion of sodium hydride in mineral oil (4.64 g of dispersion, 2.64 g of active hydride, 0.11 mol) was washed free of the mineral oil with ether. Tetrahydrofuran (300 ml) was distilled from sodium benzophenone ketyl directly into the flask containing the hydride. The mixture was cooled to 0° in an ice bath and 11.60 g (0.10 mol) of methyl acetoacetate in 25 ml of dry tetrahydrofuran was added dropwise over a 10-min period. The reaction mixture was stirred 10 min at 0°, and then 75 ml (0.11 mol) of 1.5 *M* *n*-butyllithium in hexane was injected dropwise over a 5-min period and the red suspension was stirred for 15 min at 0°. Then a solution of 22.8 g (0.09 mol) of iodomethyl phenyl sulfide in 50 ml of dry tetrahydrofuran was added dropwise over a 20-min period. The reaction mixture was stirred for 1 hr at 0° and then poured into a mixture of 100 ml of 3 *N* hydrochloric acid and 200 ml of ice water and extracted with 2 × 300 ml of ether. (Note: During alkylation, the temperature of the reaction mixture should not be allowed to rise above 0°). The combined ether layers were washed with 4 × 100 ml of saturated aqueous sodium chloride solution and dried over magnesium sulfate. Solvent was removed by rotary evaporation *in vacuo* to give 22.5 g of brown oil. Preparative tlc of a 0.523-g portion of this sample with chloroform (R_f 0.28) yielded 0.394 g (79%) of sulfide **2**.

Column chromatography allowed easy purification. (This simple filtration through silica gel is required. When it was omitted, oxidation proceeded smoothly, but the thermal elimination of sulfoxide proceeded in poor yield.) A 17.2-g sample of the crude alkylation product was applied directly to the top of a dry-packed silica gel column (29 g in a 2.0 × 34 cm column) and covered with 4 cm of sand. Elution with 270 ml of pentane removed the less polar impurities. Changing to 2% ether in pentane (v/v) eluted the sulfide (*ca.* 2 l.). Chromatography was discontinued when the sulfide showed contamination with more polar impurities. In this way, 10.4 g (63%, based on iodomethyl phenyl sulfide) of pure methyl 5-phenylthio-3-oxopentenoate (**2**) was obtained.

Methyl 3-Oxo-5-phenylsulfinylpentanoate. A solution of 9.80 g (41.1 mmol) of methyl 3-oxo-phenylthiopentanoate(**2**) in 220 ml of methanol (reagent grade) was immersed in an ice bath and stirred with a mechanical stirrer while 100 ml of saturated aqueous sodium metaperiodate solution (*ca.* 15 g, 65.1 mmol) was added in 5-ml portions over a 5-min period. A thick white precipitate formed almost immediately upon completion of the addition. The ice bath was removed after 10 min and stirring was continued at room temperature for 12.5 hr. The reaction mixture was then diluted with 500 ml of water and extracted with 4 × 200 ml of chloroform. The combined chloroform layers were washed once with 200 ml of saturated sodium chloride solution and dried over magnesium sulfate. Solvent was removed by rotary evaporation *in vacuo* at room temperature to give 10.2 g (98%) of sulfoxide of sufficient purity to be used without further purification (Note: Because of the facility of elimination which occurs slowly even at room temperature, the sulfoxide should not be heated above room temperature): ir (CCl_4) 1754 (ester C=O), 1724 (ketone C=O), 1053 (S=O), 690 cm^{-1} (Ph); nmr ($CDCl_3$) δ 7.6 (m, 5 H, Ph), 3.68 (s, 3 H, $-CO_2CH_3$), 3.5 (s, 2 H, $-COCH_2CO_2-$), 3.0 (m, 4 H, $-SCH_2CH_2CO-$).

