The distillate was diluted with petroleum ether (30–60°), the solution washed with three portions of water, dried over magnesium sulfate, and distilled to remove solvent. The residual oil was fractionated using a short packed column. A fraction (6.7 g.) with b.p. 96–140° (0.5–0.8 mm.) was collected as crude recovered starting material, and two fractions (total of 12.5 g.) with b.p. 140–146° (0.8–0.9 mm.) and 126–130° (0.3 mm.) were taken as crude product. Fractionation of the recovered starting material afforded 5.4 g. of water-white methyl 12-tridecenoate, b.p. 99–100° (0.4 mm.) which showed an infrared absorption curve identical with that of the starting material. Fractionation of the higher boiling material through a 2-inch Vigreux column yielded (a) 2.5 g. of a straw-yellow liquid, b.p. 92–133° (0.25–0.35 mm.), n^{25}_{D} 1.4790, and (b) 6.8 g. (25%; corrected for recovered starting material, 35%) of yellow liquid, b.p. 133–136° (0.35–0.45 mm.), n^{25}_{D} 1.4804.

Anal. Calcd. for $C_{14}H_{25}O_2Br$: C, 55.08; H, 8.26. Found: (a) C, 62.32; H, 9.14; (b) C, 56.10; H, 8.21.

Further fractional distillation of these and other samples of brominated tridecenoic ester afforded no analytically pure product. Analysis of various fractions, with n^{25}_{D} ranging from 1.4796 to 1.4805, yielded C and H values of 55.52–56.63 and 7.97–8.42, respectively.

In every distillation, considerable amounts of non-volatile tar were left in the still. The distillates, orginally yellow in color, gradually became darker and finally black. It was also noted that a petroleum ether insoluble oil developed on standing at room temperature.

Coupling Reaction with Methyl Bromotridecenoate.—Over a period of one hour, 42.4 ml. of 0.524 *N* ethereal pentylmagnesium bromide (0.0222 mole) was added to a boiling solution of 5.63 g. (0.0185 mole) of freshly distilled methyl bromotridecenoate in 20 ml. of absolute ether. After warming the mixture for an additional hour, it was poured over ice and dilute sulfuric acid. The organic material was taken up in ether, the ether extracts were washed with water and dried. Removal of ether solvent left 5.8 g. of residual oil.

This material was heated on the steam-bath with 6 ml. of pyridine for 1.5 hours. To the cooled deep-red mixture was added 100 ml. of ether followed by dilute sulfuric acid. The acid mixture was extracted thoroughly with ether, and the extract was washed first with dilute acid and then with water until neutral. After drying the solution (magnesium sulfate), it was boiled to remove solvent. The amber-colored residue was then distilled in a small Claisen flask under reduced pressure.

To saponify the ester product, the distillate (3.0 g.) was boiled for one hour with a solution of 3 g. of sodium hydroxide in 45 ml. of 60% alcohol. The clear amber solution, after dilution with water and extraction with two portions of petroleum ether (30–60°), was acidified with dilute sulfuric acid and the organic acids extracted with petroleum ether. The petroleum ether solution was shaken with water until free of sulfuric acid and then dried with magnesium sulfate. Removal of solvent left 2.2 g. of a yellow oil.

Crystallization of this material from acetone at −15 to −20° afforded 0.43 g. of a white crystalline solid, m.p. 38–43.5° (preliminary sintering). Two further crystallizations from 5-ml. portions of acetone at −20° yielded 0.23 g. of vaccenic acid, m.p. 45–45.5° (sintering at 44°). A third crystallization brought the melting point to 45–45.5° (sintering at 44.5°).

Anal. Calcd. for $C_{18}H_{34}O_2$: C, 76.5; H, 12.1. Found: C, 76.7; H, 12.1.

A mixed melting point determination of this material with the synthetic vaccenic acid (m.p. 43–44°) prepared according to Ahmad, Bumpus and Strong[13] was carried out by Dr. Strong, who reported the first appearance of oily drops at 42.5°, and the sample completely liquid at 44°.

Infrared Absorption.—The infrared absorption curves were taken on a Baird infrared recording spectrophotometer which covered the range from 2–16 μ. Carbon tetrachloride solutions of approximately 2.5% by weight were used in a 0.1-mm. rock-salt cell.

