cipitated, which after several recrystallizations from ethanol–ether, melted at 174–177°.

Anal. Calcd. for $C_{14}H_{22}NCl$: C, 70.12; H, 9.25. Found: C, 70.06; H, 9.33.

***trans*-9-Keto-1,2,3,4,4a,9,10,10a-octahydrophenanthrene** (V).—The crude acid products isolated from the hydrolysis of the ester obtained in the above described Friedel–Crafts reaction (9.5 g.) were dissolved in 48 ml. of concentrated sulfuric acid, and heated on the steam-bath for 15 minutes. The cooled mixture was poured onto ice, and extracted with ether. The ether extract was washed with water, dilute alkali, dried, and concentrated. A small amount of the ketone was obtained, the quantity depending on the conditions of the Friedel–Crafts reaction from which the acid material was derived. If the Friedel–Crafts reaction was carried out at room temperature for 24–36 hours about 5% of the ketone was obtained; if refluxing temperature conditions were employed approximately 10% of the ketone was obtained. On the assumption that higher temperatures increased the yield of the 2-phenylcyclohexaneacetic acid, the Friedel–Crafts reaction was carried out in refluxing benzene–nitrobenzene. The yield of ketone upon cyclization of this acid product led to 1% or less of the ketone.

The ketone, twice recrystallized, and once sublimed, melted at 95.5–97.5°. This sample gave no melting point depression with an authentic sample which had been kindly supplied by Dr. W. E. Bachmann.

A 2,4-dinitrophenylhydrazone was prepared in the usual manner and recrystallized several times from toluene–methanol mixtures. It melted at 267–269° (no depression in mixed melting point with authentic sample).

Anal. Calcd. for $C_{20}H_{20}O_4N_4$: C, 63.15; H, 5.30. Found: C, 63.21; H, 5.35.

The Preparation of Spirocyclohexane-1,1-indanone-3 (VII).—Unrecrystallized 1-phenylcyclohexaneacetic acid (6 g.) was dissolved in 157 ml. of concentrated sulfuric acid and heated on a steam-bath. The temperature was maintained at about 85° for 25 minutes, after which the mixture was cooled and poured slowly with stirring over ice.

The product was extracted with ether; the ethereal solution was washed with 10% potassium hydroxide, and dried over anhydrous magnesium sulfate. After filtering, the ether was removed and the residue seeded with an authentic crystal of the indanone.

The white solid, obtained by cooling the seeded concentrate in an ice-bath, was dissolved in 30–60° petroleum ether and decolorized with Norite. Recrystallization was effected by chilling the filtrate in an acetone–Dry Ice-bath; yield 3.8 g. (69.1%).

An analytical sample, prepared by sublimation at 60–75° (0.1 mm.) melted at 58–59° (literature 58–59°[7] no depression on mixed m.p. with an authentic sample).

The oxime and semicarbazone derivatives were prepared in the usual manner and melted at 138–139° and 210–213°, respectively, and mixed m.p. with authentic sample gave no depressions.

β-(1-Phenylcyclohexane)-ethylamine.—1-Phenylcyclohexaneacetic acid was dissolved in 30 ml. of dry benzene and 3.5 ml. of thionyl chloride added. The solution was heated on a steam-bath for 2 hours and then concentrated under reduced pressure. The oily residue was added dropwise with stirring to a cold solution of 250 ml. of concentrated ammonium hydroxide. The stirring was continued overnight. Since the product was an oil, it was extracted with benzene, washed and dried over anhydrous magnesium sulfate. The benzene solution was added to 50 ml. of 1 molar lithium aluminum hydride in ether and refluxed for 18 hours, cooled and decomposed with water. The benzene–ether layer was separated, dried and hydrogen chloride gas passed into the solution. The amine hydrochloride (1.5 g.) was obtained, which after recrystallization from absolute alcohol–ether melted at 250–254° (dec.). Bachmann and Fornefeld[1] report m.p. 253–254° (dec.).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Open-chain Acylals, Formals and Ethers Containing Terminal Double Bonds

BY CHARLES D. HURD, LEONARD G. GINGER,[1a] LEON L. GERSHBEIN[1b] AND W. A. YARNALL

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Allyl chloromethyl ether, a hemiacetal chloride, was used in the synthesis of several new acylals, formals and ethers. Reactions were with carboxylic salts, with alcohols in the presence of pyridine, and with butadiene in the presence of zinc chloride. The reaction of allyl chloroformate and 2-allyloxy-1-ethanol was studied.

