A second experiment, conducted in the same manner, except that the Grignard was used directly without titration, assuming 100% conversion, resulted in a 57% yield of crude acids. Fractional crystallization gave 27.2% of III and 20.1% of II.

Reaction of I with Ethyl Chlorocarbonate.—The general procedure employed by Gaertner[5] for the isomeric thenyl Grignard was used. I, prepared in the cyclic reactor from 17.7 g. (0.1 mole) of 3-thenyl bromide, was allowed to react with 53 ml. (0.56 mole) of resistilled ethyl chlorocarbonate, and 8.1 g. (57%) of crude acid was obtained. Two crystallizations from 10% acetic acid yielded 7.5 g. (52.8%) of pure III melting at 145–146°.

Extraction of the mother liquors of recrystallization with ether and evaporation produced only a trace of crude solid acid melting above 90°, which was discarded.

Reaction of I with Acetyl Chloride.—Following the procedure of Gaertner[5] for the isomer, the 3-thenyl Grignard prepared in the cyclic reactor from 45 g. (0.25 mole) of 3-thenyl bromide was allowed to react with 71.5 ml. (1.0 mole) of redistilled acetyl chloride, and the product, a pink oil (32 g.), was distilled under reduced pressure. A fore-fraction, b.p. 28–52°/0.5 mm., weighed 7.3 g. but gave a negative ketone test with 2,4-dinitrophenylhydrazine reagent, and a negative iodoform test. The major fraction, weighing 19.3 g. (55%), was collected between 57° and 90°/0.5 mm., n^{26}_{D} 1.5650. Hartough and Conley[16] report 3-methyl-2-acetothienone (IV), b.p. 72–73°/2 mm., n^{20}_{D} 1.5618. About 5 ml. of dark viscous residue remained in the distillation flask. The middle fraction was redistilled, giving 15 g. of colorless oil boiling from 52–57° at 0.3 mm., n^{26}_{D} 1.5637.

A semicarbazone was prepared and found to melt at 207–208°, as previously reported[16] for the semicarbazone of IV. A mixed melting point with a semicarbazone prepared from an authentic sample[17] of IV, prepared by the method of Hartough and Kosak,[18] was not depressed.

Oxidation of 3.5 g. (0.025 mole) of the ketone with sodium hypochlorite solution, as described by Hartough and Conley,[16] gave 2.7 g. (77%) of III, m.p. 146°, after two recrystallizations from 10% acetic acid. Extraction of the mother liquors with ether and concentration under vacuum left only a trace of nonacidic oil.

Reaction of I with Formaldehyde.—Following the Gaertner procedure,[5] a solution of I prepared from 36.8 g. (0.21 mole) of 3-thenyl bromide in the cyclic reactor, was treated with gaseous formaldehyde generated from 50 g. of paraformaldehyde and swept into the reaction mixture with a slow stream of nitrogen, as described by Gilman and Catlin.[19] It was necessary to dry the nitrogen by passing it through an alkaline drying train of calcium chloride, calcium sulfate, and sodium hydroxide pellets, since the sulfuric acid drying tower described[19] caused polymerization of the products in the reaction.

The reaction produced a yellow oil from which a colorless distillate, b.p. 80–83°/3 mm., n^{25}_{D} 1.5520, weighing 10.3 g. (40%) was obtained. One gram of the fresh distillate was treated with α-naphthyl isocyanate, and the α-naphthylurethane which crystallized was recrystallized from carbon tetrachloride twice. It melted sharply at 139°.

Anal. Calcd. for $C_{17}H_{15}NO_2S$: C, 68.64; H, 5.08; N, 4.71. Found: C, 68.58; H, 5.02; N, 4.75.

3-Methyl-2-thenyl alcohol (V).—A Grignard reagent was prepared from 17.7 g. (0.1 mole) of 2-bromo-3-methylthiophene, and excess gaseous formaldehyde passed through the reaction mixture under nitrogen. The mixture was then treated as previously described and the colorless distillate, b.p. 70–74°/1.5 mm., n^{25}_{D} 1.5524, weighed 9.0 g. (70%).