Summary

Directions are given for the preparation of methyl bromoundecenoate and methyl bromotridecenoate by allylic bromination of the terminally unsaturated eleven-carbon and thirteen-carbon esters. The coupling of methyl bromoundecenoate with heptylmagnesium bromide yields a 1:1:4 mixture of elaidic, oleic and 9-vinylpalmitic acids. Coupling of methyl bromotridecenoate with pentylmagnesium bromide yields a mixture from which vaccenic acid may be isolated.

BOSTON, MASSACHUSETTS RECEIVED JUNE 12, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

Some Addition Reactions of Chalcones. II. The Preparation of Some γ-Ketoselenides

BY HENRY GILMAN AND LOUIS F. CASON

Incidental to some studies carried out in these laboratories¹ on the addition of unsymmetrical reagents to α,β-unsaturated ketones the reactions of selenols and benzeneseleninic acid with chalcones were investigated.

The addition of thiols and sulfinic acids to α,β-unsaturated compounds is well established.[2] However, similar reactions involving the selenium analogs have not been reported. By reason of the location of selenium and sulfur in the same periodic family it seemed probable that the course of addition of the selenols to chalcones would closely parallel that described for the corresponding sulfur compounds. In addition, it was of interest to explore the possibility of masking the extreme toxicity of the selenium atom in the effort to synthesize products of pharmacological value.

We found that aryl selenols add readily to chalcones in ethanol without the aid of a catalyst. The products were well-defined, sharp melting crystalline compounds which were obtained in yields varying from 44 to 80% (see Table I). No product resulted when the addition of benzeneselenol to an *o*-substituted chalcone, 2-chloro-4′-methoxychalcone, was attempted.

There is little doubt that the formation of these γ-ketoselenides takes place by the mechanism of 1,4-addition to the conjugated system as in the case of the formation of the corresponding ketosulfides.[2] However, in order to establish the conclusive proof of their structure, β-phenyl-β-(4-chlorobenzeneseleno)-propiophenone was prepared by an alternate method involving the alkylation of sodium *p*-chlorobenzeneselenoxide with β-phenyl-β-bromopropiophenone. The product obtained in this manner was identical (mixed m. p.) with that resulting from the addition of *p*-chlorobenzeneselenol to benzalacetophenone.

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(1) Gilman and Cason, THIS JOURNAL, **72**, 3469 (1950).

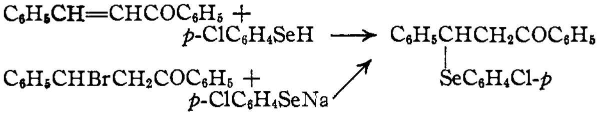
(2) (a) Posner, *Ber.*, **34**, 1395 (1901); *ibid.*, **35**, 799 (1902); (b) Ruhemann, *J. Chem. Soc.*, **87**, 17, 461 (1905); (c) Nicolet, THIS JOURNAL, **53**, 3066 (1931); (d) *ibid.*, **57**, 1098 (1935); (e) Gilman and King, *ibid.*, **47**, 1136 (1935).

TABLE I

γ-KETOSELENIDES—$RCH(SeR'')CH_2COR'$

No.	R	R′	R″	M. p., °C.[a]	Yield, %	Formula	Analyses, %[b] Calcd.	Found
1	C_6H_5	C_6H_5	C_6H_5	120	76	$C_{21}H_{18}OSe$	Se, 21.64	21.88
2	C_6H_5	p-ClC_6H_4	C_6H_5	100–101	58	$C_{21}H_{17}OClSe$	Cl, 8.77	8.95
3	C_6H_5	C_6H_5	p-ClC_6H_4	105	80	$C_{21}H_{17}OClSe$	Cl, 8.77	8.75
4	p-$CH_3OC_6H_4$	C_6H_5	p-ClC_6H_4	97–98	44	$C_{22}H_{19}OClSe$	Cl, 8.16	8.02
5	C_6H_5	p-ClC_6H_4	p-ClC_6H_4	110	52	$C_{21}H_{16}OCl_2Se$	Cl, 16.33	16.00
6	p-$CH_3OC_6H_4$	C_6H_5	C_6H_5	87–88	69	$C_{22}H_{20}O_2Se$	Se, 20.00	19.76

