If), b.p. 107–108° (20 mm.); N-(3,3-dimethylbutyl)-*n*-heptylamine (from Ig), b.p. 118° (8 mm.), n^{20}D 1.4377; N-(3,3-dimethylbutyl)-aniline (from Ih), b.p. 138–139° (17 mm.); N-(3,3-dimethylbutyl)-α,α-dimethylpyrrolidine (from Ii), b.p. 81–85° (18 mm.); N-(3,3-dimethylbutyl)-di-*n*-butylamine (from Ij), b.p. 116–118° (18 mm.), n^{20}D 1.4291–1.4310 and di-*n*-butylamine, b.p. 53–56° (18 mm.), n^{24}D 1.4181, phenylthiourea derivative, m.p. 84–85° (reported 86°)[46]; N-(3,3-dimethylbutyl)-N-methylaniline (from Ik), b.p. 77–79° (0.2 mm.), n^{20}D 1.5180; thiophenol (from Io), b.p. 87° (60 mm.), n^{20}D 1.5840 (also identified by odor); *n*-hexyl mercaptan (from Ip), b.p. 70–72° (60 mm.), n^{20}D 1.4460. No olefin could be detected from Iq or its semicarbazone. No olefin could be detected from Ir, but colorless prisms (from ethanol) were collected, m.p. 86–87.5°, which did not depress the melting point of an authentic sample of methyl-*p*-tolylsulfone (69% yield). The hydrazones of 3,3-dimethyl-1-N-piperidyl-2-butanone (Ia) and 3,3-dimethyl-1-phenoxy-2-butanone (II) furnished the same yields of olefin as did the ketones.

URBANA, ILLINOIS

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[46] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 174, 234.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

Enol Esters of α-Haloketones

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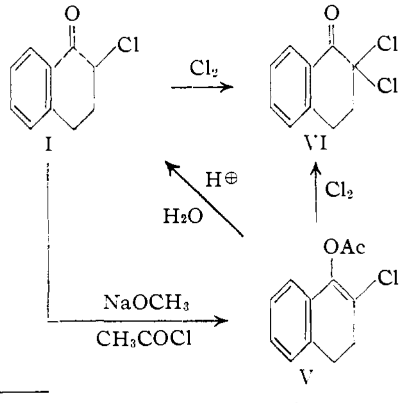
The preparation of enol esters from the following cyclic α-haloketones is reported: 2-chloro-α-tetralone (I), 2-bromo-α-tetralone (II), 2-bromo-1-indanone (III) and 2-chlorocyclohexanone (IV). Stable enolate ions, obtained at low temperatures from the reactions of I, II, III and IV with anhydrous, powdered sodium methoxide in anhydrous ether, were acylated to obtain enol acetates from I, II and III, and an enol caproate from IV.

While the preparation of enol acetates from ketones which contain an enolizable α-hydrogen atom has long been known, a practical preparation for such enol esters from α-haloketones has not been reported. Lyle[2] recently described the isolation of an enol acetate from 2,2-diphenyl-7-bromocycloheptanone, but the yield was poor (9%).

While investigating the reaction of 2-chloro-α-tetralone (I) with anhydrous, powdered sodium methoxide in anhydrous ether at −80°, it was noted that the heterogeneous sodium methoxide–ether slurry became homogeneous at once upon the addition of I. The solution became greenish-yellow in color and this color, coincident with homogeneity, was thought to have arisen from the formation of an enolate ion produced by the action of the base on the α-proton of I. This belief was confirmed upon the addition of acetyl chloride. A precipitate of sodium chloride appeared immediately and 1-acetoxy-2-chloro-3,4-dihydronaphthalene (V) was isolated from the ethereal portion in 65% yield.

The elemental analyses and infrared spectrum were compatible with structure V, and chemical evidence for O-acylation rather than C-acylation was obtained by hydrolysis to the parent α-haloketone I. Also, chlorination of V gave 2,2-dichloro-α-tetralone (VI).



This reaction constitutes another useful procedure involving the enolate ion of an α-haloketone, the ion being relatively stable at low temperature. Previously, the enolate ion has been proposed as an intermediate in the glycidic-ester type self-condensation of phenacyl halides.[3] The reaction has added significance in view of the profusion of reactions involving the action of bases on α-haloketones: epoxyether formation,[4] Favorski-type rearrangement,[5] elimination,[6] substitution,[7] carbon skeleton rearrangement not of the Favorski-type,[8] and functional group rearrangement.[9]

The scope of this type of O-acylation was extended and shown to be practical for α-bromoketones as well as for α-chloroketones. 1-Acetoxy-2-bromo-3,4-dihydronaphthalene (VII) was obtained from 2-bromo-α-tetralone (II) in 47% yield and 1-acetoxy-2-bromoindene (VIII) from 2-bromo-1-indanone (III) in 23% yield. Bromination of VII and VIII gave 2,2-dibromo-α-tetralone (IX) and 2,2-dibromo-1-indanone (X), respectively, in excellent yields. Both IX and X were prepared independently by bromination of II and III, respectively.