Anal. Calcd. for C_6H_8OS: C, 56.22; H, 6.29. Found: C, 56.55; H, 6.55.

This oil formed glistening plates of an α-naphthylurethane melting sharply at 144°. A mixture melting point with the urethane previously prepared was 140–142°.

β-(**3-Thienylethanol (VIb)**.—Following the procedure of Nystrom and Brown[20] for the reduction of carboxylic acids, a solution of 8.4 g. (0.059 mole) of 3-thienylacetic acid[3] in 100 ml. of absolute ether was added dropwise to 4.6 g. (0.12 mole) of lithium aluminum hydride in 200 ml. of dry ether at such a rate as to maintain gentle refluxing of the solution. After addition was complete and refluxing had subsided, water was slowly added followed by 10% sulfuric acid until a clear aqueous layer was formed. This was separated and washed with two 50-ml. portions of ether. The combined ether layers were dried over anhydrous magnesium sulfate, concentrated, and the residual oil distilled. The product was a colorless oil boiling at 67°/0.5 mm. It weighed 6.0 g. (79%).

Anal. Calcd. for C_6H_8OS: C, 56.22; H, 6.29. Found: C, 55.69; H, 6.50.

The compound formed an α-naphthylurethane having a melting point at 108–109°, which was depressed to 95–105° when mixed with the urethane melting at 139°, obtained from the product of I and formaldehyde.

Anal. Calcd. for $C_{17}H_{15}NO_2S$: N, 4.71. Found: N, 4.83.

A 3,5-dinitrobenzoate was also prepared from VIb. It melted at 110° after two recrystallizations from ethanol and water.

Anal. Calcd. for $C_{13}H_{10}N_2O_6S$: N, 8.69. Found: N, 8.68.

Acknowledgment.—The authors are indebted to the Sterling-Winthrop Research Institute for the Fellowship in support of this research.

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[16] H. D. Hartough and L. G. Conley, *J. Am. Chem. Soc.*, **69**, 3096 (1947).

[17] We are indebted to Dr. R. L. Patrick for this preparation. See R. L. Patrick, Ph.D. thesis, Indiana University, 1949.

[18] H. D. Hartough and A. Kosak, *J. Am. Chem. Soc.*, **69**, 3093 (1947).

[19] H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 188.

[20] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

Reactions of Mercuric Carboxylates with Trivalent Phosphorus Compounds

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Reactions of mercuric carboxylates with triethyl phosphite or with tertiary phosphines have been studied. When mercuric acetate was treated with triethyl phosphite, acetic anhydride was obtained in good yield along with mercury and triethyl phosphate. Similarly, the reaction of mercuric acetate with tri-*n*-butylphosphine resulted in the formation of acetic anhydride, mercury, and tri-*n*-butylphosphine oxide. In addition, it was found that, when mercurous propionate was treated with triethyl phosphite or with tri-*n*-butylphosphine, propionic anhydride was formed in good yield along with mercury, and triethyl phosphate or tri-*n*-butylphosphine oxide, respectively. Mechanisms of these reactions are discussed.

Deoxygenation reactions of diphenylfuroxane, isocyanates, and diphenyl ketene into diphenylfurazan, isonitriles, and tolane, by means of tertiary phosphites have been described in a previous paper.[1]

In the present study, the deoxygenation by tertiary phosphites was tested on ethylene carbonate under the assumption that it would, when deoxygenated, yield ethylene and carbon dioxide.[2] But it was found

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[1] T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).

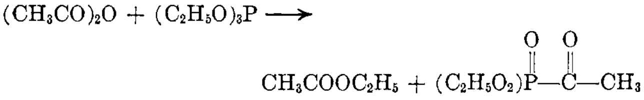
[2] It was reported that ethylene carbonate was deoxygenated by tertiary phosphine to yield ethylene and carbon dioxide. P. T. Keough and M. Grayson, *ibid.*, **27**, 1817 (1962).

that ethylene carbonate did not react with triethyl phosphite even at the boiling point. Then the two compounds were subsequently treated in the presence of a catlalytic amount of either mercuric oxide or mercuric acetate. It was found that the expected deoxygenation could not be effected by the catalysts, but mercuric oxide or mercuric acetate was always reduced to mercury.