Relatively few simple hemiacetal chlorides, $ROCH_2Cl$, have been reported (R = methyl, ethyl, isopropyl, *s*-butyl, cyclohexyl, 2-chloroethyl), the general synthesis being the interaction of formaldehyde, an alcohol and hydrogen chloride. The allyl analog was prepared in the present work. Distillation gave rise to a product (b.p. 107°) analyzing 1.5% low in chlorine, probably because of entrained allyl alcohol. However, most of the latter was removable by benzoylation to yield a product containing 0.8% less chlorine than the theoretical. Its derivatives were generally of acceptable purity.

Acylals were prepared by metathesis of allyl chloromethyl ether with sodium salts

$$CH_2{=}CHCH_2OCH_2Cl + RCOONa \longrightarrow CH_2{=}CHCH_2OCH_2OCOR + NaCl$$

The salts included the acetate, acrylate, oxalate, α-acetoxypropionate and phthalate. Details followed the general procedure of Hurd and Green.[2] Similar treatment of the formate gave a product which resisted purification, perhaps owing to the presence of allyl formal, $CH_2(OC_3H_5)_2$.

Several other formals were prepared by interaction of the chloride with various alcohols in the presence of a base such as pyridine

$$CH_2{=}CHCH_2OCH_2Cl + ROH + C_5H_5N \longrightarrow CH_2{=}CHCH_2OCH_2OR + C_5H_5NHCl$$

The alcohols investigated were 2-ethoxy-1-ethanol, 2-allyloxy-1-ethanol, ethyl lactate and allyl lactate.

The reaction of allyl chloromethyl ether with 1,3-butadiene in the presence of zinc chloride presumably involved a 1,4-addition, but this point is unsettled. The expected product would be 5-allyloxy-1-chloro-2-pentene

$$CH_2{=}CHCH_2OCH_2Cl + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow CH_2{=}CHCH_2OCH_2{-}CH_2CH{=}CHCH_2{-}Cl$$

This reaction is analogous to the one reported by Straus and Thiel,[3] namely, the addition of methyl α-chlorobenzyl ether to butadiene to form 5-

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[1] Pittsburgh Plate Glass Company research associates: (a) 1944, (b) 1943–1944.

[2] C. D. Hurd and F. O. Green, THIS JOURNAL, **63**, 2201 (1941).

[3] Straus and Thiel, *Ann.*, **525**, 151 (1936).

TABLE I

PHYSICAL CONSTANTS AND ANALYSES

	B.p.,				Calcd.		Found[b]	
Acylals	°C.	Mm.	d^{23}_{20}	n_D (°C.)	C	H	C	H
Allyloxymethyl formate	136–138	Atm.	1.021	1.4170 (23)	51.7	6.90	53.4	7.02
	50.5–52.5	23						
Allyloxymethyl acetate	145–146	Atm.	0.989	1.4154 (23)	55.4	7.70	55.9	7.49
Allyloxymethyl acrylate	74–76	20	1.004	1.4400 (23)	..	..	..	..
Allyloxymethyl oxalate	152–153	18	1.137	1.4493 (22)	52.2	6.13	51.9	5.88
	136	4	...	....	..	..	..	..
	93–96	0.1	...	1.4454 (31)	..	..	..	..
Allyloxymethyl 2-acetoxypropionate	115–118	0.5	...	1.4452 (22)	53.5	6.98	53.7	6.96
Allyloxymethyl pththalate	100–125[a]	0.001	...	1.5078 (22)	62.7	5.92	62.8	5.75
Formals								
Allyl 2-ethoxyethyl formal	74–75	13	0.919	1.4180 (23)	60.0	10.00	60.4	9.77
Allyl 2-allyloxyethyl formal	94–96	14	0.933	1.4343 (23)	62.9	9.30	63.0	8.68
Ethyl O-(allyloxymethyl)-lactate	90–91	10	...	1.4210 (26)	57.4	8.57	57.8	8.19
Allyl O-(allyloxymethyl)-lactate	111.5–112.5	13	0.998	1.4369 (23)	..	..	60.1	7.66
	119–120.5	20	...	1.4380 (21)	60.0	8.05	60.4	7.66
Ethers								
Allyl 2-allyloxyethyl carbonate	121	17	1.03 d^{26}_{20}	1.4378 (26)	..	..	..	..
	117.5	14	...	....	58.1	7.52	58.6	7.44
5-Allyloxy-1-chloro-2-pentene	90–92	25	0.9829 d^{24}_{20}	1.4590 (24)	Cl: 22.1		Cl: 21.8	

