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

AUGUST STURZENEGGER, JOSEPH ZELAUSKAS, AND ALFRED OFNER

Technical Development Department of Hoffmann-La Roche, Inc., Nutley 10, New Jersey

Received May 31, 1962

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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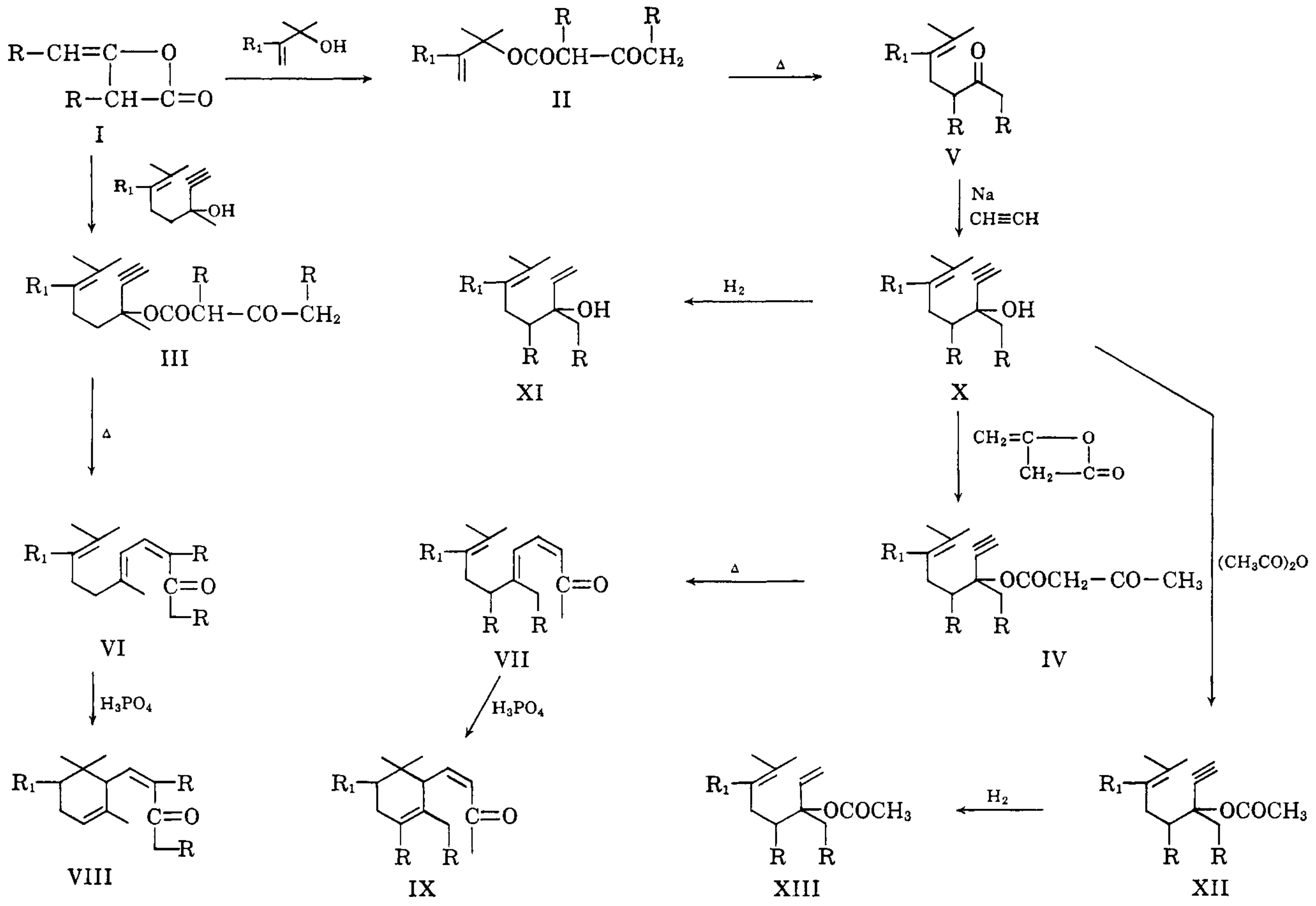
[13] Boiling points are uncorrected.



R = Methyl, ethyl, or *n*-hexyl
R_1 = Methyl or H

A stirred mixture of ligroin (2 l.) and the requisite acid chloride (3.9 moles) was treated with triethylamine (404 g., 4.0 moles), added dropwise during 1 hr. A rise in temperature from 25° to about 60° occurred with propionyl chloride. Agitation was continued overnight (higher homologs required 2 days) after which the triethylamine hydrochloride was removed by filtration and the solvent evaporated. Then the product (I) was isolated by distillation at reduced pressure or used immediately (in the crude state) in the next step.