Attempts to prepare the enol acetate of α-chlorocyclohexanone (IV) in a pure state were unsuccessful because of difficulties encountered in separating

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[1] Supported in part by a Grant-in-aid from the Research Corporation of New York and the Research Council of Ontario, Canada.

[2] R. E. Lyle and R. A. Covey, THIS JOURNAL, **75**, 4973 (1953).

(3) (a) V. Fritz, *Ber.*, **28**, 3028 (1895); (b) J. Berson, THIS JOURNAL, **74**, 5175 (1952); (c) H. H. Wasserman, *et al.*, *ibid.*, **75**, 96 (1953); *J. Org. Chem.*, **19**, 515 (1954); (d) C. L. Stevens, R. Church and V. J. Traynelis, *J. Org. Chem.*, **19**, 522, 533 (1954).

(4) (a) T. I. Temnikova and E. N. Kropacheva, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **19**, 1920 (1949); (b) C. L. Stevens, W. Malik and R. Pratt, THIS JOURNAL, **72**, 4758 (1950).

(5) (a) A. Favorski, *J. Russ. Phys. Chem. Soc.*, **26**, 559 (1894); (b) R. B. Loftfield, THIS JOURNAL, **73**, 4707 (1951).

(6) R. E. Lutz and C. J. Kibler, *ibid.*, **62**, 1520 (1940).

(7) (a) D. O. Dean, W. B. Dickinson, G. B. Hoey and C. T. Lester, *ibid.*, **76**, 4988 (1954); (b) C. L. Stevens and J. J. DeYoung, *ibid.*, **76** 718 (1954).

(8) (a) B. Tchoubar and O. Sackur, *Compt. rend.*, **208**, 1020 (1939), (b) C. L. Stevens and E. Farkas, THIS JOURNAL, **74**, 5352 (1952).

(9) C. L. Stevens and C. T. Lenk, *J. Org. Chem.*, **19**, 538 (1954).

the product from starting material. However, 1-caproxy-2-chlorocyclohexene (XI) was prepared in 29% yield from the reaction of caproyl chloride with the sodium enolate of IV at −50°. XI proved to be a liquid and appeared from examination of the infrared spectra of various fractions of the distillate to be a homogeneous substance. Evidence for the position of the double bond in this enol ester was obtained by permanganate oxidation to cyclohexane-1,2-dione which was isolated as the osazone in 42% yield.

The formation of XI *via* attack of methoxide as indicated at point 3 in Fig. 1 is especially interesting since α-chlorocyclohexanone is known to react with methoxide ion to give rearrangement products arising from attack of the base at the opposite hydrogen[5] (point 1, Fig. 1) as well as hydroxyketals[10] resulting from the attack of methoxide ion at the carbonyl group (point 2, Fig. 1).

Experimental

2-Chloro-α-tetralone (I).—This compound was obtained by the chlorination of α-tetralone according to the method of Beereboom.[11] From 14.6 g. (0.1 mole) of α-tetralone and 7.8 g. (0.11 mole) of chlorine in carbon tetrachloride, a yield of 70% (12.6 g.) of I (2-chloro-3,4-dihydro-1(2H)-naphthalenone) was obtained, m.p. 44–45.5°.

2-Bromo-α-tetralone (II).—This bromoketone was prepared by the dropwise addition of bromine to an ethereal solution of α-tetralone according to the procedure of Wilds.[12] From 14.6 g. (0.1 mole) of α-tetralone in 100 ml. of anhydrous ether, a yield of 80% (18.5 g.) of pure II (2-bromo-3,4-dihydro-1(2H)-naphthalenone) was obtained. Crystallization from petroleum ether (b.p. 30–60°) yielded white needles, m.p. 37–38°.

2-Bromo-1-indanone (III).—In the same manner prescribed for the preparation of II, average yields of 80% of pure III were obtained from the bromination of 1-indanone in anhydrous ether. Crystallization from petroleum ether (b.p. 30–60°) yielded white flakes,[13] m.p. 37–38.5°.