In order to study the reaction of mercuric acetate with triethyl phosphite, their equimolar reaction was tried. When triethyl phosphite was added dropwise to mercuric acetate with stirring at room temperature, a vigorous exothermic reaction took place and mercury (99%), acetic anhydride (51%), and ethyl acetate (11%) were obtained along with triethyl phosphate (63%).

$$(C_2H_5O)_3P + (CH_3COO)_2Hg \longrightarrow Hg + (CH_3CO)_2O + (C_2H_5O)_3PO + CH_3COOC_2H_5$$

It has been reported[3] that only ethyl acetate was obtained as an identified product when triethyl phosphite and mercuric acetate were allowed to react at room temperature. Lutsenko, *et al.*, explained the formation of the ester by assuming a pentavalent phosphorus intermediate. While, according to Kamai and Kukhtin,[4] the isolation of ethyl acetate in this experiment suggests that it may be attributed to the reaction of triethyl phosphite with acetic anhydride initially formed, although diethyl acetylphosphonate, theoretically expected to come out with the ester, was not obtained.



$$(CH_3CO)_2O + (C_2H_5O)_3P \longrightarrow CH_3COOC_2H_5 + (C_2H_5O_2)\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}-CH_3$$

Since the reaction by means of tertiary phosphines may not involve such a side reaction, tri-*n*-butylphosphine was chosen in place of triethyl phosphite in the above experiment. Indeed, when mercuric acetate was treated with tri-*n*-butylphosphine in *n*-hexane at room temperature, it gave mercury (88%), tri-*n*-butylphosphine oxide (91%), and acetic anhydride (74%).

$$(n\text{-}C_4H_9)_3P + (CH_3COO)_2Hg \longrightarrow Hg + (CH_3CO)_2O + (n\text{-}C_4H_9)_3PO$$

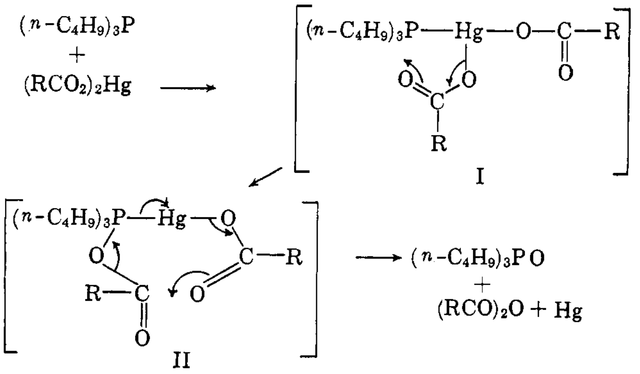
Similarly, when the mercuric salts of various carboxylic acids reacted with triethyl phosphite, tri-*n*-butylphosphine, or triphenylphosphine, the corresponding acid anhydrides were obtained in good yields except in the cases of mercuric succinate with tertiary phosphines (see Tables I–III). Further, the reaction of one molar equivalent of triethyl phosphite with two molar equivalents of mercurous propionate was found to give propionic anhydride (59%), triethyl phosphate (78%), and mercury (97%).

$$2C_2H_5COOHg + (C_2H_5O)_3P \longrightarrow 2Hg + (C_2H_5CO)_2O + (C_2H_5O)_3PO$$

Similarly, when tri-*n*-butylphosphine was used in place of triethyl phosphite in the above experiment, propionic anhydride (67%) was obtained along with tri-*n*-butylphosphine oxide (95%) and mercury (87%).

It can be noted that the mercuric and mercurous salts of carboxylic acids can be reduced by triethyl phosphite or tertiary phosphines under comparatively mild conditions to yield the corresponding acid anhydrides in about 60–80%.