[a] All melting points are uncorrected. [b] Analyses for chlorine were made by the macro Parr bomb method. The selenium analyses were run according to the procedures of Banks and Hamilton, THIS JOURNAL, 61, 2306 (1939), and of Fredga, *Uppsala Univ. Arsskrift*, No. 5, 232 (1935) [*C. A.*, 29, 7281 (1935)].



$$C_6H_5CH{=}CHCOC_6H_5 + p\text{-}ClC_6H_4SeH \longrightarrow C_6H_5\underset{\displaystyle SeC_6H_4Cl\text{-}p}{CH}CH_2COC_6H_5$$

$$C_6H_5CHBrCH_2COC_6H_5 + p\text{-}ClC_6H_4SeNa \nearrow$$

It is interesting to note that the formation of β-phenyl-β-benzeneselenopropiophenone from 0.02 mole of benzeneselenol and an equivalent amount to benzalacetophenone in 40 ml. of ethanol required only nine minutes. Under identical conditions no addition product was obtained from benzenethiol and the ketone after allowing the reaction to stand for five hours. The introduction of a few drops of piperidine brought about the immediate precipitation of the γ-ketosulfide. Generally, the addition of thiols to conjugated ketones is quantitative, and the products are sparingly soluble in ethanol. The γ-ketoselenides, on the other hand, were obtained in lower yields and were recrystallized from ethanol without difficulty. As in the case of their sulfur analogs[2d] the selenides decomposed into the corresponding selenol and the unsaturated ketone after standing at room temperature in the presence of dilute (approximately 1 N) alcoholic sodium hydroxide. Refluxing with phenylhydrazine in glacial acetic acid gave the corresponding 1,3,5-triarylpyrazolines. No definite products resulted from the oxidation of β-phenyl-β-benzeneselenopropiophenone with 30% hydrogen peroxide, nitric acid or potassium permanganate, respectively.

In contrast to the smooth addition of the selenols to chalcones, no reaction was observed when benzeneseleninic acid was used. These negative results are not surprising after considering some distinct differences in the reactions of certain organic selenium compounds from those of their sulfur analogs. For example, in contrast to the behavior of aromatic sulfides, the selenides upon oxidation exhibit a tendency to remain in the tetravalent state.[3] The sulfides, however, are oxidized to the corresponding sulfones under comparatively mild conditions. Only one aryl selenone has been described in the literature,[3b,c] and the reactions of this compound are characteristic of a peroxide rather than those of the relatively inert sulfone. Benzeneseleninic acid crystallizes from concentrated nitric acid as its nitrate,[3b] $C_6H_5SeO_2H\cdot HNO_3$, conditions under which the corresponding sulfinic acid would be most unstable.

In the older literature, the structure of the sulfinic acid was a subject of much controversy. Some reactions indicated an unsymmetrical arrangement for the compound while others could be best explained by assuming that the hydrogen is attached to sulfur. There is little doubt that the 1,4-addition of the sulfinic acids to conjugated unsaturated molecules is made possible by the latter arrangement. It is highly probable that the sulfinic and seleninic acids are not similarly constructed and that the latter do not possess the structural requirement necessary for their addition to α,β-unsaturated ketones. The fact that the unsymmetrical ethyl ethanesulfonate is obtained from ethyl iodide and silver sulfite while under the same conditions silver selenite yields the symmetrical diethyl selenite[3c] is partial support for this point of view.

Experimental

Preparation of the Aryl Selenols.—The selenophenols employed in this investigation were prepared according to the general method described by Foster[4] for the preparation of selenophenol.

β-Phenyl-β-benzeneselenopropiophenone.—The procedure which follows is typical of the preparation of all of the γ-ketoselenides described in this paper. To a solution of 4.2 g. (0.02 mole) of benzalacetophenone in 25 ml. of ethanol there was added with shaking 3.2 g. (0.02 mole) of benzeneselenol dissolved in 15 ml. of ethanol. After allowing the reaction mixture to stand at room temperature for nine minutes, the addition product began to crystallize from the solution. Within an additional ten minutes the entire contents of the flask became a solid mass of crystals. The yield of the crude product was 5.5 g. (76%); m. p. 118–120°. Two recrystallizations from ethanol gave 4.2 g. (58.5%) of the pure product which melted at 120–120.5°.