2-Chlorocyclohexanone (IV).—The method of Newman[14] was used to prepare this haloketone. From 50 g. (0.51 mole) of cyclohexanone mixed with 150 ml. of water, a yield of 60% (40 g.) of IV was obtained on fractional distillation, b.p. 78–82° (6 mm.).

The 1-Acetoxy-2-chloro-3,4-dihydronaphthalene (V).—Freshly cut sodium (1.3 g., 0.055 g.-atom) was dissolved in 30 ml. of anhydrous methanol. This operation was carried out in a predried, round-bottomed, three-necked, 500-ml. flask which was equipped with a Hershberg stirrer, a vacuum take-off tube, and a reflux condenser (drying tube attached). After the sodium had dissolved, the reflux condenser was replaced by a solid rubber stopper and the methanol was removed *in vacuo*. An infrared lamp as a source of heat aided in the removal of last traces of methanol. The Hershberg stirrer served as an excellent means of powdering the lumps of sodium methoxide.

After about five hours of constant stirring and the application of heat under reduced pressure, the sodium methoxide assumed the form of a fine powder. The pressure was equalized by allowing air to pass into the system through a large calcium chloride drying tube. Approximately 300 ml. of anhydrous ether was added, the calcium chloride drying tube was replaced, and the temperature of the sodium methoxide–ether slurry was lowered to −80° by means of a Dry Ice–ether bath.

An equimolar amount of I (10 g.) was dissolved in 30 ml. of anhydrous ether and added in one portion with stirring to the reaction flask. When the mixture became homogeneous (within a few seconds), an excess of acetyl chloride (10 g.) was added rapidly in one portion. Immediately a precipitate of sodium chloride appeared. The reaction mixture was allowed to warm to room temperature, the salts were removed by centrifugation, and the ether solution was concentrated *in vacuo*. The remaining solid was recrystallized from petroleum ether (b.p. 30–60°). Colorless prisms of V were obtained in 65% yield (8.0 g.), m.p. 61–62°.

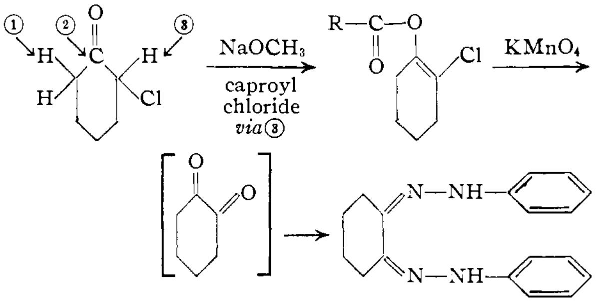

Fig. 1.—O-Acylation of α-chlorocyclohexanone.

Anal. Calcd. for $C_{12}H_{11}ClO_2$: C, 64.72; H, 4.98; Cl, 15.92. Found: C, 64.75; H, 5.38; Cl, 15.97.

Hydrolysis of 1-Acetoxy-2-chloro-3,4-dihydronaphthalene (V).—To a solution of 2.0 g. (0.009 mole) of V in 40 ml. of acetic acid, a solution of 25 ml. of water containing 2 ml. of concentrated hydrochloric acid was added. The reaction mixture was heated on a steam-bath for 4 hours and allowed to stand overnight. It was then poured on cracked ice and the precipitate of 2-chloro-α-tetralone (I) was removed by filtration. Recrystallization of I from petroleum ether (b.p. 30–60°) yielded needles, 1.2 g. (83%), m.p. 43–44.5°. A mixture melting point determination with a known sample of I was not depressed. The infrared spectra were also identical.

Chlorination of 1-Acetoxy-2-chloro-3,4-dihydronaphthalene (V).—The enol acetate (V) (1.0 g., 0.0045 mole) was dissolved in 10 ml. of anhydrous carbon tetrachloride. A few crystals of benzoyl peroxide were added. To this solution a few drops of a concentrated solution of chlorine in carbon tetrachloride were added. After a variable induction period, the reaction mixture was decolorized. Application of sunlight increased the rate of decolorization. The addition of the concentrated chlorine–carbon tetrachloride solution was continued until absorption of chlorine ceased. The carbon tetrachloride was removed *in vacuo*. The remaining oil was dissolved in 10 ml. of acetic acid and poured on cracked ice. The precipitate which formed was removed by filtration and recrystallized from petroleum ether (b.p. 30–60°), m.p. 74–76°. The average yield of three runs was 41% of recrystallized 2,2-dichloro-α-tetralone (VI).