These experiments show that the reaction may proceed through an initial formation of intermediate (I) resulting from the mercuric salt and trivalent phosphorus compound. An intramolecular nucleophilic attack of carbonyl oxygen on positively charged phosphorus occurs concomitant with a migration of carboxyl group and intermediate (II) resulted as shown in Scheme I.

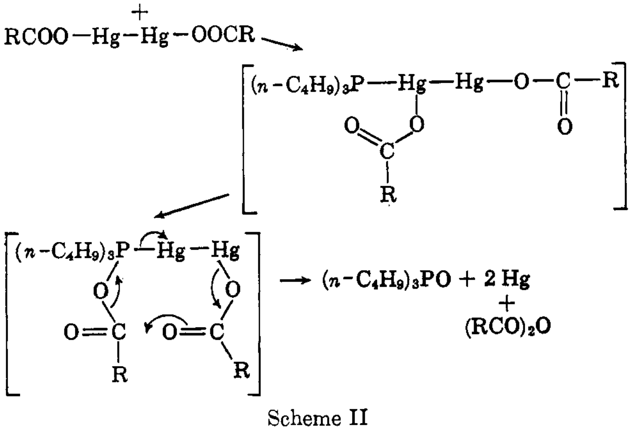


Scheme I

The intermediate (II) decomposes to give the corresponding acid anhydride, mercury, and triethyl phosphate or tertiary phosphine oxide, conceivably by way of internal nucleophilic displacement as sketched (Scheme I).

In the case of the reaction between mercuric phthalate and triethyl phosphite, a solid material which was identified to be an 1:1 adduct of the starting materials was isolated. Since it decomposes to yield phthalic anhydride, mercury, and triethyl phosphate almost quantitatively on heating, it is considered to be an intermediate corresponding to I or II.

With regard to the mercurous salt, a mechanism involving a similar intermediate may be suggested as shown in Scheme II.



Scheme II

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[3] I. F. Lutsenko, R. M. Khomutov, and L. V. Eliseeva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 181 (1956); *Bull. Akad. Sci. USSR, Div. Chem. Sci.*, 173 (1956).

[4] G. Kamai and V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **102**, 283 (1955).

Table I

The Reactions of Triethyl Phosphite with Mercuric Carboxylates

Mercuric carboxylate	Reaction condition			Yield, %		
	Solvent	Time, hr.	Temp., °C.	Anhydride (b.p. or m.p., °C.)	Hg	$(C_2H_5O)_3PO$
Acetate[a]	None	1.5	Room temp.	51 (137–140°)	99	63
Propionate	None	1.5	Room temp.	65 (77–79°/30 mm.)	83	78
Benzoate	Dioxane[b]	0.25	100°	73 (42° m.p.)	95	78
Phthalate	Dioxane[b]	1.0	100°	76 (129–131° m.p.)	82	69
Succinate	Dioxane[b]	1.0	100°	51 (118–119° m.p.)	89	66

[a] Mercuric acetate gave ethyl acetate in 11% yield, but other mercuric carboxylates did not give the corresponding esters. [b] Anhydrous dioxane.

Table II

The Reactions of Tri-*n*-butyl Phosphine with Mercuric Carboxylates

Mercuric carboxylate[b]	Reaction condition			Yield, %		
	Solvent	Time, hr.	Temp., °C.	Anhydride (b.p. or m.p., °C.)	Hg	$(n\text{-}C_4H_9)_3PO$
Acetate	*n*-Hexane	1.0	69°	74 (61–62°/50 mm.)	88	91
Propionate	*n*-Hexane	1.0	69°	81 (77–78°/40 mm.)	87	91
Butyrate	*n*-Hexane	1.0	69°	82 (87–88°/20 mm.)	85	93
Benzoate	*n*-Hexane	1.0	69°	73[a]	95	70
Phthalate	*n*-Hexane	1.0	69°	63[a]	79	76

[a] Since anhydrides could not be separated from tri-*n*-butylphosphine oxide by fractional distillation, their yields were determined from weights of the corresponding anilides derived from anhydrides. [b] In the case of mercuric succinate, colored tarry product was formed and succinic anhydride was not obtained.