Anal. Calcd. for $C_{21}H_{18}OSe$: Se, 21.64. Found: Se, 21.88.

The preceding reaction was run concurrently with a second one in which 2.2 g. (0.02 mole) of benzenethiol[2a,b] was used in place of the selenol. No addition occurred after allowing the solution to stand at room temperature for five hours. The introduction of a few drops of piperidine brought about the instantaneous precipitation of the ketosulfide. The yield of this product was 6.3 g. (quantitative); m. p. 118°. (The reported melting point for the compound is 121°.[2a,b]) β-Phenyl-β-phenylthiopropiophenone was difficultly soluble in ethanol.

Although the addition of benzeneselenol to benzalacetophenone took place without the aid of a catalyst, the introduction of a few drops of piperidine hastened the reaction but caused no significant increase in the yield of the product.

Preparation of β-Phenyl-β-(4-chlorobenzeneseleno)-propiophenone from Sodium p-Chlorobenzeneselenoxide and β-Phenyl-β-bromopropiophenone.—A solution of sodium p-chlorobenzeneselenoxide prepared from 2 g. (0.01 mole) of p-chlorobenzeneselenol and 0.4 g. (0.01 mole) of sodium

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[3] Foster and Brown, THIS JOURNAL, **50**, 1182 (1928); (b) Krafft and Vorster, *Ber.*, **26**, 2813 (1893); (c) Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 2280 (1928).

[4] Foster, *Org. Syn.*, **24**, 89 (1944); see also Foster, *Rec. trav. chim.*, **53**, 405 (1934).

hydroxide in 25 ml. of ethanol was refluxed under nitrogen with 2.8 g. (0.01 mole) of β-phenyl-β-bromopropiophenone.[5] After filtering to remove the sodium bromide, the solution was placed in the ice-box. The crystalline product thus obtained was filtered and recrystallized from fresh ethanol. Three grams (62%) of the product was obtained; m. p. and mixed m. p. (with product obtained from addition of *p*-chlorobenzeneselenol to chalcone) 105°.

Reaction of β-Phenyl-β-benzeneselenopropiophenone with Alkali.—Five-tenths of a gram (0.0013 mole) of the ketoselenide was dissolved in 15 ml. of ethanol to which 2.5 ml. of 20% sodium hydroxide had been added. The solution was allowed to stand at room temperature for one hour and then diluted with water. Benzalacetophenone (mixed m. p.) was recovered from the reaction, and the characteristic odor of the selenol was evident in the filtrate after acidification.

Reaction of β-Phenyl-β-benzeneselenopropiophenone with Phenylhydrazine.—Five-tenths of a gram (0.0013 mole) of the selenide was refluxed for 15 minutes with 0.5 g. (0.0045 mole) of phenylhydrazine in 15 ml. of glacial acetic acid. 1,3,5-Triphenylpyrazoline crystallized from the solution on dilution with water and cooling. After recrystallization from ethanol, the pure product melted at 134° and showed no depression of melting point when mixed with an authentic sample prepared from benzalacetophenone and phenylhydrazine.[6]

Attempted Addition of Benzeneseleninic Acid to Benzalacetophenone.—Benzeneseleninic acid and its nitrate were prepared according to the procedure of Pyman.[7] The products obtained melted at 118–120° and 114–115°, respectively. Previous investigators have reported melting points of 121° and 124–125° for the free acid and 112° for the nitric acid salt.[7a,b]

Equivalent quantities of benzeneseleninic acid and benzalacetophenone were dissolved in ethanol and allowed to stand at room temperature for several hours. The only product isolated from the reaction was the unreacted ketone (mixed m. p.). No addition product was obtained when benzene or glacial acetic acid was used as the solvent nor when benzeneseleninic acid nitrate was employed in the reaction.

The authors are grateful to Parke, Davis and Company for arranging for the pharmacological testing.

