Experimental

The carbon diselenide used initially in this work was prepared in this laboratory by the method of Ives, *et al.*[4] Subsequently, experimental quantities of carbon diselenide were obtained from Noranda Research Centre, Pointe Claire, Quebec.

It has been our experience that redistilled carbon diselenide has an odor very similar to that of carbon disulfide. However, when carbon diselenide vaporizes and becomes mixed with air, extremely repulsive stenches are gradually formed. Many of the reaction residues gave foul odors that were rather persistent. By using an effective hood and working with rather small quantities of materials, as well as using a charcoal trap, Dry Ice trap, or a potassium hydroxide decontamination bath whenever it seemed advisable, pleasant working conditions were maintained.

It should be noted that some of the volatile selenium compounds produced may be extremely toxic as well as foul. For example, hydrogen selenide, a by-product of the reactions described, is about as toxic as hydrogen cyanide. An effective hood, therefore, is essential from a safety standpoint and a trap containing caustic solution is advisable, especially when larger quantities are involved.

1,3-Diphenylselenourea.—A solution of 0.32 ml. (0.005 mole) of carbon diselenide in 100 ml. of carbon tetrachloride was added dropwise over a 1-hr. period with stirring to a refluxing solution of 4.6 ml. (0.05 mole) of aniline in 50 ml. of carbon tetrachloride. The refluxing was continued 30 min. longer, whereupon hydrogen selenide evolution could no longer be detected by moistened lead acetate paper. A stream of nitrogen was passed through the reaction mixture during the entire period. At the end of the reflux period, the mixture was cooled and filtered to give 1.36 g. (98%) of 1,3-diphenylselenourea, m.p. 190–192° dec. The product was colored pale gray from a trace of elemental selenium. Recrystallization from ethanol, using a stream of nitrogen to displace air, gave a colorless product with no increase in melting point.

Modifications of the above procedure for the preparation of other products are given in Table I. Small amounts of black elemental selenium were sometimes removed by filtering the hot reaction mixtures. In some cases the solutions were concentrated on a rotating evaporator and taken up in the recrystallization solvent in order to obtain crystalline products.

Seleno-2-benzoxazolinone.—A mixture of 0.32 ml. (0.005 mole) of carbon diselenide and 0.44 g. (0.004 mole) of *o*-aminophenol in 100 ml. of benzene was refluxed with stirring under nitrogen for 16 hr. The mixture was filtered while hot to remove a small amount of insoluble impurities. The filtrate upon cooling yielded 0.48 g. of nearly colorless needles, m.p. 198–200° dec. Concentration of the mother liquors to 25 ml. yielded an additional 0.14 g., m.p. 194–196° dec. The total yield was 78%. Recrystallization of the product from benzene gave colorless needles, m.p. 201–203° dec.

Seleno-2-benzothiazolinone was prepared similarly.

1,1-Diethyl-3-benzylselenourea.—A solution of 0.32 ml. (0.005 mole) of carbon diselenide in 50 ml. of benzene was added dropwise over a 20-min. period with stirring to 1.6 ml. (0.015 mole) of benzylamine in 100 ml. of benzene at room temperature under nitrogen. A solution of 51.5 ml. (0.50 mole) of diethylamine in 100 ml. of benzene was then added over a 15-min. period with stirring at room temperature. After the addition was complete, the mixture was refluxed for 16 hr. The resulting dark brown mixture was concentrated to a sirup, redissolved in 100 ml. of benzene, and filtered to remove a small amount of black precipitate. The clear yellow filtrate was washed with 60 ml. of 0.2 *N* hydrochloric acid followed by three washings with 50 ml. of distilled water. The benzene layer was dried over anhydrous magnesium sulfate, concentrated to a sirup, and cooled. Filtration followed by washing with a benzene–pentane mixture gave 1.15 g. of 1,1-diethyl-3-benzylselenourea as pale yellow needles, m.p. 62–67°. A second crop of 0.15 g., m.p. 65–68°, was obtained by the addition of pentane to the mother liquor. The total yield was 96%. Recrystallization of the first crop from a benzene–hexane mixture gave 0.91 g., fine colorless needles, m.p. 93–94°, that was used as an analytical sample.