Table III

The Reactions of Triphenylphosphine with Mercuric Carboxylates

Mercuric carboxylate[a]	Reaction condition			Yield, %		
	Solvent	Time, hr.	Temp., °C.	Anhydride (b.p. or m.p., °C.)	Hg	$(C_6H_5)_3PO$
Propionate	Dioxane[b]	1.0	100°	81 (77–79°/40 mm.)	85	92
Benzoate	Dioxane[b]	1.0	100°	61 (42° m.p.)	74	73

[a] In the case of mercuric succinate, colored tarry product was formed and succinic anhydride was not obtained. [b] Anhydrous dioxane.

Table IV

The Reactions of Mercurous Propionate with Triethyl Phosphite or with Tri-*n*-butylphosphine

R'_3P	Reaction condition			Yield, %		
	Solvent	Time, hr.	Temp., °C.	Anhydride (b.p., °C.)	Hg	$R_3'P{=}O$
$(C_2H_5O)_3P$	None	1.0	Room temp.	59 (75–77°/28 mm.)	97	78
$(n\text{-}C_4H_9)_3P$	*n*-Hexane	1.0	69°	67 (77–78°/40 mm.)	87	95

Experimental

Materials.—Triethyl phosphite (b.p. 53–54°/14 mm.) and tri-*n*-butylphosphine (b.p. 125–126°/18 mm.) were prepared by the methods of Ford-Moore[5] and Davies.[6] Triphenylphosphine and mercuric acetate were obtained from commercial sources and purified by recrystallization.

Preparation of the Mercuric or Mercurous Salts of Carboxylic Acids.—The mercuric salts of propionic and butyric acid were prepared as follows: 1 mole of mercuric oxide and 3 moles of the acid were heated until mercuric oxide was dissolved. After cooling, the precipitate of the mercuric salt was collected and purified by recrystallization from water and a small amount of the acid.

Mercuric phthalate was prepared according to the method of Ekeley[7] and mercuric succinate was prepared by essentially the same method.

Mercuric benzoate was prepared as follows: a solution of 0.1 mole of sodium benzoate in 100 ml. of water was added to a solution of 0.06 mole of mercuric acetate in 300 ml. of water. A white precipitate of mercuric benzoate was filtered and washed several times with aqueous ethanol and dried *in vacuo*.

Mercurous propionate was prepared according to the method of Varet.[8]

Reaction of Mercuric Acetate with Triethyl Phosphite.—When triethyl phosphite (8.30 g., 0.05 mole) was added at once to mercuric acetate (15.95 g., 0.05 mole) with vigorous shaking at room temperature, the reaction started soon with liberation of heat. Then the reaction mixture was allowed to stand at room temperature for 1.5 hr. with occasional shaking and mercury was filtered off. It weighed 9.91 g. (99%). Distillation of the filtrate gave ethyl acetate, 0.47 g. (11%), b.p. 75–80°, and acetic anhydride, 2.54 g. (51%), b.p. 137–140°. The residue was further distilled *in vacuo* giving triethyl phosphate, 5.70 g. (63%), b.p. 106–108°/24 mm. The products were identified by gas chromatography.

By a similar procedure, various acid anhydrides were obtained from the equimolar reactions of triethyl phosphite and the mercuric salts of the corresponding carboxylic acids. The results are listed in Table I.

Reaction of Mercuric Acetate with Tri-*n*-butylphosphine.—When tri-*n*-butylphosphine (4.0 g., 0.02 mole) was added dropwise to a suspension of mercuric acetate (6.4 g., 0.02 mole) in 20 ml. of *n*-hexane, the reaction started soon with liberation of heat and mercury began to precipitate. After refluxed for an additional hour, mercury (3.5 g., 88%) was filtered and the filtrate was concentrated. The residue was then distilled *in vacuo* giving acetic anhydride, 1.5 g. (74%), b.p. 61–62°/50 mm., and tri-*n*-butylphosphine oxide, 4.0 g. (91%), b.p. 137–139°/0.8 mm.