Summary

Aryl selenols undergo 1,4-addition to chalcones without the aid of a catalyst. The course of reaction is analogous to that previously described for the addition of thiols to α,β-unsaturated carbonyl compounds. The resultant γ-ketoselenides are crystalline, sharp melting compounds which decompose into their original components on treatment with dilute alkali. Refluxing these addition products with phenylhydrazine in glacial acetic acid gives rise to the selenium-free 1,3,5-triarylpyrazolines.

No addition product was obtained from benzalacetophenone and benzeneseleninic acid or its nitrate.

AMES, IOWA RECEIVED JULY 5, 1950

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(5) Vorländer and Tubandt, *Ber.*, **37**, 1644 (1904).

(6) Knorr and Laubmann, *ibid.*, **21**, 1205 (1888).

(7) (a) Pyman, *J. Chem. Soc.*, **115**, 166 (1919); (b) Stoecker and Krafft, *Ber.*, **39**, 2197 (1906).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXXI. The Reaction of Butenyl Chlorides with Diethylamine and Triethylamine

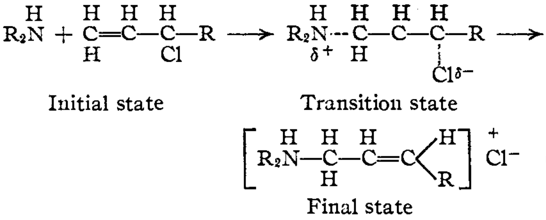
BY WILLIAM G. YOUNG, I. D. WEBB[1a] AND HARLAN L. GOERING[1b]

The reaction of α- and γ-ethylallyl chlorides with secondary amines has been described by Meisenheimer and Link,[2] and is of interest due to the abnormal substitution product resulting from secondary chloride. These workers showed that the same product was obtained from either allylic chloride, and identified the product as the γ-ethylallyl isomer by reduction to the corresponding *n*-amylamine. Thus it was established that the primary halide yielded normal products, whereas abnormal products were produced from the secondary chloride. More recently Jones, *et al.*,[3] have observed the formation of abnormal products from the reaction of diethylamine on the halides I (R = H or n-C_4H_9). Normal products were obtained with aniline, ammonia and ethylamine. The abnormal

$$RC{\equiv}CCH{=}CHCHClCH_3 \qquad \text{I}$$

products from I may arise from isomerization of an initially formed normal product since treatment of the normal secondary amine, from I (R = H) and ethylamine, with ethyl bromide gives the abnormal product, $RC{\equiv}CCHN(Et)_2CH{=}CHCH_3$.

Analogous to the cases mentioned above, we have known for some time that the reaction of α-methylallyl chloride (II) with diethylamine results in an abnormal substitution product. Due to the lack of necessary evidence, especially kinetic evidence, any conclusions regarding the mechanism of the reactions leading to the abnormal products were necessarily speculative. However, as has been previously suggested,[4] the available facts could be accommodated by an abnormal bimolecular substitution (S_N2') mechanism formulated in equation (1).



$$R_2\overset{H}{N} + \underset{H}{\overset{H}{C}}{=}\overset{H}{C}{-}\underset{Cl}{\overset{H}{C}}{-}R \longrightarrow R_2\underset{\delta+}{\overset{H}{N}}\cdots\underset{H}{\overset{H}{C}}{-}\overset{H}{C}{-}\underset{Cl^{\delta-}}{\overset{H}{C}}{-}R \longrightarrow \left[R_2N{-}\underset{H}{\overset{H}{C}}{-}\overset{H}{C}{=}C{<}^{H}_{R}\right]^{+} Cl^{-} \qquad (1)$$

In view of recent explanations advanced for the non-existence of the S_N2' mechanism[5,6] and the more recent demonstration of its operation in the

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[1] (a) Polychemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware. (b) Postdoctorate Fellow, 1948–1950. Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

(2) Meisenheimer and Link, *Ann.*, **479**, 211 (1930).

(3) Jones, Lacey and Smith, *J. Chem. Soc.*, 940 (1946).

(4) Kepner, Winstein and Young, THIS JOURNAL, **71**, 115 (1949).

(5) Catchpole, Hughes and Ingold, *J. Chem. Soc.*, 8 (1948).

(6) Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 86.