The Claisen Rearrangement of Allyl Ethers of α-Hydroxybenzalacetophenones[1]

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The allyl ethers of several phenylbenzylglyoxals have been prepared and rearranged to the corresponding C-allyl glyoxals. The electron-donating CH_3–O– group in the *o*- and *p*-position of the benzyl nucleus promotes the rearrangement, whereas the similarly placed electron-withdrawing NO_2– group retards the rearrangement.

The Claisen rearrangement has been shown to be intramolecular,[3–6] and the kinetics of the reaction have been established as first order.[7] Studies of a series of *p*-X-phenyl ethers[8] and *p*-X-cinnamyl phenyl ethers[9] indicate that both the aryloxy and allyl groups assume partial radical character in the transition state.

While the allyl ethers of the enolic modification of β-diketones have been subjected to the Claisen rearrangement, those of the α-diketones have not. Since the allyl ethers of the α-diketones possess the structural requirements necessary for this rearrangement, one might expect them to rearrange.

In order to test this hypothesis, the chalcones (I–VII) were prepared by condensing the appropriate aldehyde and acetophenone. The chalcones were converted to the corresponding oxides (VIII–XIV). Oxide (VIII) was converted to the glyoxal (XV) by way of the chlorohydrin; oxides (IX–XIV) were isomerized with alkali to the diketones (XVI–XXI). These glyoxals in turn were treated in acetone solution in the presence of potassium carbonate with allyl bromide, yielding the allyl ethers (XXII–XXVIII), which were subjected to the conditions of rearrangement (p. 1645).

The ethers were refluxed in N,N-dimethylaniline in an atmosphere of nitrogen for twenty-four hours. The extent to which rearrangement occurred is

$$
\begin{array}{lcll}
\text{XXII} & \longrightarrow & \text{XXIX} & 18\% \\
\text{XXIII} & \longrightarrow & \text{XXX} & 20 \\
\text{XXIV} & \longrightarrow & \text{XXXI} & 75 \\
\text{XXV} & \longrightarrow & \text{XXXII} & 80 \\
\text{XXVI} & \longrightarrow & \text{XXXIII} & 0 \\
\text{XXVII} & \longrightarrow & \text{XXXIV} & 0 \\
\text{XXVIII} & \longrightarrow & \text{XXXV} & 60
\end{array}
$$

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(2) In partial fulfillment of the requirements for the Ph.D. degree.

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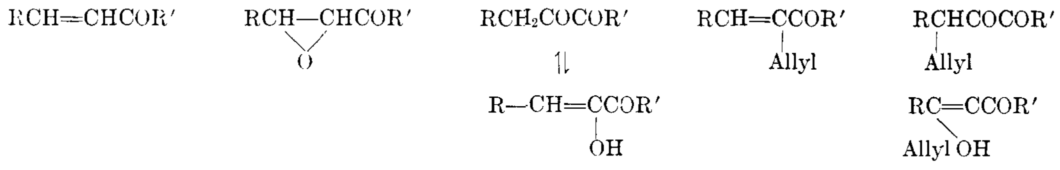

$$\mathrm{RCH{=}CHCOR'} \qquad \mathrm{RCH{-}CHCOR'}\ (\text{-O-}) \qquad \mathrm{RCH_2COCOR'} \rightleftharpoons \mathrm{R{-}CH{=}C(OH)COR'} \qquad \mathrm{RCH{=}C(Allyl)COR'} \qquad \mathrm{RCH(Allyl)COCOR'} \rightleftharpoons \mathrm{RC(Allyl){=}C(OH)COR'}$$

(I-VII) (VIII-XIV) (XV-XXI) (XXII-XXVIII) (XXIX-XXV)

I, VIII, XV, XXII, XXIX, R = C_6H_5; R′ = C_6H_5
II, IX, XVI, XXIII, XXX, R = C_6H_5; R′ = Mes
III, X, XVII, XXIV, XXXI, R = o-$CH_3OC_6H_4$; R′ = Mes
IV, XI, XVIII, XXV, XXXII, R = p-$CH_3OC_6H_4$; R′ = Mes
V, XII, XIX, XXVI, XXXIII, R = o-$NO_2C_6H_4$; R′ = Mes
VI, XIII, XX, XXVII, XXXIV, R = p-$NO_2C_6H_4$; R′ = Mes
VII, XIV, XXI, XXVIII, XXXV, R = Mes; R′ = C_6H_5

When N,N-diethylaniline was substituted for N,N-dimethylaniline, ethers XXVI and XXVII rearranged to XXXIII and XXXIV to the extent of 5% and 6%, respectively.