Methyl 3-Oxo-4-pentenoate (1). A solution of 10.2 g (39.8 mmol) of methyl 3-oxo-5-phenylsulfinylpentanoate in 100 ml of chloroform was refluxed for 12 hr. The solution was concentrated to approximately 20 ml by distillation of chloroform at atmospheric pressure. This solution was then transferred to a 50-ml round-bottom flask equipped with a 6-cm Vigreux distillation head and distillation was continued at 50° (80–120 (80–120 mm) until the chloroform was totally removed. The receiver flask was then immersed in a Dry Ice–isopropyl alcohol bath and the pressure was reduced slowly to 2 mm. A colorless liquid distilled at 35–39° (1–2 mm) [lit.[5] bp 78–81° (18 mm)] to give 4.92 g (97% yield) of methyl 3-oxo-4-pentenoate (**1**): ir (CCl_4) 1736 (C=O ester), 1661 (α,β-unsaturated ketone C=O), 1642 (C=C), 1582 (enol), 1232 (CO ester), 976 cm^{-1} (C=CH_2); nmr (CCl_4) δ 6.1 (m, 2 H, $-HC=CH-$), 5.5 (dd, 1 H, =CH–), 5.0 (s, 1 H, enol $-CHCO_2-$), 3.65 (s, 3 H, $-CO_2CH_3$), 3.55 (s, 1 H, keto $-CH_2CO_2-$) (*cf.* ref 8).

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Registry No.—**1,** 37734-05-7; **2,** 51849-20-8; 3-phenylthiopropionic acid, 5219-65-8; β-propiolactone, 57-57-8; phenyl mercaptan, 108-98-5; 3-phenylthiopropionyl chloride, 51849-21-9; iodomethyl phenyl sulfone, 51849-22-0; thioanisole, 100-68-5; trimethylsilyl 2-methoxycarbonylacetate, 51849-23-1; methyl acetoacetate, 105-45-3; methyl 3-oxo-5-phenylsulfinylpentanoate, 51849-24-2.

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Synthesis of Some Derivatives of 1,2-Diaza-3,5-phospholene 3-Oxides. A New Heterocyclic System[1]

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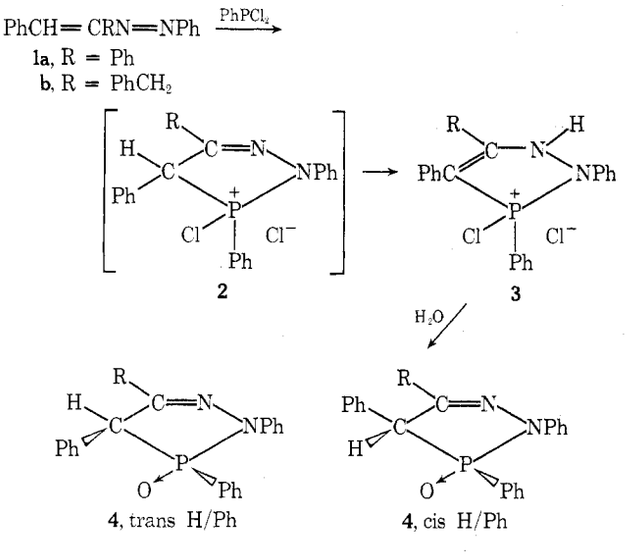
In our study of phosphorus heterocycles from phosphines, we have obtained a new five-membered diazaphospholene by a cycloaddition similar to that reported by McCormack with conjugated dienes and phosphonous dihalides.[2,3] All the isomers of phenylazostilbene[4,5] (**1a**) and of 2-phenylazo-1,5-diphenylpropene[6] (**1b**) easily react with phenyldichlorophosphine at room temperature to form cycloadducts (**2** and **3**). These adducts are quenched with water and give (75% total yield) a mixture of cis and trans[7] phospholene oxides **4** (Scheme I). That an isomer mixture

Scheme I



was obtained was readily apparent from the proton nmr spectrum, which showed two PCH doublets. The two isomers were isolated in pure form by fractional crystallization or by silica gel column chromatography. They formed colorless needles; the infrared spectra showed bands characteristic of P═O and PPh groups. The nmr spectrum ($CDCl_3$) showed for the crude hydrolyzed product mixture **4a** and **4b** an isomer ratio of about 3:2 (cis:trans) and 5:2, respectively. The isomer ratio may sometimes vary, and probably depends on the mode of quenching or on the amount of water present in the reagents. Analogous variations have been observed[8] in the case of phosphetanium salts.