The results from the equimolar reactions of the other mercuric salts of carboxylic acids and tri-*n*-butylphosphine or triphenylphosphine are shown in Table II and III.

Reaction of Mercurous Propionate with Triethyl Phosphite.—When triethyl phosphite (1.66 g., 0.01 mole) was added to mercurous propionate (5.48 g., 0.02 mole) with vigorous shaking at room temperature, an exothermic reaction started at once and

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[5] A. H. Ford-Moore and B. J. Perry, *Org. Syn.*, **31**, 111 (1951).

[6] W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 33 (1929).

[7] J. B. Ekeley and C. Banta, *J. Am. Chem. Soc.*, **39**, 766 (1917).

[8] R. Varet, *Ann. chim. phys.*, [7] **8**, 135 (1896).

mercury began to precipitate. The reaction mixture was allowed to stand at room temperature for 1 hr. with occasional shaking. Mercury (3.88 g., 97%) was filtered and filtrate was distilled *in vacuo* giving propionic anhydride, 0.76 g. (59%), b.p. 75–77°/28 mm., and triethyl phosphate, 1.41 g. (78%), b.p. 107–110°/28 mm.

Similarly, propionic anhydride was obtained by the reaction of mercurous propionate with tri-*n*-butylphosphine. The results are shown in Table IV.

Preparation of the Adduct of Triethyl Phosphite and Mercuric Phthalate.—Triethyl phosphite (3.32 g., 0.02 mole) was added to a suspension of mercuric phthalate (7.30 g., 0.02 mole) in 20 ml. of anhydrous dioxane with stirring at room temperature. The stirring was continued for 15 min. at room temperature, and then heated at 100° for 30 min. After cooling, the precipitate was separated and dioxane was removed *in vacuo*. When the residue was treated with 40 ml. of dry ether, a white precipitate, the adduct of triethylphosphite and mercuric phthalate, formed. It weighed 4.20 g. The adduct was freely soluble in cold water, ethanol, and dioxane, and insoluble in ether and petroleum ether. The sample for elemental analysis was purified by recrystallizafrom dioxane–ether. It melted at 104–107° and decomposed at 120° to yield mercury.

Anal. Calcd. for $C_{14}H_{19}O_7PHg$: P, 5.8; Hg, 37.8. Found: P, 6.0; Hg, 39.2.

Pyrolytic Decomposition of the Adduct.—When the adduct (3.50 g.) was heated at 140° for 10 min., mercury, 0.67 g. (51%), triethyl phosphate, 0.44 g. (37%), b.p. 105–107°/25 mm., and phthalic anhydride, 0.40 g. (41%), b.p. 157–159°/25 mm., m.p. 129–130°, were obtained.

Substituted Pseudoionone Homologs and Related Compounds from Substituted Diketenes

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The preparations of a series of ketones related to 6-methyl-5-hepten-2-one with 1,3- and 1,3,5-substitution are described. Also reported are related ethynyl- and vinylcarbinols, their acetates, pseudoionones, pseudoirones, α-ionones, and α-irones. These compounds are of interest to the essential oil industry.

In order to expand on the work on pseudoionone homologs reported by Kimel, *et al.*,[1–3] we investigated the use of various substituted ketene dimers in place of diketene in order to produce a novel series of pseudoionone homologs. In addition, various intermediates related to compounds having vital interest to the essential oil industry were isolated. By the varied introduction of the substituted ketene dimers we arrived, through novel intermediates, at pseudoionone homologs of type VI and type VII. They were ring-closed finally to α-irones and α-ionones of type VIII and type IX.