These results indicate that rearrangement is facilitated by the electron donating methoxyl group and retarded by the electron withdrawing nitro group, and that temperature is a factor.

Experimental

Preparation of the Chalcones. I,[10] II,[11] III,[12] IV,[13] V, VI, and VII.[14]—Chalcones V and VI were prepared in the conventional manner by adding slowly a solution of 2.0 g. of sodium hydroxide in 6 cc. of water to a stirred alcoholic solution of 7.5 g. of the nitrobenzaldehyde and 8.0 g. of acetomesitylene. After standing overnight, the mixture was stirred, chilled, filtered, washed with water until free of alkali, dried, and recrystallized from alcohol.

The yellow o-nitrochalcone melted at 93°; the yellow p-isomer melted at 116–117°.

Anal. Calcd. for $C_{18}H_{17}O_3N$ (V): C, 73.3; H, 5.8. Found: C, 73.1; H, 5.8.

Anal. Calcd. for $C_{18}H_{17}O_3N$ (VI): C, 73.3; H, 5.8. Found: C, 73.2; H, 5.9

Preparation of the Oxides. VIII,[15] IX,[11] X,[12] XI,[13] XII, XIII, and XIV.[14]—Oxides XII and XIII were prepared according to the method of Barnes and Lucas,[12] and recrystallized from methanol. The o-nitro compound melted at 115°; the p-isomer melted at 118°.

Anal. Calcd. for $C_{18}H_{17}O_4N$ (XII): C, 69.5; H, 5.5. Found: C, 69.8; H, 5.8.

Anal. Calcd. for $C_{18}H_{17}O_4N$ (XII): C, 69.5; H, 5.5. Found: C, 69.8; H, 5.8.

Preparation of the Glyoxals. XV,[16] XVI,[11] XVII,[12] XVIII,[13] XIX, XX, and XXI.[14]—Glyoxals XIX and XX were prepared according to Barnes.[11] The resulting yellow crystalline solids produced a red color with alcoholic ferric chloride. The o-nitro compound melted at 120°; the p-isomer melted at 122°. The o-nitro isomer was 80% enolic according the modified Kurt H. Meyer method[17]; the p-isomer was 99% enolic.

Anal. Calcd. for $C_{18}H_{17}C_4N$ (XIX): C, 69.5; H, 5.5. Found: C, 69.8; H, 5.8.

Anal. Calcd. for $C_{18}H_{17}O_4N$ (XX): C, 69.5; H, 5.5. Found: C, 69.4; H, 5.2.

Preparation of the Allyl Ethers of the Glyoxals. XXII, XXIII,[11] XXIV, XXV, XXVI, XXVII, and XXVIII.—All of the allyl ethers were prepared according to Barnes.[11] After refluxing the glyoxal and allyl bromide in acetone solution with anhydrous potassium carbonate, the inorganic salts were removed by filtration and the acetone by distillation. The residue was dissolved in ether and extracted with Claisen's alkali in order to remove any unchanged glyoxal. The ethereal solution was dried over anhydrous sodium sulfate, filtered, and distilled. The residual oil was crystallized from methanol where possible. (See Table I.)

TABLE I

Allyl ether	M.p., °C.	Reaction with Alc. FeCl₃	Analysis			
XXII	Yellow oil	Negative	$C_{18}H_{16}O_2$ Calcd.:	C, 81.8;	H, 6.1
			Found:	C, 81.5;	H, 6.6
XXIV	103–104	Negative	$C_{22}H_{24}O_3$ Calcd.:	C, 78.6;	H, 7.1
			Found:	C, 78.8;	H, 7.3
XXV	73–74	Negative	$C_{22}H_{24}O_3$ Calcd.:	C, 78.6;	H, 7.1
			Found:	C, 78.8;	H, 7.2
XXVI	80–81	Negative	$C_{21}H_{21}O_4$ Calcd.:	C, 71.8;	H, 6.0
			Found:	C, 71.9;	H, 5.7
XXVI	119	Negative	$C_{21}H_{24}O_4N$ Calcd.:	C, 71.8;	H, 6.0
			Found:	C, 72.0;	H, 5.7
XXVIII	Light yellow	Negative	$C_{21}H_{22}O_2$ Calcd.:	C, 82.3;	H, 7.2
			Found:	C, 82.9;	H, 7.3