[a] Bath temperature for molecular still of the type described by Hurd, Liggett and Gordon, THIS JOURNAL, **63**, 2657 (1941).
[b] The C, H analyses were performed by Dr. T. S. Ma.

methoxy-5-phenyl-1-chloro-2-pentene: $CH_3OCH(C_6H_5)CH_2CH{=}CHCH_2Cl$. Although these authors employed mercuric chloride as catalyst, only a slight conversion was promoted by the latter in the present work.

The reaction of allyl chloroformate with 2-allyloxy-1-ethanol was included also in this study. The product formed was allyl 2-allyloxyethyl carbonate, $CH_2{=}CHCH_2O{-}CO{-}O{-}CH_2CH_2OCH_2CH{=}CH_2$.

Experimental

Allyl Chloromethyl Ether.[4]—A 3-necked liter flask was fitted with stirrer, calcium chloride drying tube and gas inlet tube. Thirty-six grams of dry hydrogen chloride was passed into 116 g. of chilled allyl alcohol with stirring and then 30 g. of paraformaldehyde was introduced. In the latter operation, gentle occasional stirring was employed; emulsions often followed too vigorous agitation. This addition was followed by another 36 g. of hydrogen chloride and finally 30 g. of paraformaldehyde. In view of the insolubility of some of the latter, more hydrogen chloride was used to dissolve it. The two liquid phases were separated and the ether layer was dried for several hours with calcium chloride. The crude yield was 82 g. (77%).

Distillation under diminished pressure removed some allyl alcohol in the forerun. The main fraction boiled at 106–107°, but this is only 10° higher than the b.p. of allyl alcohol. Since 31.8% of chlorine was found in this product (calcd. for C_4H_7ClO: Cl, 33.3) this pointed to allyl alcohol as contaminant. Accordingly, it was refluxed one hour with benzoyl chloride and dimethylaniline, then distilled: b.p. 107–108°, n^{23}_D 1.431, d^{23}_{20} 1.025. Analysis for chlorine was 32.5%. This material was of acceptable purity for the syntheses below.

Acylals.—A 250-cc., 3-necked flask was equipped with condenser, mercury-sealed stirrer and a dropping funnel which was protected with a calcium chloride tube. About 0.1 to 0.3 mole of the anhydrous salt (sodium acetate, sodium acrylate, etc.) was placed in the flask and air in the system was displaced by dry nitrogen. Benzene (or toluene) was added to facilitate stirring and an equivalent quantity of allyl chloromethyl ether was dropped into the stirred and cooled reaction flask during half an hour. A trace of hydroquinone or pyrogallol was introduced as an inhibitor against polymerization. This mixture was then heated to reflux temperature for two hours (stirring), cooled, filtered from sodium salts and fractionally distilled. Pertinent data are recorded in Table I. Yields ordinarily were 60–90%. Yields with the oxalate were low (only 16%) if benzene was used, but an 80% yield was obtained by using no solvent and heating one hour at 115° followed by one hour at 150°.

In purifying the oxalate, it was necessary to use two vacuum distillations to give an acylal of analytical purity. The crude 2-acetoxypropionate required a sodium bicarbonate scrubbing followed by drying prior to distillation.

The formate was never obtained completely pure. Possibly allyl formal (of comparable boiling point) was the impurity. Its presence to the extent of 10% could account for the analytical figures.

These changes were noticed in some of the samples when they were allowed to stand for several months in the absence of an inhibitor. Allyloxymethyl acrylate polymerized to a clear solid. Considerable polymerization of the oxalate also was apparent. The formate remained liquid but contained a flocculent precipitate.