2. **Allyl and Ethynyl Acetoacetates (Table II).**—Over-all yields of the esters (based on the acyl chlorides) were better from the crude ketene dimers than from the distilled ones.

Table II

Vinylcarbinyl and Ethynylcarbinyl Acetoacetates

Compound	R	R_1	Boiling points °C.	Mm.	$n^{25}D$	% Yield
IIa	CH_3	H	60	0.4	1.4345	82
b	C_2H_5	H	45	.007	1.4378	77
c	*n*-C_6H_{13}	H	dec.	.007	1.4500 (crude)	88 (crude)
d	CH_3	CH_3	43	.007	1.4437	60
IIIa	CH_3	H	69	.007	1.4615	60
b	C_2H_5	H	88	.006	1.4612	61
c	CH_3	CH_3	84	.007	1.4664	61
d	C_2H_5	CH_3	dec.	.007	...	56 (crude)
IVa	CH_3	H	dec.	.007	1.4720	97 (crude)
b	C_2H_5	H	dec.	.007	1.4723	98 (crude)
c	CH_3	CH_3	dec.	.007	1.4754	97 (crude)

The crude substituted ketene dimer (I), obtained from the appropriate acid chloride (3.0 moles) was converted immediately by addition, during 1 hr., to a mixture of the unsaturated carbinol (1.5 moles), pyridine (6.6 cc.) and glacial acetic acid (6.6 cc.). The temperature rose from 30° to 40°. After stirring the mixture for 12 hr., it was diluted with ether and washed successively with sulfuric acid (5%), sodium carbonate (5%), and water until neutral. Distillation under reduced pressure afforded the acetoacetates (II, III, or IV).

It is interesting to note the higher stability of acetoacetates with substitution in the acid moiety compared to acetoacetates with even lower molecular weights substituted in the alcohol portion. For example, IIIb is more stable than IVa.

3. **Unsaturated Ketones (Table III).**—The allylic acetoacetate, II, (1.0 mole) was heated with aluminum isopropoxide[1,3] (3.0 g.) at 150–160° with vigorous stirring until gas evolution stopped—about 3 hr. The mixture was diluted with ligroin and washed successively with sulfuric acid (15%), water, sodium carbonate (5%), and water until neutral. The product, V, was obtained by fractional distillation.

4. **Ethynylcarbinols (Table VI).**—These acetylenic tertiary alcohols were prepared essentially according to Ruzicka and Fornasir.[14]

Sodium (1.2 g.-atom) was dissolved in liquid ammonia (700 cc.). Then acetylene was introduced until the blue color disappeared, after which a solution of V (1.0 mole) in ether was added over a period of a few hours. The reaction was allowed to continue overnight. One half of the ammonia was evaporated and ethynylcarbinol liberated with ammonium chloride. The remainder of the ammonia was removed, water was added, and the layers were separated. The aqueous layer was extracted with ether. The combined organic layers were washed successively with sulfuric acid (5%), sodium carbonate (5%), and water until neutral. X was isolated by distillation.

5. **Vinylcarbinols (Table VII).**—The ethynylcarbinol, X, was dissolved in hexane (1:2). Lindlar catalyst,[15] 5% by weight, was added and the hydrogenation was carried out at atmospheric pressure until 1 mole of hydrogen was absorbed. The vinylcarbinol, XI, was obtained by fractional distillation.

6. **Ethynylcarbinyl Acetates (Table VI).**—These were prepared according to the method of Ofner, Chase, and Weber.[16]

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[14] L. Ruzicka and V. Fornasir, *Helv. Chim. Acta*, **2**, 182 (1919); *Cf.* also H. Rupe and G. Lang, *ibid.*, **12**, 133 (1929).

[15] H. Lindlar, *ibid.*, **35**, 446 (1952).

[16] A. Ofner, G. Chase, and J. Weber, *Compt. rend. congr. intern. chimie ind. 31ᵉ Liege*, **II**, 644 (1958).

TABLE III

UNSATURATED KETONES

Compound	R	R_1	Boiling points °C.	Boiling points Mm.	$n^{25}D$	% Yield	Microanalyses Theory C	Microanalyses Theory H	Microanalyses Found C	Microanalyses Found H
Va	CH_3	H	46	2.0	1.4401	77	77.87	11.76	77.56	11.56
b	C_2H_5	H	66	1.2	1.4421	62	79.06	12.16	78.99	12.13
c	n-C_6H_{13}	H	121	0.1	1.4508	56	81.56	13.01	81.05	12.82
d	CH_3	CH_3	51	.8	1.4484	44	78.51	11.98	78.78	12.00