Rearrangement of the Allyl Ethers. XXII–XXVIII to the α-Allylglyoxals XXIX–XXXV.—A solution of 2.0 g. of the allyl ether in 20 cc. of N,N-dimethylaniline was refluxed in an atmosphere of nitrogen for 20 hr. The dimethylaniline was vacuum distilled under a stream of nitrogen, and the residue was dissolved in benzene. The benzene solution was extracted with Claisen's alkali. The alkaline extract was neutralized with dilute hydrochloric acid and extracted with ether. The ethereal extract was dried over anhydrous sodium sulfate, filtered, and the ether removed by distillation. The residue was crystallized from methanol where possible.

Recovery of the unchanged ether was effected in good yield from the benzene solution which had been extracted with Claisen's alkali. The benzene was distilled and the residue was crystallized where possible. When the recovered allyl ether could not be crystallized, it was hydrolyzed to the glyoxal by refluxing with dilute hydrochloric acid and alcohol.

In the case of ethers XXVI and XXVII where no rearrangement occurred, recovery was effected to the extent of more than 90%. When N,N-diethylaniline was substituted for N,N-dimethylaniline, ethers XXVI and XXVII rearranged to the extent of 5% and 6%, respectively, and recovery of unchanged ether was effected to about 90%. (See Table II.)

TABLE II

α-Allyl-glyoxal	M.p., °C.	% Conversion	Reaction with Alc. FeCl₃	Analysis		
XXIX	Oil	18	Red	$C_{18}H_{16}O_2$ Calcd.:	C, 81.8;	H, 6.1
				Found.	C, 81.5;	H, 6.6
XXX	109	20	Red	$C_{21}H_{22}O_2$ Calcd.:	C, 82.3;	H, 7.2
				Found:	C, 82.9;	H, 7.4
XXXI	Oil	75	Red	$C_{22}H_{24}O_3$ Calcd.:	C, 78.6;	H, 7.1
				Found:	C, 78.8;	H, 7.3
XXXII	113–114	80	Red	$C_{22}H_{24}O_3$ Calcd.:	C, 78.6;	H, 7.1
				Found:	C, 78.8;	H, 7.2
XXXIII	Oil	5		$C_{21}H_{24}O_4N$ Calcd.:	C, 71.8;	H, 6.0
				Found;	C, 72.0:	H, 5.7
XXXIV	Oil	6		$C_{21}H_{21}O_4N$ Calcd.:	C, 71.8;	H, 6.0
				Found:	C, 72.0;	H, 5.7
XXXV	Oil	60	Red	$C_{21}H_{22}O_2$ Calcd.:	C, 82.3;	H, 7.2
				Found:	C, 82.9;	H, 7.3

Spectroscopic Analysis.—Infrared absorption measurements were made using a Perkin-Elmer infrared spectrophotometer, Model 21. The solvent used was carbon tetrachloride.

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(10) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 78.

(11) R. P. Barnes, *J. Am. Chem. Soc.*, **57**, 937 (1935).

(12) R. P. Barnes and W. M. Lucas, *ibid.*, **64**, 2260 (1942).

(13) R. P. Barnes and H. Delaney, *ibid.*, **65**, 2155 (1943).

(14) R. P. Barnes and R. J. Brown, *ibid.*, **65**, 412 (1943).

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(16) E. P. Kohler and R. P. Barnes, *J. Am. Chem. Soc.*, **56**, 211 (1934).

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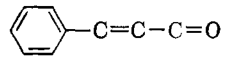
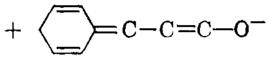
Bands were found at 3.425 and 6.00 μ for the chalcones which are regions of C—H and conjugated carbonyl absorptions, respectively. The enols absorbed at 2.95, 3.425, and 6.00 μ. The diketone (XXI)[11] which is 100% ketonic, adsorbed at 3.425, 5.85, and 5.95 μ. There was no band at 2.95 μ. These observations are in agreement with the findings of Barnes and Pinkney.[18] When the enols were converted to the allyl ethers, the band at 2.95 μ disappeared in each case. Upon equilibration of the enols with deuterium oxide, the band at 2.95 μ disappeared. This observation justified the assignment of this band to O—H stretching frequency.