The Formals.—One-quarter mole of the alcohol (2-ethoxy-1-ethanol, 2-allyloxy-1-ethanol,[5] ethyl lactate, allyl lactate) was dissolved in 0.3 mole of dry pyridine at 5–10°. A total of 0.25 mole of allyloxymethyl chloride was added dropwise and with stirring during 90 minutes, after which the mixture was maintained at 100° for 1–2 hours. Two layers formed, the lower layer solidifying at room temperature with the first two compounds listed. The top layer was separated and any formal was extracted from the salt layer with ether. The ether solution was washed with dilute hydrochloric acid, sodium bicarbonate solution, and was dried over sodium sulfate. The ether was removed and the product distilled under reduced pressure. Yields were 30–45%. Samples of these compounds did not polymerize on standing for five months in the absence of an inhibitor.

Similar results were obtained when pyridine was the reagent that was added dropwise.

The same method was used with allyl alcohol, but the yield of allyl formal, $CH_2(OC_3H_5)_2$, was only 10–15%. It was collected at 38–39° (14 mm.), n^{23}_D 1.4211, d^{23}_{20} 0.886.

Allyl 2-Allyloxyethyl Carbonate.—To a chilled mixture of 21 g. of 2-allyloxy-1-ethanol, b.p. 60–63° (15 mm.), and 18 g. of dry pyridine was slowly added 25 g. of freshly distilled allyl chloroformate. Pyridine hydrochloride separated. The mixture was stirred for two hours at room tem-

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[4] L. N. Bauer and H. T. Neher, U. S. pat. appl. 773,922; *C. A.* **44**, 10730 (1950), describe this compound as boiling at 104–109°, and its reaction with sodium methacrylate to yield allyloxymethyl methacrylate of b.p. 78–82° (16 mm.).

[5] C. D. Hurd and M. A. Pollack, THIS JOURNAL, **60**, 1905 (1938).

perature before adding dry ether and filtering off the solid. The ether solution was washed with cold, dilute hydrochloric acid and aqueous sodium bicarbonate, then was dried over sodium sulfate, and distilled. A 73% yield of allyl 2-allyloxyethyl carbonate was collected at 124–125° (18 mm.). The molar refractivity was 47.69 as compared to a calculated value of 47.77. A sample without inhibitor did not undergo polymerization over a period of five months.

5-Allyloxy-1-chloro-2-pentene (?).—To a mixture of 80 cc. of cold carbon disulfide, 27 g. of 1,3-butadiene and 1.5 g. of anhydrous zinc chloride was slowly added 42.5 g. of allyl chloromethyl ether with thorough chilling and stirring. After a resting period of 15 hours at 5–15° the product was poured into ice. The organic layer was removed, dried, and a trace of pyrogallol was added. Distillation yielded 21 g. (33%) of a constant boiling fraction: b.p. 90–92% (25 mm.). The molecular refractivity (44.65) conforms with that calculated (44.72) for $C_8H_{13}ClO$.

The halogen in this compound reacted in aqueous alcohol solution with aqueous silver nitrate. Silver chloride precipitated instantly.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Mechanism of the Reaction of α-Haloketones with Weakly Basic Nucleophilic Reagents

BY RALPH G. PEARSON, STANLEY H. LANGER, FORREST V. WILLIAMS AND WILLIAM J. MCGUIRE

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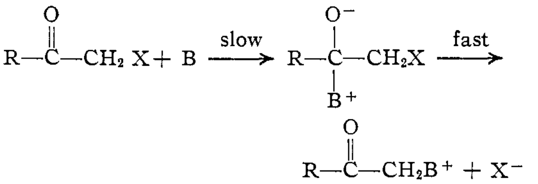
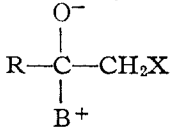
The second-order rate constants for the reactions of pyridine and thiourea with a number of organic bromides, including several in which the bromine is alpha to a carbonyl group, have been determined. It is found that the haloketones and haloesters are relatively more reactive toward the weakly basic but easily polarized thiourea than are the other halides. This is interpreted as meaning that the activating influence of the carbonyl group is largely electrostatic in nature. Arguments are presented against an epoxide intermediate in the reaction of haloketones with weakly basic nucleophilic reagents and against a rate determining addition of the reagent to the carbonyl group.