Anal. Calcd. for $C_{10}H_8Cl_2O$: C, 55.84; H, 3.75. Found: C, 56.05; H, 4.01. A mixture melting point determination with a known sample[10] of VI was not depressed. The infrared spectra were also identical.

1-Acetoxy-2-bromo-3,4-dihydronaphthalene (VII).—This enol acetate was prepared from II in the manner previously described for the preparation of V. The temperature was held at −60° by means of a Dry Ice–chloroform mixture. From 10 g. (0.044 mole) of II a yield of 47% (5.55 g.) of VII was obtained after recrystallization from petroleum ether (b.p. 30–60°), m.p. 80–81°.

Anal. Calcd. for $C_{12}H_{11}BrO_2$: C, 53.95; H, 4.15; Br, 29.92. Found: C, 53.55; H, 4.12; Br, 29.89.

Bromination of 1-Acetoxy-2-bromo-3,4-dihydronaphthalene (VII).—The enol acetate (VII) (2.67 g., 0.01 mole) was dissolved in 15 ml. of acetic acid. Bromine was added dropwise with warming and stirring until absorption ceased. The reaction mixture was poured on cracked ice and the solid was removed by filtration. Recrystallization of the crude product from an ether–petroleum ether (b.p. 30–60°) solvent pair yielded 2.5 g. (82%) of 2,2-dibromo-α-tetralone[15] (IX), m.p. 59–60°. A mixture melting point determination with an authentic sample (prepared from the

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[10] C. L. Stevens and J. Tazuma, THIS JOURNAL, **76**, 715 (1954).

[11] C. L. Stevens, J. J. Beereboom and K. G. Rutherford, *ibid.*, **77**, in press (1955).

[12] A. L. Wilds, *ibid.*, **64**, 1421 (1942).

[13] F. S. Kipping, *Trans., J. Chem. Soc.*, **65**, 500 (1894), reports m.p. 38–39°.

[14] M. S. Newman, M. D. Farbman and H. Hipsher, *Org. Syntheses*, **25**, 22 (1945).

[15] F. Krollpfeiffer and A. Müller, *Ber.*, **68**, 1175 (1935), reports m.p. 59–60°.

bromination of II in acetic acid) was not depressed. The infrared spectra were also identical.

3-Acetoxy-2-bromoindene (VIII).—This enol acetate was prepared in 23% yield from III, following exactly the procedure outlined for the preparation of V. When excess acetyl chloride was added to the ether solution of the enolate ion, the reaction mixture turned deep purple and sodium chloride precipitated. During removal of the ether, a solid crystallized. A small amount of petroleum ether (b.p. 30–60°) was added and the solid was filtered. Recrystallization of this solid from petroleum ether (b.p. 30–60°) gave an average yield of 1.6 g. of 2,2-dibromo-1-indanone[16] (X), m.p. 130–131.5° (recorded 132–133°),[13] from several 10 g. runs of III. A mixture melting point determination with an authentic sample of X which was prepared by the bromination of III was not depressed.

Crystallization of the original petroleum ether extract yielded colorless prisms of VIII, m.p. 80–81°. An average of 2.25 g. (23%) was obtained from several 10-g. runs.

Anal. Calcd. for $C_{11}H_9BrO_2$: C, 52.20; H, 3.59; Br, 31.58. Found: C, 52.05; H, 3.67; Br, 31.40.

Bromination of 3-Acetoxy-2-bromoindene (VIII).—Following the procedure outlined for the bromination of VII a crude yield of 88% (2.6 g.) of 2,2-dibromo-1-indanone (X), m.p. 126–130°, was obtained from 2.53 g. of VIII. Recrystallization from petroleum ether (b.p. 30–60°) yielded prisms, m.p. 131–132°.

1-Caproxy-2-chlorocyclohexene (XI).—An ether slurry of anhydrous, powdered sodium methoxide was prepared, following the directions used for the preparation of V; the volume of ether was 300 ml. Increasing the volume of ether increases the tendency for the enolate salt of 2-chlorocyclohexanone (IV) to precipitate. The temperature of the reaction mixture was lowered to −50° by means of a Dry Ice–chloroform bath. IV (13.2 g., 0.1 mole) was added in one portion. When the reaction mixture became homogeneous (2 minutes), an excess (15 g.) of caproyl chloride was added. After centrifugation of the salts and removal of the ether, the oil which remained was fractionally distilled. After a lower-boiling forerun, XI distilled as a colorless oil at 86–87° (0.05 mm.), n^{25}_{D} 1.4707. The yield was 8 g. (29%).

Anal. Calcd. for $C_{12}H_{19}ClO_2$: C, 62.46; H, 8.30; Cl, 15.36. Found: C, 62.56; H, 8.34; Cl, 15.56.