TABLE IV

PSEUDOIONONES AND PSEUDOIRONES

Compound	R	R_1	Boiling points °C.	Boiling points Mm.	$n^{25}D$	% Yield
VIa	CH_3	H	100–104	0.1	1.4931–1.4956	55
b	C_2H_5	H	131–135	.8	1.4857–1.4876	39
c	CH_3	CH_3	109	.35	1.5120	45
d	C_2H_5	CH_3	135	.5	1.5081	20
VIIa	CH_3	H	94–104	.09	1.5051–1.5194	54
b	C_2H_5	H	111	.1	1.4960–1.5160	57
c	CH_3	CH_3	100–110	.08	1.5081–1.5212	51

TABLE V

α-IONONES AND α-IRONES

Compound	R	R_1	Boiling points °C.	Boiling points Mm.	$n^{25}D$	% Yield	Microanalyses Theory C	Microanalyses Theory H	Microanalyses Found C	Microanalyses Found H
VIIIa	CH_3	H	90	0.09	1.4960	35				
b	C_2H_5	H	99	.2	1.4935	33	82.20	11.36	82.20	11.40
c	CH_3	CH_3	111	1.0	1.4970	77				
d	C_2H_5	CH_3	124	0.9	1.500	84 (crude)				
IXa	CH_3	H	83	.09	1.5019	68	62.98[a]	7.05	63.34	6.75
b	C_2H_5	H	109	.4	1.4971	53	82.20	11.36	82.61	11.04
c	CH_3	CH_3	94	.2	1.5010	67	81.99	11.18	82.64	11.16

[a] Analyzed as the 2,4-dinitrophenylhydrazone.

TABLE VI

ETHYNYLCARBINOLS AND ACETATES

Compound	R	R_1	Boiling points °C.	Boiling points Mm.	$n^{25}D$	% Yield	Microanalyses Theory C	Microanalyses Theory H	Microanalyses Found C	Microanalyses Found H
Xa	CH_3	H	65	0.3	1.4680	71	79.94	11.18	80.17	11.00
XIIa	CH_3	H	65	.08	1.4592	90				
Xb	C_2H_5	H	77	.5	1.4672	81	80.71	11.61	80.46	11.33
XIIb	C_2H_5	H	92	.5	1.4611	82	76.75	10.47	76.96	10.45
Xc	CH_3	CH_3	62	.1	1.4730	75	80.35	11.41	80.00	11.47

TABLE VII

VINYLCARBINOLS AND ACETATES

Compound	R	R_1	Boiling points °C.	Boiling points Mm.	$n^{25}D$	% Yield	Microanalyses Theory C	Microanalyses Theory H	Microanalyses Found C	Microanalyses Found H
XIa	CH_3	H	63	0.5	1.4664	91	79.06	12.17	79.18	12.46
XIIIa	CH_3	H	65	.09	1.4568	90	74.95	10.78	74.72	10.86
XIb	C_2H_5	H	75	.4	1.4664	90	79.94	12.46	80.12	12.72
XIIIb	C_2H_5	H	81	.3	1.4584	80	76.14	11.18	76.16	10.78
XIc	CH_3	CH_3	60	.6	1.4725	81				

X (1.0 mole) and 85% phosphoric acid (1.8 g.) were mixed, then acetic anhydride (1.5 moles) was added dropwise at 25–30°. The mixture was allowed to react for 1 day, then was diluted with water (200 cc.) and hexane (400 cc.). After the layers were separated, the organic layer was washed with sodium carbonate (10%) to pH 11, then washed neutral with water. Fractionation under reduced pressure yielded XII.

7. Vinylcarbinyl Acetates (Table VII).—The ethynylcarbinyl acetates XII were selectively hydrogenated, as described for XI, to yield the vinylcarbinyl acetates, XIII.

8. Pseudoionones and Pseudoirones (Table IV).—These compounds were prepared by the pyrolysis of the requisite acetoacetates[1,2] (III and IV) under conditions similar to those used for the synthesis of V.

At a temperature of 170–180°, a mixture of III (1.0 mole) or IV (1.0 mole), decalin (260 cc.), aluminum isopropoxide (0.3 g.), and propionic acid (3.0 g.) was pyrolyzed until the gas evolution stopped. The mixture was worked up as for V and upon fractionation either VI or VII was isolated.

9. α-Ionones and α-Irones (Table V).—These ketones were obtained by cyclization, according to Royals,[17] of VI and VII.

To 85% phosphoric acid (600 cc.) at 0°, one added VI or VII (1.0 mole) during 0.5–1 hr. The mixture was agitated for 0.5 hr. at 40–50°, poured onto ice-water (2 l.) and extracted with toluene. The toluene extract was washed with sodium carbonate (5%) and water. Distillation afforded the ring-closed product VIII or IX.

Acknowledgment.—The authors wish to thank Dr. Al Steyermark and his staff of the Roche Microchemical Laboratories for the carbon and hydrogen analyses.

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