The well known reactivity of α-haloketones and α-haloesters toward nucleophilic reagents has been the subject of several discussions. Hughes[1] and Ingold have ascribed the reactivity to a polar effect in which the electron-attracting carbonyl group induces a positive charge on the carbon atom holding the halogen. This then facilitates the bringing up of a reagent with a negative center to a position where it can push out the halogen by the usual back-side displacement process. Baker[2] has postulated a mechanism involving addition of the basic reagent to the carbonyl group in a rate determining step, followed by a rapid intramolecular displacement



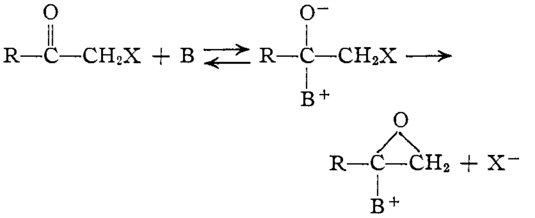
$$R-\overset{O}{\overset{\|}{C}}-CH_2X + B \xrightarrow{slow} R-\underset{B^+}{\overset{O^-}{C}}-CH_2X \xrightarrow{fast} R-\overset{O}{\overset{\|}{C}}-CH_2B^+ + X^- \quad (1)$$

Winstein, Grunwald and Jones[3] have mentioned the possibility of contributions from structures such as

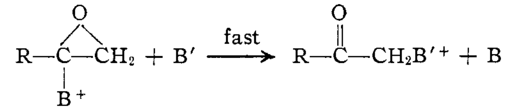


$R-\underset{B^+}{\overset{O^-}{C}}-CH_2X$ in the transition state for the displacement of X by B in haloketones.

The recent isolation of a moderately stable epoxide[4] in the reaction of an α-haloketone with sodium methoxide and the evidence that the epoxide is an intermediate in the formation of other products of the reaction[5] leads to another possible mechanism for the reaction of α-haloketones and esters with bases:



$$R-\overset{O}{\overset{\|}{C}}-CH_2X + B \rightleftarrows R-\underset{B^+}{\overset{O^-}{C}}-CH_2X \longrightarrow R-\overset{\diagup O \diagdown}{\underset{B^+}{C}-CH_2} + X^- \quad (2)$$



$$R-\overset{\diagup O \diagdown}{\underset{B^+}{C}-CH_2} + B' \xrightarrow{fast} R-\overset{O}{\overset{\|}{C}}-CH_2B'^+ + B \quad (3)$$

If some stage of reaction (2) is slow then this mechanism can agree with the second-order kinetics which have always been found for reactions of α-haloketones, etc., with nucleophilic reagents.[6] A key point in this mechanism is that the reagent B′ need not be the same as the reagent B.

In criticism of Hughes and Ingold's explanation it can be mentioned that substitution of an electron-attracting group in a halide frequently *deactivates* toward nucleophilic displacement reactions. Thus α-halosulfones and α-halonitroparaffins are quite unreactive. Also as Hinshelwood, Laidler and Timm[7] have pointed out, for a neutral reagent one might well predict that a negative substituent would deactivate by causing the negative halogen to be held more tightly.

Baker's mechanism can be ruled out as a general one by the observation that phenacyl bromide is 54 times as reactive as phenacyl chloride toward pyridine in ethanol at 55.6°.[8] This is inconsistent

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[1] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[2] J. W. Baker, *ibid.*, **37**, 643 (1941).

[3] S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

[4] (a) Temnikova and Kropacheva, *J. Gen. Chem. U.S.S.R.*, **19**, 1917 (1949); (b) C. L. Stevens, W. Malik and R. Pratt, THIS JOURNAL, **72**, 4758 (1950).

[5] Reference 4 and A. M. Ward, *J. Chem. Soc.*, 1541 (1929).

[6] (a) J. W. Baker, *ibid.*, 1148 (1932); 1128 (1933); (b) H. T. Clark, *ibid.*, **97**, 416 (1910); (c) J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 232 (1924).

[7] C. N. Hinshelwood, K. J. Laidler and E. W. Timm, *J. Chem. Soc.*, 848 (1938).

[8] Reference 6 (b); also we have observed that phenacyl bromide reacts 126 times as fast as phenacyl chloride with thiourea in methanol at 35°.