Oxidation of 1-Caproxy-2-chlorocyclohexene (XI).—XI (1.4 g., 0.006 mole) was dissolved in 40 ml. of reagent-grade acetone. To this solution, a water solution (40 ml.) containing an equivalent of potassium permanganate (0.98 g.) was added. Although the permanganate was decolorized rapidly, the reaction mixture was allowed to stir for two hours at room temperature. A few crystals of sodium sulfite were then added to decompose any unreacted permanganate. The inorganic material was removed by filtration and the water–acetone solution was made basic by the addition of sodium carbonate. The reaction mixture was extracted three times with 50-ml. portions of ether. The ether extracts were combined and dried over anhydrous sodium sulfate. The sodium sulfate was removed by filtration and the ether was removed *in vacuo*.

The remaining oil was dissolved in 7 ml. of 95% ethanol, and phenylhydrazine (1.3 g.) was added. Distilled water was added dropwise until the solution became turbid. Acetic acid was then added dropwise until the solution became clear. The reaction mixture was heated on a steam-bath for 3 hours and allowed to stand overnight whereupon yellow needles of the osazone of cyclohexane-1,2-dione, m.p. 145–148°, crystallized in a yield of 42% (0.75 g.) based on the starting enol caproate XI. Recrystallization from ethanol gave yellow needles,[17] m.p. 150–151° (recorded 152–153°).

Anal. Calcd. for $C_{18}H_{20}N_4$: C, 73.94; H, 6.90. Found: C, 74.06; H, 7.01.

DETROIT, MICHIGAN

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[16] C. Revis and F. S. Kipping, *Trans., J. Chem. Soc.*, **71**, 243 (1897). The disproportionation of an α-bromoketone into an α,α-dibromoketone and an unbrominated ketone in the presence of base has been noted recently by Lyle and Covey, ref. 2.

[17] O. von Wallach, *Ann.*, **437**, 174 (1924).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

C^{14}-Tracer Studies in the Rearrangements of Unsymmetrical α-Diketones. V.[1] Substituted Benzils[2]

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RECEIVED APRIL 1, 1954

Four unsymmetrically substituted benzils, each labeled with carbon-14 in the carbonyl group adjacent to the unsubstituted phenyl ring have been studied to determine the migration preferences of the aryl group. The percentages migration of the substituted groups as opposed to phenyl were found experimentally to be: *p*-methoxyphenyl, 31.3; *p*-methylphenyl, 38.8; *p*-chlorophenyl, 67.2; *m*-chlorophenyl, 81.2. The migration ratios, corrected for isotope effect, were found to be capable of correlation by the Hammett equation. These data emphasize the importance of the point of attack of hydroxyl ion in determining the course of the reaction and cast doubt on the postulation that the attack is reversible.

The benzilic acid rearrangement, though apparently the earliest recognized[5] organic rearrangement and though much discussed since its discovery, is still poorly understood mechanistically. The confusion is apparently due equally to the dearth of experimentation and to the wealth of discussion, for the tendency has prevailed to force this reaction into a common class with others to which it bears only the faintest resemblance.[6]

The present paper, which presents the results obtained in the study of four unsymmetrically substituted carbon-14 labeled benzils, records no solution to the question of the mechanism of this reaction but rather indicates the need for a new interpretation of the accumulated evidence.

The transformation of benzil to benzilic acid is known to occur in aqueous solution in the absence of base,[7] and in certain basic media in the absence

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[1] Previous paper in this series: E. C. Hendley and O. K. Neville, THIS JOURNAL, **75**, 1995 (1953).

[2] This document is based upon work performed under contract W-7405 eng. 26, for the Atomic Energy Commission at the Oak Ridge National Laboratory.

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[4] Nuclear Instrument and Chemical Corporation, 223 West Erie, Chicago, Ill.

[5] J. von Liebig, *Ann.*, **25**, 27 (1838).

[6] J. U. Nef, *ibid.*, **298**, 372 (1897); G. Schroeter, *Ber.*, **42**, 2344 (1909); M. Tiffeneau, *Rev. Gen. Sci.*, 585 (1907); H. Staudinger and A. Binkert, *Helv. Chim. Acta*, **5**, 703 (1922); A. Michael, THIS JOURNAL, **42**, 813 (1920); F. C. Whitmore, *ibid.*, **54**, 3274 (1932).

[7] H. Klinger, *Ber.*, **19**, 1868 (1886); A. Jena, *Ann.*, **155**, 78 (1870).