The substituted ketene dimers were prepared by dehydrohalogenating the appropriate aliphatic acid chlorides with triethylamine.[4–7] The asymmetric dimerization of the methyl-, ethyl-, and *n*-hexylketenes gave rise to the liquid forms of the dimers which exist as the vinylaceto-β-lactones (I).[8–11]

The route to an α-irone, type VIII, required the following sequence of reactions. Methylketene dimer (Ia) (R = CH_3) was treated with 3,6,7-trimethyl-6-octen-1-yn-3-ol[3] to yield the corresponding 2,4-dialkylacetoacetate, 1-ethynyl-1,4,5-trimethyl-4-hexen-1-yl 2-methyl-3-oxovalerate (IIIc). On pyrolysis IIIc afforded the pseudoirone homolog, 4,7,10,11-tetramethyl-4,6,10-dodecatrien-3-one (VIc). Upon ring closure of VIc, we obtained the corresponding α-irone, 1-(2,5,6,6,-tetramethyl-2-cyclohexen-1-yl)-2-methyl-1-penten-3-one (VIIIc).

In order to arrive at a pseudoionone of type VII the subsequent path was followed. Ethylketene dimer (Ib) (R = C_2H_5) and 2-methyl-3-buten-2-ol[1] were allowed to react to yield the 2,4-dialkylacetoacetate, 1,1-dimethylallyl 2-ethyl-3-oxohexanoate (IIb). Pyrolysis of IIb led to the unsaturated ketone, 5-ethyl-8-methyl-7-nonen-4-one (Vb). The tertiary carbinol (Xb) resulting from the ethynylation of Vb was treated with diketene to yield an acetoacetate (IVb) which on pyrolysis afforded the desired substituted pseudoionone, 7-ethyl-10-methyl-6-propyl-3,5,9-undecatrien-2-one (VIIb). Ring closure led to the corresponding α-ionone homolog (IXb).

We synthesized a typical α-irone of type IX in the following manner. The reaction of methylketene dimer (Ia) with 2,3-dimethyl-3-buten-2-ol[12] gave the corresponding 2,4-dialkylacetoacetate (IId). Pyrolysis and subsequent ethynylation led to the ethynylcarbinol (Xc), which was treated with diketene. The acetoacetate (IVc) was converted to the pseudoirone (VIIc) in the usual manner. Ring closure afforded the α-irone (IXc).

Experimental[13]

1. **Substituted Ketene Dimers (Table I).**—These compounds were prepared as described by Sauer[5] and Wedekind and Miller.[4]

TABLE I

SUBSTITUTED DIKETENES

Compound	R	Boiling points °C.	Boiling points Mm.	$n^{25}D$	% Yield
Ia	CH_3	50	15	1.4339	42
b	C_2H_5	40	0.1	1.4380	58
c	n-C_6H_{13}	85	.008	1.4520	56

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(1) W. Kimel, N. Sax, S. Kaiser, G. Eichmann, G. Chase, and A. Ofner, *J. Org. Chem.*, **23**, 153 (1958).

(2) W. Kimel and N. Sax, U. S. Patent 2,661,368 (December 1, 1953).

(3) W. Kimel, J. Surmatis, J. Weber, G. Chase, N. Sax, and A. Ofner, *J. Org. Chem.*, **22**, 1611 (1957).

(4) E. Wedekind and Miller, *Ber.*, **39**, 1631 (1906); **42**, 1269 (1909).

(5) J. C. Sauer, *J. Am. Chem. Soc.*, **69**, 2444 (1947).

(6) A. T. Blomquist and R. D. Spencer, *ibid.*, **69**, 472 (1947).

(7) N. Rabjohn and H. M. Molotsky, *J. Org. Chem.*, **23**, 1642 (1958).

(8) R. L. Wear, *J. Am. Chem. Soc.*, **73**, 2390 (1951).

(9) C. M. Hill, M. E. Hill, H. I. Schofield, and L. Haynes, *ibid.*, **74**, 166 (1952).

(10) J. Bregman and S. H. Bauer, *ibid.*, **77**, 1955 (1955).

(11) R. B. Woodward and G. Small, *ibid.*, **72**, 1297 (1950); A. D. Jenkins, *J. Chem. Soc.*, 2563 (1952); E. Enk and H. Spes, *Angew. Chem.*, **73**, 334 (1961).

(12) K. A. Ogloblin, *J. Gen. Chem. USSR*, **18**, 2153 (1948); *Chem. Abstr.*, **43**, 3777 (1949).

(13) Boiling points are uncorrected.