Assignment of Configuration. The steric configurations of the diazaphospholenes have been made on the basis of nmr spectra. The difference between the chemical shifts of the methine proton in the two isomers of **4a** is 0.45 ppm, with the upfield signal at δ 4.55 ppm, while in the two isomers of **4b** it is 0.40 ppm, with the upfield signal at δ 4.29 ppm. The cis configuration was assigned to the isomer showing an upfield methine signal, since only in this isomer is the phenyl ring capable of shielding the methine proton.

Compound *trans*-**4a** has a significantly higher coupling constant (J_{PCH} = 22.5 Hz) than *cis*-**4a** (J_{PCH} = 7.5 Hz). The same large difference was observed for the two isomers **4b** (22.8 and 6 Hz).

This correlation permits the assignment of the trans configuration to the isomers having high J_{PCH} and cis to those having a low value. Examples of analogous assignments are reported in the literature for similar systems.[9] The same effects, less marked, are observed in the benzyl methylene protons of the isomers **4b.** The benzylic protons appeared as the AB portion of an ABX pattern (where X = ^{31}P), with $J_{AX} = J_{BX}$ = 1 Hz, δ_A 3.82 ppm, δ_B 3.36 ppm, J_{AB} = 15 Hz for *cis*-**4b** and J_{AX} = 2 Hz, $J_{BX} < 1$ Hz, δ_A 3.85 ppm, δ_B 14 Hz for *trans*-**4b.**

The ABX signal persisted at 150°, indicating that the magnetic nonequivalence arises from proximity of the benzylic group to an asymmetric center rather than to restricted rotation. Preliminary results showed little tendency for cis–trans interconversion in **4a** or **4b.** This will be subject of further study.

The adducts **3** are highly reactive toward water and are not readily characterized. We have, however, succeeded in obtaining the pmr spectrum in deuteriochloroform when all operations were conducted under a dry nitrogen atmosphere. Although isomeric diazaphospholene oxides are produced on hydrolysis, the nmr spectra of the cycloadducts did not show the presence of an isomeric mixture. The signals of the methine protons were not present but signals of the amine protons were. Rearrangement must therefore occur during subsequent hydrolysis. The nmr spectra are in agreement with the tautomeric structure **3** and the large downfield shifts of protons (see Experimental Section) suggests that in these adducts, at least in solution, phosphorus is ionic rather than covalent.

Experimental Section

All operations involving trivalent phosphorus compounds were performed under a nitrogen atmosphere. Hexane was dried by distillation over sodium. Phenyldichlorophosphine was obtained from Alfa Inorganic Derivatives. **1a** and **1b** were obtained by published procedures.[4-6] The nmr spectra were determined on a Jeol J.M.MC 60-HL spectrometer. Proton nmr chemical shifts are expressed in parts per million from internal TMS. Ir spectra were run as KBr disks on a Perkin-Elmer 337 with NaCl optics. The microanalyses were performed on mixture of the isomers as well as on pure isomers. The results obtained were pratically identical.

Synthesis of 3a and 4a. Phenyldichlorophosphine (3.74 g, 0.02 mol) was added to **1a** (5.68 g, 0.02 mol) in 400 ml of dry hexane. After 1 hr at room temperature the adduct began to separate as a crystalline solid. The reaction was completed in a 24–26-hr period (until the orange color of the solution disappeared). A small por-