Ferguson and Barnes[19] studied the ultraviolet spectra of some 1,3-diketones and related intermediates. They observed that the main chromophoric system in the chalcones is



probably due to the resonating form



They concluded that groups such as alkoxyl which readily accept a positive charge, will have a bathochromic effect while negative groups such as NO_2 will have the opposite effect.

Spectra in the ultraviolet region were obtained using the Beckman Model DU spectrophotometer with 95% ethanol as the solvent. The effects observed by Barnes and Ferguson[19] were also observed in the following cases with the exception of the *p*-nitrobenzalacetomesitylene (VI) and the α-hydroxy-*p*-nitrobenzalacetomesitylene (XX). Complete agreement with the observation was obtained in the allyl ethers of the enols. The completely ketonic glyoxal (XXI) absorbs at 255 mμ. (See Table III.)

TABLE III

WAVE LENGTH OF THE MAXIMUM ABSORPTION BANDS

		λmax, (mμ)
I.	$C_6H_5CH{=}CHCOC_6H_5$	305 (313)[a]
II.	$C_6H_5CH{=}CHCO$ Mes	292
III.	$o\text{-}CH_3OC_6H_4CH{=}CHCO$ Mes	335
V.	$o\text{-}O_2NC_6H_4CH{=}CHCO$ Mes	250 (252)[b]
VI.	$p\text{-}O_2NC_6H_4CH{=}CHCO$ Mes	305
XVI.	$C_6H_5CH{=}\underset{OH}{C}\ CO$ Mes	318
XVII.	$o\text{-}CH_3OC_6H_4CH{=}\underset{OH}{C}\ CO$ Mes	345
XIX.	$o\text{-}O_2NC_6H_4CH{=}\underset{OH}{C}\ CO$ Mes	295
XX.	$p\text{-}O_2NC_6H_4CH{=}\underset{OH}{C}\ CO$ Mes	345
XXI.	Mes $CH_2COCOC_6H_5$	255
XXIV.	$o\text{-}CH_3OC_6H_4CH{=}\underset{O\text{—}Allyl}{C}\ CO$ Mes	335
XXVI.	$o\text{-}O_2NC_6H_4CH{=}\underset{O\text{—}Allyl}{C}\ CO$ Mes	265
XXVII.	$p\text{-}O_2NC_6H_4CH{=}\underset{O\text{—}Allyl}{C}\ CO$ Mes	275

[a] See ref. 20. [b] See ref. 19.

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Structures of Substituted Fulvenes. The Reaction Products from Acetone and Dimethylfulvene

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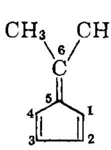
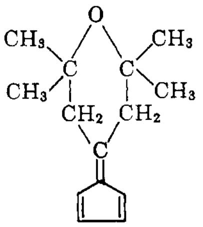
Acetone has been shown to substitute on to the ring carbons of 6,6-dimethylfulvene rather than the side-chain carbons. The structures of the mono-, di-, tri-, and tetrasubstituted 6,6-dimethylfulvenes are discussed. The presence of methanol in the reaction medium leads to the formation of ethers.

In 1906, Thiele[1] reported that, in addition to the production of 6,6-dimethylfulvene (I), the reaction of acetone and cyclopentadiene in a basic methanolic solution led to the formation of an ether whose analysis corresponded closely to that of $C_{14}H_{20}O$. A compound of very similar properties could be obtained after some purification from acetone and 6,6-dimethylfulvene in a basic alcoholic solution. The analysis, the typical fulvene physical properties of color and oxygen uptake, and the fact that the ether appeared to be composed of one cyclopentadiene and three acetone moieties led Thiele to postulate II for the structure of the ether. Courtot[2] speculated that compounds of structure III were possible when aldehydes (RCHO) reacted with cyclopentadiene under basic conditions. Ziegler[3] therefore considered II, IV, and V as possible structures for Thiele's ether and showed that the reaction product,



I



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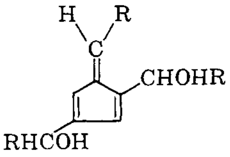
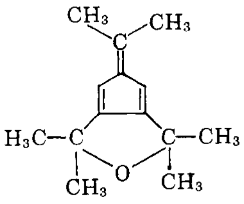
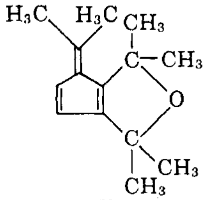


III



IV



V

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